2009 APS March Meeting
Pittsburgh, Pennsylvania
http://www.aps.org/meetings/march/index.cfm
8:00AM A4.00001 Ion solvation and its effects on the miscibility of binary polymer blends
ZHENGANG WANG, Division of Chemistry and Chemical Engineering, California Institute of Technology — We study the effects of adding salt ions on the miscibility of a binary blend of polymers having different dielectric constants. The competition between the preference of the ions to be solvated by the component of the higher dielectric constant and the entropic tendency for the ions to be distributed uniformly results in non-trivial effects on the miscibility. We first study the thermodynamics of the polymer blend-ion mixture using a simple Born model in a uniform dielectric medium of the average composition of the polymer blend. We then study the effect of local enrichment of the higher dielectric constant polymer near the ion. We find that when the dielectric constants of the polymers are both low, adding salt decreases the miscibility, while when the dielectric constants of the polymers are both high, the addition of salt enhances the miscibility. When the blend consists of a high dielectric constant polymer and a low dielectric constant polymer, miscibility is decreased if the low dielectric constant component is the majority and is increased if the high dielectric constant component is the majority. The effect becomes significant as ion concentrations corresponding to an order of one ion per polymer chain. The quantitative change in the effective $\chi$ parameter depends on the functional form of the composition dependence of the dielectric constant of the mixture. We also illustrate the difference between fixed ion concentration and fixed chemical potential of the ions.

8:36AM A4.00002 The Nanostructure of Nafion for Fuel-Cell Membranes from Small-Angle Scattering and NMR Analysis
KLAS SCHMIDT-ROHR, Ames Laboratory and Dept. of Chemistry, Iowa State University, Ames, IA 50011. USA — We have investigated the long contentious nanometer-scale structure of the Nafion ionomer used in proton exchange membranes of H$_2$/O$_2$ fuel cells. Using a simple algorithm based on 3D numerical Fourier transformation, we have quantitatively simulated previously published small-angle scattering data of hydrated Nafion. The characteristic “ionomer peak” arises from long, parallel but otherwise randomly packed water channels surrounded by the partially hydrophilic sidebranches, forming inverted-micelle cylinders. The channels are stabilized by the considerable stiffness of the Nafion backbones, detected by $^{13}$C and $^{1}$H NMR. An upper limit of 300 nm to the persistence length of the water channels has been estimated from $^{2}$H NMR of $^{2}$H$_2$O in the channels. At 20 vol% water, the water channels have diameters between 1.8 and 3.5 nm, with a 2.4-nm average. The hydration-induced changes in small-angle scattering patterns and in the surface-to-volume ratio have also been analyzed in quantitative detail. Nafion crystallites (~10 vol%), which form physical crosslinks crucial for the mechanical properties of Nafion films, are elongated and parallel to the water channels, with cross sections of (~5 nm)$^2$. Simulations for a dozen other models of Nafion, including Gierke’s cluster and the polymer-bundle model, do not match the scattering data. The water-channel model is the first without exceptions to all observations in quantitative detail. Nafion crystallites (~10 vol%), which form physical crosslinks crucial for the mechanical properties of Nafion films, are elongated and parallel to the water channels, with cross sections of (~5 nm)$^2$. Simulations for a dozen other models of Nafion, including Gierke’s cluster and the polymer-bundle model, do not match the scattering data.

9:12AM A4.00003 New Materials and Approaches for Solution-Processed Organic Solar Cells
YUE-LIN LOO, Princeton University — Organic solar cells have been proposed as low-cost and sustainable alternatives for power generation. To realize the low cost aspects of organic solar cells, conventional vacuum deposition technologies are to be replaced with solution processing. Our group has focused on the development of solution processable conductive polymers. Conductive polymers, like polyaniline, are generally doped with small-molecule acids. Though highly conductive, such materials are not processable. To overcome this intractability, polymer-acid dopants have replaced small-molecule acids. While the dopant increases the conductivity, the low solubility of the conductive polymer in organic solvents makes it difficult to cast a film of sufficient thickness. By introducing an additional polymer that solvates the dopant, we were able to cast films of the organic solar cell. We have investigated the efficiency of these materials as a function of the dopant and the solvent.

9:48AM A4.00004 Charge Transport and Storage within Radical Redox Polymers as Electroactive Materials in Energy Devices
HIROYUKI NISHIDE, Waseda University — No abstract available.

10:24AM A4.00005 Polymers as active components in harnessing solar energy
JAYANT KUMAR, University of Massachusetts, Lowell — In the last couple of decades molecular and polymeric photovoltaic cells have attracted considerable attention as a possible low cost alternative to conventional semiconductor solar cells. While considerable advances in improving device efficiencies have been made, significant challenges in developing efficient, reliable and low cost solar cells using polymers as an active component remain. Some of these advances and challenges as well as on-going efforts to mass manufacture solar cell modules will be discussed.

Monday, March 16, 2009 8:00AM - 11:00AM —
Session A18 DPOLY: Bulk Block Copolymers

8:00AM A18.00001 Order-order transition among lamellae, Fddd, and gyroid in diblock copolymer melts
MIKIHIITO TAKENAKA, MYUNG IM KIM, TSUTOMU WAKADA, SATOSHI AKASAKA, SHOTARO NISHITSUJI, KENJI SAIJO, HIROKAZU HASEGAWA, Kyoto University, KAZUKI ITO, Riken, KYOTO TEAM, RIKEN TEAM — We firstly found a Disorder-Gyroid-Lamellae transition behavior found poly(styrene-isoprene) (SI) diblock copolymer melts in previous study. In this study, we will present the dynamics of order-order transition (OOT) among lamellae, Fddd, and gyroid. We investigated the dynamics of OOT by using time-resolved small angle X-ray scattering with Synchrotron radiation X-ray source. We found that Fddd structure was formed as a metastable structure during the OOT from lamellae to gyroid induced by temperature jump.

8:12AM A18.00002 Determination of Fddd phase boundary in polystyrene-block-polysoprene diblock copolymer
MIKIHIITO TAKENAKA, MYUNG IM KIM, SATOSHI AKASAKA, TSUTOMU WAKADA, MIKIHIITO TAKENAKA, HIROKAZU HASEGAWA, Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University — We previously reported the discovery of a novel bicontinuous microdomain structure with Fddd symmetry in polystyrene-block-polysoprene (SI) diblock copolymer. In this study, we investigated the phase behavior of eight SI diblock copolymer samples having slightly different compositions (0.627 ≤ f_{PI} ≤ 0.653) by SAXS and TEM to determine the phase boundary of the Fddd structure in the phase diagram of SI. The SI having the lowest $f_{PI}$ (0.627) showed only disorder-lamella (L) transition but no order-order transition. The SI having the largest $f_{PI}$ (0.653) showed disorder-gyroid (G)-L transition with decreasing temperature, but did not show Fddd phase. The other six SI samples having $f_{PI}$ values between these two exhibited disorder-G-Fddd-L transition with decreasing temperature. Consequently, we could determine the compositional region where Fddd phase is thermally stable, which is in good agreement with that predicted by SCFT.
8:24AM A18.00003 Stabilization of Bicontinuous Phases in Diblock Copolymer Systems, FERNANDO ESCOBEDO, FRANCISCO MARTINEZ-VERACOECHEA, Cornell University — We used a coarse-grained description of the copolymer chains (i.e., dissipative particle dynamics fluid), together with continuum-space Monte Carlo and Molecular Dynamics methods, to study systems of diblock copolymers melts that have been “filled” with selective additives (i.e., homopolymer, and nanoparticles). Approximate phase boundaries were found via free-energy calculations. We focus on the stabilization of bicontinuous phases and the strikingly different phase behavior observed when the nature of the selective filler is changed. Our results elucidate the origins of the packing frustration that limits the viability of the gyroid, double-diamond, and plumbmer’s nightmare phases and provide insights for future experiments. Attention also focused on directly determining the areas of phase diagram where macro- phase separation occurs. We compare the particle-based simulation results with the results obtained by means of self-consistent field theory calculations.

8:36AM A18.00004 Structure-Properties Relationship in Proton Conductive Sulfonated Polystyrene-Poly(ethylene-co-methyl methacrylate) Block Copolymers, LAURENT RUBATAT, CHAOXU LI, HERVE DIETSCHE, University of Fribourg, Switzerland, ANTTI NYKAINEN, JANNE RUOKOLAINE, Helsinki University of Technology, Finland, RAFFAELE MEZZENGA, University of Fribourg, Switzerland — We report on the dependence of proton conductivity on the morphologies of sulfonated polystyrene-poly(methyl methacrylate) (sPS-P(MMA)) diblock copolymers. Three diblock copolymers of varying molecular weight and block volume fraction were studied, for each one several sulfonation degrees of the PS block were considered. The investigation of the morphologies of the self-assembled sPS-P(MMA) diblocks was carried out by means of small angle neutron scattering and transmission electron microscopy. Depending on molecular weight and sulfonation degrees, isotropic phase (ISO), lamellar phase (LAM), cylindrical hexagonal phase (HEX) and hexagonally perforated lamellae (HPL) were observed. Proton conductivity, normalized by the volume fraction of the conductive domains (formed by PS, sPS and water), was shown to rise monotonically with the following sequence of morphologies: ISO to HEX to HPL to LAM.

8:48AM A18.00005 Morphology of Sulfonated Styrenic Pentablock Copolymer Solutions and Membranes, ARUN KOTA, KAREN WINEY, Department of Materials Science and Engineering, University of Pennsylvania — We report a systematic investigation of the morphology of sulfonated styrenic pentablock copolymer solutions and membranes obtained from Kraton Polymers LLC. The polymer studied was poly(t-butyl-styrene)-b-(ethylene-r-butylene)-b-(styrene-r-styrene sulfonate)-b-(ethylene-r-butylene)-b-(t-butyl-styrene). Small angle x-ray scattering (SAXS) revealed that the solutions exhibited micellar morphologies. The solution SAXS data was modeled using the Kinning-Thomas model to obtain radius of the micelle core, the radius of closest approach between two micelles and the volume fraction of micelles. The membranes exhibited anisotropic morphologies with different d-spacings in-plane and through-plane. A good linear correlation was observed between the radius of closest approach between two micelles in the solutions and the d-spacings in the membranes. Efforts are underway to characterize the type of morphology in the membranes using electron microscopy and correlate them to the transport properties.

9:00AM A18.00006 Thermodynamic Behavior of Poly(styrene-b-styrene sulfonate) Block Copolymers With Varying Counterions, KEVIN CAVICCHI, The University of Akron, KEVIN POLLACK, Carleton College — A series of poly(styrene-b-styrene sulfonate) (PS-b-PSS) block copolymers have been prepared by RAFT polymerization. The counterions in the PSS block have been varied by neutralizing the sulfonate groups with alkyl amines or quaternary ammonium ions. The choice of counterion has a strong effect on the lipophilicity of the PSS block. This presentation will focus on the resulting morphology and bulk thermodynamic behavior of these polymers as a function of the PSS counterion. The use of these materials for preparing ion-exchange membranes will be discussed.

9:12AM A18.00007 Salt Doping in PEO Containing Block Copolymers: Counterion and Concentration Effects, WEN-SHUE YOUNG, THOMAS EPPS, University of Delaware — Salt-doped poly(ethylene oxide)-based block copolymers are promising candidates for lithium battery polymer electrolytes, which require high ionic conductivities and adequate mechanical integrity. We studied the phase behavior of poly(styrene-b-ethylene oxide) block copolymers doped with various lithium salts over a range of [EO]:[Li] ratios. Small-angle X-ray scattering, transmission electron microscopy, and differential scanning calorimetry experiments were used to characterize the phase behavior of our samples. Specimens were prepared in an argon atmosphere and rigorously dried to reduce the effects of moisture uptake on phase behavior. We found that we can tune the copolymer microstructure by varying the lithium counterion as well as the salt doping ratio. Using strong segregation theory, we estimated an effective interaction parameter for the salt-doped copolymers, which varies linearly with salt concentration, where the slope is influenced by the nature of the counterion.

9:24AM A18.00008 Ion transport through block copolymer electrolytes, SCOTT MULLIN, ASHOUTOSH PANDAY, NITASH BALSAUR, UC Berkeley — Poly(styrene-b-ethylene oxide) (PSSP) is a candidate material for electrolytes for rechargeable lithium metal batteries. The PS phase suppresses lithium dendrite growth on the anode during recharge, and the PEO phase solvates lithium bis(trifluoromethane)sulfonimide (LiTFSI) salt to form conducting pathways. Complete electrochemical characterization of PEO/LiTFSI mixtures requires measurement of conductivity, salt diffusion coefficient, and lithium ion transference number. The present study covers PEO/LiTFSI mixtures with different LiTFSI concentrations. A good linear correlation was observed between the radius of closest approach between two micelles in the solutions and the d-spacings in the membranes. Efforts are underway to characterize the type of morphology in the membranes using electron microscopy and correlate them to the transport properties.

9:36AM A18.00009 Morphology of Novel Semicrystalline Ethylene-α-Olefin Block Copolymers, SHENG LI, RICHARD REGISTER, Princeton University, BRIAN LANDES, Dow Chemical Company — In semicrystalline block copolymers, the solid-state structure can be set either by block incompatibility or by crystallization of one or more blocks. Depending on the block interaction strength, a wide array of solid-state morphologies may be observed, ranging from spherulitic to confined crystallization within preexisting microphase-separated domains. Dow Chemical has recently developed a novel chain shuffling polymerization process to produce olefin block copolymers with alternating amorphous and semicrystalline chain segments, where each block exhibits the most-probable distribution. We examined the melt and solid-state morphologies of these novel olefin block copolymers, having a high octene content in the amorphous block, using two-dimensional synchrotron small-angle and wide-angle x-ray scattering on specimens oriented by channel die compression. Multiblock and diblock copolymers with near-symmetric compositions showed well-ordered lamellar structures at room temperature with long periods exceeding 100 nm, with little dependence on thermal history, indicating the presence of a mesophase-separated melt which templates crystallization.

9:48AM A18.00101 Self-assembly of crystalline bioinspired block copolymers, A.M. ROSALES, H.K. MURNEK, Dept. of Chemical Engineering, University of California - Berkeley, R.N. ZUCKERMAN, Molecular Foundry, Lawrence Berkeley National Laboratory, R.A. SEGALMAN, Dept. of Chemical Engineering, University of California - Berkeley — Polypeptoids are sequence-specific biologically inspired polymers based on N-substituted glycines for which monodisperse, polymeric molecular weights can be achieved. Sequence control allows for a degree of tunability in both the self-assembly and thermal properties not available in classical polymer systems. We demonstrate that a series of homopolypeptoids are thermally stable to 300°C and are crystalline with melting transitions ranging from 150°C to 250°C. The introduction of defects at precise locations in the polymer sequence (as a side chain substitution) allows crystallization and hence the melting temperature to be suppressed. Symmetric block copolymers with two crystalline polypeptoid blocks exhibit co-crystallization of the two blocks but distinct melting behaviors, indicating a disordered melt. If samples are carefully prepared to allow for microparticle separation, block copolymer lamellae with long range order are formed with an order-disorder transition temperature well below the melting transition temperature of the polymer.
10:00AM A18.00011 Crystallization, Crystal Orientation and Morphology of Poly(ethylene oxide) under 1D Defect-Free Nanoscale Confinement , MING-SIAO HSIAO, The University of Akron, JOSEPH X. ZHENG, RYAN M. VAN HORN, RODERIC P. QUIRK, EDWIN L. THOMAS, MIT, BERNARD LOTZ, Institute Charles Sadron, STEPHEN Z. D. CHENG — One-dimensional (1-D) defect-free nanoscale confinement is created by growing single crystals of PS-b-PEO block copolymers in dilute solution. Those defect-free, 1-D confined lamellae having different PEO layer thicknesses in PS-b-PEO lamellar single crystals (or crystal mats) were used to study the polymer recrystallization and crystal orientation evolution as a function of recrystallization temperature ($T_{rx}$) because the $T^P$ in the PS-b-PEO single crystal. The results are summarized as follows. First, by the combination of electron diffraction and known PEO crystallography, the crystallization of PEO only takes place at $T_{rx} < -5\degree C$. Meanwhile a unique tilted PEO orientation is formed at $T_{rx} > -5\degree C$ after self-seeding. The origin of the formation of tilted chains in the PEO crystal will be addressed. Second, from the analysis of 2D WAXD patterns of crystal mats, it is shown that the change in PEO c-axis orientation from homeotropic to homeotropic at higher $T_{rx}$ transitions sharply, within 1\degree C. The mechanism inducing this dramatic change in crystal orientation will be investigated in detail.

10:12AM A18.00012 Gradient Architecture as Means of Phase Diagram Manipulation in Copolymers: Accessing Both LCOT and UCOT in High Molecular Weight Styrene/n-Butyl Acrylate Systems , MICHELLE MOK, WESLEY BURGHARDT, Northwestern University, CHRISTOPHER ELLISON, University of Texas at Austin, JOHN TORKELSON, Northwestern University — Traditionally, phase transitions of block copolymers could only be tuned through molecular weight and relative block length. Here, we introduce comonomer sequence design through gradient compositions as a means of further manipulating phase diagram boundaries. In such gradient copolymers, the reduced repulsion between chain segments allows access to phase transitions even at high molecular weights (MW). Rheological and x-ray scattering studies were performed to study the impact of comonomer sequence on phase behavior in styrene/n-butyl acrylate (S/nBA) systems. In S/nBA block copolymers, only upper critical ordering behavior was observed. In contrast, by using a gradient architecture of higher MW we observed both upper and lower ordering transitions similar to those seen in very weakly segregating S/n-butyl methacrylate block copolymers, where such dual ordering transitions were first detected by Russell et al. This is the first study to access a miscibility gap in gradient copolymers. Access to such behavior is very rare in blends and block copolymers, limited to low MW and/or very weakly segregating systems.

10:24AM A18.00013 Effects of polydispersity on the order-disorder transition of diblock copolymer melts , TOM BEARDSLEY, MARK MATSEN, University of Reading — The effect of polydispersity on an AB diblock copolymer melt is investigated using lattice based Monte Carlo simulations with parallel tempering (PT) techniques. We consider melts where the B blocks are monodisperse and the A blocks are polydispers with a Schultz-Zimm distribution. Expanding our previous work on polydisperse melts of symmetric composition, we now construct a polydisperse phase diagram, investigating the size of the domains and locations of the order-disorder (ODT) and order-order (OOT) transitions. The PT method has yielded a number of benefits over single-processor temperature scans, including: simulating a number of temperatures simultaneously, annealing out defects in the configurations more readily and capturing the distinctive spike in the heat capacity that occurs at the ODT, allowing the location of the transition to be determined more accurately than in previous studies. The results are compared to those of experiment and to the predictions of self-consistent field theory (SCFT).

10:36AM A18.00014 Dynamics of Disordered PI-PtBS Diblock Copolymer , HIROSHI WATANABE, Kyoto University — Viscoelastic ($G''$) and dielectric ($\varepsilon''$) data were examined for a LCST-type diblock copolymer composed of polyisoprene (PI; $M = 53K$) and poly(p-tert- butyl styrene) (PtBS; $M = 42K$) blocks disordered at $T \leq 120\degree C$. Only PI had the type-A dipole parallel along the chain backbone. Thus, the $G''$ data reflected the global motion of the PI block, while the $G''$ data detected the motion of the copolymer chain as a whole. Comparison of these data indicated that the PI block relaxed much faster than the PtBS block at low $T$ and the dynamic heterogeneity due to PtBS was effectively quenched to give a frictional nonuniformity for the PI block relaxation. The $G''$ data were thermo-rheologically complex at low $T$, partly due to this nonuniformity. However, the block connectivity could also lead to the complexity. For testing this effect, the $\varepsilon''$ data were reduced at the iso- frictional state defined with respect to bulk PI. In this state, the $G''$ data of the copolymer at low and high $T$, respectively, were close to the data for the star-branched and linear bulk PI. Thus, the PI block appeared to be effectively tethered in space at low $T$ thereby behaving similarly to the star arm while the PI block tended to move cooperatively with the PtBS block at high $T$ to behave similarly to the linear PI, which led to the complexity of the $\varepsilon''$ data. The PtBS block also exhibited the complexity (noted from the $G''$ data), which was well correlated with the complexity of the PI block.

10:48AM A18.00015 Morphology of Renewable Polylactide / Soybean Oil Blends Compatibilized by Block Copolymers , MEGAN ROBERTSON, KWANHO CHANG, MARC HILLMYER, University of Minnesota-Twin Cities — Renewable composites derived from polylactide and soybean oil (soy) were prepared by melt blending. The blend morphology was tuned with the addition of poly(isoprene-b-lactide) block copolymers. Due to the extreme differences in the viscosities of soy and polylactide, a critical block copolymer block ratio was found to induce a phase inversion in which the morphology changed from soy droplets in a polylactide matrix to polylactide droplets in a soy matrix, even though soy was the minority component. This transition was not only due to the thermodynamic interactions between the block copolymer and the two immiscible phases, but also was a result of shear forces acting on the mixture during melt blending. The droplet size of the soy droplets in the polylactide matrix was also highly dependent on the block copolymer composition. In binary polylactide/soy blends there was a limiting concentration of soy which could be incorporated into the polylactide matrix (5 percent of the total blend weight) due to the mismatch in viscosities resulting in the loss of soy during mixing. The addition of block copolymer with an appropriate block ratio allowed full incorporation of soy up to 20 percent of the total blend weight.

1 We acknowledge the EPSRC (EP/E010342/1) for financial support.

10:36AM A18.00014 Dynamics of Disordered PI-PtBS Diblock Copolymer , HIROSHI WATANABE, Kyoto University — Viscoelastic ($G''$) and dielectric ($\varepsilon''$) data were examined for a LCST-type diblock copolymer composed of polyisoprene (PI; $M = 53K$) and poly(p-tert- butyl styrene) (PtBS; $M = 42K$) blocks disordered at $T \leq 120\degree C$. Only PI had the type-A dipole parallel along the chain backbone. Thus, the $G''$ data reflected the global motion of the PI block, while the $G''$ data detected the motion of the copolymer chain as a whole. Comparison of these data indicated that the PI block relaxed much faster than the PtBS block at low $T$ and the dynamic heterogeneity due to PtBS was effectively quenched to give a frictional nonuniformity for the PI block relaxation. The $G''$ data were thermo-rheologically complex at low $T$, partly due to this nonuniformity. However, the block connectivity could also lead to the complexity. For testing this effect, the $\varepsilon''$ data were reduced at the iso- frictional state defined with respect to bulk PI. In this state, the $G''$ data of the copolymer at low and high $T$, respectively, were close to the data for the star-branched and linear bulk PI. Thus, the PI block appeared to be effectively tethered in space at low $T$ thereby behaving similarly to the star arm while the PI block tended to move cooperatively with the PtBS block at high $T$ to behave similarly to the linear PI, which led to the complexity of the $\varepsilon''$ data. The PtBS block also exhibited the complexity (noted from the $G''$ data), which was well correlated with the complexity of the PI block.

10:48AM A18.00015 Morphology of Renewable Polylactide / Soybean Oil Blends Compatibilized by Block Copolymers , MEGAN ROBERTSON, KWANHO CHANG, MARC HILLMYER, University of Minnesota-Twin Cities — Renewable composites derived from polylactide and soybean oil (soy) were prepared by melt blending. The blend morphology was tuned with the addition of poly(isoprene-b-lactide) block copolymers. Due to the extreme differences in the viscosities of soy and polylactide, a critical block copolymer block ratio was found to induce a phase inversion in which the morphology changed from soy droplets in a polylactide matrix to polylactide droplets in a soy matrix, even though soy was the minority component. This transition was not only due to the thermodynamic interactions between the block copolymer and the two immiscible phases, but also was a result of shear forces acting on the mixture during melt blending. The droplet size of the soy droplets in the polylactide matrix was also highly dependent on the block copolymer composition. In binary polylactide/soy blends there was a limiting concentration of soy which could be incorporated into the polylactide matrix (5 percent of the total blend weight) due to the mismatch in viscosities resulting in the loss of soy during mixing. The addition of block copolymer with an appropriate block ratio allowed full incorporation of soy up to 20 percent of the total blend weight.

1 Funding provided by Toyota Motor Inc.
8:12AM A19.00002 Theoretical analysis of dispersing of aggregated nanorods in shear flow in presence of AC electric or magnetic fields, VICTOR PRYAMITSYN, VENKAT GANESAN, The University of Texas at Austin — Efficient dispersion of nanotubes in polymeric matrices is a critical problem confronting the development of modern polymer nanocomposites. The nanotube-nanotube interactions usually promote aggregation, which also depends on factors such as the chemical makeup of the polymer matrix and the size of nanotubes. High intensity mechanical mixing such as shear pulverization are commonly used for dispersion of nanotubes. The main disadvantage of such processes is the degradation of polymer matrix, which may downgrade the final properties of PNC’s. In this work, we theoretically explore a novel strategy to reduce the shear stresses required for dispersion of rodlike fillers. Explicitly, we found that simultaneous applications shear flow and AC electric field oriented at an angle to each other may cause rotational instabilities of the rods suspension and lead to the dispersion of the rods. We demonstrate this idea through Brownian dynamics simulations of aggregating nanorods and a complementary theoretical analysis using a 2D Smoluchowski equation. Our results suggest that an optimal dispersion may be achieved at a shear-E field orientation of $\beta = -45^\circ$ with an optimal amplitude of AC electric field which is proportional to the rotation Peclet number of nanorods suspension.

8:24AM A19.00003 Effective Interactions, Structure and Phase Behavior of Polymer Nanocomposites with Nonspherical Fillers, LISA M. HALL, KENNETH S. SCHWEIZER, University of Illinois at Urbana-Champaign — The Polymer Reference Interaction Site Model is applied to study polymer-mediated inter-nanoparticle interactions, fluid structure, and miscibility of nonspherical filler particles in a melt of adsorbing freely-jointed chains. The behavior of hard rod, disk, and cube-like nanoparticles are compared. The depletion contact aggregation, dispersed, and polymer bridging mediated nanoparticle network states of organization are sensitive to filler shape. A detailed study of thin rod fillers, including the rod-rodd potential of mean force and second virial coefficient, $B_2$, as a function of polymer-rod and rod-rod attraction strengths, has also been performed. A primary goal is to identify design rules for dispersing nanotubes in polymer melts. Shortening the spatial range of rod-rod attraction compared to polymer-rod attraction increases miscibility. The transition from positive to negative $B_2$ at low polymer-rod interfacial attraction (entropic depletion) occurs more readily (at higher attraction strength) as rod-rod attraction is increased. However, the transition to negative $B_2$ at high polymer-rod attraction strength, driven by polymer-induced enthalpic bridging of rods, is relatively invariant to inter-rod attraction strength. Increasing rod length reduces the stabilizing consequences of polymer adsorption and the attendant steric repulsion.

8:36AM A19.00004 Polymer-tethered nanoparticle “shape amphiphiles”: A new class of macromolecular building block for self-assembly, SHARON GLOTZTER, University of Michigan — Fabricating complex ordered structures from nanoparticles requires controlling nanoparticle interactions for self-assembly over multiple length scales. Here we exploit both building block shape and interaction anisotropy for self-assembly, and explore the use of polymer “tails” attached to nanoparticle “head groups” to create a new kind of amphiphile that self-assembles into structures like those seen in surfactant and block copolymer systems, but with important differences arising from nanoparticle shape, and tethered nanoparticle geometry and topology. We investigate the impact of nanoparticle size polydispersity and show that it can both help hinder formation of certain complex phases. Using simulation, we investigate tethered spheres, rods, cubes, triangles, and other shapes, and provide design rules for the predicted self-assembly of a range of chiral and achiral structures, including helical scrolls, gyroid, square arrays, and ionic crystal-like structures.

9:12AM A19.00005 Control of the Spatial Distribution of Nanoparticles in Fluorescent Polymer Nanocomposites, CHELSEA CHEN, PETER GREEN, University of Michigan, Ann Arbor — In a brush-coated nanoparticle (NP) / polymer nanocomposite system, the spatial distribution of the NPs is largely determined by the entropic and enthalpic interactions between the brush and polymer host chains. We examined the miscibility between polystyrene (PS) homopolymer chains and a fluorescent polymer poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and found that in thin films, low molecular weight (MW) PS and MEH-PPV are miscible, whereas high MW mixtures exhibit phase separation. Consequences of this behavior were examined with regard to the effect on the morphology of nanocomposite thin films composed of MEH-PPV and thiolated polystyrene grafted Au nanoparticles of varying sizes. We were able to achieve complete dispersion, as well as interfacial segregation, of the Au-PS nanoparticles within MEH-PPV hosts. Through control of the morphology, we were able to “tune” the optical properties of the MEH-PPV/Au-PS nanocomposites.

1 Supported by DOE#DE-FG02-07ER46412 and NSF#DMR 9871177.

9:24AM A19.00006 Importance of Chain Connectivity in the Formation of Non-covalent Interactions between Polymers and Single-Walled Carbon Nanotubes, DIAS LINTON, BRAD C. MILLER, HUIMIN LI, CHARLES FEIGERLE, Department of Chemistry, University of Tennessee, Knoxville, TN 37996, BOBBY G. SUMPTER, Oak Ridge National Laboratory, Oak Ridge, TN 37831, MARK D. DADMUN, Department of Chemistry, University of Tennessee, Knoxville, TN 37996 and Oak Ridge National Laboratory, Oak Ridge, TN 37831 — Our work is focused on understanding and utilizing non-covalent electron donor-acceptor (EDA) interactions between polymers and SWNT to optimize interfacial adhesion and homogeneity of nanocomposites without modifying the SWNT native surface. Nanocomposites with polymer bound electron donating 2-(dimethylamino)ethyl methacrylate or electron accepting acrylonitrile and cyanostyrene moieties leads to improved SWNT dispersion if the SWNT to optimize interfacial adhesion and homogeneity of nanocomposites without modifying the SWNT native surface. Nanocomposites with polymer bound electron donating 2-(dimethylamino)ethyl methacrylate or electron accepting acrylonitrile and cyanostyrene moieties leads to improved SWNT dispersion if the interacting functional group is a minor component of a copolymer matrix. Correlation of experimental (Raman mapping, Raman D* band peak shifts, and optical microscopy) and computational results indicates that chain connectivity is critical in controlling the accessibility of the functional groups to form EDA interactions. Thus, controlling the amount of e− donating or withdrawing moieties throughout the polymer chain will direct the extent of EDA interaction, which enables tuning the SWNT dispersion.

9:36AM A19.00007 The Structure of Amphiphilic Polymers Interacting with Carbon Nanotubes, YACHIN COHEN, MEIRAV GRANITE, Technion, Israel, WIM PYCKHOUT-HINTZEN, AUREL RADULESCU, Fz. Juelich, Germany — Dispersion of single-walled carbon nanotubes, necessary for their beneficial utilization, is often based on amphiphilic copolymers. We have successfully utilized the following systems: an alternating copolymer of styrene and sodium maleate, exhibiting alternating hydrophobic and hydrophilic groups, amphiphilic block copolymers such as Pluronic F108 and a synthetic short polypeptide (FFDD)$_n$, containing alternating hydrophobic blocks of two phenylalanine (FF) and hydrophilic block of two aspartic acid (DD). Cryo-transmission electron microscopy images reveal isolated, very small bundles of carbon nanotubes, with diameters range from 1 to 5 nm and approximately 500 nm length. Small-angle neutron scattering experiments were conducted at different D$_2$O/H$_2$O content of the dispersing medium. The scattering patterns suggest a complex entity with an heterogeneous structure. For the alternating copolymer, loose adsorption of polymer coils is indicated, contrary to published ideas on “polymer wrapping” of nanotubes. For the Pluronic block copolymers, the data suggest that even below the critical micellization temperature there is a dense coating on the nanotube surface and the hydrophilic blocks are highly extended. The polypeptide also forms a dense coating with an apparently “spongy” structure.
10:00AM A19.00009 Effects of nanoparticles on chain dynamics and glass transition in athermal polymer nanocomposites1. HYUN JOON OH, PETER GREEN, University of Michigan, Ann Arbor — Chain relaxation dynamics and the glass transition of mixtures of polystyrene (PS) homopolymer with PS-grafted gold nanoparticles were examined using broadband dielectric spectroscopy, differential scanning calorimetry and capacitive scanning dilatometry. Through changes in the nanoparticle core size, D, grafting density, σ, degree of polymerization of grafted chains, N, and the nanoparticle concentration, φ, both the chain relaxation time, τ, and the T_g could be induced to undergo significant changes, increases or decreases, in magnitude. These results will be discussed in light of dynamics in other polymer/nanoparticle systems. In addition, the role of particle size and the role of the melt/brush interfacial interactions on the dynamics will be discussed.

1Work supported by the US DOE (DE-FG02-07ER46412) and by the NSF (DMR-0601890).

10:12AM A19.00010 Dynamics in Nanoparticle Liquids. PETER MIRAU, AFRL/RXBN, Air Force Research Lab, BioNano Branch, Wright-Patterson AFB, OH 45433, MICHAEL JESPERSEN, RICHARD VAIA, AFRL/RXBN, ROBERT RODRIGUEZ, EMMANUEL GIANNELIS, Materials Science & Engineering, Cornell University, Ithaca, NY 14853 — Nanoscale Ionic Materials (NIMS) are organic-inorganic hybrids in which a nanometer-sized core is functionalized with a covalently attached corona and an ionically tethered canopy. NIMS can be engineered to be liquids at ambient temperature in the absence of solvent and are of interest for a variety of applications. We have used NMR relaxation and pulse-field gradient NMR to measure the dynamics of NIMS made from a 20 nm silica core modified with propyl sulfonic acid groups and amino-terminated ethylene oxide/proplylene oxide block copolymers. Carbon NMR studies show that the block copolymer canopy is quite mobile both in the bulk and the nanoparticle liquid. The carbon spin-lattice relaxation times, as a function of temperature and nanoparticle size, are determined. The correlation times for reorientation of the block copolymer are the same as the diffusion constant for the nematic component of the copolymer. These data suggest that the liquid-like behavior in NIMS is due to rapid exchange of the block copolymer canopy between the ionically modified silica nanoparticles.

10:24AM A19.00011 Hierarchically Structured Block Copolymer \ Silicate Nanocomposites. ROSS BEHLING, ERIC COCHRAN, Iowa State University — In this contribution we functionalized MMT with a bromine terminated alkylamine and subsequently polymerized polystyrene-b-poly(tert-butyl acrylate) via graft-from atom transfer radical polymerization. Hierarchical assembly of these composites was facilitated through targeted graft density, polymer block size, and MMT intrinsic properties. The high graft density on the MMT surface results in confinement effects which force growing polymer chains into highly extended conformations. Block copolymer (BCP) brushes were chosen because they inherently offer an easily tunable method for producing self-assembled structures on the order of tens of nanometer. Montmorillonite (MMT) in its raw state is composed of negatively charged tactoid stacks 100-300 nm in diameter and 1-2 nm thick resulting in BCP/silicate nanocomposites particles arranged under shear into structures spanning several hundreds of nanometers. The equilibrium structures were influenced by the MMT platelet curvature and the BCP interaction parameter, χ. BCP nanocomposites were observed via transmission electron microscopy to display novel morphologies with multiple systems exhibiting interpenetrating networks reminiscent of “worm micelles”.

10:36AM A19.00012 Effect of Copolymer-Nanoclay Interactions on Interfacalization Kinetics1. LOAN VO, HARI S RETSOS, EMMANUEL GIANNELIS, Cornell University — We use X-ray diffraction to measure the melt intercalation kinetics of a series of surface-modified clay nanoparticles (nanolayer) with styrene-butadiene-rubber (SBR). Since SBR is a copolymer, both the styrene and the butadiene components interact with the nanoparticles contributing to the nanolayer miscibility and the intercalation kinetics. We are able to directly measure the butadiene-nanoclay interaction strength by using dielectric relaxation spectroscopy to probe the butadiene-nanoclay interfacial relaxation mode, and by varying the nanoclay surfactant and copolymer composition, we can indirectly measure the styrene-nanoclay interaction strength. We will present the spectroscopy results and discuss the relation to the intercalation kinetics.

1Michelin

10:48AM A19.00013 Polymer Nanocomposites Containing Carbon Nanotubes and Exfoliated Nanoplatelets1. HUNG-JUE SUE, DAZHI SUN, Texas A&M University, PROF. SUE’S TEAM — We report a simple and efficient method to disperse carbon nanoparticles (CNTs) into an epoxy matrix through exfoliated nanoplatelets. Pre-oxidized CNTs were first dispersed in the presence of exfoliated nanoplatelets in water, followed by re-dispersion in epoxy matrix. Both individual CNTs and nanoplatelets are exfoliated and well dispersed in epoxy, which is confirmed by high-resolution transmission electron microscopy. The possible mechanisms responsible for the CNT dispersion in polymers are proposed. The epoxy nanocomposites containing CNTs and nanoplatelets show exceptional mechanical properties: significant improvements in both modulus and strength over a wide range of nanoparticle and CNT concentrations and composition. The amount of CNT dispersion in our epoxy nanocomposites is also discussed.

1We thank Kaneka and Defense Logistic Agency (SP0103-02-D-0003) for their partial financial support of this research.

Monday, March 16, 2009 8:00AM - 10:24AM – Session A20 DPOLY: Spatially Confined Polymer Materials 321

8:00AM A20.00001 Field-Based Simulations of Confined Block Copolymers. GLENN FREDRICKSON, UC Santa Barbara — This presentation will discuss field-theoretic simulation methods that can be used to analyze the self-assembly behavior of thin block copolymer films, including films that are laterally confined on a flat substrate and curved films on a spherical manifold. Our studies of lateral confinement have revealed strategies for epitaxially templating microdomain patterns with long-range in-plane order and minimal defects (“graphoepitaxy”), and methods for diversifying the set of stable 2D lattice structures. On the sphere, we have found defective ground state block copolymer morphologies that are analogous to spherical crystalline packings in other contexts, e.g. the Thompson problem and viruses. The methods and findings have applications in block copolymer lithography and in dispersion technology of polymer-stabilized nanoparticles and colloids.
We gratefully acknowledge funding from the National Science Foundation (DMR 0606086, CBET-0609087) and Petroleum Research Fund (46204-AC7).
10:12 AM A20.00010 Newtonian drop deformation in a viscoelastic matrix under shear1, SHAHRIAR AFKHAMII, PENGTAO YUE, YURIKO RENARDY, Virginia Tech — When a Newtonian drop is sheared in a viscoelastic matrix, the direct numerical simulation produces a viscoelastic “wake” at the interface in the front and back of the drop. In the case of a drop reaching a stationary state, the stresses in the wake and the viscous shear balance out the interfacial tension force. When a viscoelastic drop is sheared in a Newtonian matrix, numerical simulations exhibit an overshoot in the transient evolution of drop deformation. Experimental observations also show that an overshoot can occur when a Newtonian drop is sheared in a viscoelastic matrix. However, these overshoots do not appear for 3D drop computations. In this work, we investigate how drop deformations in 3D do not display overshoots.

1 NSF-DM-0456086, NCSC TG-CTS060013N

Monday, March 16, 2009 11:15AM - 1:51PM – Session B4 DPOLY: Polymer Translocation 306/307

11:15AM B4.00001 Polymer Translocation: What Can We Learn From An Exactly Solvable One-Dimensional Model?1, GARY W. SLATER, University of Ottawa — The translocation of a polymer through a narrow hole or channel is generally not a quasi-static process (as we have shown using a detailed Molecular Dynamics simulation with explicit solvent). Nevertheless, numerous analytical models have relied on this approximation/assumption in order to make progress. A simple approach is then to describe the problem in terms of the translocation coordinate (e.g., the number of monomer on the trans side of the wall), which effectively makes it a one-dimensional problem with an external driving field and a entropy-related potential landscape. Our group has exploited this simple idea to its fullest using a lattice Monte-Carlo-like model that provides exact numerical results, even for extremely rare events. In this presentation, I will explain how this simplified model is built and how it can be modified to include a variety of additional effects such as polymer stiffness or the differences between the various monomer types in a biopolymer like DNA. I will review the main results obtained to date, focusing on the transitions between the low- and high- field regimes, and between the short- and long- polymer chain limits. Finally, I will examine the role of attractive interactions between the polymer and specific sites inside the channel.

1Supported by NSERC - Canada.

11:51AM B4.00002 DNA translocation through small channels and pores from molecular models. Hydrodynamic, electrostatic, and hybridization considerations, . JUAN DE PABLO, University of Wisconsin — The flow and translocation of long DNA molecules are of considerable applied and fundamental interest. Design of effective genomic devices requires control of molecular shape and positioning at the level of microns and nanometers, and understanding the manner in which DNA is packaged into small channels and cavities is of interest to biology and medicine. This presentation will present an overview of hierarchical models and computational approaches developed by our research group to investigate the effects of confinement, hydrodynamic interactions, and salt concentration, on the structure and properties of DNA, both at equilibrium and beyond equilibrium. The talk will include a discussion of coarse grain descriptions of the flow of DNA in microfluidic and nanofluidic channels over multiple length and time scales, and results of detailed, emerging models that are capable of describing melting and rehybridization at the single nucleotide level, as well as the packaging of DNA into viral capsids and small pores.

12:27PM B4.00003 Simulation studies of DNA translocation through a nanopore (†), ANIKET BHATTACHARYA, University of Central Florida — The experimental studies of voltage driven translocation of a single stranded DNA through a α-hemolysin pore, have stimulated a lot of activities as the phenomenon is rich in fundamental science involved and its prospective technical applications for detecting DNA/RNA sequences. While it is the attributes of heteropolymer translocation that are the key ingredients for prospective new sequencing methods, these experiments have generated stimulating theoretical and numerical studies directed toward a seemingly much simpler problem of homopolymer translocation through a nanopore. The earlier theoretical work of Muthukumar, Sung and Park, and by Kardar and his collaborator2 have been supplemented by more recent theoretical work by Dubbeldam et. al and Panja et. al3. During this talk I will show results from Langevin dynamics simulation carried out on a coarse-grained bead-spring model of DNA-polymer both for the unbiased and driven translocation4. During the first part of the talk, after a brief review of the current theories of DNA translocation, specifically mentioning the underlying assumptions, I will compare simulation results with those predicted by different theories. Particularly, I will show numerical results for the translocation exponent α defined as ⟨r⟩ ∼ Nα and the exponent for the s-coordinate β defined as ⟨s2n⟩(β) ∼ sβ, and discuss how the numerical values differ as one chooses slightly different pore width and geometry. In the second part of my talk I show how a model attractive nanopore can distinguish the sequence of a heteropolymer4 and discuss possibility of making a device based on this idea.

1 work done in collaboration with Kaifu Luo, Tapio Ala-Nissila, See-chen Yin, Andrey Milchev and Kurt Binder

1:03PM B4.00004 Anomalous dynamics of polymer translocation1, GERARD BARKEMA, University of Utrecht — We study the passage times of a translocating polymer of length N in three dimensions, while it passes through a narrow pore. We show that the behavior of the polymer stems from the polymer dynamics at the immediate vicinity of the pore — in particular, the memory effects in the polymer chain tension imbalance across the pore. We take as a reaction coordinate the number s of the monomer residing in the pore, in the case of unbiased translocation, these memory effects cause the mobility of s to be anomalous diffusion for times up to the Rouse time $T_R \sim N^{1+2\nu}$ or Zimm time $T_Z \sim N^{3\nu}$ without or with hydrodynamics, respectively. Here, $\nu$ is the Flory exponent. Beyond this time, the dynamics becomes ordinary diffusion. As a consequence, the pore blockade time scales with $T_T \sim N^{3+2\nu}$. If a force of sufficient strength is pulling on one end, the pore blockade time scales as $T_T \sim N^{2}$ in the absence of hydrodynamics. If a voltage is applied across the pore, which drives the charged polymer, the pore blockade time scales as $T_T \sim N^{1+2\nu}(1+\nu)$ without, and $T_T \sim N^{3\nu/(1+\nu)}$ with hydrodynamics. In these cases, the pore blockade time decreases inversely with force and field strength, respectively. Our theoretical framework is substantiated with high-precision computer simulations. We will show that memory effects similar to those governing translocation, also play a role in the dynamics of dense polymer solutions and polymer melts.

1 in collaboration with D. Panja
STM study of stereoselective oligomeric chains on cobalt oxide templates , DAEJIN EOM, HUI ZHOU, KWANG T. RIM, MICHAEL LEFENFELD, COLIN NUCKOLLS, GEORGE W. FLYNN, TONY F. HEINZ, Columbia University — Stereoselective oligomeric chains of cis-1,4-poly(2,3-dimethyl-1,3-butadiene) have been grown using the cobalt oxide surface as a template. The chains were formed by vacuum deposition of the monomer on an oxidized Co(0001) surface held at room temperature. The geometric structure of the 1-dimensional chains — Stereoselective oligomeric chains of cis-1,4-poly(2,3-dimethyl-1,3-butadiene) have been grown using the cobalt oxide surface as a template. The chains were formed by vacuum deposition of the monomer on an oxidized Co(0001) surface held at room temperature. The geometric structure of the 1-dimensional chains was controlled, which provides advantages in comparison to bare glass substrates. These include much reduced deposition time, a high degree of coverage, and the ability to accommodate both negatively and positively charged particles. Moreover, patch production yield is consistently 99 %. Rapid coating methods are polymerized by UV exposure after nanotube alignment to form the polymer matrix. X-ray scattering and optical spectroscopy are used to characterize the polymer films. The present system may have additional applications for polymer reinforcement using carbon nanotubes. For instance, are predicted to exhibit high flux and salt rejection through size exclusion of hydrated ions. Current fabrication techniques, however, are unable to realize the vertical assembly of narrow diameter SWNTs. Here, we direct the vertical alignment of SWNTs in thin films by using magnetic field aligned lyotropic surfactant mesophases as structure directing templates. The short alkyl tails of the surfactant impart negative diamagnetic anisotropy to worm-like micelles and lead to parallel alignment of the liquid crystalline (LC) director in an applied magnetic field. The nanotubes orient preferentially with their long axis parallel to the director field of the mesophase, thus promoting their vertical alignment in the system. The LC mesophase incorporates monomers that are polymerized by UV exposure after nanotube alignment to form the polymer matrix. X-ray scattering and optical spectroscopy are used to characterize the field-guided assembly process. The present system may have additional applications for polymer reinforcement using carbon nanotubes.
12:51PM B18.00007 Breath-figure-templated assembly of holey polymer films, VIVEK SHARMA, Hatsopoulos Microfluids Laboratory (HML), Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge MA 02139, MOHAN SRINIVASARAO, School of Polymer, Textile and Fiber Engineering, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta GA 30332.

— Breath figures formed on evaporating polymer solutions exposed to the blast of humid air involve growth and self-assembly of water drops that are non-coalescent. The hexagonally close packed, nearly monodisperse drops, eventually evaporate away, leaving a polymer film with ordered array of pores. We provide the first quantitative attempt at elucidating the mechanism of this breath-figure-templated assembly. The dynamics of drop nucleation, growth, noncoalescence and self-assembly are modeled by accounting for various transport and thermodynamic processes. The theoretical framework developed in this study allows one to rationalize and predict the structure and size of pores formed in different polymer-solvent systems under given airflow conditions. 1

1 Funded by NSF-DMR

1:03PM B18.00008 Gelation in Semiflexible Polymers, VENKAT PADMANABHAN, SANAT K. KUMAR, Columbia University — Discrete Molecular Dynamics/Collision Dynamics has been employed to study the formation of a physical gel by semi-flexible polymer chains. The formation of a geometrically connected network of bundles of chains is investigated as a function of temperature. As the temperature is lowered, a percolated homogeneous solution phase separates to form a non-percolated nematic fluid and upon further decrease in the temperature, it goes back to a percolated gel state. For longer temperatures, it is due to the dynamic arrest of chains, preventing them from completing the phase separation process. The cooling rate also plays an important role in deciding the final outcome. Quenching the system, to the final temperature, at a faster rate yields gelation while slower quenches result in phase separation.

1:15PM B18.00009 Highly Ordered Block Copolymer Templates for the Generation of Nanostructured Materials, E. HOJE GOWD, BHANU NANDAN, NADJA C. BIGALL, ALEXANDER EYCHMULLER, MANFRED STAMM, LEIBNIZ INSTITUTE OF POLYMER RESEARCH DRESDEN, HOHE STRASSE 6, 01069 DRESDEN, GERMANY TEAM, PHYSICAL CHEMISTRY, TU DRESDEN BERGSTRASSE 66B, 01062 DRESDEN, GERMANY TEAM — Among many different types of self-assembled materials, block copolymers have attracted immense interest for applications in nanotechnology. Block copolymer thin film can be used as a template for patterning of hard inorganic materials such as metal nanoparticles. In the present work, we demonstrate a new approach to fabricate highly ordered arrays of nanoscopic inorganic dots and wires using switchable block copolymer thin films. Various inorganic nanoparticles from a simple aqueous solution were directly deposited on the surface reconstructed block copolymer templates. The preferential interaction of the nanoparticles with one of the blocks is mainly responsible for the lateral distribution of the nanoparticles in addition to the capillary forces. Subsequent stabilization by UV-irradiation followed by pyrolysis in air at 450°C removes the polymer to produce highly ordered metallic nanostructures. This method is highly versatile as the procedure used here is simple, eco-friendly and provides facile approach to fabricate a broad range of nanoscaled architectures with tunable lateral spacing.

1:27PM B18.00010 Polymeric nanocomposite comprising size-controlled organic nanostructures via copolymer-directed self-assembly, DEQUAN XIAO1, KUNHUA LIN, Department of Chemistry, Sichuan University, Chengdu, 610064 China, QIANG FU, Department of Polymer Science and Engineering, Sichuan University, State Key Laboratory of Polymer Materials Engineering, Chengdu, 610065 China, QINJIAN YIN, Department of Chemistry, Sichuan University, Chengdu, 610064 China — Inspired by inorganic nanomaterials, low-dimensional organic nanostructures have emerged as a new field of nanomaterials with the presence of size-dependent physical properties. Here, we report a polymeric nanocomposite comprising size-controlled organic nanostructures, formed by copolymer-directed self-assembly. By TEM and SEM images, we found the near-spherical shapes of the zero-dimensional organic nanoparticles. A strongly broadened Raman shift band was probed, suggesting the presence of size-dependent quantum confinement effect. By proof-of-principle quantum chemical calculations, we further explain that the strong Raman broadening is caused by the heterogeneous size-distribution of the organic nanoparticles. The present polymeric nanocomposite opens a new route for exploring low-dimensional organic nanostructures with size-dependent physical properties.

1 current address: Department of Chemistry, Duke University, Durham, NC 27708

1:39PM B18.00011 Orientational Change of Microphase-Separated Domains of Block Copolymer Thin Films Placed on Ordered Nanoparticle Monolayers, KOOKHEON CHAR, TAEHEE KIM, Seoul National University — Orientation of microphase-separated domains of diblock copolymer (BCP) thin films deposited on ordered nanoparticle (NP) monolayers was investigated. Ordered NP monolayers were prepared on silicon substrates with the Langmuir-Blodgett deposition technique. Parallel orientation of anisotropic microdomains (cylinders and lamellae) of BCP thin films with respect to the substrate is preferred on bare silicon substrates due to the preferential enthalpic interaction with one of BCP blocks, while the perpendicular orientation is preferred on the lattice-like ordered NP monolayers due to the roughness induced from the NP monolayers which can exert elastic deformation on the parallel-oriented microdomains, suppressing the substrate-induced parallel orientation. The effects of NP size as well as BCP film thickness on the orientation of BCP domains were systematically studied. Subsequent stabilization by UV-irradiation followed by pyrolysis in air at 450°C removes the polymer to produce highly ordered metallic nanostructures. This method is highly versatile as the procedure used here is simple, eco-friendly and provides facile approach to fabricate a broad range of nanoscaled architectures with tunable lateral spacing.

1:51PM B18.00012 Directed self-assembly of block copolymers for resolution enhancement and pattern rectification, JOY CHENG, CHARLES RETTNER, DANIEL SANDERS, ALSHAKIM NELSON, HOA TRuong, HO-CHEOL KIM, WILLIAM HINSBERG, SELF-ASSEMBLY TEAM — Directed polymer self-assembly which combines lithographically defined substrates and self-assembled polymers has been considered as a potential candidate to extend conventional lithography techniques. Self-assembled block copolymer domains can multiply the spatial frequency and improve pattern quality of the underlying resist prepattern. Lamella-forming PS-b-PMMA is spin-cast on patterned substrate with the Langmuir-Blodgett deposition technique. The rectification of perpendicularly oriented BCP microdomains onto underlying NP lattices was analyzed with SEM for thin BCP films. We observe the rectification of the perpendicular BCP microdomains on NP lattices with a variation of NP size and BCP film thickness.

2:03PM B18.00013 Tetragonal Ordering in Block Copolymer-Homopolymer Blend Films Laterally Confined in a Square Well, SU-MI HUR, CARLOS GARCÍA-CERVERA, ED KRAMER, GLENN FREDRICKSON, UCSB — Self-consistent field theory (SCFT) simulations are presented for a melt blend of AB diblock copolymers and A homopolymers in a thin film confined to a square well. The work aims to guide self-assembly towards tetragonal ordering, which is a pattern of technological interest in block copolymer lithography. By using suitable A homopolymer additives, we have succeeded in achieving square lattices of cylinders not observed in the confined or bulk pure diblock system. A phase diagram is presented that shows the region of stability of the tetragonal phase as a function of chain length and volume fraction of the homopolymer additive, in addition to several other interesting phases that result from a competition between surface and bulk contributions to the free energy. Results are also presented on the effect of line edge roughness in the square confinement well on the achievement of robust and defect free tetragonal order.
Monday, March 16, 2009 11:15AM - 2:03PM –
Session B19 DPOLY: Focus Session: Polymers and Ionic Liquids

11:15AM B19.00001 Block Copolymers and Ionic Liquids: A New Class of Functional Nanocomposites1, TIMOTHY LODGE, University of Minnesota — Block copolymers provide a remarkably versatile platform for achieving desired nanostructures by self-assembly, with length scales varying from a few nanometers up to several hundred nanometers. Ionic liquids are an emerging class of solvents, with an appealing set of physical attributes. These include negligible vapor pressure, high chemical and thermal stability, tunable solvation properties, high ionic conductivity, and wide electrochemical windows. For various applications it will be necessary to solidify the ionic liquid into particular spatial arrangements, such as membranes or gels, or to partition the liquid into coexisting phases, such as microemulsions and micelles. One example includes formation of spherical, cylindrical, and vesicular micelles by poly(butadiene-b-ethylene oxide) and poly(styrene-b-methyethacrylate) in the common hydrophobic ionic liquids [BMI][PF6] and [EMI][TFSI]. This work has been extended to the formation of reversible micelle shuttles between ionic liquids and water, whereby entire micelles transfer from one phase to the other, reversibly, depending on temperature and solvent quality. Formation of ion gels has been achieved by self-assembly of poly(styrene-b-ethylene oxide-b-styrene) triblocks in ionic liquids, and by the thermoreversible system poly(N-isopropylacrylamide-b-ethylene oxide-b-N-isopropylacrylamide), using as little as 4% copolymer. Further, these gels have been shown to be remarkably effective as gate dielectrics in organic thin film transistors. The remarkably high capacitance of the ion gels (> 10 µF/cm²) supports a very high carrier density in an organic semiconductor such as poly(3-hexylthiophene), leading to milliamp currents for low applied voltages. Furthermore, the rapid mobility of the ions enables switching speeds approaching 10 kHz, orders of magnitude higher than achievable with other polymer-based dielectrics such as PEO/LiClO4. Finally, we have shown that ordered nanostructures of block copolymers plus ionic liquids show the characteristic self-assembly properties of strongly-segregated systems. Prospects for anisotropic ionic conductivity are also being explored.

1Supported by the National Science Foundation

11:51AM B19.00002 Phase Behavior of Block Copolymer Solutions in an Ionic Liquid, J.M. VIRGILI, M.L. HOARFROST, N.P. BALSARA, R.A. SEGALMAN, UC Berkeley — Incorporation of ionic liquids into block copolymers is of interest for applications such as high temperature fuel cell membranes. We investigate the lyotropic and thermotropic phase behavior of solutions of poly(styrene-b-2-vinyl pyridine) (SZVP) block copolymers in an ionic liquid consisting of imidazole and bis(trifluoromethane)sulfonamide (HTFSI). Using small angle X-ray scattering (SAXS) and static birefringence, we find that the ionic liquid behaves as a selective solvent, preferentially solvating the poly(2-vinyl pyridine) segment of the block copolymer. At moderate to high concentrations (> 40 wt%) of copolymer, we observe lyotropic phase transitions to lamellar and cylindrical (hcp) morphologies. At low concentrations of SZVP copolymer (< 30 wt%), we observe poorly ordered, microphase-separated structures, which do not resemble the face-centered cubic or body-centered cubic spherical micelles observed in block copolymer solutions in molecular solvents. We observe that the order-disorder transition temperature of the series of SZVP copolymers does not depend strongly on the concentration of the block copolymer solution in ionic liquid.

12:03PM B19.00003 Ordering of Triblock Copolymer Surfactants by Blending with a Room Temperature Ionic Liquid1, DANIEL MIRANDA, JAMES WATKINS, THOMAS RUSSELL, University of Massachusetts Amherst — Well-ordered block copolymer microdomains were obtained by blending Pluronic® PEO-PPO-PEO triblock copolymer surfactants with the room temperature ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate. The selective association of the ionic liquid with the PEO blocks increases the segregation strength by increasing the effective interaction parameter between the blocks. The neat copolymer is phase-mixed in the melt whereas the addition of ionic liquid to the copolymer results in phase segregation, forming well-ordered microdomains. The ionic liquid was confirmed to interact with the PEO blocks by a depression in the melting point of the blends with increasing ionic liquid concentration. Further, small angle x-ray scattering experiments show a decrease in the breadth of the first order peak, as well as the appearance of higher order peaks, with increasing ionic liquid concentration. These results confirm the formation of well-ordered microdomains.

1MRSEC, CHM

12:15PM B19.00004 Phase separation induced by polymer-ionic molecule complexation, ISSEI NAKAMURA, AN-CHANG SHI, McMaster University — The miscibility of polymers in ionic solutions has attracted long standing interest in polymer science. In particular, it has been demonstrated experimentally that phase separation can be driven by complexation of polymers and ionic molecules. Thermally reversible strong forces such as hydrogen bonding and electrostatic force are often employed to induce the complexation. In this study, we developed a self consistent field theory for polymers which are capable of binding small ionic molecules. Specifically, poly(vinyl alcohol) and borate ion in aqueous solution with sodium chloride are used as a model system. Binding isotherm, phase diagrams, as well as comparisons with experiments, will be presented. The theory provides a closed-loop region for an instability of the homogeneous phase in the phase diagram. Implications of our results to the sol-gel transition arising from the correlation between unoccupied and occupied ion-binding sites of polymers are discussed.

12:27PM B19.00005 Morphology and Ion Transport in Mixtures of Polymers and Ionic Liquid, JAE-HONG CHOI, Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6272, LIANG GWEE, YOSSEF A. ELABD, Department of Chemical and Biological Engineering, Drexel University, Philadelphia, PA 19104, KAREN I. WINEY, Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6272 — Mixtures of polymers and ionic liquid have been prepared using homopolymers, random copolymers, and block copolymers: poly(methyl methacrylate), poly(methyl methacrylate-ran-styrene), and poly(methyl methacrylate-b-styrene). The ionic liquid is 1-ethyl-3-methylimidizolium bis(trifluoromethylsulfonyl)imide. These mixtures are investigated using X-ray scattering and electron microscopy. Mixtures of the homopolymer and random copolymer with the ionic liquid are homogeneous and amorphous morphology with excess scattering as content of ionic liquid increases. The block copolymer and ionic liquid mixtures show ordered structures typical of block copolymers that vary with ionic liquid content. The morphologies of the copolymer-ionic liquid mixtures will be correlated with the conductivities.

12:39PM B19.00006 Dissolving Polymers in Ionic Liquids, DAVID HOAGLAND, JOHN HARNE, Univ. of Massachusetts Amherst — Dissolution and phase behavior of polymers in ionic liquids have been assessed by solution characterization techniques such as intrinsic viscosity and light scattering (static and dynamic). Elevated viscosity proved the greatest obstacle. As yet, whether principles standard to conventional polymer solutions apply to ionic liquid solutions is uncertain, especially for polymers such as polyelectrolytes and hydrophilic block copolymers that may specifically interact with ionic liquid ions or cations. For flexible polyelectrolytes (polymers releasing counterions into high dielectric solvents), characterization in ionic liquids suggests behaviors more typical of neutral polymer. Coil sizes and conformations are approximately the same as in aqueous buffer. Further, several globular proteins dissolve in a hydrophilic ionic liquid with conformations analogous to those in buffer. General principles of solubility, however, remain unclear, making predictions of which polymer dissolves in which ionic liquid difficult; several otherwise intractable polymers (e.g., cellulose, polyvinyl alcohol) dissolve and can be efficiently functionalized in ionic liquids.
12:51PM B19.00007 Polyester Spherulite Crystallization in Ionic Liquids, KATHY SINGFIELD, SHAWNA MITCHELL, Saint Mary’s University — A series of polyesters have been crystallized in ionic liquids. Spherulites of the polyesters have been grown isothermally from different ionic liquids after cooling the single phase polymer/ionic liquid system from above the polymer melting point temperature. To the authors’ best knowledge this is the first reported account of polyester spherulites grown from these non-traditional solvents. The combination of physical properties of the crystallizing system supports the un-restrained branching/splitting volume-filling growth in all radial directions of the suspended crystallizing entity. The morphology of the collected spherulites at various stages of their formation was examined using scanning electron microscopy (SEM). The SEM results provide a clear visual inspection of the early-stage growth forms and the branching/splitting patterns involved in their evolution to the final spherical form.

1:03PM B19.00008 Understanding Ion Transport in Polymerized Ionic Liquids using Dielectric Spectroscopy, U. HYEOK CHOI, Penn State University, HONG CHEN, Drexel University, WENJUAN LIU, Penn State University, YOSEF A. ELABD, Drexel University, RALPH H. COLBY, Penn State University — In order to deduce the mechanism of ion conduction in ion-containing polymers, not only the conductivity needs to be measured but also the number density and mobility of conducting ions must be determined using broadband dielectric spectroscopy, covering broad frequency and temperature ranges. To obtain a transference number of unity, one ionic charge is covalently bonded to the polymer so that only the counterions can contribute to ion conduction. In this study, imidazolium-containing monomer was synthesized and polymerized to make a cationic homopolymer with either tetrafluoroborate or bis(trifluoromethanesulfonyl)imide anionic counterions. These ions can associate into pairs and larger aggregates. The degree of ion pairing can be estimated from the temperature dependence of the dielectric constant and knowledge of the dipole moment of the ion pair, using the 1936 Onsager equation. Using the 1953 Macdonald model makes it possible to determine concentration and mobility of mobile counterions from analysis of electrode polarization in dielectric spectroscopy.

This material is based upon work supported in part by U.S. Army Research Office under grant number W911NF-07-1-0452 Ionic Liquids in Electro-Active Devices (ILEAD) MURI.

1:15PM B19.00009 Enhanced ionic conductivity of polyurethane ionomers by self-solvating cations, SHIH-WA WANG, RALPH COLBY. Pennsylvania State University — We study the effect of different cations on ionic conductivity and dielectric properties of polyurethane ionomeric single-ion conductors with para-phenyl diisocyanate and anionic diols (carboxylate or phosphonate) constituting the hard segments and poly(ethylene glycol) as the soft segment. Bulky cations such as tetra-alkyl ammonium can increase ionic conductivity compared to metallic cations like sodium because bulky cations have lower interaction energy with anions, allowing more dissociation from the anions. In order to increase the conductivity even more, ether oxygens, which are well-known to solvate cations, are incorporated in the alkyl tail of ammonium-type cations. By comparing cations like sodium because bulky cations have lower interaction energy with anions, allowing more dissociation from the anions. In order to increase the conductivity even more, ether oxygens, which are well-known to solvate cations, are incorporated in the alkyl tail of ammonium-type cations. By comparing cations like sodium because bulky cations have lower interaction energy with anions, allowing more dissociation from the anions.

1:27PM B19.00010 Weakening Ion Interactions in Ionomers using Ionic Liquid Counterions, GREGORY TUDRYN, RALPH H. COLBY, Penn State University — Anionic poly(ethylene oxide)-based ionomers are candidate materials for electro-active devices due to the ability of ether oxygens to solvate conducting cations. Conventional alkali metal cations in sulfonated PEO-ionomers are exchanged to ionic liquid counterions and electrical and mechanical properties are measured. Electrode polarization in dielectric spectroscopy is used to determine number density and mobility of conducting counterions. Conductivity and mobility increase with counterion size and exhibit Vogel temperature dependences, meaning counterion motion is coupled with polymer segmental motion. Conducting ion concentrations show Arrhenius temperature dependences, with activation energy reduced as counterion size increases. Oscillatory shear and SAXS suggest ions do not microphase separate, presumably due to ether oxygen solvation of cations. Ionomers with small counterions have higher plateau moduli than larger counterions, suggesting small counterions form more stable quadrupoles. Such studies allow fundamental design of ion conductors for actuators, as ionic liquids provide larger strains and faster response for electro-active devices.

1:39PM B19.00011 Processing of Natural Polymer-nanocomposites using Ionic Liquids as “Green Solvents”, SAMEER RAHATEKAR, NIST, ASIF RASHEED, FDA, RAHUL JAIN, Georgia Tech, K. KOZIOL, ALAN WINDLE, University of Cambridge, PAUL TRULOVE, US Naval Academy, SATISH KUMAR, Georgia Tech. JEFFREY GILMAN, NIST, NIST COLLABORATION, GEORGIA TECH COLLABORATION, UNIVERSITY OF CAMBRIDGE COLLABORATION — We report fiber spinning of natural polymers such as cellulose and silk using ionic liquids. Ionic liquids can dissolve cellulose and silk and are less hazardous than the traditional solvents used for dissolving cellulose. We use imidazolium-based ionic liquids as a common solvent to process natural polymers and carbon nanotubes. Cellulose/carbon nanotubes based fibers are spun using wet spinning process. The rheological, mechanical thermal and electrical properties of the fibers are measured. We also characterize the cellulose nanocomposites fibers using ionic liquids by SEM/TEM, X-ray diffraction, TGA and FTIR analysis. Silk and carbon nanotubes fiber processing is also reported using ionic liquids as common solvent.

51PM B19.00012 Biocompatible Ionic Liquid-Derived Conducting Polymers, MILLICENT FIRESTONE, CHRISTOPHER BURNS, SUNGWOON LEE, Argonne National Laboratory — A significant and frequently encountered challenge when making an electrical connection to a protein is that its electron-transfer sites are buried within the polypeptide matrix and thus, are not readily accessible to bulk metal electrodes. A further complicating factor is that inorganic (i.e., metallic) electrodes are often incompatible with biological samples. These obstacles might be overcome by the use of conducting oligomers and/or polymers, which are flexible, offering a means to access remote redox centers. These oligomers can be readily modified to include chemical moieties that can connect covalently to sites near redox centers. In addition, conducting polymers can be made to be environmentally responsive (dynamic), processable (conformal coating, soluble) and mechanically durable, thus enabling them to function as an electrical conduit (wire or electrode) to biomolecules. In this work, we describe the design, synthesis and electrochemical properties of thiophene-based ionic liquid monomers and their bulk polymerization by chemical oxidation to yield cationic, aqueous-soluble polymers. Preliminary studies evaluating the electropolymerization of these monomers into nanostructured thin films will also be presented.

3This work was performed under the auspices of the Office of BES, DMS, US-DOE, under contract No. DE-AC02-06CH11357.
Organic photovoltaics have received much attention recently due to their promise of affordable and flexible solar power. A major component of these devices is the bulk heterojunction: an interconnected mixture of an electron donor, a highly conjugated polymer, and an electron acceptor, generally a fullerene derivative. We have performed neutron reflectivity experiments on 200 nm thick films of poly(3-hexylthiophene) and [6,6]-phenyl-C71-butyric acid methyl ester (P3HT:PCBM) and poly[N-(4′-heptadecyl)-2,7-carbazole-alt-5,5-(4,7-di-2-thienyl-2,7-di-3-benzothiadiazole)] : [6,6]-phenyl-C71-butyric acid methyl ester (PCDTBT:PC70BM).

We demonstrate that domain orientation of polymer electrolyte membranes made from poly(styrenesulfonate-b-methylbutylene) (PSS-PMB) copolymers can be tuned by controlling sulfonation level and moisture content of the air. Increasing the sulfonation level results in a transition from perpendicular to parallel orientation. Our conclusion is based on three-dimensional characterization of membranes using electron microscopy of samples prepared by the shadow focused ion beam technique, grazing incident small angle x-ray scattering, and electron tomography.

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1:03PM B20.00008 Photo-induced improvement of Bulk Heterojunction Polymeric Solar Cells . KAMIL MIECZKAREK, ALEXANDER COOK, ANVAR ZAKHIDOV, University of Texas at Dallas, NANOTECH INSTITUTE TEAM — The effectiveness of BHJ polymeric solar cells depends highly on the formation of continuous three dimensional interconnecting networks of electron donor (typically RR P3HT) and acceptor (typically PCBM) materials. This process is controlled by post-processing heat treatment to induce phase separation of the materials. We demonstrate in this presentation, that in-situ photo-excitation of the BHJ structure during the annealing process controls both the maximal photocurrent and filling factor of the BHJ solar cell. We have found that variations in intensity and spectral composition of the photo excitation affect the resulting morphology of BHJ. The increased diffusivity of constituents and photo-modulation of the carrier recombination upon annealing is discussed as one of the causes of the observed morphology improvement.

1:15PM B20.00009 High-Vacuum Annealing of Polythiophene:Methanofullerene Bulk Heterojunction Solar Cells . JENNIFER SEGUI, State University of New York - Stony Brook, IOANA GEARBA, Brookhaven National Laboratory, MIRIAM RAFAILOVICH, State University of New York - Stony Brook, CHARLES BLACK, Brookhaven National Laboratory — Solar cell device architectures incorporating photoactive layers of immiscible blends of organic semiconductors achieve improved photovoltaic power conversion efficiency compared to planar device geometries. We have fabricated bulk heterojunction solar cells with active layer blends of poly-3 hexylthiophene (P3HT) and the fullerene derivative, [6,6] phenyl C61-butyric acid methyl ester (PCBM). Spin casting the blend from a chlorobenzene solution forms nanometer-scale domains of electron donor and acceptor phases in the device active layer. We solution process the active layers in ambient atmospheric conditions prior to aluminum contact evaporation resulting in inevitable oxygen adsorption in the P3HT bulk and interfaces. We have investigated several device post-fabrication thermal treatments for driving oxygen from the device active layer, including different temperatures, times, and vacuum pressures. We evaluate the efficacy of this technique in improving Al contact quality, film morphology, solar cell efficiency, and reproducibility via analysis of device current-voltage characteristics and tapping mode atomic force microscopy.

1:27PM B20.00010 Optimizing Ionic Electrolytes for Dye-Sensitized Solar Cells , XIAOJUAN FAN, SARAH HALL, Dept. of Physics, Marshall University — Dye-sensitized solar cells DSSCs provide next generation, low cost, and easy fabrication photovoltaic devices based on organic sensitizing molecules, polymer gel electrolyte, and metal oxide semiconductors. One of the key components is the solvent-free ionic liquid electrolyte that has low volatility and high stability. We report a rapid and low cost method to fabricate ionic polymer electrolyte used in DSSCs. Poly(ethylene oxide) (PEO) is blended with imidazolium salt without any chemical solvent to form a gel electrolyte. Uniform and crack-free porous TiO2 thin films are sensitized by porphrine dye covered by the synthesized gel electrolyte. The fabricated DSSCs are more stable and potentially increase the photo-electricity conversion efficiency.

1:39PM B20.00011 Improved thermally crosslinked polythiophene conductivity by thermal crosslinking for solar cell applications . I.R. GEARBA, C.-Y. NAM, R. PINDAK, C.T. BLACK — Organic photovoltaic device power conversion efficiencies are limited in part by low charge mobility within the constituent active layer. For example, the p-type polythiophene polymers used in the highest efficiency organic photovoltaic devices have transverse hole mobilities of only 10−4−10−5 cm2/V-s, despite showing significantly higher values (~0.1 cm2/V-s) in a lateral FET geometry. This reactivity anisotropy is caused by poor overlap of π−π orbitals in the transverse direction, which impedes charge hopping between polymer chains. We have improved this transverse hole conductivity by as much as three times by incorporating the radical initiator di-tert-butyl peroxide into polythiophene thin films. The initiator promotes thermal crosslinking upon annealing at 170C. Crosslinked polythiophene films maintain a similar absorption spectrum to the uncrosslinked material. Grazing incidence X-ray measurements correlate film structural changes to the measured electronic properties, and reveal two possible mechanisms for increased π−π overlap in crosslinked films. We have increased the power conversion efficiency of planar photovoltaic devices composed of p-type polythiophene and n-type C60 by about three times (from 0.09% to 0.27%) by crosslinking the polythiophene material. Moreover, crosslinked polythiophene films are rendered insoluble and thus amenable to the further material processing.

1:51PM B20.00012 Modeling photocurrent transients in organic solar cells . INCHAN HWANG, NEIL GREENHAM, Cavendish Laboratory, Department of Physics, University of Cambridge, J. J. Thomson Ave., Cambridge CB3 0HE, United Kingdom — We investigate the transient photocurrents of organic photovoltaic devices by numerical modeling of the drift-diffusion equations. Understanding charge transport in organic solar cells is one of the major interesting issues relevant to improving performance of organic devices. We demonstrate the simulation of the transient photocurrents in a response to a sharp turn-on illumination. Our results show the transient time in photocurrents is determined not only by free charge transport, but also by geminate charge pair dynamics. The dissociation probability of geminate charge pairs is a key parameter in determining the performance of organic devices, controlling the efficiency at low intensity, and also governing the fate of charge pairs formed by bimolecular recombination at high intensity. Bimolecular recombination appears to shorten the typical distance traveled by free charges from where they are generated to the electrode, leading to a reduced turn-on time at high intensity.

2:03PM B20.00013 Conjugated Polymer Organic Solar Cells made using Low Bandgap Vinylene-linked Benzothiadiazole-thiophene . N. C. HESTON, Univ of Florida, J. MEI, S. VASILYEVA, J. R. REYNOLDS, Univ. of Florida — With over 70% of the solar photon flux occurring at wavelengths beyond 700 nm, the broad absorption spectra of low bandgap conjugated polymers offers an additional path towards improving organic photovoltaic efficiencies. Here, we report on polymer solar cells fabricated using a vinylene-linked benzothiadiazole-thiophene polymer and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) blends. We have fabricated cells with various blend film polymer to PCBM ratios as well as film thicknesses and architectures. The performance of these cells was investigated using both AM 1.5 and incident photon to current efficiency measurements. Surface morphologies were characterized using atomic force microscopy. A strong correlation was observed between the percentage of polymer in the blend and the resulting film morphology. We observed photon-generated currents at wavelengths greater than 800nm, though we have not yet obtained high overall power conversion efficiencies.
2:42PM D18.00002 Interfacial Charge Transfer in Nanoscale Polymer Transistors . JEFFREY WORNE, RAJIV GIRDHARAGOPAL, KEVIN KELLY, DOUGLAS NATELSON, Rice University, JOHN ANTHONY, University of Kentucky — Interfacial charge transfer plays an essential role in establishing the relative alignment of the metal Fermi level and the energy bands of organic semiconductors. While the details remain elusive in many systems, this charge transfer has been in a number of photoemission experiments. We present electronic transport measurements in very short channel (L < 100 nm) transistors made from poly(3-hexylthiophene) (P3HT). Channel length is reduced, the evolution of the contact resistance and the zero gate voltage conductance is consistent with such charge transfer. Short channel conduction in devices with Pt contacts is greatly enhanced compared to analogous devices with Au contacts, consistent with charge transfer expectations. Alternating current scanning tunneling microscopy (ACSTM) provides further evidence that holes are transferred from Pt into P3HT, while much less charge transfer takes place at the Au/P3HT interface. We have also begun to use these same techniques to investigate the nature of interfacial charge transfer between metal electrodes and pentacene. We use these data together with our previous results to develop a more complete picture of metal/organic interfaces.

2:54PM D18.00003 Ab initio study of molecular packing of organic semiconducting materials . SEFA DAG, LIN-WANG WANG, Lawrence Berkeley National Laboratory — The self-organizing and electronic properties of organic semiconducting material, poly(3-hexylthiophene) (P3HT), have been investigated in terms of Ab initio density functional calculations. We found that thiophene-thiophene interaction in adjacent layers has a strong influence to create stacked planar structures. Our calculations showed that P3HT chains tend to stack into planar structures, in which adjacent thiophene-thiophene rings along the stacking direction are 180° rotated with respect to each other. Theoretical powder diffraction profile of this structure showed same structure with experimental reflection peaks. We also showed enhanced transport resulting from the organization of P3HT chains.

3:06PM D18.00004 Electrical Noise in Individual Conducting Polymer Nanowires . ALEXEY KOVALEV, YANYAN CAO, THERESA MAYER, THOMAS MALLOUK, Penn State University — Electrical property characterizations of conducting polymer nanostructures have been limited primarily to resistance measurements. Electrical noise is one aspect that is usually overlooked, yet critical to their device performance. Moreover, electrical noise is more sensitive to the polymer doping and microstructure than resistance, which makes it particularly interesting for sensor applications. In this talk, we will present the results on the electrical noise measurements of individual multilayered electrodeposited nanowires based on Poly(3,4-ethylenedioxythiophene) (PEDOT) [1]. The polymer was electrochemically doped with either poly(4-styrenesulfonic acid) (PSS) or perchlorate (ClO4-). The nanowires had gold contacts on both ends and were measured in four-point and two-point configurations. We found that the electrical noise behavior is typical of 1/f noise, with a spectral density that depends on the polymer structure and is affected by the ambient conditions. Our data show that the contact noise represents a significant contribution to the total noise level. We will discuss the interpretation of these results assuming that the polymer is a disordered conductor. [1] Cao et al., Nano Letters Article ASAP.
4:06PM D18.00009 Fullerene-based anchoring groups for molecular electronics, CHRISTIAN MARTIN, DAPENG DING, Leiden University and Delft University of Technology, The Netherlands, JAKOB SORENSEN, THOMAS BJORNHOLM, University of Copenhagen, Denmark, JAN VAN RUITEMBEEK, Leiden University, The Netherlands, HERRE VAN DER ZANT, Delft University of Technology, The Netherlands — We present results on a new fullerene-based anchoring group for molecular electronics. Using lithographic mechanically controllable break junctions in vacuum and at RT we have studied the electrical properties of 1,4-bis(fullero(c)pyrrolidin-1-yl)benzene. The compound can be self-assembled from solution and forms molecular junctions with a low-bias conductance of $3 \cdot 10^{-4}$ $\Omega$. Compared to 1,4-benzenedithiold it exhibits a considerably lower conductance spread. Statistical analyses of the breaking process confirm the stability of the fullerene-gold bond.

4:18PM D18.00010 An organic nanoparticles transistor behaving as a spiking synapse, DOMINIQUE VUILLAUME, FABIEN ALIBART, IEMN-CNRS, CHRISTOPHE NOVEMBRE, CEA-LIST, DAVID GUERIN, CNRS-IEMN, STEPHANE PLEUTIN, KAMAL LIMMOUNI, IEMN-CNRS, CHRISTIAN GAMRAT, CEA-LIST, IEMN-CNRS TEAM, CEA-LIST TEAM — We demonstrate that an organic transistor, made of metal nanoparticles (NP) embedded into an organic semiconductor channel, behaves as a spiking synapse. We demonstrate that this device exhibits the main behavior of a biological synapse. For instance, it can be programmed to work as an excitatory or inhibitory synapse; it exhibits shot-term plasticity as well as spike timing dependent plasticity. This behavior is obtained by virtue of the combination of two properties: the transconductance gain of the transistor and the memory effect due to charges stored in the NP. The gold NP are immobilized into the source-drain channel by using surface chemistry (self-assembled monolayers) and they were subsequently covered by a thin film of pentacene. In a biological synapse, the excitatory behavior means that an incoming signal with a given frequency and duty cycle induces a post-synaptic signal having an increasing trend, whereas in the case of an inhibitory synapse, the post-synaptic signal tends to decrease. This behavior is exactly what we demonstrated for the ONTs.

4:30PM D18.00011 The role of the oxygen/water redox couple in suppressing electron conduction in field-effect transistors, PIERRE L. LEVESQUE, Université de Montréal, CARLA M. AGUIRRE, École Polytechnique de Montréal, MATHIEU PAILLET, FRANÇOIS LAPIONTE, Université de Montréal, BENOÎT C. ST-ANTOINE, PATRICK DESJARDINS, École Polytechnique de Montréal, RICHARD MARTEL, Université de Montréal — Much like with organic semiconductor FETs, a characteristic of carbon nanotube based devices has been their almost exclusive p-type character in air. Electron transport can be observed only under certain conditions, for instance devices annealed in vacuum. We investigated the impact of the chemical nature of the substrate and of ambient adsorbats on the field-effect switching behavior of both nanoscale and thin-film FETs. Our study, using carbon nanotubes as the testbed, revealed that the intrinsic material properties are modified when an adsorbed water layer containing solvated oxygen is present on the SiO$_2$ surface and lead to the reduction of n-type conduction. This finding demonstrates that an electrochemical charge transfer reaction between the semiconducting channel and the aqueous oxygen redox couple is the underlying phenomenon governing the suppression of electron conduction in these devices. This effect should be considered when measuring the transport properties of nanostructures such as nanowires, organic materials, nanotubes, graphene conducted on SiO$_2$ or Si substrates.

Monday, March 16, 2009 2:30PM - 5:30PM — Session D19 DPOLY: Focus Session: Grazing Incidence Scattering and New Imaging Techniques 320

2:30PM D19.00001 Probing small-angle x-ray scattering, JIN WANG, Argonne National Laboratory — Synthesizing complex nanocomposites and superstructures is of great interest in all areas of materials science and involving biology, chemistry, physics and engineering applications such as the fabrication of novel electronic, magnetic, and photonic devices. Since the entire synthesis and assembly process can take place far from equilibrium conditions, a controlled process has to be guided by a thorough understanding of the kinetics and dynamics in the composites. This requires measurement of the structure in situ and in real time with subnanometer spatial resolution and millisecond to subsecond temporal resolution. As an increasingly important structural-characterization technique, grazing-incidence small-angle x-ray scattering (GIXS) finds vast applications in the research of nanostructures and nanocomposites at surfaces and interfaces. Most significantly, as a complementary method to conventional surface-sensitive tools such as scanning probe microscopy and electron microscopy, GIXS can be used in situ and in real time to monitor the formation of the nanostructure or nanocomposite, which makes it most suitable for studying the kinetics of nanoscale processes. The GIXS technique can also be an integral part of numerous research, for example, those involving kinetics of mesoscale ordered block copolymer thin films, kinetics of sol-gel processes, quantum dots, nanoparticles in ultrathin films, and dynamics and phase transitions 2D nanocrystal superlattices. Here, we will focus on the applications of GIXS in real-time structure characterization, the dynamics in polymer/nanoparticle nanocomposites, and the challenges to elucidate nanostructure formation in nanoscience and nanotechnology.

2 This work and the use of the Advanced Photon Source are supported by the U. S. Department of Energy (DoE), Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

3:06PM D19.00002 Single beam approach for GIXS, BYEONGDU LEE, CHIEH-TSUNG LO, Argonne National Laboratory, PAPPANAN THIYAGARAJAN, ZHONGWEI NIU, QIAN WANG, University of South Carolina — The multiple scattering effects present in the grazing incidence small-angle x-ray scattering (GIXS) data are addressed theoretically as well as experimentally with measurement of a series of patterns at different incident angles, referred to as “incident-angle-resolved GIXS” (IAR-GIXS). We found that under certain conditions, it is possible to extract the correct structural features of the materials from the GIXS data using the kinematic SAXS formalisms assuming a single beam, without the need to use the distorted wave Born approximation (DWBA) to account for the scattering by the reflected beam. Furthermore, the Kiessig fringes in GIXS enable the measurement of average distance between the particle and the substrate, similar to the measurement of film thickness using the fringes in the x-ray reflectivity data. We believe that the methods developed here will expand the application of GIXS as they enable the use of model-independent and kinematic SAXS theories to nanostructured 2D-ordered films.

3:18PM D19.00003 Surface Dynamics of Free PS Chains on Chemically Identical Polymer Brushes: An XPCS Study, GOKCE UGUR, Department of Polymer Science, The University of Akron, Akron, OH 44325-3909, BULENT AKGUN, Center for Neutron Research, National Institutes of Standards and Technology, Gaithersburg, Maryland 20899, ZHANG JIANG, SURESH NARAYANAN, Experimental Facilities Division, Argonne National Laboratory, Argonne, IL 60439, WILLIAM J. BRITTAIN, MARK D. FOSTER, Department of Polymer Science, The University of Akron, Akron, OH 44325-3909 — We found no relaxation of fluctuations of the brush surfaces within the range of time (0.2 - 1100 s) and length scale (0.6-3 um) studied by X-ray photon correlation spectroscopy/XPCS). This is true for PS brushes of thicknesses of 9 - 101 nm and grafting density of 0.12-0.6 chains/nm$^2$ at temperatures up to 130C above bulk $T_g$. Results on the dynamics of a layer of un tethered 2.2k PS chains on top of a PS brush surface show that placing the PS chains atop the brush dramatically slows down the surface relaxations of the film surface. As the ratio of the thickness of the layer of tethered chains to the thickness of the highly dense brush drops below $\approx$0.5, the surface relaxations become too slow to be observed readily with XPCS. Reducing grafting density of the underlying brush markedly slows the surface dynamics. The surface dynamics of the layer of “free” PS chains are coupled with those of the underlying brush.
3:30PM D19.00004 X-ray Standing Wave Studies of Stability and Dynamics in Poly(4-bromostyrene)/Poly(4-vinylpyridine) Thin Films, YAN SUN, KENNETH SHULL, Northwestern University, JIN WANG, Argonne National Laboratory — The thermodynamic stability and wetting behavior in systems consisting of two or three distinct layers of polymeric thin films have been investigated with atomic force microscopy (AFM) and x-ray standing waves (XSW) generated via total external reflection from an x-ray mirror. We have probed the structural evolution of thin poly(4-bromostyrene) (PBrS) films with various degrees of bromination, prepared on top of a poly(4-vinylpyridine) (P4VP) layer whose dynamics is influenced by its interaction with the underlying substrate and couples to that of PBrS. The addition of a top poly(styrene) (PS) layer was also used in some cases. The samples were subjected to annealing treatments above the polymer glass transition temperatures. Reflectivity and x-ray fluorescence from bromine markers in the PBrS layer were tracked. Dewetting of the PS occurred with sufficient annealing time, though the results suggest that this proceeded faster with low PBrS bromination. AFM studies on the PBrS/P4VP system revealed a clear PBrS thickness dependence on the dewetting morphology and dynamics of this layer.

3:42PM D19.00005 Quantitative electron tomography and its application to polymer nanostructures, HIROSHI JINNAI, Department of Macromolecular Science and Engineering, Kyoto Institute of Technology — The transmission electron microtomography (TEMT) is a powerful tool to visualize three-dimensional (3D) structures in many fields of materials science. Recently, researchers are trying not only to visualize 3D nano-structures but also to quantify them in order to seek a possible correlation between the 3D structures and materials’ properties. However, one of the serious problems that prohibit TEMT from truly quantitative 3D images is the “missing wedge” in the Fourier space that is caused by the limitation of angular range available in transmission electron microscopes (TEM). Please note that the computerized tomography (CT), on which TEMT is based, requires projections from entire tilt angles, i.e., ±90°. Thus, the most faithful tactics for the CT is to tilt specimen over ±90°. In order to realize such requirement, a rod-shaped ZrO2/polymer nano-composite whose diameter is ca. 150 nm was attached at the tip of a specially modified specimen holder without any supporting film. A complete set of tomograms has been generated for the first time from the 181 projections that were taken over the angular range of ±90°. One of the structural parameters characterizing the nano-composite, a volume fraction of ZrO2, ϕ, was measured as a function of the maximum tilt angle, α. It was found that ϕ was in excellent agreement with the known volume fraction of ZrO2 when α=90°, i.e., ±90° tilt, while ϕ increased with decreasing α. When α=60° that is a typical maximum tilt angle, the measured ϕ was larger by 20–30% than the true value. In addition to the above TEMT experimental technique, some applications of TEMT to polymer nano-structures will be presented at the conference time.

4:18PM D19.00006 Three-dimensional subwavelength imaging with phase-less power extinction tomography, ALEXANDER A. GOVYADINOV, GEORGE Y. PANASYUK, JOHN C. SCHOTLAND, University of Pennsylvania — Modern near-field methods extend the spatial resolution of optical microscopes beyond the classical diffraction limit. However the majority of these methods only recover two-dimensional maps of optical intensity near the sample surface. The interpretation of these maps for manifestly inhomogeneous samples has been proven to be problematic. Here we derive an analytical technique which allows unique subwavelength 3D reconstruction of both real and imaginary parts of susceptibility two-dimensional maps of optical intensity near the sample surface. The reconstruction is based on simple measurements of the power extinguished from illuminating waves in the total internal reflection mode and is intrinsically nondestructive.

4:30PM D19.00007 Helium ion microscopy and its application to organic materials, STEVEN HUDSON, ANDRAS VLADAR, BIN MING, NIST, Gaithersburg, MD 20899 — Helium ion microscopy (HeIM) is a new scanning probe microscopy that uses a He+ ion beam. This microscope has improved resolution and depth of field in comparison to SEM, as demonstrated through imaging of metal particles. Organic materials, including patterned polyelectrolyte multilayers and organic semiconductor crystals, have also been imaged. The surface sensitivity, image contrast and qualitative secondary electron yield have been evaluated, in an effort to understand beam/specimen interactions and compare them with electron beam/sample interactions.

4:42PM D19.00008 Robust Tips for High Resolution Chemical Imaging1, CARLOS BARRIOS, ANDREY MALKOVSKYI, ALEXANDER KISLIUK, ALEXEI SOKOLOV, MARK FOSTER, Department of Polymer Science, The University of Akron — Tip enhanced Raman spectroscopy (TERS) combines scanning probe microscopy with Raman spectroscopy, taking advantage of apertures near-field optics. A plasmonic structure at the apex of a sharp tip provides signal amplification required for chemical imaging. Plasmonic structure characteristics such as roughness, shape, and radius determine the spatial resolution and signal enhancement. Unfortunately, noble metal nanostructures have limited lifetimes due to mechanical, chemical, and thermal degradation. Lifetime extension requires slowing degradation processes while minimizing unfavorable influences on the optical response. An ultrathin SiO2 protective coating provides lifetime improvement of silver plasmonic nanostructures on SPM tips. Controlled physical vapor deposition (PVD) of Al can be used to create ultrathin (~2-3 nm) Al2O3 coatings that improve significantly the stability and wear resistance of plasmonics structures without substantial degradation of optical properties. Such a coating completely prevented decay in plasmonic activity after 40 days of use.

1 Research support from the Army Research Office (W911NF-07-1-0470) is gratefully acknowledged.

5:04PM D19.00009 Broadband CARS microscopy, MARCUS CICERONE, JOUNG LEE, YEON HO KIM, SAPUN PAREKH, NIST — Coherent anti-Stokes Raman scattering (CARS) microscopy has exciting potential for rapid chemical imaging of materials and noninvasive imaging of biological systems, both in vivo, and as these systems interact with materials. Although CARS is as much as 104 times more sensitive that spontaneous Raman scattering, it is accompanied by a nonresonant background (NRB) signal which can mask the resonant signal of interest. This background is generally of sufficient amplitude to make chemical imaging of biological systems difficult or impossible. We will present recent advances made in our lab, both experimental and in numerical data recovery, towards ameliorating the negative aspects of the NRB and facilitating non-invasive chemical microscopy for cell-material interactions.

5:06PM D19.00010 Intensity Fluctuations of Optical Microscopy as a Means to Measure Axial Diffusion, MALVIKA BIHARI, PSE, UMASS Amherst, THOMAS RUSSELL, PSE,UMASS Amherst, DAVID HOAGLAND, PSE UMASS Amherst — Via optical microscopy, geometrically hindered motions of a single large solute (particle or polymer) can be imaged in real time. Here, intensity fluctuations of confocal fluorescence microscopy admit another way to probe such motions, one convenient when motions are perpendicular to a planar substrate. The focal plane is positioned within the substrate (lying on the microscope stage) and intensity fluctuations arise from motions in-and-out of the focal volume. Two experiments illustrate the new approach, diffusion within pores of a planar membrane or in solution near a solid wall. In the first, diffusion coefficients of spherical particles were measured inside pores of a track-etched polycarbonate membrane as functions of particle and pore size. In the second, anisotropic diffusion (perpendicular/parallel) of the same particles was measured within a few particle diameters of a solid boundary. Theory for hydrodynamically hindered diffusion in both cases is well developed, and data are compared to predictions. Two ways to assess particle/polymer motion, tracking single particles and correlating intensity fluctuations, will be discussed.
Three-Dimensional Imaging of Polymeric Nanostructures by Molecular Switching in Far Field Fluorescence Microscopy

CHAITANYA ULLAL, ROMAN SCHMIDT, ALEXANDER EGNER, BENJAMIN HARKE, JAN KELLER, Max Planck Institute for Biophysical Chemistry, DOUGLAS ADAMSON, University of Connecticut, LARS KASTRUP, STEFAN HELL, Max Planck Institute for Biophysical Chemistry — Morphological studies of self-assembled polymeric structures with length scales of interest below 100 nm have typically been conducted either by scattering-based techniques or electron and scanning probe microscopes. These techniques, however, do not provide easy access to truly 3D-structural information. In contrast, Far-field optical methods retain the advantage of simultaneously providing local, dynamic, and in situ three-dimensional (3D) structural information. The diffraction limited resolution of its standard variants, however, restricts the minimum feature size that can be examined. We exploit molecular transitions of the fluorophores to circumvent the diffraction barrier and demonstrate the power of emerging far-field fluorescence microscopy with nanoscale resolution for the study of self-assembly. We simultaneously improve both the lateral (x,y) and the axial (z) resolution of stimulated emission depletion (STED) microscopy. The increased 3D resolution is used to unambiguously map the morphology of self assembed polymeric nanostructures in a facile manner.

Monday, March 16, 2009 2:30PM - 5:18PM — Session D20 DPOLY: Polymers and Energy: Photovoltaics, Fuel Cells, Batteries II

2:30PM D20.00001 Simulation study of proton transport in stretched nanocomposite ionomer fuel-cell membranes

PHILIP TAYLOR, ELSHALL ALLAHYAROV, Case Western Reserve University — We have used coarse-grained simulation methods to investigate the effect of inclusions of nanoparticles on the stretching-induced structure orientation and on the proton conductivity of polymer electrolyte membranes. Uniaxial stretching of a Nafion film containing no inclusions causes a modest increase in proton conductivity in the direction of stretching. This effect does not persist to any significant degree after removal of the stretching stress. Stretching of a Nafion film containing spherical nanoparticles, on the other hand, causes a large increase in proton conductivity in the direction of stretching, and this effect persists to a much greater extent after the removal of the stretching stress. Simulations were performed with monodisperse nanoparticles whose diameters were in the range from 17 to 28 nm, and whose surfaces were either hydrophilic, neutral, or hydrophobic. The greatest effect in causing enhancement of the proton conductivity and in causing persistent ordering was found for hydrophilic nanoparticle inclusions of 28 nm diameter.

2:42PM D20.00002 The role of nanoparticle-membrane coupling in nanocomposite ionomers

ELSALL ALLAHYAROV, PHILIP TAYLOR, Case Western Reserve University — Coarse-grained simulation methods have been used to investigate the effect of inclusions of spherical nanoparticles on the properties of Nafion®,like membranes. We find the clustering of the sulfonate head groups to be strongly affected by the presence of a monodisperse array of spheres when the sphere diameters lie in the range from 17 to 28 nm. This change in morphology enhances the proton conductivity of the membrane through the formation of channels connecting adjacent clusters. This effect was characterized in terms of the distribution of chain lengths of the hydrophilic phase. Simulations were performed for Nafion containing spherical nanoparticles whose surfaces were either hydrophilic, neutral (hard core), or hydrophobic. The diameters of the nanoparticles were changed while keeping fixed the volume fraction of inclusions. We find that the proton conductivity of these nanocomposites is always higher than the conductivity of ionomers without additives. This effect becomes most pronounced in nanocomposites containing particles whose surfaces are hydrophilic, and whose diameters are in the larger part of the range of sizes examined.

2:54PM D20.00003 Multi-Lamellar Structures in Nafion

JOSEPH A. DURA, NIST - Center for Neutron Research, VIVEK S. MURTHI, UTC Power Corp., MICHAEL R. HARTMAN, University of Michigan, Nuclear Engineering and Radiological Sciences, SUSHIL K. SATIJA, CHARLES F. MAJKRZAK, NIST - Center for Neutron Research — Both proton conductivity and gas diffusion are key factors in the performance of a fuel cell proton exchange membrane, PEM. They are critically dependent on water content and morphology, especially in the three phase region where catalyst, PEM, and gases such as fuel or oxidizer co-exist. Here we show that lamellar structures composed of thin alternating water rich and Nafion rich layers exist at the interface between SO₂ and the hydrated Nafion film. Lamellae thickness and number of layers increase with humidity. Some lamellae remained in the film after dehydration. Multilayer lamellae are not observed for Nafion on Au or Pt surfaces. Instead, a thin partially hydrated single interfacial layer occurs and decreases in thickness to a few angstroms as humidity is reduced to zero. The absorption isotherm of the rest of the Nafion film is similar to that of bulk Nafion for all three surfaces investigated.

3:06PM D20.00004 RT-TDDFT simulation of the optical properties of a model organic photovoltaic device

F. VILA, J.J. REHR, U. of Washington — Organic solar cells are attracting much interest because of their potential as cost-effective photovoltaic devices. Prototypical cells consist of a bilayer of p- and n-type materials. The conversion of light into a current is initiated by the absorption of a photon in the p-type donor, mediated by the creation, diffusion and dissociation of an exciton, and finally by a charge transfer to the n-type acceptor, with subsequent transport to the electrodes. To explore this effect, we simulate the optical response of a model bilayer cell composed of a polythiophene(pT)/C₆₀ donor/acceptor pair using an efficient implementation of real-time TDDFT. We find that the chain twist induced by the C₆₀ on the pT shifts the absorption onset from 1.8 to 2.0 eV. This shift is larger and of opposite sign compared to that induced by the inclusion of either regioregular or random side-chains in pT, and by the interaction between two pT chains. Finally, we discuss extensions for the simulation of charge transport and exciton mobility.

3:18PM D20.00005 Collecting photo-generated charge carriers from metallo-organic materials

A.R. CARTER, J.H. PARK, Dept. of Physics, The Ohio State University, Columbus, Ohio 43210-1117, Y.-H. CHOU, Y. GHOSH, C.R. REED, L.M. MIER, T.L. GUSTAFSON, M.H. CHISHOLM, Dept. of Chemistry, The Ohio State University, Columbus, Ohio 43210-1185, A.J. EPSTEIN, Dept. of Physics and Dept. of Chemistry, The Ohio State University, Columbus, Ohio 43210-1117 — Organic photovoltaic materials continue to garner attention as potential low cost and tunable alternatives to conventional inorganics. We report progress in utilizing hybrid metallo-organic materials that incorporate metal-metal (M-M) quadruply bonded units into oligothiophenes via carboxylate linkers. Varying the metal (M = Mo, W) or the ligands shifts the energetics and can be exploited to extend absorption into the infrared. These materials have high absorbivity from 300 nm (4.1 eV) to 900 nm (1.4 eV). We present the results of photophysical studies of structures that employ these materials.

1Supported by DOE Grants DE-FG03-08GO18011 (FV and JJR), DE-FG02-97ER45623 (JJR).

This work is supported by the Wright Center for Photovoltaic Innovation and Commercialization [TECH-07-026].

3:30PM D20.00006 Monolithic Tandem Organic Photovoltaic Cell Utilizing Transparent Carbon Nanotube Interlayer, KAMIL MIELCZAREK, University of Texas at Dallas, Physics Department, Nanotech Institute, SENKU TANAKA, Shimane University, Center for Integrated Research in Science, RAQUEL OVALLE ROBLES, ALEXANDER KUZNETSOV, University of Texas at Dallas, Nanotech Institute, BRIAN WANG, University of Texas, DEAN HSU, University of Texas at Dallas, RAY BAUMGAIMAN, ANVAR ZAKHIDOV, University of Texas at Dallas, Nanotech Institute, ALAN G. MACDIARMID NANO TEC H INSTITUTE TEAM — We demonstrate an organic photovoltaic multijunction cell in a monolithic parallel tandem structure in which transparent multi- and single-walled nanotube sheets are used as an interlayer electrode connecting two cells; polymeric photovoltaic (PPV) cell or organic low molecular PV (OPV). Each cell is characterized independently and the short circuit current density of the tandem is shown to be larger than individual cells for the PPV-MWCNT-OPV tandem*. Overall efficiency is increased attributed to effective use of transparent CNTs and enhanced spectral sensitivity due to differing active layer materials. Computer model circuit simulation is used to analyze the parameters of cells in parallel and series configurations. Advantages of a parallel connection is shown for PV cells with differing photocurrents. The PPV-PPV and OPV-OPV cells are also created and described. *S.Tanaka, K Mielczarek, et.al., APL. (submitted 2008, October).

3:42PM D20.00007 Tandems of solid dye-sensitized solar cell with carbon nanotubes interlayer1, CHAO-CHEN YUAN, JIANGBIN XIA, ANVAR ZAKHIDOV, Univ. of Texas at Dallas NanoTech Institute — The light-to-electron conversion efficiency of the dye-sensitized solar cell (DSC) was recently improved up to 11.1%. However, this efficiency is not sufficient for cost-effective commercial production, so the expansion of the absorption region of the solar cell is needed. For transparent carbon nanotubes, parallel-connected tandem DSCs is developed. Novel parallel type of tandem cell structure is created. We create a parallel combination for cells using different dyes. The top cell is transparent and the bottom cell only uses light passing through the top cell. Instead of a common platinum counter electrode as interlayer, we use transparent carbon nanotubes (CNTs) coated on hole transport layers of each sub-cell, as an interlayer counter electrode. With high enough conductivity and high optical transparency, the compatibility of CNTs work as the interlayer counter electrode performing even better than Pt. The short-circuit current density (Jsc) for the tandem cell is demonstrated to be higher than that of separate the front and back photo electrodes. A model using light energy absorbed by the photo electrode is NT19 top cell and a black-dye bottom cell is developed. Now the prototype of DSC tandem cell has been proved with the efficiency of 0.293% with 0.2 cm² area.

1 The novel material as an interlayer for tandem cell - Carbon nanotubes

3:54PM D20.00008 NEXAFS Spectroscopy of Biomimetic Dyes for Solar Cells, PETER COOK, XIAOSONG LIU, FRANZ HIMPSEL, Physics Department, University of Wisconsin Madison — Organic photovoltaics hold the potential for an inexpensive alternative to traditional silicon solar cells. A group of such dyes is investigated systematically including porphyrins, phthalocyanines, and cytochrome c, all of them characterized by a transition metal atom surrounded by a cage of four nitrogen atoms. X-ray absorption spectroscopy of the transition metal 2p and the nitrogen 1s absorption edges reveals the LUMO, the oxidation state of the transition metal, and its spin state. In addition, the sensitivity of these molecules to damage by photon-induced hot electrons is investigated. While the nitrogen cage is rather robust, the peptide bonds between the one hundred amino acids in cytochrome c are easily damaged. This finding suggests minimizing the size of biologically-inspired molecules for photovoltaic applications.

4:06PM D20.00009 Semiconductor Conjugated Polymer-Quantum Dot Nanocomposites at the Air/Water Interface and Their Performance in Thin Film Solar Cells, ZHIQUIN LIN, MATTHEW GOODMAN, JUN XU, JUN WANG, Iowa State University — Organic-inorganic nanocomposites consisting of electroactive conjugated polymer, poly(3-hexylthiophene) (P3HT) interpenetrated region, and self-assembled quantum dot (i.e., P3HT-CdSe nanocomposites at the air/water interface) Langmuir isotherms were explored for the first time. The P3HT-CdSe nanocomposites displayed a high pressure plateau in the Langmuir isotherm, illustrating their complex packing at the air/water interface. Furthermore, photovoltaic devices fabricated from the LB depositions of the P3HT-CdSe nanocomposites exhibited a relatively high short circuit current, Jsc, while maintaining a thin film profile. These studies provide insights into the fundamental behaviors of semiconductor organic-inorganic nanocomposites confined at the air/water interface as well as in the active layer of an organic-based photovoltaic device.

4:18PM D20.00010 Effect of polymer mobility on conductivity of single-ion conductors, KOKONAD SINHA, JANNA MARANAS, The Pennsylvania State University — Scientists are turning to the use of polymers as substitutes for liquid electrolytes in lithium ion batteries, because of their mechanical flexibility and non-toxic properties. Physical mixtures of lithium salt and poly(ethylene oxide) (PEO + LiClO4) are commonly chosen because they have potential for high ionic conductivities. However, high mobility of ions in these mixtures results in electrode polarization, which affects battery performance. To isolate the effect of the cation and to reduce the obstacle of concentration polarization, the anion is chemically incorporated into the backbone of the polymer, thereby rendering it immobile. These single-ion conductors are called ionomers. Neutron scattering experiments have been conducted on ionomers to observe the relationship between ionomer mobility and ionic conductivity. Results show that with increasing ion content, there arises a new process at smaller length scales. Comparisons with PEO + LiClO4 systems hint at the formation of cation-PEO-anion complexes which are significantly slower in dynamics than the segmental motion of the polymer. This interaction between the cation and the polymer chain is of vital importance in understanding the fundamental mechanism of ion conduction in polymers.

4:30PM D20.00011 Electrochemical Characterization of poly (styrene-b-ethylene oxide)/LiTFSI Lamellar Diblock Copolymer Electrolyte System, NITASH BALSARA, University of California, Berkeley, CA, ASHOUTOSH PANDAY, Lawrence Berkeley Lab, Berkeley, CA, SCOTT MULLIN, NISITA WANKUJILE, University of California, Berkeley, CA — We present the electrochemical characterization studies of symmetric poly (styr e n e - b - e th y l e n e o x i d e ) co polymer s ( S E O ) an d Li[N(SO2CF3)2] (LiTFSI). The molar ratio of Li to ethylene monomers, r, was varied from 0.02 to 0.10. The ionic conductivity of these electrolytes increases with molecular weight over the entire range of temperatures and r values evaluated. Preliminary data suggest that the salt diffusion coefficient also increases with increasing MW of PEO block.

4:42PM D20.00012 Progress toward few-molecule photochemistry with a low temperature STM.1, DAVID DAUGHTON, DONGHUN LEE, JAY GUPTA, The Ohio State University — Photochemistry at interfaces provides insight into molecular binding and charge transfer with future implications for organic photo-active devices. We have developed a novel instrument combining a low-temperature scanning tunneling microscope (STM) with a maneuverable, high numeric aperture lens in proximity to the tunnel junction for the study of photoactive systems with single-molecule sensitivity. We will present the results of our initial efforts on the electronic and photo-induced polymerization of C60 islands, tunneling and photo-induced isomerization of thiadieno, and the effects of well-defined optical nanostructures on photochemical processes. http://www.physics.ohio-state.edu/~jgupta

1Supported by the Beckman Foundation.
4:54PM D20.00013 Confinement-Induced Fast Discharge and Low Dielectric Losses in Ferroelectric PVDF Graft Copolymers1. LEI ZHU, FANGXIAO GUAN, ZHONGZHE YUAN. Polym. Program, Inst. of Mater. Sci. and Dept. of Chem., Mater. and Biomolecular Eng., University of Connecticut, Storrs, CT 06269-3136 — The relatively high dielectric loss of poly(vinylidene fluoride) (PVDF) and its copolymers limits their range of application as a high energy density capacitor material, although a high electric energy density was recently reported for millisecond discharge. In this work, we report time independent (or fast) discharge and reduced losses in ferroelectric poly(vinylidene fluoride) (PVDF) graft copolymer dielectric films. Experimental results suggested that the fast discharge and low losses were results of an increased amorphous content and nanoscale confinement of ferroelectric PVDF crystals.

1This work is supported by ONR (N00014-05-1-0338).

5:06PM D20.00014 ABSTRACT WITHDRAWN —

Tuesday, March 17, 2009 8:00AM - 11:00AM — Session H2 DPOLY: Polymer Physics Prize Symposium Honoring Steve Granick Spirit of Pittsburgh Ballroom BC

8:00AM H2.00001 Polymer Physics Prize Talk: Polymer Mobility at Surfaces and in Confined Environments. STEVE GRANICK, University of Illinois at Urbana-Champaign — Rich new chemistry and physics emerge when one considers confined fluids, where the environment is distinctly different than in bulk. The intuition of what to expect based on bulk properties is found to break down. This talk will emphasize recent findings using a combination of single-particle imaging and fluorescence correlation spectroscopy of polymers at hard surfaces (mica), soft surfaces (phospholipid bilayers) and random network environments. A surprising dependence is found on the polymer molecular weight and concentration, as well as on the substrate makeup.

8:36AM H2.00002 Engineered Colloids Having Particles of Controlled Size, Shape, and Chemistry1. JOSEPH DESIMONE, UNC Chapel Hill — This lecture will focus on opportunities for complex particles made using a novel “top-down” fabrication method called PRINT (Particle Replication In Non-wetting Templates). PRINT enables the production of monodisperse, shape-specific nano- and micro-particles from an extensive range of organic and inorganic liquid precursors. The assembly of colloidal particles has long been a rich and continuously growing area of materials science, with great potential for a broad range of applications including electronics, control systems, optics and biotechnology. Within this field, the bulk of research has been devoted to studying the assembly of isotropic spherical particles. In spite of this, there has been a growing interest in studying the assembly of anisotropic particles due to the more complex and useful structures that these particles can potentially assemble into. There are few reports on the assembly of anisotropic particles, in part because of the lack of effective fabrication processes for the preparation of these particles with the monodispersity, control and range of compositions required for in-depth study. Herein we will discuss the use of PRINT to fabricate monodisperse, nanometer- and micron-sized particles of varying size, shape and composition. PRINT stands out because of the high degree of molding resolution, the broad range of chemistries that can be molded, and the ease with which reel-to-reel technology can be incorporated for scalability. Thus, it is ideally suited to the synthesis of unique, highly anisotropic nanoparticles in a wide range of compositions. Within this discussion we use the discussion of dielectrophoresis to study the assembly of highly anisotropic polymer particles: rods, discs, hexnuts and boomerangs, fabricated with the PRINT process. In addition, the discussion will focus on the details and opportunities for loading shape controlled particles with magnetite and their manipulation when dispersed in various liquid media.

1Departments of Chemistry & Pharmacology, University of North Carolina at Chapel Hill; Dept. of Chemical & Biomolecular Engineering, North Carolina State University

9:12AM H2.00003 Polymers under Cylindrical Confinement. THOMAS RUSSELL, University of Massachusetts — Anodized alumina oxide (AAO) membranes offer a unique platform to investigate polymers under confinement. AAO membranes have been prepared where the diameters of the nanofibers in the membrane have been varied from 8 to 50 nm by varying the anodization conditions. Capillary force is sufficiently large to draw high molecular weight polymers into the membrane, producing either nanotubes or nanorods. Polymer solutions can also be used place a thin film on the walls of the nanotubes, forming nanotubes. With pore diameters less than the radius of gyration, a quantitative understanding of perturbations to chain dynamics due to geometric constraints was examined. We found a weak molecular weight-dependent mobility of polymers confined within AAO nanotubes having diameters smaller than the dimension of the chains in the bulk. The measured mobility of polymers in the confined geometry was much higher than the mobility of the unconfined chain. Rayleigh instabilities in thin polymer films confined within nanoperforated alumina membranes were also found where periodic undulations on the film surface were found to increase with time, eventually bridging across the cylindrical nanopore, resulting in the formation of polymer nanorods with a periodic array of encapsulated holes. With microphase separated block copolymers, where the characteristic period of the BCP morphology is comparable to the pore diameter, significant deviations from the bulk morphology as revealed by electron tomography. Small angle neutron scattering was also used to investigate the influence of cylindrical confinement on the order-to-disordered transition. This work was done in collaboration with T. J. McCarthy (UMass), K. Shin (Seoul National University), H. Jinnai (Kyoto University), D. Chen, J. Chen, H. Xiang, T. Kim, and P. Dobryal, and was supported by the DOE, NSF MRSEC, NSF CHM.

9:48AM H2.00004 The Challenge of Understanding the “Complexity” of Polymeric Fluids and Solutions. JACK DOUGLAS, Polymers Division, National Institute of Standards and Technology — It is well known that the complexity of polymer conformational shapes makes this class of molecules prone to glass formation and that high molecular mass polymers exhibit rubbery viscoelastic flow properties associated with their topological and packing interactions. Many natural and synthetic polymers also exhibit complex associative interactions arising from the variation of chemical species and the presence of charged and polar groups within the molecule that can give rise to polymer supermolecular organization into a wide range of fragile structures at the nanoscale and larger. There are changes in both the thermodynamics and dynamics of these fluids associated with these general patterns of “complex fluid” behavior that provide a fundamental challenge for theoretical understanding so that this field remains at the frontier of materials science. The high level of regularity observed in the relatively high frequency glassy dynamics of polymer fluids, and other glass forming liquids more broadly, and in the viscoelastic properties that define chain “entanglement” in high molecular mass polymers, provides some hope for a general theoretical framework describing the complex fluid dynamics of polymeric fluids. Specifically, it is argued, and supported by evidence, that the complex fluid behavior underlying glass formation, entanglement and self-assembly in polymeric fluids all involve emergent collective behavior taking the form of supermolecular polymer structures forming and disintegrating in dynamic equilibrium. This “dynamic heterogeneity” paradigm, which is not addressed by conventional mean field theories such as the mode-coupling model of glass formation and the reptation model, provides a framework for understanding many aspects of the linear and non-linear dynamics of polymer complex fluid behavior such as stretched exponential stress relaxation, and shear thinning and “aging” following cessation of flow. It also provides a framework for understanding the influence of nanoparticles, and other additives to polymeric fluids, that modify the fluid mesoscale structure, often with significant changes in material properties.
10:24AM H2.00005 Anisotropic Self-Assembly of Nanoparticle Amphiphiles1, SANAT KUMAR, Columbia University — It is easy to understand the self-assembly of particles having anisotropic shapes or interactions, such as Co nanoparticles or proteins, into highly extended structures. However, there is no experimentally established strategy for creating anisotropic structures from common spherical nanoparticles. We demonstrate that spherical nanoparticles, uniformly grafted with macromolecules, robustly self-assemble into a range of anisotropic superstructures when they are dispersed in the corresponding homopolymer matrix. This phenomenon is driven by the microphase separation between the inorganic nanoparticles and the (organic) polymeric chains grafted to their surfaces in a fashion similar to block copolymers. This microphase separation driven self-assembly provides a unique means of controlling the global nanoparticle dispersion state in polymer nanocomposites. The relationship between the state of particle dispersion and nanocomposite properties can thus be critically examined, and in particular we focus on the mechanical reinforcement afforded when particles are added to polymers. Grafted nanoparticles are thus versatile building blocks for creating tunable and functional particle superstructures with significant practical applications. With Pinar Akcora, Hongjun Liu, Yu Li, Brian Benicewicz, Linda Schadler, Thanos Panagiotopoulos, Jack Douglas, P. Thiyagarajan and Ralph Colby.

1Supported by NSF—DMR.

Tuesday, March 17, 2009 8:00AM - 10:48AM –

Session H18 DPOLY: Block Copolymer Thin Films I

8:00AM H18.00001 Polymer Physics Prize Symposium Break –

8:36AM H18.00002 Analysis of block-copolymer thin film ordering through a moving thermal zone, KEVIN YAGER, NATHANIEL FREDIN, RONALD JONES, Polymers Division, National Institute of Standards and Technology — Block-copolymer thin films self-assemble into well-defined structures at the nanometer lengthscale. It has been shown that the morphology, orientation, and degree of order resulting from assembly is sensitive to a variety of preparation parameters, including annealing time and temperature, solvent exposure, substrate surface energy, application of electric fields, etc. A moving thermal zone can also strongly affect the ordering. We have shown that relatively “cold” zone annealing (CZA) conditions (above the glass-transition but well below the disordering temperature) can induce a preferential orientation of the microdomains in thin films. We further analyze this effect by measuring the ordering through the thermal front, using atomic force microscopy and scattering techniques (reflectivity and GI-SAXS), which are combined to quantify the order and 3D orientational distribution. Zone annealing leads to increased grain sizes and substantially faster coarsening kinetics, as compared to oven annealing. Moreover, the evolution of order through the thermal front constrains models which aim to explain the CZA’s ability to induce orientational bias.

8:48AM H18.00003 Neutral Parameter Window for Perpendicularly Oriented Block Copolymer Resists Deposited on Organosilicate Substrates with Tunable Surface Energy, HYOSEON SUH, KOOKHEON CHAR, Seoul National University, HILMA KANGS-PARK, F. NEALEY, University of Wisconsin — Balancing the interfacial interactions of a block copolymer (BCP) with a substrate as well as the free surface can induce the perpendicular orientation of microdomains, allowing the BCP films to serve as templates for nanofabrication. However, it is known that such orientation of microdomains is quite sensitive to the film thickness. In this presentation, we investigated the effect of film thickness on the orientation of microdomains in lamellae-forming P(S-b-MMA) thin films placed on thermally cured organosilicate (OS) substrates. For the film thickness of a P(S-b-MMA) ranging from 1 L0 up to 2.5 L0, we varied the surface energy of the OS substrate around the value close to the enthalpically neutral condition by controlling the substrate cure temperature. We will demonstrate the origin of the observed thickness effect by taking into account the increase in surface area at the free surface when P(S-b-MMA) films make holes or islands depending on the incommensurable conditions of the BCP film. This analysis allows us to define a more accurate neutral window for the P(S-b-MMA) in terms of both substrate surface energy and BCP film thickness.

9:00AM H18.00004 Effect of Surface Energetics on Block Copolymer Thin Film Phase Behavior1, JULIE LAWSON, MICHAEL BANEY, THOMAS EPPS, University of Delaware — The development of block copolymer materials for future nanotechnologies requires an understanding of how surface energetics affect block copolymer thin film phase behavior. In this work, we use combinatorial methods to study these effects and to identify transitions in thin film phase behavior and microstructure orientation. Surface energy gradients were created using a vapor deposition technique developed by our group in which cross-diffusion of functionalized chlorosilanes under dynamic vacuum results in a linear gradient in surface energy on a silicon substrate. These gradients were characterized using x-ray photoelectron spectroscopy (XPS) and contact angle measurements. We then cast a thin film of block copolymer on the modified substrates using a flow coating technique. Finally, we used thermal and solvent annealing conditions to affect the surface energy at the free surface. The surface morphology of the films was examined with atomic force microscopy (AFM), and morphological changes across the gradient were found.

1National Science Foundation DMR 0645586, National Science Foundation Graduate Research Fellowship

9:12AM H18.00005 Systematic tunability of self-assembled block copolymer patterns, YEON SIK JUNG, CAROLINE ROSS, Massachusetts Institute of Technology — The morphology and length scale of diblock copolymers (BCPs) are determined by the chain lengths, and therefore to obtain different geometries and feature sizes, polymers with different chain lengths or BCP/homopolymer blends have been employed. Here, we report on the solvent vapor induced tunability of pattern dimension and morphology of thin films of polystyrene-polydimethylsiloxane (PS-b-PDMS) BCPs, which provide robust patterns with exceptionally good ordering due to their large interaction parameter. Vapor pressure can control the interfacial interaction between the two blocks, and a mixed solvent can manipulate the effective volume fraction of each block. We show both coupled and independent control of the microdomain size and the periodicity by changing the vapor pressure and the mixing ratio of a selective (heptane) and a partially selective (toluene) solvent. We also demonstrate the transformations from spheres to cylinders and from cylinders to perforated lamellar structures by increasing the portion of selective solvent in the vapor. These results are supported by a theoretical model.

9:24AM H18.00006 Solvent annealing of Micropatterned PS-b-PEO copolymer films1. TAE HEE KIM, HIMADRI ACHARYA, HEE JUNE JOENG, CHEOLMIN PARK, Yonsei University — Solvent annealing of block copolymer thin films have been known as an effective way to control both orientation of microdomains with respect to the surface and their registration into a well ordered periodic lattice structure. We have recently demonstrated hierarchically ordered microdomains in a thin poly(styrene-b-ethylene oxide) (PS-b-PEO) film combined with microcontact printing. The solvent annealing gave rise to well ordered spherical PEO microdomains in large area by the confined dewetting of thin PS-b-PEO films which had been micropatterned on chemically modified surface during solvent annealing. In this presentation, we intentionally prepare a micropatterned dewet film of PS-b-PEO by spincoating a block copolymer solution on a topographic PDMS pre-pattern. Convex lens shaped spherical caps of PS-b-PEO individually located on each PDMS mesa were successfully transferred to a Si substrate by a conventional transfer printing technique. We investigate the effect of solvent on not only film wettability but also formation of hierarchical nanostructures.

1This research was supported by National Research Program for Memory Development and “SYSTEM2010” project sponsored by Korea Ministry of knowledge and economy and Samsung Electronics, Co., Ltd.

9:36AM H18.00007 Transition Behavior of Block Copolymer Thin Films. DU YEOL RYU, CHANGHAK SHIN, HYUNGJU AHN, JUNE HUH, Yonsei University, Korea, KWANG-WOO KIM, Pohang Accelerator Laboratory, Korea, THOMAS RUSSELL, University of Massachusetts, Amherst, YONSEI UNIVERSITY COLLABORATION, POHANG ACCELERATOR LABORATORY COLLABORATION, THE COLLABORATION. — The phase transitions in block copolymers (BCPs), like the order-to-disorder transition, occur when the enthalpic term of free energy of mixing is equal to the entropic term. In thin films, interactions at the substrate/polymer and polymer/air interfaces influence this free energy balance, resulting in a change in the transition behavior. Here, we report on the transition behavior of BCP thin films. The thickness dependence of the transition temperature shows that the free energy due to the entropic term overwhelms that due to the enthalpic term. In thin films, the free energy due to the entropic term becomes much more important than that due to the enthalpic term. The transition behavior of the BCP thin films is controlled by the thickness of the film.

9:48AM H18.00008 Thin Film Morphology of Diblock and Triblock Copolymers with Bulk Order-Order Transition (OOT). K.E. SOHN, R.C. COFFIN, G.C. BAZAN, E.I. KRAMEER, UCSB, K. KOJIO, Nagasaki, B.C. BERRY, A. KARIM, NIST, M. SPRUNING, J. WANG, ANL — The thin film morphology of SEB and SEBS block copolymers that have an OOT in the bulk from cylinders to spheres as the annealing temperature is increased was studied as a function of increasing film thickness using AFM and GISAXS. For both SEB and SEBS, the morphology is the same no matter if the film is annealed above or below the bulk OOT. The SEB morphology is governed by the free energy penalty due to chain stretching, showing spheres when the film thickness is less than that of a monolayer of cylinders. The cylindrical morphology dominates the regime of the film thickness that is larger than that of a monolayer of cylinders. On the other hand, the SEBS morphology is governed by the free energy penalty due to the mixing of the midblocks in the film. Spheres require a lower fraction of midblocks to loop at the surface than cylinders, therefore spheres pay a lower free energy penalty due to chain looping and were found for all film thicknesses studied (up to ~100nm).

10:00AM H18.00009 UV-Induced Order-to-Order Transition (OOT) in Thin Films of Supramolecular Diblock Copolymer Assemblies Containing 2-(4'-Hydroxyphenylazo)benzoic Acid. WEI CHEN, JIA-YU WANG, XINYU WEI, ANNA BALAZS, THOMAS RUSSELL — Long-range lateral ordering and orientation in block copolymer thin films, which are highly desired for applications requiring addressability, as in magnetic storage, may be obtained in a controlled way via an order-to-order transition (OOT), i.e., a morphological transition in a microphase-separated system. The phase transition is controlled by the strength of the azobenzene photoisomerization. The UV-induced OOT in the supramolecule-assembled thin films of 2-(4'-hydroxyphenylazo)benzoic acid and polystyrene-block-poly(2-vinylpyridine) diblock copolymer. Grazing incidence small angle X-ray scattering demonstrated that the transition from lamellae to hexagonally packed cylinders occurred at 150 °C after UV radiation for 1 hour due to a significantly enhanced interfacial fluctuation induced by photoisomerization as evidenced by X-ray Reflectivity. This suggested that UV light can be utilized to control OOT in the supramolecule-assembled thin films and, hence, to fabricate long-range ordered nanostructures, and even smart responsive surfaces.

10:12AM H18.00010 Dilute Micelle Arrays in Block Copolymer Thin Films. JOHN PAPALIA, RICHARD REGISTER, Princeton U., DOUGLAS ADAMSON, U. Connecticut, PAUL CHAIKIN, NYU — Thin films of sphere-forming block copolymers are attractive templates for surface patterning and nanofabrication. While the areal density of spheres (micelles) can be adjusted through the diblock's molecular weight, sparse micelle arrays are quite difficult to achieve. Instead, we blend the diblock with matrix homopolymer in the “dry brush” regime, which eliminates the “terracing” (island/void formation) pattern in films of the neat diblock. Furthermore, by choosing a system where the sphere-forming block wets the substrate and/or free surface, we can achieve very sparse micelle arrays. We use x-ray scattering to determine the micelle density at each thickness, rather than the blend ratio. Specifically, we employ a polystyrene-polyisoprene diblock (PS/PI blocks of 68/12 kg/mol), blended with PS homopolymer. The PI block wets both the free surface and the SiOx substrate. For sufficiently thin films (~60 nm for 50 wt% homoPS), all the block copolymer goes to form brush-like layers at the two surfaces, yielding no micelles. For thicker films, sufficient block copolymer remains to form spherical microdomains between the brushes; the areal density of micelles can be continuously tuned via the film thickness. We evaluate this approach by preparing a film with a thickness gradient, and apply a simple model to the measured areal densities of micelles.

10:24AM H18.00011 Surface Dynamics of Segregation Layer in Blockcopolymer Films. SANG-HOON SONG, WONSUK CHA, Sogang University, Korea, ZHANG JIANG, SURESH NARAYANAN, Advanced Photon Source, ANL, ADRIAN RUEHM, Max Planck Institute for Metal Research, Germany, SUNIL K. SINHA, Univ. of California, San Diego, HYUNJUNG KIM, Sogang University — We have investigated the surface dynamics of supported block copolymer films of poly(styrene)-b-poly(dimethylsiloxane) (PS-b-PDMS) in the spherical phase, i.e., PDMS cores surrounded by PS shells by x-ray photon correlation spectroscopy (XPCS) in grazing angle geometry. The experiment was performed at the beamline 8ID-1 in Advanced Photon Source. We found that the PDMS-rich layer near the surface appears at the temperature higher than the glass transition temperature. We applied the nanoscale bilayer diode modified surface to study the surface capillary waves on simple viscoelastic liquid films. The viscoelasticity obtained in this study is compared with that from the rheology measurement for bulk films.

1This work was supported by Korea Research Foundation, Korea Science & Engineering Foundation, and Seoul Research and Business Development Program (10816).

10:36AM H18.00012 Block Copolymer Brushes1. MARK MATSEN, University of Reading — Using self-consistent field theory (SCFT), we examine dry brushes of AB diblock copolymer, where the B ends are uniformly grafted to a planar substrate. Four different morphologies are predicted, which are conveniently described as the uniform, stripe, hexagonal, and inverted hexagonal phases on the basis of the patterned formed at the air surface by the A-rich domain. Phase diagrams are calculated for different grafting densities and for different A-segment surface affinities. In contrast to unanchored diblock-copolymer films, the brush system has a much greater tendency to form chemically-patterned surfaces.

1Sponsored by EPSRC (grant no. EP/F029616/1)
Behavior in Glassy Polymers

Controlling the relative timescale of the relaxational process by altering the polymer network structure alters both the rate and the mode of penetrant transport. To this end, the effects of the basic network parameters of PMMA, including the degree of crosslinking, polymer mesh size, and the crosslink size, on the integral sorption of methanol were studied utilizing both gravimetric data and in situ ultra-high-resolution X-ray computed tomography studies. The effects of sub-Tg annealing/aging, temperature, and the presence of un-reacted monomer were also investigated. Controlling the relative timescale of the relaxational process by altering the polymer network structure is shown to directly influence the Case II front propagation velocity and the nature of the observed transport behavior.

On the Nature of Gas Transport of Ethylene Vinyl Alcohol Copolymers

SERGEI NAZARENKO, JUSTIN BRANDT, BRIAN OLSON, University of Southern Mississippi, ALEXANDER JAMIESON, Case Western Reserve University — Historically, all the approaches describing gas diffusion in polymers can be roughly divided in two categories, based on free volume models and the activation molecular models, which take into account the cooperative penetrant-polymer chain motions, chain rigidity and intermolecular forces. Although gas transport characteristics exhibit a general correlation with free volume, alone free volume cannot adequately describe gas barrier. The chain rigidity and the strength of intermolecular interactions are two additional important factors which are manifested via activation energy. The main objective of this work was to develop a quantitative understanding of the manner in which a polymer’s network structure alters the rate and the mode of penetrant transport. To this end, the effects of the basic network parameters of PMMA, including the degree of crosslinking, polymer mesh size, and the crosslink size, on the integral sorption of methanol were studied utilizing both gravimetric data and in situ ultra-high-resolution X-ray computed tomography studies. The effects of sub-Tg annealing/aging, temperature, and the presence of un-reacted monomer were also investigated. Controlling the relative timescale of the relaxational process by altering the polymer network structure is shown to directly influence the Case II front propagation velocity and the nature of the observed transport behavior.

8:48AM H19.00003 Twinkling Fractal Theory of the Glass Transition: Applications and Insights

RICHARD WOOL, University of Delaware — The new perspective on the Glass Transition of amorphous materials offered by the Twinkling Fractal Theory (TFT). [R. P. Wool, J. Polym. Sci, Part B: Polym Phys. 46, 2765 (2008)] is examined in several applications. The TFT describes Tg in terms of the autocorrelation relaxation function for the spatio-temporal solid-liquid fluctuations which are related to the vibrational frequencies (“twinkles”) described by the Orbach vibrational density of states for a fractal. The twinkling frequencies for solid-liquid interchange are due to Boltzmann energy populations of interatomic oscillators interacting through anharmonic potentials U(x) with energy D∇; order 1-5 kcal/mol. Tg occurs when the activation energy for the solid-liquid transition goes to zero at the inflection point of U(x) and is given by Tg = 2D/6k. The applications include: (a) group contributions to Do, (b) the rate and temperature dependence of yielding and fracture, (c) shear thickening fluids, (d) rate dependence of dynamical mechanical properties, particularly the tan delta damping peak used to measure Tg, (e) derivation of the empirical WLF time-temperature superposition empirical relation, (f) thermal expansion and (g) physical aging.

9:00AM H19.00004 Cooperativity and fragility in glass forming systems: not a simple relationship

LIANG HONG, ALEXANDER KISLIUK, ALEXEI SOKOLOV, Department of Polymer Science, The University of Akron, Akron, Ohio 44325-3909, USA, DR. SOKOLOV’S TEAM — Understanding the sharp increase of the main structural relaxation time τ on approaching the glass transition temperature (Tg) remains a great challenge. Traditionally this relaxation is considered as a cooperative process, with larger cooperativity leading to a steeper temperature dependence of τ around Tg, i.e. higher fragility. On the other hand, the boson peak, a collective vibration in the pico-second time region, is also described as a cooperative motion. In this study we estimate the structural correlation length for various glass forming systems from the collective vibration. The obtained values are in good agreement with the dynamic heterogeneity length estimated by 4 dimensional NMR for the main structural relaxation. Thus the two different motions appear to have very similar length scale for cooperativity. Direct comparison of cooperativity to fragility reveals no correlation. However, we discover that cooperativity correlates with the pure volume contribution to fragility. This result explains why many earlier attempts to find direct relationship between fragility and cooperativity fail. A possible origin for the observed correlation is discussed.

9:12AM H19.00005 Molecular Interpretations of Observed non-Fickian Penetrant Transport Behavior in Glassy Polymers

ADAM EKENSEAIR, RICHARD KETCHAM, NICHOLAS PEPPAS, The University of Texas at Austin — The relative rates of the diffusional and relaxational processes during the absorption of penetrant molecules in glassy polymers determine the nature of the transport process and lead to Fickian, Case II, and anomalous absorption behavior. While previous models account for anomalous behavior, there is still a disconnect between theory and experiment, as data must be fit to the model with previously determined independent parameters. With trends leading to smaller device scales and increasingly complex polymer structures, there is a need for a quantitative understanding of the manner in which a polymer’s network structure alters both the rate and the mode of penetrant transport. To this end, the effects of the basic network parameters of PMMA, including the degree of crosslinking, polymer mesh size, and the crosslink size, on the integral sorption of methanol were studied utilizing both gravimetric data and in situ ultra-high-resolution X-ray computed tomography studies. The effects of sub-Tg annealing/aging, temperature, and the presence of un-reacted monomer were also investigated. Controlling the relative timescale of the relaxational process by altering the polymer network structure is shown to directly influence the Case II front propagation velocity and the nature of the observed transport behavior.

9:24AM H19.00006 On the Nature of Gas Transport of Ethylene Vinyl Alcohol Copolymers

SERGEI NAZARENKO, JUSTIN BRANDT, BRIAN OLSON, University of Southern Mississippi, ALEXANDER JAMIESON, Case Western Reserve University — Historically, all the approaches describing gas diffusion in polymers can be roughly divided in two categories, based on free volume models and the activation molecular models, which take into account the cooperative penetrant-polymer chain motions, chain rigidity and intermolecular forces. Although gas transport characteristics exhibit a general correlation with free volume, alone free volume cannot adequately describe gas barrier. The chain rigidity and the strength of intermolecular interactions are two additional important factors which are manifested via activation energy. The main objective of this work was to develop a fundamental understanding of oxygen transport in a broad range of EVOH copolymers as it is related to free volume characteristics studied by positron annihilation lifetime spectroscopy and hydrogen bonding interaction.
elastic modulus is the inverse of the decaying characteristic relaxation time. Parameter of the isothermal ripening process is the "ripening time", $t$, scaling function with two pronounced powerlaw regions, a fast ripening process ($\sim G$ that gradually approaches its equilibrium. The ripening process accelerates at elevated temperature. After rescaling (Rheol Acta 45:331-338, 2006), the complex clay sheets through the action of end-functionalized ("sticky") polymer molecules. A freshly mixed sample quickly forms a sample-spanning network structure scaling relations for the slow ripening of an out-of-equilibrium model colloidal solid that consists of clay particles that swell and exfoliate into randomly oriented H. HENNING WINTER, University of Massachusetts Amherst, X. WANG, G. XUE, Nanjing University, China, P. SUN, Nankai University, China — We explore average of the moduli of the two pure components. As in recent studies of monodisperse systems (R. S. Hoy and M. O. Robbins, Phys. Rev. Lett. G hardening have been a matter of great controversy in recent years. Recent experiments and our earlier simulations have suggested that the hardening modulus system of deformation on the potential energy landscape and find qualitatively different behaviors when we deform at constant stress versus constant strain rate. Additionally, we explore the effects of each mode of deformation on the potential energy landscape and find qualitatively different behaviors when we deform at constant stress versus constant strain rate. Finally, we provide a brief comparison of our simulation results to recent experiments and demonstrate that the simulations are capable of reproducing all of the behaviors observed in the experiments.

THEODOROU, National Technical Univ. of Athens — Craze formation occurs during fracture of many polymers and leads to a substantial increase in the fracture energy. Models of craze formation usually assume that entanglements act like permanent chemical crosslinks. This model is tested by following the evolution of entanglements using the Contour Reduction Topological Analysis (CReTA) algorithm. The CReTA algorithm shortens each chain until further shortening would require chains to pass through each other. The contacts between chains that limit further shortening are identified as entanglements or topological constraints. Unlike related algorithms, the chain shortening has little effect on the craze structure, allowing the entanglements to be followed in real space, as well as along chains. CReTA is applied to molecular simulations of crazing using a coarse-grained bead-spring polymer model. The number of beads in each chain $N$ and the entanglement length $N_e$ are varied. Our results show that entanglements do not act like fixed chemical crosslinks. There is a systematic loss in entanglements during craze formation that does not occur when chains are deformed affinely and is nearly independent of $N/N_e$. The role of chain length, $N$, Ne, interchain friction and other parameters in determining the degree of entanglement loss is discussed.

10:36AM H19.00012 A Model of Glassy Polymers that Includes both Spatial and Temporal Fluctuations, GRIGORI MEDVEDEV, JAMES CARUTHERS, Purdue University — Glass forming polymers near and below $T_g$ are dynamically heterogeneous as has been found via a number of experimental techniques, where the dynamic heterogeneity is the probable cause of the non-exponential decay of the orientation correlation function of probe molecules embedded in polymer matrix as well as "breaking" of the Stokes-Einstein relations for rotational and translational diffusion. Although dynamic heterogeneity in glassy polymers is well established, constitutive models for describing the mechanical behavior employ quantities that ignore fluctuations. Consequently, the mechanical implications of dynamic heterogeneity are largely unexplored. In this talk we report on a finite element type model, where the local relaxation times in the material experience fluctuations, i.e. both the temporal and spatial nature of the fluctuations is explicitly acknowledged. The stochastic force between neighboring domains is assumed to be uncorrelated; however, since neighboring domains tile space, there is spatial and temporal correlation in the stochastic response of the system. The mechanical response of the sample under different deformation histories, including constant strain rate tensile and compressive loading as well as creep under constant load, will be presented.

9:36AM H19.00007 Photochemical Crosslinking of Preformed Glassy and Amorphous Polymers Through bis-Benzophenone Mediated Covalent Bridging, NICHOLAS CARBONE, MARY DICKSON, JEFFREY LANCASTER, University of Groningen, GREG CARROLL, University of Groningen, JEFFREY KOBORSTEIN, Columbia University — We show that bis-benzophenone (bis-BP) is an effective method to photochemically crosslink essentially any solvent-free glassy or amorphous preformed polymer system that contains abstractionable hydrogen atoms. When bis-BP is mixed into a polymer and exposed to UV radiation, it abstracts hydrogen atoms from any chains in proximity, thereby initiating a cascade of free radical reactions that include several mechanisms that can lead to covalent polymer crosslinking. Herein we study the early stages of branching reactions that precede gelation by following molecular weight changes in bis-BP modified glassy polystyrene (PS) and amorphous poly(n-butyl acrylate) (PNBA) thin films on silicon wafers by Gel Permeation Chromatography. Quantitative molecular weight changes in PS-bis-BP and PNBA-bis-BP thin films are studied as a function of irradiation time, polymer:bis-BP molar ratio, and film height. Increases in molecular weight and polydispersity are quantified and model equations are developed.

We gratefully acknowledge support of the NSF-IGERT fellowship program.
Anomalous crack propagation in reinforced natural rubber. Paul Sotta, CNRS/Rhodia Research and Technology, France, Brice Gabrielle, Didier Long, Loïc Vanel, CNRS/Rhodia Research and Technology, Pierre-Antoine Albouy, CNRS/University Paris XI, Francesca Pedditto, Rhodia Operations — In reinforced natural rubber, crack propagation in mode I exhibits rotation of the tear in a direction perpendicular to the usual one. Our objective is, first, to understand the impact of this phenomenon on fracture toughness of the material, and, secondly, to understand how this phenomenon is related to the specific properties of reinforced natural rubber. To this aim, we combine measurements of ultimate properties, measurements of the number and length of tear rotations as a function of loading velocity and temperature, and investigation of material heterogeneities at sub-micrometric scales, originating both from fillers and strain-induced crystallites (strain-induced crystallinity is measured up to failure by X-ray diffraction), in natural rubber samples reinforced by nanometric aggregates. Observations suggest that tear rotation is related both to the mechanical anisotropy induced by strain-induced crystallinity and to the dissipative properties of the material at high strain.

Tuesday, March 17, 2009 8:00AM - 11:00AM — Session H20 DPOLY: Electrically and Optically Active Polymers 321

8:00AM H20.00001 Polymer Physics Prize Symposium Break

8:36AM H20.00002 Soliton and polaron induced 3D conformational changes in conjugated polymers1. André Leitao Botelho, Xi Lin2, Boston University — We perform ab initio calculations on polyacetylene (PA), polypyrrole (PPY), and polyaniline (PANI) to examine the 3D conformational change as a function of injected charge. We find that self-localized solitons and polarons in their ground states are dispersed along the chain to minimize the localized charge Coulomb repulsion and the strain repulsion due to chain terminations. Each polaron in PPY or PANI progressively straightens each chain from their neutral bent state, where PPY and PANI are shown to have analogous conformations due to subsequent twisting along non-collinear axes. Solitons in PA are able to fully utilize the zigzag backbone geometry to minimize Coulomb repulsions, by alternating from one side of the chain to the other. This causes bending in alternating directions, leading to a sinusoidal shape, while maintaining a straight chain axis on average. Since PPY and PANI can change from a coil to a straight rod, these polymers can achieve strains about an order of magnitude higher than PA.

1This work was supported by Honda R&D Co., Ltd.

2Corresponding author

8:48AM H20.00003 Conjugated Polymer based sensor for detecting explosives such as RDX (1,3,5-Trinitrohydro-1,3,5-triazine)1, Abhishek Kumar, Department of Physics, University of Massachusetts Lowell, Robinson Anandkather, Center for Advanced Materials, Jayant Kumar, Department of Physics — Conjugated polymers are an important class of materials and have attracted great scientific interests because of their unique optical and electrical properties. Synthesis of various conjugated polymers has been reported for detecting DNT and TNT. Here, for the first time, we report the synthesis and characterization of a conjugated polymer based on thiophene, Poly[2-(3-thienyl)ethanol n-butoxycarbonylmethylurethane] (PURET), for the detection of RDX via fluorescence quenching. The incorporation of judiciously chosen bulky butoxycarbonylmethyl urethane side group in the back bone of polythiophene reduces the aggregation, improves the solubility of the polymer in the organic solvents and quantum yield of fluorescence. We have observed a 15 % decrease of fluorescence in 60 sec in thin films of PURET exposed to the saturated vapor of RDX at room temperature. The large exciton diffusion length and interaction between side group and the quencher molecule are believed to be the reasons for enhanced RDX detection. Sensitivity below 5 parts per trillion (ppt) has been demonstrated for RDX at room temperature. The effect of nanostructures (electrospun nanofibers and stamped 1 D periodic pattern) on sensitivity and response time will also be discussed.

1National Science Foundation

9:00AM H20.00004 Charge-transfer excitons in strongly coupled organic semiconductors. Paul-Ludovic Karsenti, Jean-François Glöwe, Carlos Silva, University of Montreal — Time-resolved and temperature-dependent photoluminescence measurements on one-dimensional sexithiophene lattices reveal intrinsic branching of photoexcitations to two distinct species: self-trapped excitons and dark charge-transfer excitons (CTX; \( \gtrsim 5\% \) yield), with radii spanning 2–3 sites. The significant CTX yield results from the strong charge-transfer character of the Frenkel exciton band due to the large free exciton bandwidth (~ 400 meV) in these supramolecular nanostructures.

9:12AM H20.00005 Highly Conductive Polymer Films by Post-Processing Solvent Annealing and Their Broad Applications in Organic Electronics. Joong Eun Yoo, Kwang Seok Lee, Enrique Gomez, Kimberly Baldwin, Yangming Sun, Chang Suk Kim, Hong Meng, Yueh-Lin Loo, Princeton University Team, University of Texas at Austin Team, Dupont Collaboration, Governor Livingston High School Team — The electrical conductivity of polyaniline (PANI) that is template synthesized with a polymer acid of poly(2-acrylamido-2-methyl-1-propanesulfonic acid), PAAMPSA, is enhanced by more than two orders of magnitude with post-processing solvent annealing. Such solvent annealing allows the conducting polymer to rearrange from the globular structure that is arrested by strong ionic interactions during synthesis to the conformationally more favorable structure that dramatically enhances charge transport. This solvent annealing is general; we demonstrate conductivity enhancement with this process for at least two common classes of conducting polymers, including poly(3,4-ethylenedioxythiophene), PEDOT, as well as PANI. The treated conducting polymer films make efficient source and drain electrodes and anodes for organic thin-film transistors and organic solar cells, respectively.

9:24AM H20.00006 Electrochemical Stability of Polyaniline Beyond pH 9. Jacob Tarver, Joong Eun Yoo, YUEH-LIN LOO, Department of Chemical Engineering, Princeton University — Conductive polymer films are promising candidates for solution-based biosensor and organic electrochemical transistor devices. For many conducting polymers, however, stable electrochemical activity often demands restrictively acidic solutions. This need has in turn limited the use of conductive polymers in near-neutral and physiological conditions. Using spectroelectrochemical methods, we studied the stability of polyaniline that is template synthesized on poly(2-acrylamido-2-methyl-1-propanesulfonic acid) as a function of pH. Transitions between the different oxidation states of polyaniline are stable and reversible in solutions as high as pH 10. This range of sustained electroactivity far exceeds that of previously reported polyaniline systems. In comparison, polyaniline that is doped with small-molecule acids loses its electroactivity in solutions beyond pH 4. Immobilezation of polyaniline within a polymer acid matrix retards dopant diffusivity and reduces proton mobility. The preservation of local acidic conditions within the film greatly extends the pH range of stable electroactivity.
9:36AM H20.00007 Quadratic Electro-optic Effect in a Novel Nonconjugated Conductive Polymer, iodine-doped Polynorbornene. ANANTHAKRISHNAN NARAYANAN, MRINAL THAKUR, Photonic Materials Research Laboratory, Auburn University, AL — Quadratic electro-optic effect in a novel nonconjugated conductive polymer, iodine-doped polynorbornene has been measured using field-induced birefringence at 633 nm. The electrical conductivity of polynorbornene increases by twelve orders of magnitude to about 0.01 S/cm upon doping with iodine. The electro-optic measurement has been made in a film doped at the medium doping-level. The electro-optic modulation signal was recorded using a lock-in amplifier for various applied ac voltages (4 kHz) and the quadratic dependence of the modulation on the applied voltage was observed. A modulation of about 0.01% was observed for an applied electric field of 3 V/micron for a 100 nm thick film. The Kerr coefficient is determined as about 1.7×10⁻¹¹ m/V². This exceptionally large Kerr coefficient has been attributed to the confinement of this charge-transfer system within a sub-nanometer dimension. 1. A. Narayanan, A. Palthi and M. Thakur, J. Macromol. Sci. – PAC, accepted.

9:48AM H20.00008 Quadratic Electro-optic Measurements in Nonconjugated Conductive Polymers, iodine-doped Polyisoprene and Pol(y-pinene) at 1.55 μm. ANANTHAKRISHNAN NARAYANAN, JITTO TITUS, MRINAL THAKUR, Photonic Materials Research Laboratory, Auburn University, AL — Exceptionally large near-resonant (at 633nm) quadratic electro-optic effects in nonconjugated conductive polymers, iodine-doped pol(y-pinene) and 1,4-cis-polyisoprene have been previously reported. In this report, we discuss the quadratic electro-optic effects in these polymers at 1.55μm. The measurements were made using the field-induced birefringence technique. A modulation depth of about 0.1% was observed for a 1 μm thick sample of doped pol(y-pinene) at an applied field of 1V/μm. The Kerr coefficient as determined was about 1.6×10⁻¹⁰ m/V². For polyisoprene samples the modulation was slightly smaller. These exceptionally large Kerr coefficients at a technologically important wavelength make these polymers promising for guided-wave applications in electro-optics. Techniques for longer-term stability of the samples have been established. The large optical nonlinearities as observed have been attributed to the sub-nanometer confinement of these charge-transfer systems.

10:00AM H20.00009 ABSTRACT WITHDRAWN

10:12AM H20.00010 Ultrasonic Solution Processed Polymer Photodetectors. XIONG GONG, MING-HONG TONG, GANG YU, CHAN-LONG SHIEH, BOO NILSSON, ALAN HEEGER, CBRITE INC TEAM, UC SANTA BARBARA TEAM — Semiconducting polymer optoelectronic and electric devices have evolved as a promising cost-effective alternative to silicon-based devices. Organic photodetectors have been the subject due to several inherent advantages. Some of the important advantages of these so-called “plastic” electronics include large-area detection, low cost of fabrication, ease of processing and mechanical flexibility. However, there are few reports on organic photodetectors whose performances are comparable with inorganic counterparts. will report ultrasonic solution processed photodetectors fabricated by different semiconducting polymers as the electron donors and various fullerenes derivatives and/or inorganic quantum dots as the electron acceptors. Polymer photodetectors with different photo-response and detectivity were demonstrated. One example is that polymer photodetectors have photo-response from 300nm to 1450nm, the detectivity larger than 10¹² cm Hz¹/₂/W, and linear dynamic range larger than 120 dB. All these values are comparable to or even better than their inorganic counterparts.

10:24AM H20.00011 Twin instability of Peierls distortion and its mechanical consequence on conductive polymer actuation. MINGHAI LI, ANDRE BOTELHO, XI LIN, Boston University — We prove analytically that a one-dimensional metallic chain is subject to two coupled spontaneous conformational relaxations, resulting in the well-known Peierls bond length alternation and an overall chain contraction. Using the Su-Schrieffer-Heeger (SSH) Hamiltonian, a tight-binding version of the Peierls theory, we find in a neutral defect-free polyacetylene chain these two coupled distortions work cooperatively against the backbone elastic deformation. The cooperative bond alternation and chain contraction reduce the activation barrier so they cross each other at a certain point, beyond which the barrier disappears and solitons cannot get closer to the center of the chain. The local minima energy has a larger exponent than the wash-board energy landscape when it is in the vicinity of the boundary due to its localization width shrinkage. Favoring the opposite elastic strain as the boundaries, soliton prefers staying at the center of the backbone via the Su-Schrieffer-Heeger (SSH) model and ab initio calculations. Our results confirm the conventional consensus that soliton hops over two CH bonds in one single step, maintaining wavefunction nodal structures at intermediate CH sites. Standard SSH parameters give rise to negligible migration barriers, which increases exponentially with the localization width decreases. Favoring the opposite elastic strain as the boundaries, soliton prefers staying at the center of an open chain; this ground state energy increases linearly when the chain length decreases. Starting at the center and moving towards the chain terminations, soliton first successively jumps over the Peierls bond alternations and then smoothly switches to an exponentially increased wash-board energy landscape when it is in the vicinity of the boundary due to its localization width shrinkage. The local minima energy has a larger exponent compared to that of the activation barrier so they cross each other at a certain point, beyond which the barrier disappears and solitons cannot get closer to the boundary.

10:36AM H20.00012 Soliton migration along trans-polyacetylene backbone. MINGHAI LI, YONGWOO SHIN, XI LIN, Boston University — We compute the minimum energy paths and activation barriers for the soliton migration process along trans-polyacetylene backbone via the Su-Schrieffer-Heeger (SSH) model and ab initio calculations. Our results confirm the conventional consensus that soliton hops over two CH sites in one single step, maintaining wavefunction nodal structures at intermediate CH sites. Standard SSH parameters give rise to negligible migration barriers, which increases exponentially with the localization width decreases. Favoring the opposite elastic strain as the boundaries, soliton prefers staying at the center of an open chain; this ground state energy increases linearly when the chain length decreases. Starting at the center and moving towards the chain terminations, soliton first successively jumps over the Peierls bond alternations and then smoothly switches to an exponentially increased wash-board energy landscape when it is in the vicinity of the boundary due to its localization width shrinkage. The local minima energy has a larger exponent compared to that of the activation barrier so they cross each other at a certain point, beyond which the barrier disappears and solitons cannot get closer to the boundary.

1:00PM H20.00013 ABSTRACT WITHDRAWN

Tuesday, March 17, 2009 11:15AM - 2:15PM — Session J5 DPOLY: Polymer Nanoparticle Interactions 401/402

11:15AM J5.00001 Simulations of Polymer Grafted Nanoparticles in a Polymer Matrix. GRANT SMITH, University of Utah — We have performed molecular dynamics (MD) simulations of polymer-grafted nanoparticles in a polymer melt. The model is a coarse-grained representation of spherical nanoparticles with arafted poly(methyl methacrylate)-like bead-spring polymer in a matrix of the same polymer. Simulations were performed on both a single polymer-grafted nanoparticle as well as for a pair of polymer-grafted nanoparticles. The nanoparticle has a diameter of 5 nm. We have investigated the role of the molecular weight of the grafted and matrix polymer on both brush structure and nanoparticle-nanoparticle interactions. We find that brush density profile is independent of matrix molecular weight. Furthermore, the matrix chains penetrate almost to the particle surface, and there is no extended region with zero or near-zero matrix chain density. Hence, the highly curved brush does not exhibit “dry brush” behavior that would be expected at this investigated grafting density. We observe a repulsive interaction between the nanoparticles that sets in at a separation consistent with the polymer brush height. The combined brush-brush plus matrix effect on the nanoparticle-nanoparticle interactions is repulsive at all separations. Our simulations profile reveals no matrix-induced attraction between nanoparticles that is anticipated when the brush are truly “dry”, i.e., largely non-penetrable by the matrix. Such behavior would be expected for larger particles where the surface curvature effects on brush structure and brush-melt interactions are less important. However, for small nanoparticles, our simulations reveal that surface curvature effects are very important in determining the structure of the grafted polymer as well as nanoparticle-nanoparticle interactions.

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a variety of optical, electronic, and biomedical applications. The annealing temperatures after incubation. The planar geometry of the PSCs led to Janus NP formation. A series of NP dimers, trimers and tetramers were Janus NPs and patterning these NPs using PSCs. Single crystals of thiol-terminated polyethylene oxide (PEO) were incubated in a gold sol. Au-S bonds were alternating patterning was achieved by using crystalline block copolymers. The mechanism was attributed to the crystallization induced block copolymer phase.

NHSKs can serve as templates to fabricate a variety of CNTs-containing hybrid materials with controlled patterning on the CNT surface. Sub-20 nanometer periodically decorated with PSCs, resulting in nano hybrid shish-kebab (NHSK) structures. Because the polymer kebabs can be easily removed, these unique NHSKs can serve as templates to fabricate a variety of CNTs-containing hybrid materials with controlled patterning on the CNT surface. Sub-20 nanometer alternating patterning was achieved by using crystalline block copolymers. The mechanism was attributed to the crystallization induced block copolymer phase separation. This pattern was successfully used to template nanoparticles (NP) patterning on CNTs. In the second part of the talk, I will discuss fabricating Janus NPs and patterning these NPs using PSCs. Single crystals of thiol-terminated polyethylene oxide (PEO) were incubated in a gold sol. Au-S bonds were formed between the AuNPs and the PEO single crystal surfaces. The inter-particle spacing was controlled by PEO molecular weights, the incubation time, and the annealing temperatures after incubation. The planar geometry of the PSCs led to Janus NP formation. A series of NP dimers, trimers and tetramers were synthesized. NP nanowires were also fabricated. We anticipate that this observation could lead to controlled synthesis of artificial molecules and NP chains for a variety of optical, electronic, and biomedical applications.

1:39PM J5.00005 DNA Directed Nanoparticle Assemblies. FRANCIS W. STARR, Wesleyan University — While DNA is mostly noted for carrying genetic information, a single strand of DNA is simply a polymer with chemically specific recognition. As a result, DNA is an interesting polymer to consider for the development of new materials. In particular, attaching single strands of DNA to nanoparticle offers the possibility to encode highly specific bonding between nanoparticles to create engineered building blocks, or “functionalyzed atoms.” These core units are an ideal candidate for the development of network-based, nanostructured materials. In this talk, we present results from computer simulations of a coarse-grained model examining several choices and DNA functionalization, and show how these design choices can affect dynamics, phase behavior, and the formation of crystal structures. We first discuss nanoparticles functionalized by four single DNA strands. These units give rise to a material with a hierarchy of interpenetrating networked structure and four thermodynamically distinct amorphous phases, unlike any naturally occurring pure material. On the other hand, the mechanism for the formation of the amorphous phases offers insight into anomalous networked liquids like water and silica. We also consider how varying the number of functionalizing DNA strands alters both the number and shape of these phase transitions. The formation of very low density crystals of nanoparticles tethered by DNA has recently been achieved experimentally, but the factors controlling crystal formation are still not well understood. Therefore, we also discuss the results of nanoparticles uniformly coated with DNA, similar to experimental systems. We show how the DNA strand length and stiffness affects the competition between energy and entropy that controls crystal formation.

3Support from NSF DMR-0427239.

Tuesday, March 17, 2009 11:15AM - 2:15PM —
Session J18 DMP DPOLY: Charge Transport and Optical Properties of Organic Semiconductors

11:15AM J18.00001 Light Emitting Transistors of Organic Single Crystals. YOSHIHIRO IWASA, Tohoku University — Organic light emitting transistors (OLETs) are attracting considerable interest as a novel function of organic field effect transistors (OFETs). Besides a smallest integration of light source and current switching devices, OLETs offer a new opportunity in the fundamental research on organic light emitting devices. The OLET device structure allows us to use organic single crystals, in contrast to the organic light emitting diodes (OLEDs), the research of which have been conducted predominantly on polycrystalline or amorphous thin films. In the case of OFETs, use of single crystals have produced a significant amount of benefits in the studies of pursuit for the highest performance limit of FETs, intrinsic transport mechanism in organic semiconductors, and application of the single crystal transistors. The study on OLETs have been made predominantly on polycrystalline films or multicomponent heterojunctions, and single crystal study is still limited to tetracene [1] and rubrene [2], which are materials with relatively high mobility, but with low photoluminescence efficiency. In this paper, we report fabrication of single crystal OLETs of several kinds of highly luminescent molecules, emitting colorful light, ranging from blue to red. Our strategy is single crystallization of monomeric or oligomeric molecules, which are known to have a very high photoluminescence efficiency. Here we report the result on single crystal LETs of rubrene (red), 4,4′-bis(diphenylvinyl)antracene (green), 1,4-bis(5-phenylthiophene-2-yl)benzene (ACS) (green), and 1,3,6,8-tetrathenylpyrene (TPPy) (blue), all of which displayed ambipolar transport as well as peculiar movement of voltage controlled movement of recombination zone, not only from the surface of the crystal but also from the edges of the crystals, indicating light confinement inside the crystal. Realization of ambipolar OLET with variety of single crystals indicates that the fabrication method is quite versatile to various light emitting molecular solids, providing novel opportunities to get further insight on the intrinsic optoelectronic processes in organic semiconductors.


11:51AM J18.00002 ABSTRACT WITHDRAWN —
12:27PM J18.00003 Modification of the electronic properties of rubrene crystals by extrinsic species . LEONIDAS TSETSERIS, Vanderbilt University and University of Thessaloniki (Greece), SOKRATES PANTELIDES, Vanderbilt University and Oak Ridge National Laboratory — The chemical stability of organic semiconductors is one of the most important factors for the performance of related electronic devices. Here, we report the results of first-principles calculations on the effect of some of the most typical defect culprits in the prototype system of rubrene, the current record-holder organic semiconductor in terms of carrier mobilities. We identify the most stable water and oxygen-related impurity structures, with species in either substitutional or interstitial configurations, and we analyze their complex role in changing the shape and profile of rubrene energy bands. In certain cases the impurities either give rise or help annihilate carrier traps. We discuss the relevance of our findings for the optimization of rubrene-based electronic systems, and, in particular, the possibilities for effective defect engineering. This work was supported in part by DOE Grant DEFG0203ER46096.

12:39PM J18.00004 Charge carrier transport and optical properties of SAM-induced conducting channel in organic semiconductors . VITALY PODZOROV, Rutgers University — Certain types of self-assembled monolayers (SAMs) grow directly at the surface of organic semiconductors and induce high surface conductivity in these films [1]. For example, the conductivity induced by self-assembled alkyl silanes in organic molecules reaches 10^-5 S/cm (~10 Ω cm) [2]. The observed large electronic conductivity opens new opportunities for nanoscale surface functionalization of organic semiconductors and provides experimental access to the regime of high carrier density. Here, we will discuss temperature variable measurements of SAM-induced conductivity in several types of organic semiconductors. [1]. M. F. Calhoun, J. Sanchez, D. Olaya, M. E. Gershenson and V. Podzorov, “Electronic functionalization of the surface of organic semiconductors with self-assembled monolayers”, Nature Mater. 7, 84 (2008).

12:51PM J18.00005 Infrared spectroscopy of organic semiconductors modified by self-assembled monolayers . O. KHTAB, University of California, San Diego, B. LEE, V. PODZOROV, Rutgers University, J. YUEN, A.J. HEEGER, University of California, Santa Barbara, Z.Q. LI, M. DI VENTRA, D.N. BASOV, University of California, San Diego — Recently, self-assembled monolayers (SAMs) were used to modify electronic surface properties of organic single crystals, leading to several orders of magnitude increase in the electrical conductivity. Motivated by this discovery, the same technique was applied to polymers. Here we present a thorough spectroscopic investigation of organic semiconductors based on poly(3-hexylthiophene) (P3HT) that have been treated with a fluorinated trichlorosilane SAM. Infrared spectroscopy offers access to details of charge injection, electrostatic doping, and the electronic structure that are not always available from transport measurements, which can be dominated by defects and contact effects. In polymer films, the SAM molecules penetrate into the bulk, leading to a rich spectrum of electronic excitations in the mid-infrared energy range. M. F. Calhoun, J. Sanchez, D. Olaya, M. E. Gershenson, V. Podzorov, Electronic functionalization of the surface of organic semiconductors with self-assembled monolayers, Nature Mater. 7, 84–89 (2008).

1:03PM J18.00006 Gate electric-field tuning of contact barriers between metals and organic semiconductor crystals J. TAKEYA, M. YAMAGISHI, K. NAKAYAMA, T. UEMURA, Osaka University — Metal/organic semiconductor junctions are by all means essential in many organic electronic devices such as organic transistors, reasoning importance of understanding microscopic physics of carrier injection at the boundary. In this presentation, we focus on charge conductance through the metal/organic semiconductor contacts and their gate-electric field effects, fabricating structure of interfacing hole-rich rubrene single crystal with metal electrodes. The hole-rich regions are formed at the top surface of the crystals either by field-effect accumulation using secondary gate electrodes or charge transfer from acceptor films of fluoro-silane molecular layers or F4-TCNQ layers. Application of gate voltage on the bottom surface of the crystals has given rise to a very sharp switching in the conductance through the contacts, because of very short (nanoscale) active length for the conductivity modulation. For the mechanism of the result, energy-level tuning between the metals and the hole-rich rubrene surface is suggested as the result of gradual band-bending in the direction of crystalline thickness. The minimum working length of the device is highly advantageous in high-frequency response and densities of the device integration.

1:15PM J18.00007 Controlling Grain Size in Solution-Processed Organic Semiconductors for Thin-Film Transistors . STEPHANIE LEE, CHANG SU KIM, ENRIQUE GOMEZ, Princeton University, CHENG WANG, ALEXANDER HEMER, Lawrence Berkeley National Laboratory, MICHAEL TONEY, Stanford Synchrotron Radiation Laboratory, JOHN ANTHONY, University of Kentucky, YUEH-LIN (LYNN) LOO, Princeton University — We present a novel method for controlling the grain size in solution-processed triethylsilylethylanthradithiophene (TES-ADT) films through the addition of fractional amounts of fluorinated 5,11-bis(triethylsilylethyl) anthradithiophene (FTES-ADT) films. FTES-ADT can seed the crystallization of TES-ADT during solvent-vapor annealing. The grain size in these films follows an exponential dependence on the concentration of FTES-ADT, varying the FTES-ADT concentration by 2-fold induces a 3-order of magnitude change in the grain size. For channels in which the average grain size is 200 µm, the device mobility of the organic thin-film transistors (OTFTs) is 0.05 cm²/V-s. The relationship between device mobility and grain size is well described by a composite mobility model, which assumes a high intrinsic grain mobility and a low grain boundary mobility. Grazing incidence x-ray diffraction indicates that the crystal lattice of TES-ADT is preserved despite the addition of FTES-ADT.

1:27PM J18.00008 Charge transport in crystalline organic semiconductors: using polymorphs to explore the effect of crystal packing . OANA JURCHESCU, National Institute of Standards and Technology, DEVIN MOUREY, Penn State University, SANKAR SUBRAMANIÁN, SEÁN PARKIN, University of Kentucky, BRANDON VOGEL, Bucknell University, JOHN ANTHONY, University of Kentucky, THOMAS JACKSON, Penn State University, DAVID GUNDLACH, National Institute of Standards and Technology — Organic semiconductors are a fascinating class of materials, with a wealth of properties and diverse technological potential. We present molecule organic semiconductors, charge transport is closely related to the crystal packing motif. Polymorphism is frequently encountered in these materials, given the weak intermolecular interaction energies. This represents a unique opportunity to explore phenomena related to the fundamental mechanism of charge transport in organic semiconductors, such as the influence of the crystal packing. For example, 5,11-bis(triethylsilylethyl)anthradithiophene has two polymorphs inter-convertible through phase transition that occurs at T = 294 K. We report on their crystal structure, formation, and the effect of the different molecular packing on the electronic properties. We discuss the technical implications that a room-temperature phase transition has on the performance and stability of devices fabricated with this material.

1:39PM J18.00009 A crystalline phase organic semiconductor grown from a mesophase: A test of polaron band theory . NARESH SHAKYA, CHANDRA POKHREL, Department of Physics, Kent State University, BRETTE ELLMAN, SHIN-WOONG KANG, SATYAN KUMAR, Department of Physics, Kent State University, YULIA GETMANENKO, ROBERT TWIEG, Department of Chemistry, Kent State University — We find that the hole mobility of the crystalline smectic phases of the liquid crystal 1,4-di-(5-tridecylthien-2-yl)-benzene increases exponentially with decreasing temperature. While qualitatively consistent with transport via polaron bands, we find that it is quantitatively difficult to explain the data with physically realistic parameters. In particular, the data demand either quite large typical optical phonon frequencies and/or phonon bandwidths. We also find evidence that an unusually highly ordered high temperature smectic-F phase templates the formation of crystalline smectic phases, which may have implications for device development.
1:51PM J18.00010 First-principles study of charge injection and transport through pentacene multilayers. YONG-HOON KIM, University of Seoul — Applying a combined density-functional theory and matrix-Green's function approach [1, 2], I study the coherent charge transport properties of pentacene nanowires sandwiched between Au(111) electrodes. Junction models based on pentacene trilayers in the ideal n-stacked and herringbone arrangements with the face-on and edge-on contact configurations at different contact distances are considered. I show that pentacene wires exhibit a robust p-type conductance behavior in agreement with experiments, and analyze the physical origin in terms of charge transfer between molecules and metal electrodes.


2:03PM J18.00011 Low temperature, field-dependent mobility in pentacene thin-film transistors. ADRIAN SOUTHARD, Center for Nanophysics and Advanced Materials (CNAM) and the Department of Physics (DOP), University of Maryland (UM), VINOD SANGWAN, Laboratory of Physical Sciences (LPS), CNAM, and DOP, UM, DAN LENSKI, MICHAEL FUHRER, CNAM and the DOP, UM, ELLEN WILLIAMS, LPS, CNAM, and the DOP, UM — We measure the field-effect and saturation mobility of Au bottom contact thin-film polycrystalline pentacene field-effect transistors while varying temperature, channel length, and gate voltage. We utilize Au bottom contacts without a wetting layer, and achieve contact resistance as low as 1 kΩ-cm despite disturbance of the pentacene morphology at the drain and source electrodes. By measuring multiple channel lengths, we extract a contact-resistance free mobility. We confirm this value using an alternative technique in which we short the source and drain electrodes and make two terminal measurements of the capacitance and loss between these electrodes and the gate as a function of frequency. We discuss the result of field-dependent mobility in the context of Poole-Frenkel theory to rationalize the non-linear dependence of drain current on drain voltage, and test the predictions of recently developed models for transport in such systems.

11:15AM J19.00001 Self-assembled surface patterns from organometallic-containing triblock terpolymers. VIVIAN CHUANG, CAROLINE ROSS, Massachusetts Institute of Technology. JESSICA GWYTHER, IAN MANNERS, University of Bristol — Block copolymers are useful in nanotechnology because they can self-assemble to form periodic nanoscale structures. Here, we demonstrate the formation of hollow ring arrays with a period of 54 nm from a core-shell cylindrical morphology based on poly(styrene-b-ferrocenylmethylthiophene-b-2-vinyl pyridine) (PS-b-PFS-b-P2VP) triblock terpolymer thin film. By spin-coating and solvent annealing, thin films of the polymer were self-assembled into arrays of core-shell structures oriented perpendicular to the top surface of the film. Various chemically modified substrates were employed to investigate the effects of interfacial interaction between the substrate and the film, as well as the effects of solvent annealing, on the film morphology. Results will be compared with those obtained from a poly(butadiene-b-styrene-b-methyl methacrylate) triblock terpolymer [1]. The PS core and P2VP matrix blocks were partly removed simultaneously using oxygen plasma, and the remaining PFS ring pattern was successfully transferred into a PS layer by imprinting.

11:27AM J19.00002 Improvement of Extraction Efficiency of LED with Surface Relief Nanostructure Fabricated by Self-Assembled Block Copolymer Pattern. RYOTA KITAGAWA, AKIRA FUJIMOTO, KOJI ASAKAWA, Corporate Research & Development Center, Toshiba Corporation — A surface relief nanostructure was fabricated on the emission surface of light-emitting diodes (LEDs) using a self-assembled diblock copolymer pattern. The pattern of the nanostructure possesses moderate short-range order with slightly deviation in size and spacing, which is different from conventional extraction surface structures, such as photonic crystal and randomly textured surface. The dot pattern of a self-assembled polystyrene-polyethylmethacrylate diblock copolymer (PS-b-PMMMA) was used as an etched mask. An average dot spacing was controlled by changing blend ratio of PS-b-PMMMA, homo (h-) PS, and h-PMMMA in a polymer solution. In the photoluminescence (PL) measurement, the light extraction efficiency of the nanostructure exceeded over twice, compared with a flat surface, by optimizing the average spacing of the nanostructure. It was also revealed that the nanostructure showed more than 10% higher extraction efficiency than the highly ordered nanostructure fabricated by a self-assembled nanopattern surface structure. These results can be interpreted as a contribution of structural fluctuation in the nanostructure for enhancement of extraction efficiency.

11:39AM J19.00003 Self-Assembling Block Copolymer Resist Mixtures towards Lithographic Resists for Sub-10 nm Features. CURRAN CHANDLER, VIKRAM DAGA, JAMES WATKINS, University of Massachusetts Amherst — Significant improvements in 193 nm photolithography have enabled the extension of device feature sizes beyond the 45 nm and 32 nm nodes, yet uncertainty lies beyond 22 nm features as no single replacement has emerged. Here we show that low molecular weight, nonionic block copolymer surfactants blends are capable of self-assembling into highly ordered domains with feature sizes on the order of 5 nm. These surfactants, most of which lack the required $\chi_N$ for microphase separation on their own, exhibit strong segregation and long-range order upon addition of a component capable of multi-point hydrogen bonding that is specific for one of the blocks in the copolymer. This has been demonstrated by our SAXS data for several Pluronic (PEO-b-PPO-b-PEO) and Brij (PEO-$b$-[CH$_2$]$_n$, CH$_3$) surfactants of various molecular weights and PEO volume fractions. Furthermore, we employ these highly-ordered systems as thin film, nanolithographic etch masks for the transfer of sub-10 nm patterns into silicon-based substrates. Small molecule, hydrogen bonding additives containing aromatic or silsesquioxane structure are also used to tune etch contrast between the blocks which is important for reducing line edge roughness (LER) of such small features.

11:51AM J19.00004 Directed assembly of block copolymers on chemically nanopatterned substrates: enabling science for ultra high resolution lithography. PAUL NEALEY, University of Wisconsin — Self-assembling materials based on block copolymers spontaneously form structures with well-defined dimensions and shapes at length scales of interest in nanotechnology. Unfortunately the thermodynamic driving forces for self-assembly are small and low-energy defects can get easily trapped. At issue is the extent of direction or guidance required to meet criteria related to perfection and registration for use of such materials in nanofabrication. Through fundamental understanding of the physics, chemistry, and surface and interfacial phenomena associated with equilibrating block copolymer films in the presence of chemically nanopatterned substrates, we demonstrate how block copolymers may be integrated into and advance the performance of the lithographic process. The technological importance of this approach is discussed with respect to patterned media and the fabrication of integrated circuits.
and as a daughter master for MTP, and 3) the master and daughter templates can be reused tens of times.

12:15PM J19.00006 Directed self-assembly of diblock copolymer thin films on chemically-patterned substrates for defect-free nano-patterning, MIKIHIITO TAKENAKA, Department of Polymer Chemistry, Graduate School of Engineering, Department of Chemical and Biological Engineering, University of Tokyo, SATOSHI AKASAKA, Materials Research Laboratory, Hitachi Ltd., SATOSHI YOSHIDA, Materials Research Laboratory, Hitachi Ltd., HIROKAZU HASEGAWA, Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, ELIZABETH DOBISZ, DAN KERCHER, San Jose Research Center, Hitachi Global Storage Technologies — We demonstrate that Polystyrene-block-poly(methyl methacrylate) (PS-b-PMAA) can self-assemble in a well-aligned, long-range ordered nano-pattern over arbitrarily large areas, commensurate with chemically pre-patterned templates prepared by electron beam (EB) lithography. We also demonstrate that the self-assembly process can interpolate points in between the EB generated pattern, thus multiplying the pattern density. Moreover, we show the results of the investigation about the time-evolution of the self-assembled structure during annealing process.

12:27PM J19.00007 Lamellar and Non-bulk like Morphologies in Thin Films of Block Copolymer on Chemical Nanopatterned Surfaces, GUOLIANG LIU, FRANCOIS DETCHEVERRY, JUAN J. DE PABLO, PAUL F. NEALEY, Department of Chemical and Biological Engineering, University of Wisconsin-Madison, 1415 Engineering Drive, Madison, WI, 53706 — Thin films of symmetric PS-b-PMAA (bulk lamellae period \( L_0 \)) were equilibrated on substrates patterned with periodic stripes such that the adjacent stripes are preferentially wet by the two blocks of the copolymer. The morphology of the films was quantified as a function of the following pattern characteristics: the pattern period, \( L_0 \), where \( L_0 = \delta L_0 \), \( 1 \leq \delta \leq 3 \), the width of the PMMA wetting strips, \( W \), and the interfacial energies between the blocks and the patterned stripes, \( \Lambda_{1,2} \). Under different boundary conditions we can 1) direct the assembly of lamellae perpendicular to the substrate and ordered in linear arrays so as to increase the density of features of the chemical pattern, or 2) obtain a number of stable non-bulk like structures including asymmetric lamellae, mixed orientated lamellae, dots, and check-board structures. The experimental results are compared to a phase-diagram predicted from molecular simulations.
A molecular model of block copolymer systems is used to conduct a systematic study of the morphologies that arise when thin films of symmetric, lamellar forming block copolymer materials are deposited on nanopatterned surfaces. Over 500 distinct cases are considered. It is found that, in general, three distinct morphologies can arise depending on the strength of the substrate-polymer interactions, the film thickness, and the period of the substrate pattern. The relative stability of those morphologies is determined by direct calculation of the free energy differences. The dynamic propensity of those morphologies to emerge is examined by careful analysis of simulated trajectories. The results of this systematic study are used to interpret recent experimental data for films of polystyrene-PMMA copolymers on chemically nanopatterned surfaces.

A computational calculation on the lamellae bending which provides more insights on the free energy and interfacial characteristics will be discussed as well.

1:27PM J19.00012 Pattern interpolation in thin films of lamellar, symmetric copolymers on nano-patterned substrates, FRANCOIS DETCHEVERRY, UMANG NAGPAL, GUOLIANG LIU, PAUL NEALEY, JUAN DE PABLO, University of Wisconsin — A molecular model of block copolymer systems is used to conduct a systematic study of the morphologies that arise when thin films of symmetric, lamellar forming block copolymer materials are deposited on nanopatterned surfaces. Over 500 distinct cases are considered. It is found that, in general, three distinct morphologies can arise depending on the strength of the substrate-polymer interactions, the film thickness, and the period of the substrate pattern. The relative stability of those morphologies is determined by direct calculation of the free energy differences. The dynamic propensity of those morphologies to emerge is examined by careful analysis of simulated trajectories. The results of this systematic study are used to interpret recent experimental data for films of polystyrene-PMMA copolymers on chemically nanopatterned surfaces.
11:51AM J20.00004 How do entangled polymeric liquids flow? . SHAM SUNDAR RAVINDRANATH, SHI-QING WANG, University of Akron — This work focused on investigating fundamental questions in polymer dynamics such as how entangled polymeric liquids respond to fast external deformation. By developing an effective particle tracking velocimetric (PTV) method, along with conventional rheometric measurements, new insights can be gained into the phenomenology of entangled polymers in presence of startup shear, step strain and large amplitude oscillatory shear (LAOS). During startup shear of well entangled systems, the shear field becomes inhomogeneous after the stress overshoot for a range of applied shear rates beyond the Newtonian region [1]. The emergence of shear banding after stress overshoot helped us to identify the stress overshoot as indicating yielding, whose characteristic stress level, shear strain and time scale vary inversely to the conventional perception that entangled polymers would undergo quiescent relaxation, the PTV observations reveal macroscopic motions after shear cessation [2]. The recoil-like macroscopic motions appears to reflect an elastic breakdown of the entanglement network due to sufficient build-up of retractive forces. LAOS experiments also demonstrate that entangled polymers cannot sustain a high magnitude of fast deformation without undergoing cohesive failure [3]. [1] Macromolecules 2008, 41, 2663 [2] Macromolecules 2007, 40, 8031 [3] J. Rheol. 2008, 52, 341.

12:03PM J20.00005 Diffusion in Carbon Nanofiller / Polymer Nanocomposites , MINFANG MU, Department of Materials Science and Engineering, University of Pennsylvania, NIGEL CLARKE, Department of Chemistry, Durham University, RUSSELL COMPOSTO, KAREN WINEY, Department of Materials Science and Engineering, University of Pennsylvania — Polymer tracer diffusion through carbon nanofiller / polymer nanocomposites is measured using elastic recoil detection methods. Tracer diffusion through a single wall carbon nanotube nanocomposite is strongly suppressed at low concentrations (≤ 0.4-0.8 vol%) and then increases at higher concentrations. In contrast, the typical Maxwell model predicts only a weak monotonic decrease. We propose a model for the carbon nanotube composite system wherein the SWCNTs function as cylindrical traps. Simulations of this model found that at low concentrations, the isolated traps retard polymer diffusion and at higher concentrations the percolated traps allow polymer diffusion to recover by providing continuous pathways. A comparison of our experimental and simulation results finds that (1) the strength of the trap increases with the molecular weight of the diffusing polymers and (2) the trap diameter increases with the molecular weight of the matrix polymer. Similarly, tracer diffusion through C60 / polymer nanocomposites exhibits a significant decrease at low concentrations and then slowly increases at concentrations larger than 0.7 vol%.

12:15PM J20.00006 Tunable Wetting of Polymer Nanocomposite Films , MARLA MCCONNELL, SHU YANG, RUSSELL COMPOSTO, University of Pennsylvania — Surfaces with controlled wettabillity are of growing technological importance. In this study, nanoparticles (NPs) with tunable spacing were assembled on poly(styrene-ran-acrylic acid), S-RAA, films to manipulate the composite films' wetting properties. Amine-modified silica NPs (15-200 nm) were covalently grafted to the AA moieties on the surface of the S-RAA films, in which the S phase imparts mechanical stability and the AA domains swell, increasing the roughness and surface area. By controlling surface roughness and reaction time, NP coverage ranged from 1%-70%. These films displayed NP-coverage-dependent water contact angles between 60° and 120°. The enhanced hydrophobicity is attributed to capillary climbing of S-RAA chains to cover the previously hydrophilic NP surface. Upon increasing NP diameter, the contact angle was found to increase at a fixed total coverage. This increase in effective surface area with increasing particle size. This system is utilized as a platform to create Janus particles with unique optical properties and templates for investigating molecular motors.

12:27PM J20.00007 Direct Measurement of Molecular Mobility in Actively Deformed PMMA Glasses , HAU-NAN LEE, KEEWOOK PAENG, STEPHEN SWALLEN, MARK EDIGER, Department of Chemistry, University of Wisconsin-Madison — To quantitatively understand the response of segmental motions to external stress, we performed optical measurements of dye reorientation in PMMA glasses during tensile creep deformation. Up to 1000-fold increases in mobility are observed during deformation, which supports the view that stress-induced mobility allows plastic flow in polymer glasses. Although the Eyring model describes this mobility enhancement well at low stress, it fails to capture the dramatic mobility enhancement after flow onset. In this regime, in addition to lowering the barriers for molecular motion, external stress apparently forces the shape of distribution of relaxation times to narrow significantly. The effect of stress on physical aging was also investigated. At low stress, physical aging and deformation-induced mobility act as two independent processes. However, after flow onset, the data are consistent with the view that aging has been erased by deformation.

12:39PM J20.00008 Probing Surface Glass Temperature of Polymer Films via Pentacene Growth Mode, Microstructure, and Thin-Film Transistor Performance , CHOONGIK KIM, ANTONIO FACCHETTI, TOBIN MARKS, Northwestern University — Pentacene-based organic thin-film transistors (OTFTs) have been extensively studied in organic electronics. In this study, we report the fundamental importance of the polymeric gate dielectric glass transition temperature on pentacene film growth mode, microstructure, and corresponding OTFT performance. From the knowledge that nanosкопically-confined thin polymeric films exhibit glass-transition temperature deviations from the corresponding dielectric materials, we show here that pentacene films grown on polymeric gate dielectrics at temperatures well-below their bulk glass transition temperature ($T_g$) exhibit morphological/microstructural transitions and dramatic OTFT performance variations at a well-defined temperature [herein defined as the polymer surface glass transition temperature, $T_{g(s)}$] characteristic of the polymer structure and independent of the film thickness. Our results demonstrate that TFT measurements represent a new methodology to probe polymer surface viscoelastic properties.

12:51PM J20.00009 Responsive Polymer Surfaces: Crumpling, Folding, and Snapping Films . DOUGLAS HOLMES, ALFRED CROSBY — This work focuses on understanding deformation mechanisms and responsiveness associated with folding, crumpling, and snapping of thin polymer films. By studying folding and crumpling in confined regimes, we gain insight into material properties. By developing new strategies for adhesion, optical, and patterning applications. Using a novel processing technique, microarrays of freestanding polydimethylsiloxane plates are placed in equibaxial compression and transition through crumpled morphologies that are difficult to attain through traditional patterning techniques. The microstructures also change their curvature through a snap-through instability via environmental stimuli. When triggered via osmotic pressure the snap transition time scales as the square of the plate thickness and the inverse of the plate modulus. Recently, we have transferred this knowledge into the crumpling of ultrathin polymer films. We have fabricated sharply folded films directly on elastomeric and silicon substrates. The fold width scales directly with the film thickness and applied strain. We find that normally brittle, polyethylene films can accommodate excessive compressive strains without fracture by undergoing strain-localizing fold events.

1:03PM J20.00010 Structure and mobility of PEO/LiClO4 solid polymer electrolytes , SUSAN FULLERTON, JANNA MARANAS, Penn State — Solid polymer electrolytes (SPEs) for use in rechargeable lithium-ion batteries offer many advantages over traditional liquid electrolytes, including mechanical flexibility and environmental friendliness. The practical limitation is that room temperature conductivity remains insufficient to power a portable device. While it is well-established that ion mobility is driven by polymer dynamics, high conductivity values have also been reported through fully crystalline SPEs. PEO-based SPEs have a rich phase behavior, and can form several crystalline complexes depending on the lithium concentration, temperature, and recrystallization time. We investigate the structure, mobility, conductivity, and thermal properties of both semi-crystalline and amorphous PEO/LiClO4 SPEs. Structure is measured with small-angle neutron scattering, and PEO mobility with quasi-elastic neutron scattering. We observe a decoupling of ionic conductivity and PEO mobility in a semi-crystalline sample. We also determine that PEO hydrogen atoms undergo restricted rotation on a circle. The radius of the circle is consistent with a cylindrical, crystalline structure that persists to some extent in the amorphous phase. The results suggest that directed ion transport via ordered structures is perhaps equally important as polymer mobility for increasing conductivity, provided that the structures percolate over large spatial scales.
1:15PM J20.0011 Architectural effects in strongly hydrogen bonded thermoplastic elastomers, KATHLEEN FELDMAN, CRAIG HAWKER, EDWARD KRAMER, University of California, Santa Barbara — In this work we demonstrate the synthesis of random copolymers of n-butyl acrylate with a quadruple hydrogen bonding acrylate monomer based on 2-ureido-4[1H]-pyrimidinone (UPy). Despite low Tg's and a lack of crystallinity, these materials show thermoplastic elastomer properties through the strong but thermoreversible UPy groups. Through the use of controlled radical polymerization and post-polymerization functionalization we are able to reach high UPy monomer content while maintaining low polydispersity and excellent control over the total molecular weight. It was found that the average distance between UPy's along the chain was the major determiner of the overall properties including the plateau modulus, tensile modulus, and relaxation timescale. By using a diffusional initiator it is also possible to synthesize materials containing a homopolymer midblock and random copolymer end blocks, allowing us to address the question of how the MHB group distribution along the chain affects the bulk properties. In concentrating the UPy groups near the chain ends, the plateau modulus remained constant but the crossover frequency decreased dramatically, indicating that the effective lifetime of the hydrogen bonds within the supramolecular network increased, in keeping with prior theoretical predictions.

Tuesday, March 17, 2009 2:30PM - 5:30PM – Session L1 DPOLY: John H. Dillon Medal Symposium in Honor of Venkat Ganesan

2:30PM L1.00001 Dillon Medal Prize Lecture, VENKAT GANESAN, The University of Texas at Austin — Many aspects of polymer research have undergone a paradigm shift in the past decade, with an increased emphasis on technological applications which emphasize the use of materials and devices created by controlling matter in the atomic scales to the bulk commodity level. This talk will focus on multicompontent polymer materials (block copolymers, rod-coil polymers and mixtures like polymer blends and polymer nanocomposites), which have played a central role in enabling this paradigm shift in the context of polymeric materials. In this talk, I will discuss our recent researches on developing simulation tools that can predict the structure, morphology and flow behavior of such multicompontent polymers. In contrast to conventional (“particle-based”) Monte Carlo and Molecular dynamics approaches, our methods work at a coarse-grained description of the system to predict the thermodynamics and dynamics of such multicompontent polymers. This talk will focus on an outline of the simulation strategies and present some results concerning both the equilibrium and dynamical properties of such materials.

3:06PM L1.00002 Chain Stretching and Order-Disorder Transitions in Block Copolymer Monolayers and Multilayers1, EDWARD J. KRAMER, VINDHYA MISHRA, GILA E. STEIN, KAREN E. SOHN, SUMI HUR, GLENN H. FREDRICKSON, UCSD, ERIC W. COCHRAN, Iowa State University — Both monolayers of block copolymer cylinders and spheres undergo order to disorder transitions (ODT) at temperatures well below those of the bulk. Monolayers of PS-b-P2VP cylinders undergo a “nematic” to “isotropic” transition at temperatures about 20 K below the bulk ODT while monolayers of PS-b-P2VP with P2VP spheres undergo a 2D crystal to hexatic transition at least 10 K below the bulk ODT. Bilayers of each structure disorder at temperatures well above that of the monolayers. While one is tempted to attribute all of the differences to the fact that ordered monolayers are quasi 2 dimensional while bilayers are not, an alternative explanation exists. In the cylinder monolayer the corona PS chains must stretch to fill a nearly square cross-section domain rather than a hexagonal one in the bulk, while the corona PS chains in a sphere monolayer must stretch to fill a hexagonal prism rather than an octahedron in the bulk. The more non-uniform stretching of the chains in the monolayer should increase its free energy and decrease its order-disorder temperature.

1 Supported by NSF-DMR-Polymers Program

3:18PM L1.00003 Free Energy Estimation in Field-Theoretic Simulations, GLENN FREDRICKSON, ERIN LENNON, KIRILL KATSOV, UC Santa Barbara — A new technique is presented for computing absolute and relative free energies of polymeric fluids in the context of field-theoretic simulations. Complex Langevin sampling is combined with a thermodynamic integration scheme to provide access to free energies of homogeneous and inhomogeneous polymer phases. The scheme utilizes a harmonic crystal reference state whose free energy can be computed analytically. The method is demonstrated in the context of the order-disorder transition of diblock copolymer melts.

3:30PM L1.00004 Directed Crystallization in polymer solutions, MURUGAPPAN MUTHUKUMAR, University of Massachusetts — Theoretical considerations of amyloid fibrillation in protein solutions and polymer-mediated crystallization of nanoparticles will be presented.

3:42PM L1.00005 The O2 Network by Molecular Design: CECD Tetrablock Terpolymers, FRANK S. BATES, MICHAEL BLUEMLE, GUILLAUME FLEURY, TIMOTHY LODGE, U. Minnesota — Varying the length of poly(dimethylsiloxane) in poly(cyclohexylethylene-b-ethylene-b-cyclohexylethylene-b-dimethylsiloxane) (CECD) tetrablock terpolymers between 0 and 20% produces the sequence of ordered phases: cylindrical-to-network-to-cylindrical. Small-angle X-ray scattering and transmission electron microscopy demonstrate Pnna space group symmetry and a unique network morphology stabilized by the asymmetric molecular architecture and block interactions. These results establish a new design principle for the generation of triply periodic and multiply continuous nanostructured soft material.

3:54PM L1.00006 Suppression of Segmental Relaxation as the Origin of Strain Hardening in Polymer Glasses, KENNETH SCHWEIZER, KANG CHEN, University of Illinois — A nanometer scale dynamical theory is proposed for the post-yield large amplitude strain hardening phenomenon in polymer glasses. The physical picture is that external deformation induces anisotropic chain conformations which modifies interchain packing, resulting in density fluctuation suppression and intensification of localizing dynamical constraints and activation barriers. The strain amplitude dependence of the resulting stresses are well described by classic rubber elasticity form. However, the hardening stress is of interchain origin and arises primarily from prolongation of segmental relaxation, not single strand entropic elasticity. Theoretical predictions for the magnitude, temperature and deformation rate dependence of the hardening modulus are consistent with experiments and simulations.

4:06PM L1.00007 Disappearance of high frequency modes in polymer dilute solution viscoelasticity, RONALD LARSON, University of Michigan, SEMANT JAN, Praxair — We address the problem of the “missing modes” in the high frequency rheology of dilute polymer solutions. According to the Rouse-Zimm theory, the slow viscoelastic response of dilute polymers is dominated by the collective motion of the chain, as described by a bead-spring model. However, one expects this description to break down at high frequencies at which chain motion on scales too small to be represented by beads and springs should be evident; this motion should be controlled by rotations of individual backbone bonds of the polymer. The viscoelastic response produced by these “local modes” is observable in polymer melts; however, for dilute polymer solutions, the “local modes” are absent from viscoelastic spectra, as shown by Schrag and coworkers (Peterson, et al., J. Polym. Sci. B, 39:2860 (2001)). Here we address this problem by directly simulating single polymer chains using Brownian dynamics simulations, with realistic bending and torsional potentials. We show using these simulations that the “missing modes” result from barriers to bond rotation that make the chain “dynamically rigid” at high frequencies. As a result, the “dynamical Kuhn length” of the chain exceeds the static one, and the chain at high frequencies is not able to explore local conformations as fast as would be needed for their relaxation to contribute to the mechanical relaxation spectrum.
4:18PM L1.00008 Polymer Conductivity through Particle Connectivity. YUEH-LIN LOO, Princeton University — To promote solution processability of conductive polymers, polymer acids, instead of small-molecule acids, are frequently used as dopants. Generally, the conductive polymer is synthesized in the presence of the polymer acid; sub-micron size particles that are electrostatically stabilized result during polymerization. We discovered that the molecular characteristics of the polymer acid have great implications on the structure of these conductive polymer particles. Templating the synthesis of the conductive polymer with a higher molecular weight polymer acid results in larger particles, and templating with a polymer acid having a larger molecular weight distribution results in a large size distribution in the particles. Because conduction in such conductive polymers is governed by how these particles pack, we show that the macroscopic conductivity of these films is dictated by a single parameter, i.e., the particle density, that is reducible from the various molecular characteristics of the polymer acid we explored. In the specific case of polyaniline that is doped with poly(2-acylamido-2-methyl-1-propane sulfonic acid), the particles are structurally and chemically inhomogeneous. The conductive portions of the polymer preferentially segregate to the particle surface. Conduction in these materials are therefore mediated by the particle surface and conductivity thus scales superlinearly with particle surface area per unit film volume.

4:30PM L1.00009 Modeling the Self-Assembly of Nanoparticle Amphiphiles. SANAT KUMAR, Columbia University, ATHANASSIOS PANAGIOTOPoulos, Princeton University — We demonstrate that spherical nanoparticles, uniformly grafted with macromolecules, robustly self-assemble into a range of anisotropic superstructures when are dispersed in the corresponding homopolymer matrix. Theory and simulations both suggest that this self-assembly process reflects a balance between the energy gain when particle cores approach and the entropy of distorting the grafted polymers. The effectively directional nature of the particle interactions is thus a many-body emergent property.

4:42PM L1.00010 Confinement Effects on Polymer Dynamics in Nanocomposites. RAMANAN KRISHNAMOORTI, University of Houston, TIRTHA CHATTERJEE, UC Santa Barbara, MANSOUR ABDULBAKI, University of Houston, MADHUSUDAN TYAGI, NIST — The dynamics of polymers in systems with dispersed nanoparticles is studied using inelastic and quasi-elastic neutron scattering. In this study, the role of confinement between nanoparticles and the role of nanoparticle topology are examined by considering dispersions with spherical C60 buckeyballs, rod-like single walled carbon nanotubes and plate-like graphene. The polymers examined here include bisphenol A epichlorohydrin and bisphenol F epichlorohydrin. Significant changes in the dynamics of the polymer are observed and these will be examined in the context of mode coupling theories.

4:54PM L1.00011 Long-time dynamics of chains in polymer nanocomposites. PETER GREEN, University of Michigan — In polymer nanocomposites (PNCs), the presence of the nanoparticles has a marked effect on the dynamics and the Tg. In one limit, the chains become strongly attached to the particles, and two glass transitions, and bimodal dynamics, may be observed. In the other, where the chain/particle interactions are weak, the chain friction factor, z(T) can undergo significant changes, manifested in the translational diffusion and viscosity. In the poly(methyl methacrylate (PMMA)/C60 system, the dynamics slow down, accompanied by an increase in the glass transition. At the same time, the temperature dependence of the relaxations remains the same as pure PMMA. In polystyrene (PS)/Au-thiol capped PS ligands, the dynamics and the glass transition could be induced to increase or decrease, through manipulation of molecular parameters in the system. In this presentation, we propose a mechanism to describe translational diffusion and Tg in PNC systems in which the polymer chain/nanoparticle interactions are weak.

5:06PM L1.00012 Self-Assembly of Conjugated Rod-Coil Block Copolymers for Photovoltaic Applications. R.A. SEGALMAN, B.D. OLSEN, Y. TAO, B. MCCULLOCH, UC Berkeley and Lawrence Berkeley National Laboratories — The phase behavior of conjugated rod-coil block copolymers is significantly different from that of traditional block copolymers due to the interplay between liquid crystalline interactions of the rod blocks and microphase separation of the rods and coils. A universal phase diagram for rod-coil diblock copolymers depends on the strengths of the rod aligning interactions and the rod-coil repulsive interactions as well as the geometrical ratio of rod volume to coil and aspect ratios. In this talk, the experimental phase diagram of a weakly segregated model block copolymer will be compared to that predicted by self-consistent field theory. Conjugated rod-coil block copolymers with electron donating and accepting blocks are promising for photovoltaic applications. The self-assembly of poly(thiophene-b-acrylate perylene diimide) block copolymers as well as block copolymer-nanocrystal composites result in photovoltaic active layers with controllable degrees of order. We demonstrate that short range order on the nanoscale is beneficial to device performance.

5:18PM L1.00013 Confinement Effects on Glassy-State Polymer Behavior in Thin Films, Nanocomposites, Tethered Nanoparticles, and Nanostructured Systems. JOHN TORKELSON, PERLA RIT-TIGSTEIN, SOYOUNG KIM, RODNEY PRIESTLEY, CONNIE ROTH, MANISH MUNDRA, Northwestern University — Confinement of polymers at the nanoscale and even the microscale can significantly alter the transition temperature, physical aging rate, and alpha-relaxation dynamics from bulk polymer behavior. Here we illustrate how model experiments involving several techniques applied to simple, thin polymer films help us to understand and predict qualitatively or semi-quantitatively the glassy-state response of more complex, confined systems, including nanocomposites, tethered nanospheres, nanostructured homopolymer films, and nanostructured systems consisting of more than one polymer component. We shall illustrate how the glass transition temperature can be altered by as much as 60 K and how physical aging can be nearly totally suppressed via confinement. The discovery of new confinement effects and implications for new applications of confined polymeric systems will be discussed.

Tuesday, March 17, 2009 2:30PM - 5:30PM — DMP Session L19 DMP DPOLY: Focus Session: Ionically Gated and Conventional OFETs and Related Devices 320

2:30PM L19.00001 All-Printed Low Voltage Operation Polymer Transistors and Circuits Based on Ion Gel Gate Dielectrics. YU XIA, JEONG HO CHO, MINGJING HA, Department of Chemical Engineering and Materials Science, University of Minnesota, MICHAEL RENN, Optomec, Inc, C. FRISBIE, Department of Chemical Engineering and Materials Science, University of Minnesota, OPTOMEC, INC COLLABORATION — A key challenge in the development of organic electronics lies in the realization of high quality devices with low cost. In this presentation, we demonstrate high performance polymer transistors and circuits with all components fabricated by a commercial aerosol jet printing technique. Printing saves the device manufacturing cost through its simple procedure, fast speed, high throughput and low waste of materials. Furthermore, by employing a specially designed ion gel as the gate dielectric material, ultra-high density carrier accumulation (> 10^{14} \text{ cm}^{-2}) can be achieved in the transistor channel, which results in an exceptionally large transconductance of 10 \mu S/\mu m. Our typical transistors have mobility higher than 1cm^{2}/Vs and frequency response up to 1 kHz. Inverters, NAND and NOR logic circuits and ring oscillators have been realized as well, with low operation voltage, fast speed and high gain. In addition, the high polarizability of the gate dielectric allows us to print the gate electrode of each single transistor along with its source and drain electrodes at the same time in a coplanar architecture, which significantly simplifies the fabrication procedure.
3:06PM L19.00004 Employing ‘Liquid Gap’ Transistors to Examine the Mobility-Carrier Density Relation in Polymer and Single Crystal Organic Semiconductors 1, DANIEL FRISBIE, University of Minnesota — It is generally known that the carrier mobility in organic semiconductors can depend on carrier density, but the precise relationship hinges on the degree of structural order and the dielectric polarizability at the organic/dielectric interface. We have fabricated both single crystal and polymer transistors using the PDMS stamp approach pioneered by Podzorov and Rogers [1], where we have replaced the usual ‘air gap’ in these structures with liquids having different dielectric constants. This structure allows us to examine transport in single crystals and polymer semiconductors as a function of tunable dielectric constant and also charge density. We find striking differences in transport behavior for organic single crystals versus polymer semiconductor films using these liquid dielectric transistors. For organic single crystals such as rubrene, the carrier mobility does not seem to be a function of charge density but does strongly depend on the liquid dielectric constant, in keeping with previous results reported by Morpurgo [2] on the effects of dielectric polarizability. For polymer semiconductors, the effect of charge density is overwhelming; there is a strong increase in charge mobility with increasing carrier concentration, following a power law. These results are already largely known, but the ‘liquid gap’ transistors provide a convenient testbed for examining these effects side-by-side for different materials in the same device. We will describe the device fabrication and the nature of our results, as well as discuss the origins of the very different behavior for single crystals versus polymer semiconductor films. 1) Sundar, V.C., et al. Science 303 (2004) 1643. 2) Hulea, I. N., et al. Nature Mater. 5 (2006) 982.

1This work was supported by the NSF MRSEC Program.

3:42PM L19.00005 Organic electrochemical transistors for sensing applications 2, FABIO CICOIRA, SANG YOON YANG, JOHNM A. DEFRANCO, GEORGE G. MALLIARAS, MSE/Cornell University, ORGANIC ELECTRONICS LABORATORY CORNELL TEAM — This talk describes the use of semiconducting polymer transistors to measure chemical and biological properties in aqueous solutions. We use basic transistor devices to create new chemical and biological sensors. In particular, we have developed electrochemical transistors (ECTs) that can be used to detect biomolecules, such as DNA. We also have developed an electrochemical transistor platform that can be used to detect biomolecules, such as DNA. We have also developed an electrochemical transistor platform that can be used to detect biomolecules, such as DNA. We have also developed an electrochemical transistor platform that can be used to detect biomolecules, such as DNA. The principle of operation of the electrochemical transistor is based on the change in the charge density at the liquid-gate interface. The change in charge density is proportional to the concentration of the biomolecule in the solution. The change in charge density is also proportional to the concentration of the biomolecule in the solution. The change in charge density is proportional to the concentration of the biomolecule in the solution. The change in charge density is proportional to the concentration of the biomolecule in the solution. The change in charge density is proportional to the concentration of the biomolecule in the solution.

2also at CNR/IFN Trento (Italy)

3:54PM L19.00006 Contact resistance and lifetime of organic thin film transistors 2, GVIDO BRATINA, ANDRAŽ PETROVIC, University of Nova Gorica — We have used electric charge transport measurements coupled to Kelvin force probe microscopy of pentacene organic thin film transistors (OTFTs) to monitor the evolution of contact resistance as a function of time of exposure to ambient air. Or results demonstrate that exposure of OTFTs to ambient air for extended periods of time, results in two competitive mechanisms that are responsible for observed variation in drain-current. Initially, relatively fast oxygen doping through electronegativity-related creation of holes increases the carrier concentration and therefore increases the drain current. Slower, and persistent mechanism of water diffusion in the pentacene layer induces dipole-charge carrier interactions through the creation of energetic disorder. This results in long-term irreversible reduction of drain current.

4:06PM L19.00007 Controlling charge carrier injection in solution processed pentacene transistors by molecular engineering of the electrodes 3, SANGAMESHWAR RAO SAUDARI, Department of Materials Engineering, University of Pennsylvania, CHERIE KAGAN, Department of Electrical and Systems Engineering, University of Pennsylvania — We present the device performance of pentacene transistors fabricated from a solution deposited precursor. The bottom-contact pentacene transistors are fabricated by spin-coating N-sulfinylacetamidopentacene precursor followed by thermal conversion of the precursor into pentacene. Hole mobilities \( > 0.1 \text{ cm}^2/\text{Vs} \) and \( \text{I}_{\text{on}}/\text{I}_{\text{off}} \) \( > 10^5 \) are repeatedly achieved by this process. The metal-semiconductor interface in organic transistors plays a very important role in charge carrier injection and the overall device performance. Here we have treated the metal surface with self-assembled monolayers having different head and tail chemistries prior to pentacene precursor deposition to tailor the interfacial electronic properties. We correlate monolayer chemistry with device contact resistance and threshold voltage. These studies are used to fabricate devices with high mobility, high \( \text{I}_{\text{on}}/\text{I}_{\text{off}} \) and low subthreshold swing. Device hysteresis and stability issues will also be presented.

3also at CNR/IFN Trento (Italy)
The devices show clear evidence of rectification in air and in vacuum with a turn-on voltage of 0.4 V and with rectification ratios \( \sim 2 \), suggesting that both the interfaces and the film control the transport mechanism. The temperature dependence of the current does not show a clear activated behavior, supporting the same conclusion. On the other hand, at high voltages the power-law exponent of the I-V decreases at lower thickness for constant temperature implying also that both the interfaces and the film may control the transport. Work supported by AFOSR.

This research was supported by NSF-DMR Grants 0801764 and 0400938.

4:18PM L19.00008 Infrared and Electro-Optic Properties of TIPS-Pentacene\(^1\) . E.G. BITTLE, J.W. BRILL, J.E. ANTHONY, University of Kentucky — We will discuss new measurements of the infrared and electro-optic properties of thin crystals of trisopropylsilylethynyl (TIPS) pentacene. As with THz studies of this class of materials, crystalline films were grown from saturated tetrahydrofuran solutions on a gold electrode mask. Square wave voltages were applied to the electrical contacts on the sample as well as a gate electrode below the sample, through an oxide dielectric. Changes in phonon frequencies were studied as functions of voltage, position between contacts, and frequency of applied voltage. The results are interpreted in terms of charge diffusion through the TIPS-pentacene crystals.

\(^1\)Supported by NSF, DOE and AFOSR.

4:30PM L19.00009 Crossover from recombination limited charge transport to mobility restricted charge transport in organic LED\(^1\) . VLADIMIR PRIGODIN, ARTHUR EPSTEIN, Physics Department, Ohio State University, Columbus, OH 43210-1117 — The model of bipolar charge transport in organic semiconductors where the current solely is provided by e-h recombination (LEDs structures) is studied \([1]\). We have shown that depending on recombination rate there are two basic regimes of charge transport. For recombination rate above the critical value the current is space charge limited and the current as a function of recombination rate decreases with increasing the recombination rate. At recombination rate below the critical value the recombination takes place over the whole sample volume of sample and as a result the current is only contact limited. As a function of recombination rate the current increases with increasing recombination rate. Critical value for recombination rate depends on the thickness of sample, applied voltage and on both the hole and electron mobilities. \([1]\) J.D. Bergeson et al., Phys. Rev. Lett. \textbf{100}, 067201 (2008).

4:42PM L19.00010 Interface and bulk controlled charge transport in Pd/CuPc/Pd sandwich devices , CORNELIU COLESNICT, IVAN SCHULLER, University of California San Diego, La Jolla, Ca 92093 — We present transport measurements in thin film devices of copper phthalocyanine sandwiched between palladium electrodes. The devices were grown in situ using molecular beam deposition of phthalocyanine films with the thickness ranging between 30 and 600 nanometers. The I-V characteristics as a function of temperature and thickness exhibit two distinct regions - a low voltage Ohmic region with current proportional to the voltage and a high voltage region with a power law dependence. At low voltages the current shows an inverse power dependence on thickness, I- \(n\) thickness \(^{-n}\), with the exponent \(n > 2\), suggesting that both the interfaces and the film control the transport mechanism. The temperature dependence of the current does not show a clear activated behavior, supporting the same conclusion. On the other hand, at high voltages the power-law exponent of the I-V decreases at lower thickness for constant temperature implying also that both the interfaces and the film may control the transport. Work supported by AFOSR.

4:54PM L19.00011 RC Transmission Line Characterization of Organic Semiconductors\(^1\) . DANIEL LENSKI, ADRIAN SOUTHARD, MICHAEL S. FÜHRER, Department of Physics and Center for Nanophysics and Advanced Materials, University of Maryland, College Park, MD 20742, USA. — We have characterized thin films of organic semiconductors (pentacene and poly-3-hexylthiophene) using a 3-contact transmission line configuration, in which an AC voltage is applied between the thin film and the gate, and the phase and magnitude of the current are measured. We compare the results with those obtained from simultaneous DC measurement, and find good agreement in the sheet resistance in the ON state measured using the DC and transmission line techniques, indicating that the transmission line technique is useful for obtaining sheet resistance and mobility in the ON state. Near threshold, or at high frequencies and electric fields, we observe systematic deviations of the AC impedance from the DC values. We discuss these deviations in terms of the of frequency-dependent length scale probed by the transmission line technique, and how these measurements can shed light on the properties of the semiconductor materials as well as their interfaces with contacts and substrates.

This work has been supported by the Laboratory for Physical Sciences.

5:06PM L19.00012 Organic field effect transistors having single wall carbon nanotubes electrodes , FABIO CICIOARA\(^1\) . MSE/Cornell University, CARLA M. AGUIRRE, PATRICK DESJARDINS, Genie Physique /Polytechnique Montreal, RICHARD MARTEL, Chimie/Universite de Montreal — Single Wall Carbon Nanotubes (SWCNTs) are of great interest as electrode materials in Organic Field Effect Transistors (OFETs). Thanks to their field emission properties, SWCNTs electrodes, in principle, are able to inject both electrons and holes into organics with low injection barriers, promoting tunneling injection. We well present recent result on the electrical properties of OFETs using hairy SWCNTs electrodes (see Figure 1), where the CNTs are attached on the substrate by means of metallic Ti contact pads. Devices with SWCNTs electrodes showed improved injection characteristics compared with devices using conventional metallic electrodes.

\(^1\)Also at CNR/IFN , Trento (Italy)

5:18PM L19.00013 Electrosynpin tin oxide/poly(3-hexylthiophene) nanofiber p-n diodes\(^1\) . NICHOLAS PINTO, University of Puerto Rico - Humacao — Electrosprinning is a simple technique used to prepare nanofibers of various materials, organic and inorganic. Some advantages of this method is that the nanofibers are orders of magnitude longer than that obtained via conventional means and it is easy to isolate individual nanofibers. We have used this technique to make nanoribbons of n-doped tin oxide (SnO\(_2\)) and to make nanoribbons of p-doped regioregular poly(3hexylthiophene) (P3HT) in air and within seconds. Several p - n junction nanodiodes were fabricated by crossing individual nanofibers of P3HT with individual nanoribbons of SnO\(_2\) during the electrosprinning process and electrically characterized them at room temperature. The SnO\(_2\) nanoribbons were fabricated first by electrosprinning a precursor of SnO\(_2\) and then sintering them at 700 C to convert it to SnO\(_2\) before crossing them with P3HT nanoribbons. The devices show clear evidence of rectification in air and in vacuum with a turn-on voltage of \(\sim 0.4\) V and with rectification ratios \(\sim 10\). Exposure of the diode to UV light increases the on-state current, while removing the light restores the device to its original state making it suitable as a reusable UV light sensor as well.

\(^1\)NSF, DoD

Tuesday, March 17, 2009 2:30PM - 5:18PM –
Session L20 DPOLY: Liquid Crystalline Polymers and Anisotropic Particles 321
2:30PM L20.00001 Dillon Symposium Break –
3:06PM L20.00002 Patterns on the iridescent beetle, *Chrysina gloriosa*, JUNG OK PARK, School of Polymer, Textile and Fiber Engineering, Georgia Institute of Technology, VIVEK SHARMA, Department of Mechanical Engineering, Massachusetts Institute of Technology, MATIJA CRNE, School of Chemistry and Biochemistry, Georgia Institute of Technology, MOHAN SRINIVASARAO, School of Polymer, Textile and Fiber Engineering, Georgia Institute of Technology. The brilliant metallic color of a beetle *Chrysina gloriosa* has been known to occur due to selective reflectance from a cholesteric structure on the exoskeleton. The surface also appears to have hexagonally packed structures. Crystallographic concepts and Voronoi analysis were used to determine the degree of order in different regions of the beetle. Along the hexagons in the Voronoi diagram, many clustered pentagons and heptagons were observed. Due to the surface curvature, the number of pentagons was found to be higher than the number of heptagons. The cells appear yellow in the center surrounded by a green region with a yellow edge. Confocal microscopy was used to image the underlying structure, which was found to consist of concentric arcs on a surface of a shallow cone. The observed structures resemble the defects on a cholesteric phase with a free surface, and provide an interesting explanation of structural color development in beetles, along with inspiration for the design of chiral photonic structures.

3:18PM L20.00003 Frustrated self-assembly of dendron and dendrimer-based supramolecular liquid crystals, RAFFAEE MEZZENGA, NADIA CANILIO, University of Fribourg, Switzerland, JANNE RUOKOLAINEN, Helsinki University of Technology, Finland, EDIS KASEMI, DIETER SCHLUETER, ETHZ, Switzerland, WON BO LEE, GLENN FREDRICKSON, UCSB, USA. A new inverted topological configuration is demonstrated both experimentally and theoretically for self-assembled dendron and dendrimer-based supramolecular liquid crystals in which the dendrons/dendrimers occupy the continuous domain and the ionically attached pendant chains are confined in discrete domains. All previous studies on dendrimer and dendrimer-based liquid crystals have reported normal liquid crystalline configurations in which the dendritic templates occupy discrete domains (in spherical or planar phases) or continuous struts (in bicontinuous cubic phases), while the pendant chains occupy the continuous space-filling domain. These surprising results mandate a re-examination of the packing mechanisms for this important class of materials and open new routes to unique nanostructures of possible use in existing and emerging technologies. References: R. Mezzenga, J. Ruokolainen, N. Canilio, E. Kasemi, D.A. Schlüter, W.B. Lee, G. H. Fredrickson, *Soft Matter*, in press (DOI: 10.1039/b809497k).

3:30PM L20.00004 Hydrogen-Bonded Assisted Supramolecular Self-Assembly of Double Discotic Supercumolecules, JIANJUN MIAO, LEI ZHU, Uconn — Symmetric double discotic supermolecules based on porphine (Py) and triphenylene (Tp) cores have been successfully synthesized via PyBOP-catalyzed amidination reaction. The Tp moieties had either C12- or C14-arms, and the spacer linking between the central Py and peripheral Tp was either C6 or C10. Thermal properties of these supermolecules were studied by differential scanning calorimetry, and self-assembled crystalline and/or liquid crystalline textures were confirmed by polarized optical microscopy. For samples with C12-arms in Tp, only a crystal-melt transition was observed. X-ray diffraction (XRD) on shear-oriented samples showed that Py was crystalline and Tp formed columnar liquid crystal. For samples with C14-arms in Tp, sequential crystal-liquid crystal-isotropic melt transitions were observed. XRD results indicated that the crystalline unit cells were orthorhombic for all samples, and amide hydrogen-bonding was responsible for their supramolecular self-assembly.

3:42PM L20.00005 Glassy correlations in nematic elastomers, BING LU, PAUL GODBART, University of Illinois at Urbana-Champaign, XIAOMING MAO, University of Pennsylvania. We address the physical properties of an isotropic melt or solution of nematogenic polymers that is then cross-linked beyond the vulcanization point. To do this, we construct a replica Landau theory involving a coupled pair of order-parameter fields: one describing vulcanization, the other describing local nematic order. The nematic melt correlations, present at the time of cross-linking, are trapped by cross-linking into the vulcanized network. The resulting glassy nematic fluctuations are analyzed in the Gaussian approximation in two regimes. When the localization length is shorter than the thermal nematic correlation length, the nematic correlations are well captured as glassy correlations. In the opposite regime, fluctuations in the positions of the localized polymers partially wash out the glassy nematic correlations.

3:54PM L20.00006 Orientation distribution and process modeling of thermotropic liquid crystalline copolyester (TLCP) injection-moldings, ROBERT BUBECK, Michigan Molecular Institute. JUN FANG, WESLEY BURGHARDT, Northwestern University, SUSAN BURGARD, Michigan Molecular Institute, DANIEL FISCHER, NIST. The influence of melt processing conditions upon mechanical properties and degrees of compound molecular orientation have been thoroughly studied for a series of well-defined injection molded samples fabricated from VECTRA (TM) A950 and 4,4'-dihydroxy-a-methylstilbene TLCPs. Fracture and tensile data were correlated with processing conditions, orientation, and molecular weight. Mechanical properties for both TLCPs were found to follow a “universal” Anisotropy Factor (AF) associated with the bimodal orientation states in the plaques determined from 2-D WAXS. Surface orientations were globally surveyed using Attenuated Total Reflectance — Fourier Transform Infrared (ATR-FTIR) spectroscopy and K-edge Near-Edge X-ray Absorption Fine Structure (NEXAFS). The results derived from the two spectroscopy techniques confirmed each other well. These results along with those from 2-D WAXS in transmission were compared with the results of process modeling using a commercial program, MOLDFLOW(TM). The agreement between model predictions and the measured orientation states was gratifyingly good.

4:06PM L20.00007 In Situ X-ray Scattering Measurements and Polydomain Simulations of Molecular Orientation Development during Injection Molding of Liquid Crystaline Polymers, JUN FANG, WESLEY BURGHARDT, Northwestern University, ROBERT BUBECK, Michigan Molecular Institute. We report on a coordinated experimental/computational study of injection molding of commercial thermotropic LCPS. In situ synchrotron x-ray scattering, combined with a customized injection molding apparatus, is used to track development of molecular orientation during the mold filling process for a commercial LCP, VECTRA A950, in two simple polymer melt geometries: square and T-shaped. Use of high brilliance undulator radiation at the Advanced Photon Source, coupled with a high speed CCD detector provides sufficient time resolution (~12 frames per second) to resolve the transient orientation dynamics during and following mold filling. In addition to in situ scattering measurements, ex situ 2-D wide angle X-ray scattering measurements are conducted on the same injection molded plaques. The experiments are complemented by process simulations performed using commercial mold filling software. A very close analogy between the Folgar-Tucker fiber orientation techniques confirmed each other well. These results along with those from 2-D WAXS in transmission were compared with the results of process modeling using a commercial program, MOLDFLOW(TM). The agreement between model predictions and the measured orientation states was gratifyingly good.

4:18PM L20.00008 Dynamics and rheology of active polar liquid crystalline films, LUCA GIOMI, M. CRISTINA MARCHETTI, TANNIEMOLA B. LIVERPOOL. I will discuss the dynamical and rheological properties of active polar liquid crystalline films. Like active nematic films, active polar films undergo a dynamical transition to spontaneously flowing steady-states. Spontaneous flow in polar fluids is, however, always accompanied by strong concentration inhomogeneities or “banding” not seen in nematics. In addition, a spectacular property unique to polar active films is their ability to generate spontaneously oscillating and banded flows even at low activity. The oscillatory flows become increasingly complicated for strong polarity.

1 Research is supported by NSF Grant Nos. 0521771 and 0521823.
4:30PM L20.00009 Influence of nanorods on the properties of polymeric materials, GREGORY N. TOEPPEPERWEIN, ROBERT A. RIGGLEMAN, JUAN J. DE PABLO, University of Wisconsin — Nanoscopic additions, such as metallic nanoparticles or carbon nanotubes, can dramatically impact the mechanical properties of polymeric materials, such as the plateau modulus, which is intimately related to the entanglement length of the polymer. To explore the connection between nanocomposite configurations and the dynamic mechanical effects that are difficult to probe experimentally, due to challenges associated with sample preparation and particle dispersion, we have performed extensive Molecular Dynamics and Monte Carlo simulations of polymer nanocomposites with nanoparticles whose size, shape, and concentration have been varied systematically. Calculations of the entanglement network through primitive path analysis of these composites have enabled us to connect nanorod effects on the entanglement network structure and density to the system’s dynamic properties. The main outcome of our study is a better understanding of how inclusions alter entanglements and how those entanglements are magnified in macroscopic observables.

4:42PM L20.00010 Interactions between rod-like cellulose nanocrystals and xylan derivatives: A light scattering study, JAE HYUN SIM, Virginia Tech, KATRIN SCHWIKA, THOMAS HEINZE, University of Jena, SHUPING DONG, MAREN ROMAN, ALAN ESKER, Virginia Tech — Interactions between rod-like cellulose nanocrystals and 2-hydroxypropyl-trimethylammonium (HPMA) xylan were investigated by polarized (DLS) and depolarized dynamic light scattering (DDLS). Cellulose nanocrystals were prepared by the controlled hydrolysis of black spruce pulp. Binary rod-like cellulose nanocrystal/water and ternary HPMA xylan/rod-like cellulose nanocrystal/water systems with different concentrations of cellulose nanocrystals were probed. Translational and rotational diffusion coefficients of cellulose nanocrystals in water are \( (4.8 \pm 0.4) \times 10^{-17} \text{cm}^2 \text{s}^{-1} \) and \( (526 \pm 20) \times 10^{-17} \text{cm}^2 \text{s}^{-1} \), respectively, and calculated lengths and diameters for nanocrystals are comparable to those of cellulose whiskers from cotton. At high cellulose nanocrystal concentrations, DDLS studies in ternary systems provide translational and rotational diffusion coefficients. However, at low cellulose nanocrystal concentrations, DDLS studies of ternary systems do not yield rotational diffusion coefficients. This behavior is attributed to bridging between polymer chains that causes non-linear deviation on standard decay rate (Γ) versus scattering vector magnitude (q^2) plots.

4:54PM L20.00011 Polymerization-Enhanced Alignment Order in Carbon Nanotube Composites, HOWARD WANG, YAYONG LIU, NARANYAN DAS, Binghamton University, SUNY, KUNLUN HONG, GUYULA ERES, DAVID URG, Oak Ridge National Laboratory — Polymer nanocomposites containing vertically aligned carbon nanotubes (VACNTs) have been synthesized via vacuum infiltration of monomers into confined VACNT arrays followed by in situ polymerization. The alignment order of VACNTs before and after polymerization has been quantitatively assessed using small angle neutron and x-ray scattering. The trend of continuous variation of alignment order along the height of VACNTs remains unaltered whereas the degree of order is enhanced upon polymerization. Polymerization-enhanced alignment order may assist preparing better carbon nanotube composites.

5:06PM L20.00012 Perylene diimide liquid crystals: A density functional study, JEVERSOON ARANTES, Centro de Ciencias Naturais e Humanas, Universidade Federal do ABC, Santo Andre, SP, Brazil, MATHEUS LIMA, Instituto de Fisica, Universidade de Sao Paulo, CP 66318, 05315-970 Sao Paulo, SP, Brazil, ADALBERTO FAZZIO, Centro de Ciencias Naturais e Humanas, Universidade Federal do ABC, Santo Andre, SP, Brazil, HONGJUN XIANG, SU-HUAI WEI, National Renewable Energy Laboratory, Golden, Colorado 80401, USA, GUSTAVO DALPIAN, Centro de Ciencias Naturais e Humanas, Universidade Federal do ABC, Santo Andre, SP, Brazil — Organic semiconductors (OSs) are getting each time more space in the field of electronic materials mainly due to its low manufacturing costs, the relative facility of manufacturing and in the desired way. A model for the crystal structure of perylene diimide PPEEB has been proposed, partially based on experimental observations. In this structural model, we’ve performed an ab initio calculations on the electronic structure of this material. Due to the strongly localized nature of the Oxygen atoms on the side chains, is necessary to go beyond the standard LDA and GGA calculations. With the PBE0 approach, the electronic structure becomes in agreement with previous results. The tails of the crystal molecular not only is responsible for its structural conformation, but also can be used for tuning the electronic and optical properties of the material.

Wednesday, March 18, 2009 8:00AM - 11:00AM — Session P4 DPOLY: Physics of Polymer Membranes for Water Purification 306/307

8:00AM P4.00001 Transport of water and solutes in reverse osmosis and nanofiltration membranes1, DAVID CAHILL, Department of Materials Science and Materials Research Laboratory, U. Illinois-Urbana — The polyamide active layers of reverse osmosis and nanofiltration membranes used for water purification are real-world examples of nanoscale functional materials: the active layer is only ~100 nm thick. Because the active layer is formed by a process of interfacial polymerization, the structure and composition of the membrane is highly inhomogeneous and even such basic physical and chemical properties as the atomic density, swelling in water, and the mobility of water and ions, are poorly understood. We are using Rutherford backscattering spectrometry (RBS) to determine the composition, roughness, and thickness of the membrane; reveal the surprisingly high solubility of salt ions in the polymer active layer; analyze the acid-base chemistry of charged functional groups; and determine the degree of polymer cross-linking. Measurements of mass-uptake and adsorption-induced mechanical stress of membranes in humid air enable us to determine the water solubility, specific volume of water, and the mechanical strength of the membrane. Comparisons between these equilibrium data and the permeability of the membrane to water and salts show that the mobility of water molecules in the membrane approaches the mobility of bulk water, and that the rejection of salt ions is accomplished by low mobility, not low solubility. My collaborators in this work are Xijing Zhang, Orlando Coronell, and Prof. Benito Mariñàs.

1Supported by the NSF through The Center of Advanced Materials for the Purification of Water with Systems

8:36AM P4.00002 High Flux Nanofibrous Membranes for Water Purification, BENJAMIN HSIAO, Stony Brook University — Recently, nanofibrous materials have been made more readily available in large part due to advances in electro-spinning and related technologies, including the use of a combination of electrostatic and gas-blowing forces. The non-woven structure has unique features, including interconnected pores, very large surface-to-volume ratio, and ease of surface modifications which enable such scaffolds to have many biomedical and industrial applications. The chemical composition of electrospun membranes can be adjusted by using different polymers, polymer blends or nanocomposites, made of organic or inorganic materials. In this talk, we demonstrate a breakthrough technology on thin-film nanocomposite membranes for high-flux water purification based on nanofiber scaffolds. The breakthrough incorporates two new and unique concepts of the membrane design: (1) the replacement of the conventional flux-limited porous substrate with a highly porous nanofibrous scaffold, and (2) the creation of a very thin, strong and functional nanocomposite barrier layer, imbedded with interconnected and directed water channels. Preliminary experiments on the hierarchical design and assembly of this unique nanofibrous membrane have already revealed very promising potentials. By using a hydrophilic nanocomposite barrier layer, an asymmetric electrospun nanofibrous mid-layer scaffold and a non-woven microfibrous support, the flux rate of this not yet optimized membrane system is 3-10 times better than that of the best among all known conventional ultrafiltration/nanofiltration media without losing the high rejection and low fouling criteria.

1This is a joint collaboration with Ben Chu. The work is supported by ONR.

9:48AM P4.00004 Carbon Nanotube Membranes for Water Purification. OLIGICA BAKAJIN, Biosciences and Biotechnology Division, PLS; Lawrence Livermore National Laboratory — Carbon nanotubes are an excellent platform for the fundamental studies of transport through channels commensurate with molecular size. Water transport through carbon nanotubes is also believed to be similar to transport in biological channels such as aquaporins. I will discuss the transport of gas, water and ions through microfabricated membranes with sub-2 nanometer aligned carbon nanotubes as ideal atomically-smooth pores. The measured gas flow through carbon nanotubes exceeded predictions of the Knudsen diffusion model by more than an order of magnitude. The measured water flow exceeded values calculated from continuum hydrodynamics models by more than three orders of magnitude and is comparable to flow rates extrapolated from molecular dynamics simulations and measured for aquaporins. More recent reverse osmosis experiments reveal ion rejection by our membranes. Based on our experimental findings, the current understanding of the fundamentals of water and gas transport and of ion rejection will be discussed. The potential application space that exploits these unique nanofluidic phenomena will be explored. The extremely high permeabilities of these membranes, combined with their small pore size will enable energy efficient filtration and eventually decrease the cost of water purification.

In collaboration with Francesco Fornasiero, Biosciences and Biotechnology Division, PLS, LLNL, Livermore, CA 94550; Sangil Kim, NSF Center for Biophotonics Science & Technology, University of California at Davis, Sacramento CA 95817; Jung Bin In, Mechanical Engineering Department, UC Berkeley, Berkeley CA 94720; Hyung Gyu Park, Jason K Holt, and Michael Stadermann, Biosciences and Biotechnology Division, PLS, LLNL; Costas P. Grigoropoulos, Mechanical Engineering Department, UC Berkeley; Aleksandr Noy, Biosciences and Biotechnology Division, PLS, LLNL and School of Natural Sciences, University of California at Merced.

1Prepared by LLNL under Contract DE-AC52-07NA27344, with funding from LLNL’s LDRD program, DARPA, & NSF.

10:24AM P4.00005 Hierarchical Fiber Structures Made by Electrospinning Polymers. DARRELL H. RENEKER, The University of Akron — A filter for water purification that is very thin, with small interstices and high surface area per unit mass, can be made with nanofibers. The mechanical strength of a very thin sheet of nanofibers is not great enough to withstand the pressure drop of the fluid flowing through. If the sheet of nanofibers is made thicker, the strength will increase, but the flow will be reduced to an impractical level. An optimized filter can be made with nanometer scale structures supported on micron scale structures, which are in turn supported on millimeter scale structures. This leads to a durable hierarchical structure to optimize the filtration efficiency with a minimum amount of material. Buckling coils, electrical bending coils, and pendulum coils spanning dimensions from a few microns to a few centimeters can be collected from a single jet by controlling the position and motion of a collector. Attractive routes to the design and construction of hierarchical structures for filtration are based on nanofibers supported on small coils that are in turn supported on larger coils, which are supported on even larger overlapping coils. “Such top-down” hierarchical structures are easy to make by electrospinning. In one example, a thin hierarchical structure was made, with a high surface area and small interstices, having an open area of over 50%, with the thinnest fibers supported at least every 15 microns.

Tao Han, Darrell H Reneker, Alexander L. Yarin, Polymer, Volume 48, issue 20 (September 21, 2007), p. 6064-6076.

Wednesday, March 18, 2009 8:00AM - 11:00AM —
Session P18 DPOLY: Bulk Block Copolymers II

8:00AM P18.00001 Directed Self-Assembly of Cadmium Selenide Nanocrystals in Conjugated Rod-Coil Block Copolymers. B. L. MCCULLOCH, Dept of Chemical Engineering, University of California-Berkeley, J. URBAN, Molecular Foundry, Lawrence Berkeley National Laboratory, R. A. SEGALMAN, Dept of Chemical Engineering, University of California-Berkeley — Semiconducting polymer/nanocrystal composites are attractive for many applications; however their performance relies crucially on nanoscale morphology. We demonstrate that a conjugated rod diblock copolymer can be used both to absorb light and template the location of CdSe nanocrystals. A combination of the liquid crystallinity of the conjugated rod block and the interactions of the nanocrystal ligand coat with the block copolymer control self-assembly. For example, incorporation of the nanocrystal in the rod nanodomain disrupts liquid crystallinity. In the case of a poly(alkoxy-phenylene vinylene-b-2-vinyl pyridine) (PPV-b-P2VP) block copolymer and CdSe nanocrystals, self-assembly leads to a bulk lamellar structure on the 10nm length scale. Small angle X-ray scattering confirms the addition of nanocrystals swells the domain size. We demonstrate via transmission electron microscopy the nanocrystals reside preferentially in the P2VP domain, presumably due to the strong nanocrystal surface interactions with polar P2VP and exclusion effects of the crystalline PPV phase.

8:12AM P18.00002 ABSTRACT WITHDRAWN —

8:24AM P18.00003 Nano-porous Poly(3-hexylthiophene) films: A novel route to prepare bulk heterojunction photovoltaic devices. TIRTHA CHATTERJEE, KULANDAVELU SIVANANDAN, CRAIG J. HAWKER, EDWARD J. KRÄMER, Mitsubishi Chemicals-Center for Advanced Materials, Materials Research Laboratory, University of California, Santa Barbara, CA 93106 — Conjugated polymer/nanocrystal composites are attractive for many applications; however their performance relies crucially on nanoscale morphology. We demonstrate that a conjugated rod diblock copolymer can be used both to absorb light and template the location of CdSe nanocrystals. A combination of the liquid crystallinity of the conjugated rod block and the interactions of the nanocrystal ligand coat with the block copolymer control self-assembly. For example, incorporation of the nanocrystal in the rod nanodomain disrupts liquid crystallinity. In the case of a poly(alkoxy-phenylene vinylene-b-2-vinyl pyridine) (PPV-b-P2VP) block copolymer and CdSe nanocrystals, self-assembly leads to a bulk lamellar structure on the 10nm length scale. Small angle X-ray scattering confirms the addition of nanocrystals swells the domain size. We demonstrate via transmission electron microscopy the nanocrystals reside preferentially in the P2VP domain, presumably due to the strong nanocrystal surface interactions with polar P2VP and exclusion effects of the crystalline PPV phase.

8:36AM P18.00004 The Influence of Electric Fields on the Order-Disorder Transition Temperature of Block Copolymer Systems. HEIKO SCHOBERTH, Lehrstuhl fuer Physikalische Chemie II, Universitaet Bayreuth, D-95440 Bayreuth, Germany, KRISTIN SCHMIDT, Materials Research Laboratory, University of California, Santa Barbara, CA 93106, USA, KERSTIN SCHINDLER, ALEXANDER BÖKER, Lehrstuhl fuer Physikalische Chemie II, Universitaet Bayreuth, D-95440 Bayreuth, Germany — We investigate the influence of electric fields on the phase behavior of diblock copolymers in concentrated solutions using synchrotron small-angle X-ray scattering (synchrotron SAXS). When heating the solutions through the order-disorder transition temperature $T_{ODT}$, we find a significant decrease in $T_{ODT}$ with increasing electric-field strength. In addition we found a temperature regime in which it is possible to switch between the mixed and phase separated state at constant temperature upon application of a moderate electric field.

1This work was carried out in the framework of the SFB 481 (TP A2) funded by the German Science Foundation (DFG). AB acknowledges financial support by the Lichtenberg-Program of the VolkswagenStiftung.
8:48AM P18.00005 Phase Behavior of Polystyrene-block-Poly(n-alkyl-ran-n’alkyl methacrylate) Copolymers1, HONG CHUL MOON, JUNHAN CHO2, Dankook University, JIN KON KIM, Pohang University of Science and Technology — The phase behavior of polystyrene-block-poly(n-butyl-ran-n’hexyl) methacrylate copolymers and polystyrene-block-poly(n-octyl-ran-methyl) methacrylate copolymers were investigated by using small angle X-ray scattering, birefringence and rheometry. When the total molecular weight and the composition of the random copolymers were judiciously controlled, the closed-loop phase behavior with both a lower disorder-to-order transition and an upper order-to-disorder transition was observed. These block copolymers exhibited excellent baroplasticity. The observed phase behavior was explained by a compressible mean field approach.

1This work was supported by Creative Research Initiative Program supported by KOSEF.
2Pohang University of Science and Technology

9:00AM P18.00006 Gas Pressure Effect on Phase Behavior of Deuterated Polystyrene-block-poly(n-pentyl methacrylate)1, HYE JEONG KIM, JIN KON KIM, Pohang University of Science and Technology, DU YEOL RYU, Yonsei University — The pressure effect of various gases on the phase transitions of deuterated polystyrene-block-poly(n-pentyl methacrylate) copolymer was investigated by small angle neutron scattering (SANS) and birefringence. With increasing helium gas pressure, the size of closed-loop consisting of both the lower disordered-to-ordered transition and the upper ordered-to-disordered transition was decreased, which is similar to the hydrostatic pressure effect. On the other hand, when nitrogen gas was used, the size of the closed-loop became larger with increasing pressure. These interesting results are explained by the binding energy calculation.

1This work was supported by Creative Research Initiative Program supported by KOSEF.

9:12AM P18.00007 Pressure Jump Studies of Block Copolymer Phase Transition in Selective Solvent1, YONGSHENG LIU, RAMA BANSIL, Boston University, MILOS STEINHART, Institute of Macromolecular Chemistry, CZ Republic — Synchrotron based time-resolved small angle x-ray scattering (SAXS) was used to study the kinetics of the order-disorder transition (ODT) in a 30% (w/v) solution of a diblock copolymer of poly(styrene – isoprene) (SI 18-12) in diethylphthalate (DEP), a selective solvent for the PS block using pressure jump methods. The results show that the ODT temperature increases at about 20C/kbar with pressure. Time resolved pressure jump SAXS experiments were done to study the kinetics of disorder to BCC phase transition and the reverse transition. Pressure jump from 100 bar to 800 bar at 108C from disordered state displayed a BCC structure at 30 seconds. Results of experiments with solvent viscosity increased by adding low molecular weight polystyrene will also be presented.

1Supported by NSF DMR. RB acknowledges IR/D support of NSF.

9:24AM P18.00008 Self-assembled Oniontype Multiferroic Nanostructures, SHENQIANG REN, ROBERT M. BRIBER, MANFRED WUTTIG, Dept. of Mater. Sci. & Engi. University of Maryland, College Park — Spontaneously self-assembled oniontype multiferroic nanostructures based on block copolymers as templating materials are reported. Diblock copolymer containing two different magnetoelectric precursors separately segregated to the two microdomains have been shown to form well-ordered templated lamellar structures. Onion-type multilamellar ordered multiferroic (PZT/CoFe2O4) nanostructures have been induced by room temperature solvent annealing in a magnetic field oriented perpendicular to the plane of the film. The evolution of the onion-like microstructure has been characterized by AFM, MFM, and TEM. The structure retains lamellar periodicity observed at zero field. The onion structure is superparamagnetic above and antiferromagnetic below the blocking temperature. This templating process opens a route for nanometer-scale patterning of magnetic toroids by means of self-assembly on length scales that are difficult to obtain by standard lithography techniques.

9:36AM P18.00009 Periodic Polymers for PhoXonics, EDWIN THOMAS, Department of Materials Science and Engineering, Massachusetts Institute of Technology — Exploiting the size and shape dependence of material properties and accessing multi-functionality holds great promise for the development of materials that will contribute to novel future technologies. Polymers can act as hosts for metallic and dielectric nanoparticles as well as organic molecules, resulting in nanocomposites with combinations of properties not available by other means. Periodic structural assemblies are of particular interest, due to their interesting interactions with waves: especially light and mechanical waves. Progress in this exciting area requires excellent control of structure formation. A top-down, bottom-up approach, involving interference lithography and self assembly is demonstrating good success in fabricating the requisite structures and desired properties for photonics and phononics.

9:48AM P18.00010 Hydration and phase separation of polyethylene glycol in copolymers of tyrosine derived carbonates. N. SANJEEVA MURTHY, Rutgers University, WENJIE WANG, University of Vermont, JOACHIM KOHN, Rutgers University — Effect of PEG fraction and its block size on the temperature-induced phase transitions and the hydration-induced phase separation were investigated in a copolymer of desaminotyrosyl tyrosine ethyl ester (DTE) and PEG using simultaneous SAXS/WAXS/DSC. The PEG segments crystallized when the block size was at least 2000 Daltons and present at ∼ 40 wt%, and raised the Tg of the polymer by ∼ 15 °C. The PEG blocks in dry polymers with up to 50 wt% PEG, even when crystalline, were found to be uniformly distributed with no evidence of phase separation at 10 nm length scales. The non-iodinated PEG-rich sample with 30 mole% PEG20s showed the lower critical solution temperature (LCST) behavior with PEG blocks forming a separate phase above -21 °C. In the iodinated version of this polymer, the PEG20s blocks were phase separated in the solid phase. In all samples, whether PEG was crystalline or not, hydration induced PEG to separate into 15 nm hydrated domains. Phase behavior was dependent on whether poly(DTE) or the PEG was the major (matrix) phase. Changes in the mobility of the chains brought about by water-mediated hydrogen-bonding, and modulated by heat, appear to be the common underlying explanation for the range of observed phase behavior.

10:00AM P18.00011 Robustness of Pluronic Block Copolymer Nanostructure to Structural Changes in Dispersed Nanoparticles, THERESA A. LAFOLLETTE, LYNN M. WALKER, Carnegie Mellon University — Thermoreversible block copolymers [(PEO)n-(PPO)m-(PEO)n; trade name Pluronic] self assemble into ordered micelle gels. Nanoparticles (3-10nm) are templated in the interstitial spaces of Pluronic micelle gels to form nanocomposite systems. Globular hydrophilic proteins have served as model monodisperse nanoparticles in this work. We have shown that these proteins are templated in the interstitial sites of the cubic packed micelle gels at room temperature. By raising the temperature, the proteins are denatured to study the robustness of the micelle gel to structural changes due to the unfolded protein. Nanoscale structure is determined from small angle neutron scattering (SANS). It was expected that any change in the nanoparticle size would cause a change in the packing of the Pluronic micelle gel. However in SANS experiments, the FCC and BCC Pluronic templates show no nanoscale structural differences between a room temperature sample and a sample that has been heated to denature the protein and then cooled back to room temperature. There is a change in the template at longer length scales as evidenced by a low q upturn in the scattered intensity. The robustness of the micelle gel at different length scales will be discussed.
10:12 AM P18.00012 Phase behavior of block copolymer nanocomposites. GEORGE PAPAKONSTANTOPOULOS, Arkema Inc., ANALYTICAL AND SYSTEMS, ARKEMA INC. TEAM — Incorporating nanoparticles in block copolymers can allow the creation of a material with tailored properties. In addition, the control of the nanoparticle location in a nanometer scale, can lead to novel applications for these materials. Although, the phase behavior of block copolymers in the bulk is well established, the effects of nanoparticles on their phase behavior, especially under confinement, are not well understood. We carried out a systematic study to investigate the self-assembly of block copolymer-nanoparticle composites using a coarse grain model. The results were compared in the bulk and under confinement. The dependence of the location and distribution of the nanoparticles within the block copolymer as a function of particle-polymer interaction, size and shape were examined.

10:24 AM P18.00013 Effect of Chain Architecture on Nanoparticle Miscibility in Block Copolymer Nanocomposites. JESSICA LISTAK, HYUNG JU RYU, ILHEM F. HAKEM, Carnegie Mellon University, RANGOU SOFIA, POLITAKOS NIKOLAOS, MISCHRONIS KONSTANTINOS, APOSTOLOS AVGEROPOULOS, University of Ioannina, MICHAEL R. BOCKSTALLER, Carnegie Mellon University — This contribution will present a combined experimental and theoretical analysis of the effect of block copolymer chain architecture on the miscibility and morphology of enthalpically neutralized particle mixtures. The chain architecture is found to be a critical parameter in facilitating particle dispersion imposing both direct as well as indirect constraints on the particle distribution. Continuous block configurations (such as the bridged midblocks in triblock copolymers) are found to inhibit particle compatibilization. Interestingly, the particle miscibility is found to be strongly affected by the configuration of the block adjacent to particles. Incompatibility is observed for high branching densities in the adjacent domains (such as mixtarcin chain architectures). A mean-field model will be presented to rationalize this observation as a consequence of segmental crowding that counters changes in the layer dimensions induced by particle sequestration.

10:36 AM P18.00014 Rheological and Mechanical Properties of Crosslinked Block Copolymer Nanofiber and Polystyrene Blends. SUNGWON MA, YONATHAN THIO, Georgia Institute of Technology — The mechanical and rheological properties of blends of crosslinked and uncrosslinked poly(styrene)-b-poly(isoprene) copolymer with commercially available polystyrene were studied. Cylindrical morphology of PS-b-PI copolymer was employed for generating nanoparticle morphology. Cold vulcanization process using sulfur monochloride (S<sub>2</sub>Cl<sub>2</sub>) was used to preserve the morphology. Blends of uncrosslinked PS-b-PI copolymer with neat polystyrene were also prepared. Both blend samples were prepared by solvent casting method with the filler contents varying between 0.5 and 10 wt%. The mechanical and rheological properties were characterized and the microstructures of the fiber and the systems were imaged. The dynamic moduli (G’ and G’) of the crosslinked system increased with increasing the fiber content compared to the uncrosslinked system. The results were compared to the rheological model by fitting to Cross-Williamson. This blend study indicated critical microstructures of the fiber and the systems were imaged. The mechanical and rheological properties were characterized and the microstructures of the fiber and the systems were imaged. The mechanical properties of these materials have been examined with rheological methods. The elastic contribution to the shear modulus increases while at high temperatures which we attribute to an increase in the number of NT-NT contacts. We have attempted to verify this observation by simulating the high temperature environment in the NIR-PLS measurements and looking for quenching.

10:48 AM P18.00015 Well Ordered Polymer Melts with Sub 5-Nanometer Domains upon Blending Surfactants with Selectively Associating Additives. VIKRAM DAGA, University of Massachusetts Amherst, VIJAY TIRUMALA, Polymers Division, NIST, CURRAN CHANDLER, ALVIN ROMANG, ERIC ANDERSON, University of Massachusetts Amherst, ERIC LIN, Polymers Division, NIST, JAMES WATKINS, University of Massachusetts Amherst — Applications employing block copolymers such as templating mesoporous inorganic structures and patterning would benefit from reduction in domain size formed in well-ordered block copolymer templates. The extent to which the domain size can be reduced is limited by the minimum required segregation strength, χN, where N determines the size of block copolymer chains and the domain size. This study shows that dispersed blocks that do not associate strongly can be made to undergo disorder-to-order transition by blending selectively associating homopolymers as well as small molecule additives with multi-point, non-ionic interactions. Blending with selectively associating additives result in an increase in segregation strength χN through an increase in apparent χ. The resulting domain sizes were found to be as low as 5 nm which is significantly lower than that seen for a typical block copolymer template.

Wednesday, March 18, 2009 8:00AM - 11:00AM — Session P19 D POLY: The Physics of Polymer Nanocomposites: Properties

8:00 AM P19.00001 Tuning optical properties of gold nanorods in polymer films through thermal reshaping. RUSSELL COMPOSTO, ERIC MILLS, YU LIU, University of Pennsylvania — The thermal reshaping of gold nanorods (NRs) in a poly(methyl methacrylate) (PMMA) nanocomposite film is investigated by UV-vis and TEM. To ensure dispersion, the NRs are modified with PEG brushes, and then dispersed in PMMA. Thermal annealing of the PMMA:NR film results in a blue shift of the longitudinal plasmon resonance, caused by a decrease in the length of the NR. The rate of the blue shift increases as temperature increases from 100 °C to 200 °C, and the longitudinal absorption peak approaches a constant value that scales linearly with temperature. We demonstrate a potential application by fabricating a device with a gradient in optical properties.

8:12 AM P19.00002 Quenching Photoluminescence in Single-Walled Carbon Nanotube/Copolymer Composite Materials. ANDREW SCHOCH, Material Science and Engineering Dept. Northwestern University, L. CATHERINE BRINSON, Mechanical Engineering Dept. Northwestern University, KENNETH R. SHULL, Material Science and Engineering Dept. Northwestern University — Single-walled carbon nanotubes (SWNTs) stabilized by A-B diblock and A-B-A triblock copolymers are excellent model systems for studying the relationship between nanotube dispersion and mechanical response. The SWNTs cannot be dispersed in the alcoholic solvent used here without the addition of copolymer. However, the A blocks are in good solvent conditions for all temperatures and the A blocks solvent quality decreases with decreasing temperature. This solvent quality difference drives the formation of micelles with A block cores at low temperatures. As verified by AFM, the micelles form heterogeneous micelles in solutions by incorporating the SWNTs. The dispersion has also been verified with near-IR photoluminescence spectroscopy (NIR-PLS) and the mechanical properties of these materials have been examined with rheological methods. The elastic contribution to the shear modulus increases while at high temperatures which we attribute to an increase in the number of NT-NT contacts. We have attempted to verify this observation by simulating the high temperature environment in the NIR-PLS measurements and looking for quenching.

8:24 AM P19.00003 Temperature measurements of inverse micelles coated in gold nanoparticles using fluorescence. CHAD DALEY, JAMES A. FORREST, RYAN SPELLER, TOEWS WILLIAM, PATRICK MCVEIGH, Dept. of Physics and Astronomy, University of Waterloo, TODD EMRICK, Dept. of Polymer Science and Engineering, UMass Amherst — When nanoparticles are subject to laser radiation they have the ability to efficiently absorb energy from the beam and transform this energy into heat. Photothermal therapy uses this phenomenon to irreparably damage tissue surrounding nanoparticle conjugates. Despite the promise of this technique, there is no consensus on the damage mechanism or even the local heating. Here we present an experiment designed to measure local temperatures achieved in such processes. Ligand covered Gold nanoparticles are used to stabilize inverse micelles containing fluorescence dye in the water component. The fluorescence intensity being temperature dependent provides us with a means of measuring the temperature of the micelles as a function of time immediately following a laser pulse.
8:36AM P19.00004 Magnetic and Optical anisotropy thiol-capped Au NPs embedded into a polymer , JOSÉ DE LA VENTA, MIGUEL ANGEL GARCIA, VIRGINIA BOUZAS, Materials Physics Dept. University Complutense, ANDREAA PUCCI, GIACOMO RUGGERI, Chemistry and Industrial Chemistry Department. University of Pisa — The anisotropy at the nanoscale is achieved when the shape of the objects is not spherical such as in the case of nanorods, nanotubes or nanowires. However, when they are embedded in a macroscopic matrix, the random distribution destroys the anisotropy. In this work we study the possibility of induce optical and magnetic anisotropy in a system consisting of spherical thiol capped Au NPs embedded in a polymeric matrix. The ferromagnetic-like behavior arises from the bond between the Au-S atoms and the optical response is also highly dependent on these bonds. So, modifications in the environment and in these bonds could alter the behavior of the whole system. When the NPs are embedded in a polymeric matrix, which is stretched even 40 times in one direction, SQUID and UV/Vis measurements show that arise a macroscopic anisotropy in spite of the spherical shape of the NPs. EXAFS measurements confirm that there are modifications in the Au-S bonds along the stretched direction that are responsible of the induced macroscopic anisotropy.

8:48AM P19.00005 Stability of the double gyroid phase to nanoparticle polydispersity in polymer tethered nanosphere systems1 , CAROLYN PHILLIPS, CHRISTOPHER IACOVELLA, SHARON GLOTZER, University of Michigan — Recent simulations have shown that aggregating nanospheres functionalized with polymer "tethers" can self-assemble to form the double gyroid phase also seen in block copolymer and surfactant systems. Within the gyroid domain, the nanoparticles pack in icosahedral motifs, stabilizing the gyroid phase in a small region of the phase diagram[1]. We study the impact of nanoparticle polydispersity on the properties of the double gyroid phase [2]. Here we show that a low amount of polydispersity lowers the energy of the phase. A large amount of polydispersity raises the potential energy of the system, disrupts the icosahedral packing, and eventually, destabilizes the gyroid. A study of binary gyroids indicates that the inclusion of a small population of either smaller or larger nanospheres encourages low-energy icosahedral clusters. Using a new measure for determining the volume of a component in a microphase-separated system based on the Voronoi-tessellation, we show that polydispersity compacts the gyroid domain and lowers the average coordination of the nanospheres. [1] Iacovella, et al., PRE, 2007 [2] Phillips, et al., "Stability of the double gyroid phase to nanoparticle polydispersity in polymer tethered nanosphere systems, preprint.

9:00AM P19.00006 Experimental and computational investigation of percolation in complex polymer nanocomposites , DERRICK STEVENS, LORI DOWNEN, NCSU Dept. of Physics, RUSSELL GORGA, NCSU Dept. of Textile Engineering, LAURA CLARKE, NCSU Dept. of Physics — The continuing development of polymer nanocomposites has led to increasingly complex morphology, such as the mats of composite nanofibers formed from electrospinning. The formation of particle networks within the composite volume that leads to enhanced properties, such as electrical conductivity, may be influenced by this complex sample geometry. In this work, experimental and computational efforts are utilized to understand and predict the percolation threshold (critical volume fraction) for two cases: single ultra-high aspect ratio fibers (where fiber diameter can be similar to the particle dimensions) and these same fibers arranged in a random mat with up to 80% porosity. 2D and 3D Monte Carlo simulations, modeled on to understand and predict the percolation threshold (critical volume fraction) for two cases: single ultra-high aspect ratio fibers (where fiber diameter can be similar to the particle dimensions) and these same fibers arranged in a random mat with up to 80% porosity. 2D and 3D Monte Carlo simulations, modeled on

9:12AM P19.00007 Influence on Thermal Diffusivity through a Transformation of Nanotube-like Clay Platelets in Polymer Blends , SEONGCHAN PACK, TAKASHI KASHIWAGI, TANANDORI KOGA, JONATHAN SOKOLOV, MIRIAM RAFAILOVICH, Department of Materials Science and Engineering, Stony Brook University — We have previously demonstrated that large aspect ratio nanoparticles such as clays or nanotubes can form in-situ grafts which become universal compatibilizing agents for polymer blends. Here we show how the same mechanism could be applied to producing flame retardant materials in the polymer matrix. In particular, the large aspect nanoclays prevent thermally induced phase segregation and disperse the flame retardants, which greatly decrease flammability and increase efficiency of the flame retardants during combustion due to a formation of ribbons-like structures. These structures could produce a larger thermal differential gradient between the two polymeric phases, which could change a heat specific of the system during combustion. Therefore, a small addition of the nanoclays affects the huge reduction on heat release rate and the mass loss rates. Furthermore, using a small angle X-ray scattering (SAXS), a transmission electron microscopy (TEM), and a scanning electron microscopy (SEM) shows that the clay platelets could be transformed into tubular-like rods during combustion, which would increase of the thermal diffusivity in the polymer blend.

9:24AM P19.00008 Electrical Conductivity in Polymer Composites Containing Metal Nanowires: Simulation and Experiment , SADIE WHITE, TARUN VEMULKAR, JOHN FISCHER, KAREN WINEY, University of Pennsylvania — The study of rod percolation behavior has resurfaced in recent years, because it explains electrical conductivity in polymer nanocomposites containing carbon nanotubes and metal nanowires. Common processing techniques result in fillers with L/D < 50, so traditional models, which are only strictly correct in the limit of L/D ~ ∞, are ineffective at predicting percolation in these systems. We present a simulation that constructs percolated networks of finite-aspect ratio rods and calculates their electrical conductivity. We will compare our simulation results with polymer composites containing silver nanowires with aspect ratios of ~10 and ~30. Finally, we will present the temperature-dependent electrical conductivity of these composites and interpret the results using the thermal expansion coefficients of polystyrene and silver. These materials act as "thermal switches," wherein electrical conductivity of certain composites can be manipulated by several orders of magnitude over the temperature range from 80K-425 K.

9:36AM P19.00009 Polymer Nanocomposites Made with Unmodified Graphite or Carbon Nanotubes: Role of Dispersion in Optimizing Mechanical and Thermal Properties and Electrical Conductivity , JUNICHI MASUDA, KATSUYUKI WAKABAYASHI, PHILIP BRUNNER, CYNTHIA PIERRE, JOHN TORKELSON, Northwestern University — Polymer nanocomposites made with carbon-based nanofiller have the potential to achieve unprecedented, multifunctional property enhancements in comparison with other nanocomposite systems. Here, we describe research in which we prepare nanocomposites with polymers that are not amenable to solution-based processing, such as polycarbonate and poly(ethylene terephthalate). Solid-state shear pulverization is used singly or in conjunction with melt processing to obtain well-dispersed polymer/graphite and polymer/carbon nanotube nanocomposites. We report record improvements in properties of unoriented films of polycarbonate nanocomposites, including Young’s modulus, crystalization rate, and thermal degradation temperature. We also characterize electrical conductivity of such nanocomposites and note that the dispersion characteristics necessary to achieve maximum mechanical and thermal properties differ from those needed to maximize electrical conductivity. The potential of and challenges with using unmodified graphite as a filler in polymer nanocomposites will be discussed.
9:48AM P19.00010 Conductive Paper by LBL Assembly of PSS and ITO onto Wood Fibers and its Electrical Properties through Impedance Spectroscopy and I-AFM, CHUNQING PENG, YONATHAN THIO, ROSARIO GERHARDT, Georgia Institute of Technology — Conductive paper has been fabricated by layer-by-layer (LBL) assembly of polyelectrolytes and indium tin oxide (ITO) nanoparticles onto wood fibers, followed by traditional paper making method. The wood fibers were first coated with polyethyleneimine (PEI) and then LBL assembled with poly(sodium 4-styrenesulfonate) (PSS) and ITO for several bilayers. The AC electrical properties, measured for frequencies ranging from 0.01 Hz to 1 MHz, will be reported for the in-plane (IP) and through-the-thickness (TT) directions. With 10 bilayers of PSS/ITO assembly on wood fibers, the conductivity of as-prepared paper was improved by more than six orders of magnitude and reach to 5.2 × 10⁻⁶ S cm⁻¹ in IP direction and 1.9 × 10⁻⁶ S cm⁻¹ in TT direction. The percolation phenomenon of ITO nanoparticles through the handsheet in both directions was observed through current atomic force microscopy (I-ASF). By applying a bias voltage, either on one end of the paper stripes or on one side of the paper handsheet, the current can be detected on the other end of the paper stripes or on the other side of the paper handsheet. PEI can be used to modify the ITO suspension and significantly improve the LBL procedure. The mechanism of PEI modifying ITO colloidal suspension will be discussed.

10:00AM P19.00011 Placement Control of Nanomaterial Arrays on Surface-Reconstructed Block Copolymer Thin Films, JEONG CON GON, SON, WAN KI BAE, Seoul National University, HUMAN KANG, PAUL F. NEALEY, University of Wisconsin-Madison, KOOKHEON CHAR, Seoul National University — Nanomaterials such as nanoparticles, quantum dots and nanorods/wires have recently attracted attention not only because of their unique electronic, optical, and magnetic properties depending on their size and chemical structure but also due to their possible applications to optoelectronics devices, next-generation memory devices, and biological sensors. In order to take full advantage of these useful properties for highly integrated fabrication, precise control of such nanomaterials on patterned substrates is inevitably required. In this presentation, we demonstrate a straightforward and reproducible method for the placement of nanomaterials such as nanoparticles and nanorods on patterned PS-b-PMMA block copolymer (BCP) thin films. This concept is based on the properties of surface-reconstructed BCP thin films, which could induce topographical nanopatterns induced by selective solvent vapor treatment without any etching process. The deposition conditions for high density nanomaterial patterns in the grooves of BCP nanopatterns were optimized. By treating the surface under electron beam irradiation, the pattern inversion of nanomaterial-containing BCP nanopatterns was also observed, which can be further processed to realize the dual nanomaterial patterning.

10:12AM P19.00012 Confinement and Ordering of Au Nanorods in Polymer Films, MICHAEL J. A. HORE, ERIC MILLS, YU LIIU, RUSSSEL J. COMPOSTO, Department of Materials Science and Engineering, University of Pennsylvania — Ordered arrays of gold nanorods (Au NRs) possess interesting optical properties that might be utilized in future devices. Au NRs functionalized with a poly(ethylene glycol)-thiol brush are incorporated into homopolymer or block copolymer (BCP) films. NR distribution and orientational correlations are studied as a function of nanorod concentration and spatial confinement via Rutherford backscattering spectrometry (RBS) and transmission electron microscopy, respectively. In particular, differences in the degree of nanorod ordering are presented for PMMA homopolymer films (d ~ 45 nm) versus PS-b-PMMA BCP films (L/2 ~ 40 nm), where higher ordering is seen in the case of BCP films. At moderate volume fractions of NRs, φ = 1% to 10%, the degree of ordering is moderate, and increases with increasing φ. However, coexistence between regions of higher ordering and isotropic orientations is observed. In addition to the planar confinement considered above, orientation of Au NRs confined to cylindrical P2VP domains is studied in PS-b-P2VP BCP films.

10:24AM P19.00013 Carbon nanotubes nucleate the growth of graphitic layer arrangements during carbonization of electrosynpoly(pyrrolonylitrile) nanofibers, SABINA PRILUTSKY, YACHIN COHEN, EYAL ZUSSMAN, Technion, Israel — Hybrid nanofibers with varying concentration of multiwalled carbon nanotubes (MWCNTs) in polyacrylonitrile (PAN) were fabricated using the electrospinning technique and subsequently carbonized. The morphology of the fabricated carbon nanofibers (CNFs) at different stages of the carbonization process was characterized by high-resolution transmission electron microscopy (HRTEM) and Raman spectroscopy. In-situ morphological changes during heating were followed by HRTEM using a heated stage. The polycrystalline nature of the CNFs was shown, with increasing content of ordered crystalline regions having enhanced orientation with increasing content of MWCNTs. The results indicate that MWCNTs embedded within the PAN nanofibers nucleate the growth of graphitic layers during PAN carbonization.

10:36AM P19.00014 Crystallization and melting behavior of isotactic polypropylene and carbon nanotube nanocomposites, GEORGI GEORGIIEV, Assumption College/Tufts University, YANIEL CABRERA, LAUREN WIELGUS, Tufts University, ZARNAB IFTIKHAR, MICHAEL MATTERA, PETER GATI, AUSTIN POTTER, Assumption College, JEFFREY CEBE, Tufts University, TUFTS/ASSUMPTION COLLABORATION — Polymer nanocomposites (PNCs) are the most recent development in the field of polymer science and technology. Geared toward creating novel polymer based materials, PNCs are the largest commercial application for nanotubes. Spherulitic polymer crystal growth was changed by introducing new fibrillar crystals on the surface of carbon nanotubes. Upon isothermal melt crystallization at 135°C, CNTs lead to monoclinic crystal growth perpendicularly to the long axis of the nanotubes, explained by the multiple nucleation centers formed at the interface of the carbon nanotube and the polymer chains. Using Microscopic Transmission Ellipsometry (MTE), the sign of the alpha crystallographic phase was determined as positive. Using Differential Scanning Calorimetry (DSC), a decrease in the Avrami exponent was measured with increase of concentration of nanotubes.

1Research supported by: the NASA, Polymers Program of the DMR, grant (DMR-0602473) and NASA grant (NAG8-1167).

10:48AM P19.00015 Crystallization kinetics in poly(ethylene oxide) / layered silicates nanocomposites, ELENI PAVLOPOULOU, SAPFO FOTIADOU, ELENI PAPANANOUI, KIRIAKI CHRISSOPOLOU, SPIROS H. ANASTASIADIS, Foundation for Research and Technology-Hellas and University of Crete, Heraklion Crete, Greece, GIUSEPPE PORTALE, WIM BRAS, ESRF-DUBBLE, Grenoble, France — We investigate the effect of inorganic clay on the crystalline characteristics and the crystallization kinetics of PEO in its intercalated nanocomposites with natural montmorillonite (Na+-MMT). The structure of the hybrids was investigated over multiple length scales by X-ray diffraction, small-angle X-ray scattering (SAXS) and polarizing optical microscopy (POM) as well as by DSC. The PEO within the galleries is completely amorphous whereas only the excess polymer outside the completely full galleries can crystallize at high PEO concentrations. The time resolved measurements reveal the effect of clay on crystallization. Even very small amount of the inorganic can cause a significant decrease of the spherulite size. The crystallization mechanism varies from sporadic nucleation for pure PEO to two-dimensional growth with predetermined nuclei at 10wt% clay with a higher activation barrier for low clay concentration. Sponsored by NATO’s Scientific Affairs Division, by the Greek GSRT and by the EU.

1Also at Aristotle Univ. of Thessaloniki, Thessaloniki, Greece.

Wednesday, March 18, 2009 8:00AM - 10:48AM – Session P20 DPOLY: Melts and Solutions 321
8:00AM P20.00001 Dynamics and rheology of high molar mass polyethylene oxide solutions. ABHISHEK SHETTY, MICHAEL SOLOMON, University of Michigan — We report dynamic light scattering (DLS), bulk rheology and turbulent drag reduction (TDR) measurements that investigate the structure and dynamics of high molar mass PEO solutions. Steady shear rheology of high molar mass PEO solutions, when modeled by the FENE-P constitutive equation, was consistent with viscoelastic relaxation times much larger than predicted by single polymer, dilute solution theory. DLS of dilute PEO solutions showed a single relaxation mode in the decay time distribution, which scales as $q^{-3}$ rather than the $q^{-2}$ scaling expected of diffusive dynamics. We interpret this result as consistent with the internal dynamics of large multichain domains, clusters or aggregates in the high molar mass PEO solutions. By means of DLS, we also show that the aggregation state of dilute solutions of high molar mass PEO can be manipulated by addition of the chaotropic salt guanidine sulfate or the divalent salt magnesium sulfate. Addition of these salts shifts the power law scaling of the relaxation time from $q^{-3}$ to $q^{-2}$. This shift of relaxation time scaling from one indicative of aggregate dynamics ($q^{-3}$) to one characteristic of polymer center-of-mass diffusion ($q^{-2}$) shows that these salts are effective de-aggregation agents for PEO. We discuss the results in light of the potential connection between aggregation behavior and polymer TDR of high molar mass PEO.

8:12AM P20.00002 Diffusive Properties of Dilute HPC Solutions: Comparative Study with DLS and FPR. RYAN MCDONOUGH, KIRIL STRELETZKY, Cleveland State University, PAUL RUSSO, Louisiana State University — The dynamics of HPC (Hydroxy-propyl-cellulose) solutions were studied by two fundamentally different methods: FPR (Fluorescence Photo-bleaching and Recovery) and DLS (Dynamic Light Scattering). FPR captures polymer processes by establishing a photo-bleached boundary and “seeing” only tagged particles diffusing back into bleached area, which yields a contrast function. DLS auto-correlates scattered light intensity from particles in order to determine a statistical decay function. Inverse Laplace transform (CONTIN) and stretch exponential line shape analysis (LSA) serve to quantitatively decompose decay data into different diffusion processes or modes. The first finding is that the CONTIN and LSA results on the same sample are fairly consistent. The second finding is that the modal distributions for FPR and DLS spectra on the same sample show consistent dissimilarities. This indicates a comparative limitation or sensitivity in range of detectable diffusive processes between FPR and DLS in a complex system. The third finding is that the fluorescent tag and tagging process seem to alter the diffusion processes seen by DLS in a way that is consistent; there is a slower mode apparent in non-tagged sample which does not appear in the tagged sample.

8:24AM P20.00003 Helix formation via kinetic assembly of charged block copolymer cylinders in solution. SHENG ZHONG, Department of Materials Science and Engineering and Delaware Biotechnology Institute, University of Delaware, KE ZHANG, KAREN WOOLEY, Center for Materials Innovation, Department of Chemistry and Department of Radiology, Washington University in Saint Louis, DARRIN POCHAN, Department of Materials Science and Engineering and Delaware Biotechnology Institute, University of Delaware — A multi-micrometer-long, cylinder with helical superstructure is created from coassembly of poly(acrylic acid)-block-poly(methyl acrylate)-block-polystyrene (PAA-b-PMA-b-PS) triblock copolymers with excess triethylentetramine or diethylenetriamine in the mixture of 67% volume ratio of water in tetrahydrofuran (THF). The stable pitch distance of the formed helices is due to the balance of long range electrostatic association and uniaxial tension along the cylinder, which can be efficiently tuned by varying the type and amount of the multivalent amine molecules. Double and triple helices are also formed with characteristic interhelical cylinder distances similar to what is observed as the pitch in single helices. A kinetic study shows that the formation of a helix undergoes a complex, but reproducible, nanostructure evolution, including a starting stacked structure, a transition state of very short helices with the length of tens of nanometers and a final multi-micrometer-long mature helix by connecting those short helices.

8:36AM P20.00004 Enhancing Polymer-Fullerene Miscibility Through Enthalpic Interactions. KATIE CAMPBELL, DAVID BUCKNALL, YONANTH THIO, HASKELL BECKHAM, UWE BUNZ, ADAM HÅNNÖN, ANDREW ZAPPAS, BILGE HATIBOGLU, Georgia Institute of Technology, MICHAEL KEMPF, Universität Karlsruhe — Using both theoretical and experimental methods, the use of functional groups in controlling the miscibility between various polymers and fullerenes has been investigated. Molecular dynamics simulations with unmodified C$_{60}$ and C$_{70}$ dimers indicated that the number and connectivity of phenyl rings as functional groups, polymer backbone spacing, and aromaticity are all factors in fullerene miscibility. To distinguish between entropic and enthalpic factors, UV-visible spectroscopy was used to determine fullerene solubility with a variety of solvents and to also determine association constants with solvents and polymers. A distinct time dependency for complex formation with many of the fullerene-organic materials investigated was observed as evidenced by a change in solution color with time. Stern-Volmer approximations and fluorescence quenching were used to examine the association of C$_{60}$ with a series of poly(phenylene ethynylene)s, cyclic polystyrene (PS), and linear PS. The fluorescence quenching of these materials by C$_{60}$ indicates an association between C$_{60}$ and the polymer. WAXS studies have shown the formation of C$_{60}$ aggregates in PS at concentrations of C$_{60}$ as low as 1 wt%.

8:48AM P20.00005 Modeling Thermodynamic Behavior of Nonionic Surfactants in Water. VALERY GINZBURG, PIERRE VARINEAU, Dow Chemical Company — Aqueous solutions of nonionic surfactants exhibit a non-trivial phase behavior known as lower critical solution temperature (UCST), where solutions are homogeneous at lower temperatures but become cloudy (two-phase) at higher temperatures. Conventional Flory-Huggins theory of polymer solutions fails to describe such phase behavior. We utilize the approach suggested by Dormidontova and modify Flory-Huggins theory by explicitly accounting for water-water and water-alkylene oxide hydrogen bonding. While the Dormidontova model was restricted to aqueous solutions of polyelectrolyte oxide (PEO), we extend it to include other monomers and their copolymers. With the new approach, we can semi-quantitatively predict cloud points of various nonionic surfactants (TergitolTM L and EcosurfTM series) as functions of their molecular structures. We also discuss extensions of this model to calculate micellar phase behavior and oil/water/surfactant interfacial tensions. TM Trademark of The Dow Chemical Company


9:00AM P20.00006 Role of surfactants on the assembly of amphiphilic copolymers through instabilities of organic/water interfaces. JINTAO ZHU, RYAN C. HAYWARD, Department of Polymer Science & Engineering, University of Massachusetts Amherst — We have studied the influence of aqueous surfactants on the assembly of amphiphilic copolymers through hydrodynamic instabilities of organic/water interfaces. Micropipette aspiration measurements on evaporating chloroform droplets containing polystyrene-poly(ethylene oxide) (PS-PEO) diblock copolymers revealed that the onset of interfacial instability and subsequent growth in surface area corresponded to a near vanishing of the interfacial tension. By adding another surfactant, such as sodium dodecyl sulfate (SDS), to the aqueous phase, the chloroform/water interfacial tension was reduced and the onset of instability shifted to lower concentration of PS-PEO. Varying amounts of SDS also led to qualitatively different mechanisms of growth in interfacial area and correspondingly different morphologies of the resulting copolymer assemblies.
9:12AM P20.00007 Influence of Intermolecular Interactions on Fragility of Polymers, KUMAR KUNAL, ALEXEI SOKOLOV, The University of Akron — Glass transition in polymers is a result of slowing down of segmental relaxation. Steepness of the temperature-dependence of segmental relaxation times close to the glass transition temperature, Tg, is expressed in terms of fragility parameter. A strongly non-Arrhenius temperature dependence of segmental relaxation times with steep variations close to Tg is called a ‘fragile’ behavior, and a nearly Arrhenius behavior is called ‘strong’. The existing theoretical models and experimental investigations on polymers with weak van der Waal’s interactions suggest that fragile behavior of polymers may be linked to their poor packing ability. However, the effect of strong intermolecular interactions on fragility such as polar interactions and hydrogen bonds remains unexplored. It has been predicted that polymers composed of polar monomers are likely to be highly fragile. We have studied polymers with strongly polar interactions and hydrogen bonds and found that although polar polymers do seem to have a higher Tg than their non-polar counterparts, no such conclusion can be drawn about their fragility. The different effects of polar interactions on different classes of polymers may be similar to the difference in their Tgs.

9:24AM P20.00008 Random Walk of Chain Molecules Along Pore Axis, GUIDUK YU, School of Chem. and Bio. Eng., Seoul National University, SERGEI OBUKHOV, Dpt. of Physics, University of Florida, JIUN-TAI CHEN, Dpt. of Polym. Sci. and Eng., University of Massachusetts Amherst, JUNE HUH, School of Mater. Sci. and Eng., South National University, YOO-NATAE HWANG, SOONCHUN HOK, School of Chem. and Bio. Eng., Seoul National University, PRIYANKA DOBRIYAL, Dpt. of Polym. Sci. and Eng., University of Massachusetts Amherst, PAPPANAN THIYAGARAJAN, Intense Pulsed Neutron Source Division, Argonne National Laboratory, THOMAS P. RUSSELL*, Dpt. of Polym. Sci. and Eng., University of Massachusetts Amherst, KYUSOON SHIN*, School of Chem. and Bio. Eng., Seoul National University — We investigated the overall conformation of polymer chain in cylindrical nanopores using small-angle neutron scattering. The mixture of hydrogenous PS and deuterated PS is confined in nanopores. Surprisingly, the overall conformation of polymer chains along the pore axis is observed to be the same as that in bulk. Even though the chain dimension is larger than the radius of the pores, the chains along the pore axis are not stretched, but remain to be in unperturbed state. The SANS results implicate that the interpenetration of polymer chains decreases as polymer enters nanopores. We expect the reduction of intermolecular entanglement possibly alters other physical properties of polymer under nanoconfinement.

9:36AM P20.00009 Dynamics of Cyclic Molecules Threaded into a Linear Polymer Chain, KOICHI MAYUMI, HITOSHI ENDO, The University of Tokyo, MICHICHIRO NAGAO, Indiana University and National Institute of Standards and Technology, NOBORU OSAKA, HIDEAKI YOKOKAMA, MITSUHIRO SHIBAYAMA, KOHZU IT0, The University of Tokyo — Dynamics of polyrotaxane (PR), in which cyclic molecules, cyclodextrins (CDs), are threaded on an axis linear polymer chain, poly(ethylene glycol) (PEG), are first studied by contrast variation neutron spin echo (CV-NSE). By comparing PRs of hydrogenated and deuterated PEG with different scattering contrasts, we successfully extract two diffusive modes of CDs, corresponding to self-diffusion and relative motion to the axis PEG in PR. The self-diffusion constant of CD in PR is determined to be about one-third of the free one in the absence of the axis polymer, which would reflect the space dimension of diffusion with the topological restriction on the axis chain path.

9:48AM P20.00010 Diffusion of Water through Methyl- and Hydroxy-Terminated Poly(dimethylsiloxane)1, AHMED E. ISMAIL, GARY S. GREST, DAVID R. HEINE2, MARK J. STEVENS, Sandia National Laboratories, MESFIN TSIGE, Southern Illinois University — Both experimental and numerical reports of the diffusion constant of water through poly(dimethylsiloxane) (PDMS) show variances of nearly an order of magnitude. We use molecular dynamics simulations to calculate the diffusion constant for both methyl- and hydroxyl-terminated PDMS chains. We examine the effects of both concentration and chain length. For a single water molecule, we find that diffusion depends strongly on the structure of the molecule, as the ‘caging’ phenomenon reported by Miller-Plathe can occur. At intermediate concentrations, we observe the formation of dimer and trimer water clusters, leading to lower diffusion rates; at concentrations above the reported aggregation limit of 0.1 wt %, we observe the onset of phase segregation.

1Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract No. DE-AC04-94AL85000.
2Present address: Corning

10:00AM P20.00011 Effect of Stereochemistry and Polydispersity on Diffusion in Polypropylene1, ERNST VON MEERWALL, NUMAN WAHEED, WAYNE MATTICE, Univ. Akron — We have performed dynamic Monte-Carlo (MC) simulations and pulsed-gradient diffusion (D) experiments to study the effect of stereochemical composition in linear polypropylene (PP) melts. The coarse-grained simulations were based on the rotational isomeric state model and Lennard-Jones potentials. For the non-MR diffusion measurements we obtained three PP specimens of differing molecular weight M and dispersity, with the probability of a meso diad Pm = 0.02 (syndiotactic), 0.23 (atactic), and 0.89 (nearly isotactic). The experiment supplied the fixed conversion between MC steps and real time; no dependence on Pm is expected. Both simulation and M-scaled experiment found D at high Pm several times faster than at low Pm. The constant-M simulation also showed a maximum near Pm = 0.8 due to quenched randomness. To find the source of the remaining disagreement with experiment, new simulations tracked the samples’ Pm, mean M, and polydispersity, producing modest improvement. We suspect that the GPC determination of M and its distribution, based on linear polyethylene calibration, is somewhat dependent on PP stereochemistry (via D), generating misleading results.

1Supported in part by NSF (DMR 04-55117)

10:12AM P20.00012 On chain statistics and entanglement of flexible linear polymer melts, SHI-QING WANG, University of Akron — In this work the chain statistics of most linear flexible polymers have been found to be rather universal, allowing chain entanglement to be depicted with few parameters. We first show, to our surprise, based on the literature data of most familiar linear polymers that (a) at the same number of backbone bonds most linear polymers have comparable coil size and are similarly flexible in spite of widely varying chain thickness and (b) the Kuhn length involves a similar number of backbone bonds. The packing model is found to describe the onset molecular weight Me obtained from the elastic plateau modulus whereas all other models in the literature fail to provide good correlation. It is chain thickness not stiffness that correlates with Me for over one hundred flexible linear polymers. On the other hand, other models such as percolation model appear to provide some crude correlation for M_c, to which the packing model does not apply well, where M_c denotes the point of departure in the molecular weight scaling from Rouse like to reptation like. Thus, our analysis clarified the apparent contradiction among the various models.

10:24AM P20.00013 Translational Diffusion in a Confined Polymer Melt, JANET WONG, Department of Mechanical Engineering, Imperial College London, LIANG HONG, Dow Chemical Company, SONG CHUL BAE, STEVE GRANICK, Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign — At the University of Illinois, a new experimental platform has been developed that combines the surface forces apparatus with spatially-resolved fluorescence recovery after photobleaching, giving direct measurements of translational diffusion when polymer melts are confined between mica sheets to controlled thicknesses comparable to the size of the molecules themselves. Applying this platform to poly(dimethylsiloxane) (PDMS), we find not only the anticipated dependence on film thickness but also a dependence on the local pressure; when mica sheets are pressed together so that they flatten, the diffusion of chains confined between them depends on the local pressure, being slowest near the center of the contact. The confined chains split into two populations: those that are immobile on the scale of hours, and those whose mobility is close to that of the unperturbed polymer melt.
10:36AM P20.00014 Entangled Polymer Melt Dynamics Studied By Low-Field NMR , FABIAN VACA CHAVEZ, PATRICK HUEBSCH, RONALD ZIRBS, WOLFGANG BINDER, KAY SAALWAECHTER, Martin-Luther-University Halle-Wittenberg — Proton Multiple-Quantum (MQ) NMR is a powerful technique to investigate polymer dynamics due to its sensitivity to molecular motions on very different timescales. Entangled melts exhibit dynamic processes that cover a wide range of timescales, starting from fast ps-scale segmental reorientation up to diffusive and cooperative motions on the ms-scale. In this work, we apply MQ NMR to linear poly(cis-1,4-isoprene) and poly(isobutylene) of different molecular weight above the glass transition over suitable ranges of temperature, in order to investigate the dynamic regimes predicted by the tube model, and, for the first time, to extract actual time scale information. This directly complements many neutron scattering studies, which are restricted to the sub-μs-timescale. Measurements on PIB-grafted silica particles with different molecular weights and different chain densities on the surface of the particle are also shown. The data is analyzed by establishing scaling laws which can be directly associated with different dynamic regimes predicted by the tube/reptation model. Full analytical analyses based on a correlation function which explicitly includes segmental, Rouse, and reptation dynamics are discussed.

Wednesday, March 18, 2009 11:15AM - 2:15PM —
Session Q4 DPOLY GSNP: Polymer Surface Instabilities 306/307

11:15AM Q4.00001 Elastic instabilities in rubber , ALAN GENT, University of Akron — Materials that undergo large elastic deformations can exhibit novel instabilities. Several examples are described: development of an aneurysm on inflating a rubber tube; non-uniform stretching on inflating a spherical balloon; formation of internal cracks in rubber blocks at a critical level of triaxial tension or when supersaturated with a dissolved gas; surface wrinkling of a block at a critical amount of compression; debonding or fracture of constrained films on swelling, and formation of “knots” on twisting stretched cylindrical rods. These various deformations are analyzed in terms of a simple strain energy function, using Rivlin’s theory of large elastic deformations, and the results are compared with experimental measurements of the onset of unstable states. Such comparisons provide new tests of Rivlin’s theory and, at least in principle, critical tests of proposed strain energy functions for rubber. Moreover the onset of highly non-uniform deformations has serious implications for the fatigue life and fracture resistance of rubber components.

References:

11:51AM Q4.00002 Creasing instability of solvent-swelled polymer films , RYAN HAYWARD, University of Massachusetts, Amherst — A thin layer of polymer bound to a rigid substrate develops compressive stresses when it is swelled by solvent, due to the constraint against lateral expansion imposed by the substrate. For sufficiently large stresses, the surface becomes unstable to a buckling mode in which tightly-folded “creases” form on the surface to relieve compressive stress. While this instability has been known in practice for more than a century, it remains poorly characterized and incompletely understood. I will describe experiments on model systems of surface-attached hydrogels to characterize the onset and growth mechanisms of creases, as well as methods that allow control of crease formation in both space and time. In addition to the implications that this instability has for any type of polymeric coating undergoing swelling, it also provides an opportunity to create surfaces with switchable topography and chemistry.

12:27PM Q4.00003 The macroscopic delamination of thin films from elastic substrates , PEDRO REIS, Massachusetts Institute of Technology — The wrinkling and delamination of stiff thin films adhered to a polymeric substrate have important applications in “flexible electronics.” The resulting periodic structures, when used for circuitry, have remarkable mechanical properties since stretching or twisting of the substrate is mostly accommodated through bending of the film, which minimizes fatigue or fracture. To date, applications in this context have used patterning of the substrate-film adhesion energy to produce a controlled array of delamination “blisters.” However, even in the absence of such patterning, blisters have a characteristic size. We use macroscopic experiments to study what sets the dimensions of these blisters in terms of the material properties, which we explain using a combination of scaling and analytical methods. This points to a novel method for determining the interfacial toughness. Finally, we suggest a number of design guidelines for the thin films used in flexible electronic applications.

1:03PM Q4.00004 Elastic Instability and Pattern Formation in Confined Soft Elastomeric Films , ANIMANGSU GHATAK, Department of Chemical Engineering, IIT Kanpur — When a rigid flat object or a flexible plate is removed from a thin soft film, instability patterns appear at the interface in the form of bubbles or fingers. The wavelengths of these instabilities are independent of all material and geometrical properties of the system except the thickness of the film. These observations contrast the classical Saffman-Taylor type instability in which the instability pattern depends on the viscous and surface tension forces in addition to the thickness of the liquid film. In the case of elastic instability of the kind described here, the wavelength depends on the material properties of the films only when soft films of different elastic properties are separated from each other. In the later case, a co-operative instability mode develops, which is a non-linear function of the thicknesses and the elastic moduli of both the films. In contrast to the wavelengths of these instabilities, their amplitudes are strong functions of several material and geometric properties of the system. These problems can be analyzed using regular perturbation technique to obtain the excess deformations of the film over and above the base quantities. Furthermore, by estimating the excess energy of the system, it can be shown that instability develops when the films are critically confined. This point can be illustrated by pre-stretching the film or simply by adjusting the contact width between the film and the plate. The instabilities that develop at the interface are critical to understanding adhesion and friction of soft thin films as they act like nucleated interfacial cracks. We performed a simple experiment, in which a flat rigid glass prism is sheared off a soft elastomeric film. At a given tangential force, the prism starts to slide on the elastomeric film accompanied with the formation of “bubbles” on the interface due to elastic instability. These bubbles, the lateral dimensions of which are comparable to the thickness of the film, move across the interface with speeds 1000 times faster than the overall sliding speed of the prism. The process continues till the critical condition for fracture is reached. These studies may shed some light on the fast dynamics of shear crack propagation in other systems.

1:39PM Q4.00005 Micro-Origami: Elastic Instability of Polymer Films , PASCAL DAMMAN, Université de Mons-Hainaut — Upon compression, thin (rigid) elastic membranes supported on a soft elastic solid spontaneously deviate from their flat geometry by forming regular wrinkles. How can we control the wavelength and the symmetry of the wrinkle patterns? What is the influence of defects? Why should we observe focalisation of deformation in folds for large strains? During my talk, I will review our approaches to tackle these questions.

Wednesday, March 18, 2009 11:15AM - 2:15PM —
Session Q17 DPOLY: Superconducting Qubits: Coherence and New Implementations 318
A huge cooling effect, which could be used to cool a mechanical oscillator below the energy of quantum fluctuations, has been predicted by several authors.

Numerical Monte Carlo simulations with experiment.

The superconducting qubit, which must be overcome if their promise of a scalable, reliable mesoscopic qubit is to be achieved. Recent experiments at millikelvin temperatures (S. Girvin, M. Devoret, Yale University) have demonstrated quantum coherence in a Josephson junction array circuit.

A resonator with eigenfrequency \( \omega \) can be effectively used as a cooler for another linear oscillator with a much smaller frequency \( \omega_m \ll \omega \). A huge cooling effect, which could be used to cool a mechanical oscillator below the energy of quantum fluctuations, has been predicted by several authors. However, here we show that there is a lower limit \( T^* \) on the achievable temperature, given by \( T^* = T_m \omega_m / \omega_r \), that was not considered in previous work and can be higher than the quantum limit in realistic experimental realizations. We also point out that the decay rate of the resonator, which previous studies stress should be small, must be larger than the decay rate of the cooled oscillator for effective cooling. M. Grajcar, S. Ashhab, J.R. Johansson, F. Nori. Lower limit on the achievable temperature in resonator-based sideband cooling, Phys. Rev. B 78, 035406 (2008). URL: http://link.aps.org/abstract/PRB/v78/e035406

Recent experiments at millikelvin temperatures (S. Girvin, M. Devoret, Yale University) have demonstrated quantum coherence in a Josephson junction array circuit.

We have developed and operated a new type of phase preserving parametric amplifier, the Josephson Parametric Converter, which approaches the quantum limit. Our device consists of two microwave resonators coupled to each other through a Josephson Ring Modulator. This latter element, flux-processed for superconducting qubits, has four junctions, and four active current modes instead of two. A pump line is non-resonantly coupled to one of the modes of the ring while the signal and idler are serviced by two others and are tuned in the band of the resonators. The fourth mode, which is the dc superconducting circulating current in the ring, is biased with half a flux quantum. Our design ensures that the non-linearity presented by the Ring Modulator is pure and involves the minimal number of modes, thus placing the JPC very close to the ideal non-degenerate parametric amplifier. This is supported by recent results on the amplification and frequency conversion operations. Furthermore, measurements of the noise temperature with an auto-calibrated source based on a nanowire in the hot electron regime will be presented. In combination with correlation measurements of the noise at the signal and idler ports, these results show that the JPC can perform two-mode squeezing of quantum noise.

This work was supported by the Disruptive Technology Office under grant W911NF-04-1-0204, and by DOE grant DE-FG02-04ER46107.
12:39PM Q17.00008 Josephson junction array protected from local noises.  . SERGEY GLADCHENKO, DAVID OLAYA, EVA DUPONT-FERRIER, Rutgers University, BENOIT DOUCOT, Universités Paris 6 et 7, Paris, France, LEV IOFFE, MICHAEL GERSHENSON, Rutgers University — We have developed small arrays of Josephson junctions (JJs) that can be viewed as prototypes of superconducting qubits protected from local noises [1]. The array consists of twelve superconducting loops interrupted by four sub-micron JJs. The protected state is realized when each loop is threaded by half of the magnetic flux quantum. It has been observed that the array with the optimized amplitude of quantum fluctuations is protected against magnetic flux variations well beyond linear order, in agreement with theoretical predictions [2]. 1. S. Gladchenko et al., “Superconducting Nanocircuits for Topologically Protected Qubits”, arXiv:cond-mat/0802.2295, to be published in Nature Physics. 2. L.B. Ioffe and M.V. Feigelman, Phys. Rev. B 76, 224503 (2002); B. Doucot et al., Phys. Rev. B 71, 024505 (2005); B. Doucot and L.B. Ioffe, Phys. Rev. B 76, 214507 (2007).

12:51PM Q17.00009 Optimization and characterization of protected Josephson circuits . EVA DUPONT-FERRIER, SERGEY GLADCHENKO, LEV IOFFE, MICHAEL GERSHENSON, Rutgers University — Recently, it was proposed that small Josephson arrays can operate as superconducting qubits protected from local noises [1,2]. Here we present measurements of several optimized array designs. The read-out circuit for these arrays consists of an inductively-coupled DC SQUID, which helps to minimize perturbations of the system during measurement. We will discuss the current-phase characteristics of these arrays and their response to microwave radiation. Our results indicate that the scattering of Josephson junction parameters can be made small enough to implement the symmetry-protected superconducting qubits; our theoretical model [1] captures all essential features of real devices. 1. see e.g., B. Doucot and L.B. Ioffe, Phys. Rev. B 76, 214507 (2007) and references therein. 2. S. Gladchenko, D. Olaya, E. Dupont-Ferrier, B. Doucot, L.B. Ioffe, and M.E. Gershenson, “Superconducting Nanocircuits for Topologically Protected Qubits”, arXiv:cond-mat/0802.2295, to be published in Nature Physics.

1:03PM Q17.00010 Controllable scattering of photons in a one-dimensional resonator waveguide1. C.P. SUN, L. ZHOU, Z.R. GONG, RIKEN, Japan, and CAS, China, Y.X. LIU, RIKEN, Japan, F. NORI, RIKEN, Japan, and University of Michigan, Ann Arbor, USA — We analyze the coherent transport of a single photon, which propagates in a one-dimensional coupled-resonator waveguide and is scattered by a controllable two-level system located inside one of the resonators of this waveguide. Our approach, which uses discrete coordinates, unifies low and high energy effective theories for single-photon scattering. We show that the controllable two-level system can behave as a quantum switch for the coherent transport of a single photon. This study may inspire new electro-optical single-photon quantum devices. We also suggest an experimental setup based on superconducting transmission line resonators and qubits.


1Supported in part by LPS, NSA, ARO, NSF, NSFC, CREST, & RIKEN.

1:15PM Q17.00011 Quantum two-level systems in Josephson junctions as naturally formed qubits , ALEXANDER ZAGOSKIN, Loughborough University, SAHEL ASHHAB, ROBERT JOHANSSON, FRANCO NORI — The two-level systems (TLSs) naturally occurring in Josephson junctions constitute a major obstacle for the operation of superconducting phase qubits. Since these TLSs can possess remarkably long decoherence times, we show that such TLSs can themselves be used as qubits, allowing for a well controlled initialization, universal sets of quantum gates, and readout. Thus, a single current-biased Josephson junction (CBJJ) can be considered as a multiqubit register. It can be coupled to other CBJJs to allow the application of quantum gates to an arbitrary pair of qubits in the system. We also show that using the dynamics of a driven qubit, it could be possible to characterize the nature of the two-level systems and their coupling to the phase qubit.

1:27PM Q17.00012 Topological states and braiding statistics using quantum circuits . XIAO-FENG SHI, Fudan University, JIANQIANG YOU, Fudan University & RIKEN, FRANCO NORI, University of Michigan & RIKEN — Using superconducting quantum circuits, we propose an approach to construct a Kitaev lattice, i.e., an anisotropic spin model on a honeycomb lattice with three types of nearest-neighbor interactions. We study two particular cases to demonstrate topological states (i.e., the vortex and bond states) and show how the braiding statistics can be revealed. Our approach provides an experimentally realizable many-body system for demonstrating exotic properties of topological phases.

1:39PM Q17.00013 Topological Transition in a Non-Hermitian Quantum Walk: a new test for quantumness in driven artificial atoms and Josephson arrays , MARK RUDNER, Harvard University, LEONID LEVITOV, Massachusetts Institute of Technology — We analyze a quantum walk on a bipartite one-dimensional lattice, in which the particle can decay whenever it visits one of the two sublattices. The corresponding non-Hermitian tight-binding problem with complex potential for the decaying sites exhibits two distinct phases, distinguished by a winding number defined in terms of the Bloch eigenstates in the Brillouin zone [1]. We find that the mean displacement of a particle initially localized on one of the non-decaying sites is quantized as an integer, changing from zero to one at the critical point. By mapping this problem onto a Jaynes-Cummings-type model with decay, we find that the topological transition is relevant for a variety of experimental settings, in particular for superconducting qubits coupled to high quality resonators [2]. The quantized behavior stands in contrast with the smooth dependence expected for a classical random walk, and can serve as a hallmark of coherent quantum dynamics in ladder-like multilevel systems. A real-space implementation of the quantum walk may help to verify quantum coherence in vortex transport in Josephson arrays [3]. [1] M. S. Rudner, L. S. Levitov, arXiv:0807.2048. [2] A. Wallraff et al., Nature 431, 162-167 (2004). [3] A. van Oudenaren, S. J. K. Vardy, and J. E. Mooij, Phys. Rev. Lett. 77, 4257 (1996).

1:51PM Q17.00014 Two Types of Loss Expected for Josephson Qubit Circuits . ARTHUR DAVIDSON, ECE Department, Carnegie Mellon University, Pittsburgh, PA 15213 — The energy of a coulomb blockade capacitor, or of a current biased Josephson junction, is known to depend on the difference between a continuous charge term and a discrete one. For example the energy in the coulomb blockade is the square of (ne-k), where n is an integer, e is the electron charge, and k is a continuous charge value. This suggests that there may be two types of quantum losses in the Schroedinger dynamics of these systems. One type would reduce k to ne to arrive at the ground state energy and would be the quantum analog of external classical resistance. The other type of loss would couple energy bands at constant k, minimizing n, and corresponding to tunnel losses. Historically, two quantum loss terms have been proposed: one due to Martin Kostin in 1972; and another from the present author in 1990. The Kostin type of loss affects the continuous charge term, while the Davidson type affects the discrete charge term. These properties are linked to the boundary conditions of these systems. The loss mechanisms are likely to be important for understanding coherence times in Josephson qubit circuits.
Elastomer designs were evaluated using self-consistent mean field theory. The phase diagram of a radial (A(O’DONOGHUE, Department of Chemical Engineering and the Materials Research Laboratory, University of California, Santa Barbara, DALE HANDLIN, GLENN model systems.

Although such interactions are necessary for obtaining realistic dynamics, they significantly slow down the chain relaxation towards equilibrium configurations. Furthermore, using the standard functional employed in field-theoretic models. The main features of the proposed formalism reside in its ability to enable simulations at constant stress or constant pressure, thereby permitting accurate estimation of free energies and phase boundaries.

Similar deflections in phase boundaries towards higher $f_A$ resulted.

In addition, for branched polymers the branch point mobilities are determined by the free energy, so that its position is allowed to fluctuate, and even slide through the slip-links. The resulting model exhibits primitive-path fluctuations and chain stretching, so could be applied to flow and generalized to more complicated branches or cross-linked networks without significant modifications.

11:39AM Q18.00003 Self-assembly of rod coil block copolymers under confinement. MANAS SHAH1, VENKAT GANESAN2. The University of Texas at Austin — The interplay of microphase separation and liquid crystalline ordering in rod-coil block copolymers leads to formation of complex morphologies distinct from that of conventional flexible block copolymer phases. In order to be used for organic electronic applications such as photovoltaic cells, rod-coil block copolymers must be patterned into thin films. The final morphology and the nature of orientation of rod units would now depend (in addition to the constituent interactions) on the interactions of the blocks with the confining surfaces. We combine the self-consistent field theory models of rod-coil block copolymers in a thin film framework to understand the effect of confinement on the morphology and the nature of orientation of rod units. Also, for nearly symmetric rod-coil copolymers, we analyze the parallel – perpendicular lamellae transitions using a free energy framework. Also, we consider morphologies of such block copolymers (and blends) which can be utilized for higher device efficiency in photovoltaic cells.

12:03PM Q18.00005 Fields Help Particles – Fast Off-Lattice Monte Carlo Simulations of Soft Materials. YUHUA YIN, QIANG WANG, Colorado State University — Conventional molecular simulations of multi-chain systems are hindered by “hard” excluded-volume interactions (e.g., the Lennard-Jones potential in off-lattice simulations and the self- and mutual-avoiding walks in lattice simulations). Although such interactions are necessary for obtaining realistic dynamics, they significantly slow down the chain relaxation towards equilibrium configurations and efficient sampling of the configurational space. The idea of fast off-lattice Monte Carlo (FOMC) simulations is to perform particle-based Monte Carlo simulations in continuum with a Hamiltonian commonly used in polymer field theories, where individual polymer segments are modeled as “soft” particles whose interaction energy is finite when they overlap. This leads to much faster chain relaxation and better sampling of the configurational space. Furthermore, using the same Hamiltonian in both polymer field theories and FOMC simulations enables quantitative comparisons between them without any parameter-fitting to unambiguously reveal the effects of fluctuations and correlations in the system. Here we demonstrate these great advantages of FOMC simulations using several model systems.
12:15PM Q18.00006 Particles vs. Fields – Finite-Range Interactions in Polymer Field Theories, QIANG WANG, Colorado State University — Recently, we proposed a particle-based, fast off-lattice Monte Carlo (FOMC) simulation that uses the same Hamiltonian as in polymer field theories, which has great advantages over conventional molecular simulations. However, the continuous Gaussian chain model and $\delta$-function interactions widely used in polymer field theories (such as the self-consistent field theory) cannot be directly used in FOMC simulations. We therefore extend the field theories to the discrete Gaussian chain model and finite-range interactions. Taking the microphase separation of diblock copolymers as an example, a finite interaction range increases the order-disorder transition from the well-known result of $N \approx 10.5$, as well as the bulk lamellar period. More importantly, this work allows direct comparisons between the polymer field theories and FOMC simulations without any parameter-fitting to unambiguously and quantitatively reveal the effects of fluctuations and correlations in the system.

12:27PM Q18.00007 Mean Field Theory for Ionomer Melts, ERICA SALZTMAN, SANAT KUMAR, Columbia University — Single Chain Mean Field theory is applied to melts of charged polymers. Control parameters include temperature, chain length, and monomer density. Equilibrium variations of polymer conformational, translational, and rotational degrees of freedom and counterion translational degrees of freedom are studied; in particular we are interested in conformational and morphological transitions which occur in ionomers with changes in temperature and apparently dominate their macroscopic behavior. The equilibrium theoretical results, which are compared to simulation findings of low temperature condensation of chains and counterions to form ordered sheets of charges, form the basis for stochastic theories which model the temporal evolution of these structures, with immediate relevance to measurable dynamic properties.

12:39PM Q18.00008 Equilibrium and Beyond Equilibrium Properties of Polyelectrolytes - Ewald-Like Approach for Fluctuating Hydrodynamic and Electrostatic Interactions, JUAN P. HERNANDEZ-ORTIZ, Department of Materials, Universidad Nacional de Colombia, Sede Medellin, MICHAEL D. GRAHAM, JUAN J. DE PABLO, Department of Chemical and Biological Engineering, University of Wisconsin-Madison — A method is proposed for self consistent simulations of the equilibrium and beyond equilibrium structures and transport properties of polyelectrolytes in solution. The method incorporates solution of the Nernst-Planck diffusion equation for ions and counter-ions within the solvent, and simultaneous description of fluctuating hydrodynamic interactions by means of a Green's function formalism. The proposed approach generalizes our $O(N)$ general geometry Ewald-like method to simultaneous treatment of hydrodynamics and electrostatics. With this method, we examine the transport properties of polyelectrolytes solutions at rest and in various flow fields, and we make direct comparisons to results from explicit ion Brownian dynamics simulations and experimental observations.

12:51PM Q18.00009 Self Consistent Field Theory Study of the Effect of Grafting Density on the Height of a Weak Polyelectrolyte Brush, KEVIN WITTE, YOU-YEON WON, Purdue University — The height of weakly basic polyelectrolyte brushes in the osmotic brush regime is studied as a function of the grafting density using a numerical self-consistent field (SCF) theory derived from the (semi-) grand canonical partition function. The theory is shown to properly account for the local nature of the charge equilibrium and to be able to capture the basic behaviors of polyelectrolyte brushes, including brush height variation with salt concentration and scaling with respect to degree of polymerization. However, we find, in agreement with recent experiments, that the scaling of brush height with grafting density is qualitatively different than that predicted by basic scaling arguments. This difference is attributed to the relative strength of electrostatic type interactions compared to finite segment size packing constraints.

1:03PM Q18.00010 Adsorption and depletion of polyelectrolytes in charged1, DADONG YAN, XINGKUN MAN, State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, AN-CHANG SHI, Department of Physics and Astronomy, McMaster University, NSFC COLLABORATION — Self-consistent field theory is presented to study the adsorption of flexible polyelectrolyte (PE) onto uniformly oppositely charged cylinders. We focus on the curvature effect of adsorbing surface on the adsorption-depletion phase- transition-like behavior. In terms of the scaling expression of the critical quantities, i.e., the salt concentration, the charge fraction of PE chain and the area density of surface charge, at the adsorption-depletion transition point have been obtained. Moreover, we find a critical line for the dependence of the critical radius of cylinder on the salt concentration, which separates the adsorption and depletion states. The theoretical results are in good agreement with the Monte Carlo simulations and the experimental results.

1:15PM Q18.00011 Field-Based Modeling and Simulation of Interfacial Fluctuations in Block Copolymers, AUGUST BOSSIE, Polymers Division, NIST — The Edwards-model-based, field-theoretic simulation framework of Fredrickson is the cutting edge methodology in coarse-grained, field-based simulation of fluctuating copolymer systems [V. Ganesan and G.H. Fredrickson, Europhys. Lett. 55, 814 (2001); G.H. Fredrickson, V. Ganesan, and F. Drolet, Macromolecules 35, 16 (2001)]. Coarse graining the standard Edwards model yields the classic phenomenological “phase field” model of Ohta and Kawasaki [T. Ohta and K. Kawasaki, Macromolecules 19, 2621 (1986)]. Further coarse graining, coupled with the assumption of weak segregation, yields the ubiquitous Leibler-Brazovskii-Fredrickson-Helfand model [G.H. Fredrickson and E. Helfand, J. Chem. Phys. 87, 697 (1987)]. Each of these field-based models is capable of capturing thermodynamic fluctuations; however, the applicability of each model depends on the quench depth, the molecular weight, and the composition of the constituent copolymers, among other variables. Here we examine fluctuation effects in, and limitations of field-based models in the context of measuring interfacial fluctuations in a two dimensional diblock copolymer melt.

1:27PM Q18.00012 Variational Coarse-Graining of Discretized Field Theories of Fluids, MICHAEL VILLET, GLENN FREDRICKSON, University of California, Santa Barbara — Statistical field theory models have proven to be valuable tools for studying the equilibrium behavior of polymeric fluids, but direct simulation of these field theories without use of the mean field approximation is computationally demanding. Computational resources can be extended to simulate larger systems by discretizing the field variables with a coarsely spaced lattice, but indelicate coarse graining risks truncation of important short-wavelength physics. We introduce a variational method for systematically coarse-graining discretized field theoretic models of fluids while minimizing this truncation error.

1:39PM Q18.00013 Simulation of Fluctuations in Diblock Copolymer Melts: Testing an Alternative to the Fredrickson-Helfand Theory, JIAN QIN, CEMS at University of Minnesota, DAVID MORSE, CEMS at University of Minnesota — Simulations of a bead-spring model of disordered diblock copolymer melts have been conducted to test a renormalized one-loop (ROL) theory of composition fluctuations recently proposed by the authors. The simulations use hybrid Monte Carlo (MC) / Molecular Dynamics (MD), reptonation and double-rebriding moves, combined with replica exchange, to relax chain conformations. The quantitative comparison of simulation results with theory relies on a procedure that uses perturbation theory to independently identify the self-consistent-field (or RPA) interaction parameter. For the modest chain lengths accessible to simulations ($N \leq 64$, here), results for the maximum $S(q^*)$ of the structure factor are quite different from both RPA and Fredrickson-Helfand predictions, but agree very well with renormalized one-loop predictions.
then linked with dialkyne bridge molecules using Sharpless “click” reactions.

GORDON, Dept. of Physics, Stanford University, CHRIS CHIDSEY, Dept. of Chemistry, Stanford University — Robust, repeatable metal-molecule contacts.

Wednesday, March 18, 2009 11:15AM - 2:15PM
Session Q19 DPOLY: The Physics of Polymer Nanocomposites: Rheology and Mechanical Properties 320

11:15AM Q19.00001 Influence of Nanoparticles on the Amplitude of Molecular Motions and the Fragility a Model Glass-Forming Polymer Melt. J. SEDAT GUNES, GUILLERMO JIMENEZ, SADHAN JANA, The University of Akron — We investigate the impact of the addition of nanoparticles on both the fast and slow dynamics of a coarse-grained polymer fluid by molecular dynamics. The fast dynamics is characterized by the Debye-Waller factor (the average mean square particle displacement at a characteristic time in the caged particle motion regime) and the slow structural relaxation is characterized by the coherent intermediate scattering function. Our study explores how both the polymer-particle and nanoparticle volume fraction change the amplitude of the high frequency molecular motions (relative to the pure melt reference condition) and the strength of the temperature dependence of the structural relaxation time (defining the fragility of glass formation, as well as the glass transition temperature). Substantial variations of the Debye-Waller factor are observed and we test the effectiveness of the Buchenau relation linking the Debye-Waller factor to the long time structural relaxation time. We also consider how the presence of nanoparticles in the polymer melt influence the fragility of glass formation, where a range of criteria are utilized to define fragility. Appreciable changes of fragility are observed, these changes being dependent on the nanoparticle concentration and particle-polymer interaction.

11:27AM Q19.00002 Macroscopic dynamics of polystyrene grafted silica nanoparticles in a homopolymer matrix. JOSEPH MOLL, Columbia University, PINAR AKCORA, University of Missouri, SANAT KUMAR, Columbia University, RALPH COLBY, Pennsylvania State University — Silica nanoparticles grafted with polymers, dispersed in a homopolymer matrix, and annealed over time adopt a broad range of dispersion states which depend on grafting density, annealing time, weight percent silica, and the molecular weights of the polymers. We tuned these variables to give desired dispersion states, from uniformly dispersed particles to agglomerated clusters. Rheology was used to critically determine how the dispersion state affects the mechanical reinforcement of the composite. We have run both steady shear and small amplitude oscillatory shear experiments on nanocomposites comprising a range of dispersion states. By mapping the observed reinforcement on a morphology diagram, we observe the location of a maximum in reinforcement.

11:39AM Q19.00003 Structure, ion transport and rheology of nanoparticle organic hybrids. HAIBO QI, LYNDEN ARCHER, Cornell University — We report a new class of liquid nanoparticle organic hybrid materials (NOHMs), produced by tethering an organic oligomer corona to the surface of inorganic nanoparticles, and investigate their use as electrolites. This talk focuses on the structure factor and transport properties of these materials. Specifically, because the suspending solvent is covalently tethered to the NOHMs cores, the structure factor is predicted to vanish in the limit of small q. This behavior arises fundamentally from the presence of a new entropic attraction force produced by the tethered solvent, which constrains separation of the nanoparticle cores. Additionally, we show that NOHMs based on lithium conducting corona provide high ionic conductivities and lithium transfer numbers when doped with lithium salts. The enhanced conductivity is investigated in detail by studying how the core particles affect the melting transition, rheology, and activation energy for ion transport in the corona.

11:51AM Q19.00004 Effect of filler surface properties on stress relaxation behavior of carbon nanofiber/polyurethane nanocomposites. I. SEDAT GUNES, GUILLERMO JIMENEZ, SADHAN JANA, The University of Akron — The effect of carbon nanofiber (CNF) surface properties on tensile stress relaxation behavior of CNF/polyurethane (PU) nanocomposites was analyzed. PU was synthesized from methylene disiocyanate, polypropylene glycol (PPG diol), and butanediol. CNF, oxidized CNF (ox-CNCF), and PPG diol grafted CNF (ol-CNCF) were selected as fillers, ol-CNCF was obtained by grafting PPG diol onto ox-CNF by reacting it with the carbonyl groups present on ox-CNF surface. The atomic ratios of oxygen to carbon present on the filler surfaces were 0.13 and 0.18 on ox-CNF and on ol-CNCF as compared to 0.015 on CNF, mostly due to the presence of oxygen containing polar groups on the surfaces of the former. The composites were prepared by in-situ polymerization and melt mixing in a chaotic mixer. The stress relaxation behavior of composites was determined at room temperature after inducing a tensile strain of 100%. The presence of fillers augmented the rate of stress relaxation in composites which was highest in the presence of CNF. The results suggested that relatively weak polymer-filler interactions in composites of CNF promoted higher stress relaxation.

12:03PM Q19.00005 Synthesis of metal-molecule-metal structures for single-molecule transport and spectroscopy measurements. ALEX NEUHAUSEN, Dept. of Electrical Engineering, Stanford University, DAVID GOLDBERGERG, Dept. of Physics, Stanford University, CECIL CHIDSEY, Dept. of Chemistry, Stanford University — Robust, repeatable metal-molecule contacts are an elusive yet important hurdle in the development of molecular electronic devices. This project explores the chemical synthesis of metal-molecule-metal structures for single-molecule spectroscopy and transport measurements. Conjugated thiol-azide molecules are self-assembled on gold nanoparticles, which are then linked with dialkyne bridge molecules using Sharpless “click” reactions.
12:15PM Q19.00006 Impact of Nanofillers on the Durability of Polymeric Coatings and Composites, LI-PIN SUNG, STEPHANIE WATSON, AARON FORSTER, Materials and Construction Research Division, National Institute of Standards and Technology; SHENG LIN-GIBSON, Polymer Division, National Institute of Standards and Technology — Metal oxide nanoparticles have been incorporated into polymer systems to improve durability performance properties, for example Ultra Violet (UV) degradation and scratch resistance. In this paper, we present recent research results on (1) the effect of particle dispersion and photoreactivity of TiO₂ on the UV degradation of polymeric coatings exposed to high intensity UV radiations at two different humidity conditions; (2) the impact of nano-SiO₂ concentration on surface mechanical properties (surface morphology and scratch behavior) of polymeric coatings and composites. The physical and chemical degradation of the coatings were monitored in periodic intervals using a combination of laser confocal scanning confocal microscopy (LSCM) and attenuated total reflectance-Fourier transform infrared spectroscopy. An instrumented nanoindentation and LSCM are utilized to measure surface modulus, perform scratch testing, and map scratch damage patterns. A strong impact on the durability performance in both studies was observed in the presence of nanofillers. Particularly in the scratch resistance study, the addition of nanofillers reduces surface roughness and increase scratch resistance of the nanofiller-polymer composites.

12:27PM Q19.00007 The “Music” of Silica-Poly(methyl methacrylate) Core-Shell Spheres: Eigenvibrations and Mechanical Properties at the Nanoscale, TIM STILL, Max Planck Institute for Polymer Research, Mainz, Germany (still@mpip-mainz.mpg.de); REBECCA SAINIDOU, Universite du Havre, Le Havre, France, GOETZ HELLMANN, Deutsches Kunststoffinstitut, Darmstadt, Germany, GEORGE FYTAS, MPI for Polymer Research; University of Crete and FORTH, Heraklion, Greece — We report on the measurement of elastic vibrational modes (eigenvibrations) in silica-poly(methyl methacrylate) (SiO₂–PMMA) core-shell spheres and corresponding spherical hollow capsules (PMMA) with different particle size (diameter: 232 nm–405 nm) and shell thickness (25 nm–112 nm) using Brillouin light scattering, supported by numerical calculations. [T. Still et al., Nano Lett. 8, 3194 (2008)] These localized modes allow to access the mechanical moduli of core and shell material. We observe redshifted mechanical resonances in the core-shell sphere due to thickness of a thin film coating. The peculiar behavior of the vibrational modes in the hollow capsules is attributed to antagonistic dependence on overall size and layer thickness. The present investigation of the acoustic properties of the individual core-shell particles can lead to the use of such nanoscale engineered particles in more elaborate systems to control hypersonic phonons.

12:39PM Q19.00008 A Microscopic Model for the Reinforcement and the Non Linear Behaviour of Filled Elastomers and Thermoplastic Elastomers (Payne and Mullins Effects), Didier Long, CNRS/Rhodia, Samy Merabia, CNRS/Univ. Paris Sud, Paul Sotta, CNRS/Rhodia — We present a model regarding reinforcement properties of nanostructured polymers. Then, we show how it can be solved numerically by Dissipative Particles Dynamics. The model is based on the presence of glassy layers around the fillers. Strong reinforcement is obtained when these layers overlap. Key is the life-times distribution of these glassy bridges. The latter depend on polymer-filler interaction, the thermal-mechanical history, on the temperature, on the distance between fillers, and on the local stress in the material. Under applied strain, we show how the dynamics of yield and rebirth of glassy bridges account for the non-linear Payne and Mullins effects, which are a large drop of the elastic modulus at intermediate deformations, and a progressive recovery of the initial modulus when the samples are subsequently put at rest, respectively. These mechanisms account also for dissipative properties of filled elastomers. Our model opens the way for predicting mechanical behavior of nano-filled elastomers according to the filler structures and dispersion, polymer-filler interactions and temperature, in order to prepare systems with tailored properties.

12:51PM Q19.00009 Molecular Simulation of Highly Crosslinked Epoxy Resin and POSS-Epoxy Nanocomposites, Po-Han Lin, Rajesh Khare, Department of Chemical Engineering, Texas Tech University — Generation of atomistic model structures of crosslinked epoxy at realistic density is a challenging task. In this work, we present an efficient approach for generating such model structures of highly crosslinked matrices. The approach utilizes simulated annealing optimization technique for carrying out one-step polymerization of the reaction mixture in the simulation box. The structures so generated are relaxed using a combination of molecular mechanics and molecular dynamics (MD) simulations. The developed technique is computationally efficient and has been used for creating atomistic model structures of both crosslinked epoxy and a nanocomposite formed by the incorporation of the polyhedral oligomeric silsesquioxane (POSS) molecules in the crosslinked epoxy matrix. MD simulations are used to determine the volume-temperature behavior of these structures. The density and the glass transition temperature of the simulated structures are compared with the literature and experimental data. Furthermore, the molecular packing behavior of the POSS-epoxy nanocomposite is compared with the molecular packing in the crosslinked epoxy matrix.

1:03PM Q19.00010 Reducing Strain in Electrophoretically Deposited Nanocrystal Films by Post-Deposition Incorporation of Polymers, Theodore Kramer, Department of Applied Physics and Applied Mathematics, Columbia University, Steffen Jockusch, Michael Steigerwald, Nicholas Turro, Department of Chemistry, Columbia University, Irving Herman, Department of Applied Physics and Applied Mathematics, Columbia University — We have made dense nanoparticle-polymer films and investigated their mechanical properties using nano-indentation and other methods. Electrophoretically deposited (EPD) films of cadmium selenide nanocrystals were infiltrated with network-forming monomers and subsequently exposed to UV radiation in the presence of photoinitiators to facilitate polymerization of the monomer. This hybrid material exhibits the desirable photoluminescent properties of CdSe nanocrystals but does not fracture, as do thick electrophoretically grown nanoparticle films. This may be the result of effectively reducing strain in the films via void filling. The mechanical properties of these films differ from those of EPD films without the introduction of polymer, as seen by nanindentation studies. These films offer the benefit of high particle density, as well as large film thickness (> 2 micron), and may have useful applications in the area of flexible photovoltaic devices.

1:15PM Q19.00011 Mechanics of Nanoscale composite films from stress-electrical measurements: A nanoscale foam, Chieu Nguyen, Vivek Maheshwari, Ravi Saraf, Chemical Engineering-University of Nebraska-Lincoln Team — Nanometer thin (> 100nm) composite films consisting of polymers and organic-inorganic materials such as nanoparticles, quantum dots, nanotubes and dyes are widely researched for applications in designing a bio-mimetic cell membrane, solar cells, electronic and optical sensors, ion separation membranes and coatings. Being nanoscale in dimensions the mechanical properties of the film is critically governed by its morphology at nanoscale and the mutual interaction between the constituents of the film. The assembly process and the components of the film are detrimental in defining its morphology. A vast array of film morphologies is possible due to the multitude of combinations in processing and the components available to make the film. The study of mechanical properties of the film is hence important due their application in multitude of fields and correlating it to the nanoscale morphology and properties of its constituents. Here we present the stress-electrical measurements on a nanoscale (~100nm) nanocomposite film prepared using the well known spin assisted ionic self-assembly process. The film is a stack of nanoparticle layers, spaced by dielectric layer. Each dielectric layer consists of a stack of alternating anionic and cationic polyelectrolyte layers. The separation between the nanoparticle layers can be controlled with nanometer scale precision by modulating the number of polyelectrolyte layers in each dielectric layer.
alpha phase crystals, even at low STN content. The ionic organic modifier makes STN much more effective than SWN in promoting beta phase PVDF crystals. crystals and TTT conformers, while reducing the alpha phase crystal content in ES PVDF/nanoclay composite nanofibers. STN can completely eliminate the N,N-dimethylformamide/acetone and then electrospun into nanofibers with diameters ranging from 100

are based on hectrite structure, but only STN contains an organic modifier between the hectrite layers. The PVDF was dissolved, and nanoclay was dispersed, in

sion, JIANGSHUI HUANG, Department of Physics & Department of Polymer Science and Engineering, University of Massachusetts Amherst, WIM H. DE JEU, Department of Polymer Science and Engineering, University of Massachusetts-Amherst — We have previously studied the radial wrinkling of a thin polymer film floating on the surface of water under the capillary force exerted by a drop of water placed on its surface. Here, the same surface tension both sets the radial stress in the unperturbed film as well as the source of the perturbation that leads to the wrinkling instability. We now report the effect on the wrinkling instability of a differential surface tension by using fluids with different surface tensions for the liquid the film is floating on and the drop put on the film. We use both surfactants and a variety of pure liquids to control the surface tension of water. When the base radial stress of the film floating was decreased, the length of the wrinkles increased, but the number of wrinkles decreased.

flow induced orientation behavior of concentrated dispersions of multi-wall carbon nanotube suspensions under shear flow: Effect of aspect ratio and concentration

1:51PM Q19.00014 Polymorphism in electrospun poly(vinylidene fluoride)/nanoclay composite nanofibers,

1:39PM Q19.00013 Flow induced orientation behavior of concentrated dispersions of multi-wall carbon nanotube suspensions under shear flow: Effect of aspect ratio and concentration

...and no enhancement is observed at the iPP slab surfaces; and (iii) the dielectric constant associated with the dielectric transition at the sapphire/polypropylene interfaces. Our results indicate that the dielectric transition profile at interface strongly depends on the nanoscale averaging procedure. We propose an averaging model that ensures near-locality of the dielectric function. We find that: (i) the dielectric permittivity approaches the corresponding bulk value just a few atomic layers away from the interface or surface; (ii) the dielectric constant is enhanced at the surfaces of the isolated α-Al2O3 slabs, while no enhancement is observed at the iPP slab surfaces; and (iii) the dielectric transition at the α-Al2O3/iPP is mainly confined in the α-Al2O3 side.

1:39PM Q19.00013 Flow induced orientation behavior of concentrated dispersions of multi-wall carbon nanotube suspensions under shear flow: Effect of aspect ratio and concentration

SASWATI PUJARI, WESLEY BURGHARDT, Cambridge University — We report studies of average orientation state of concentrated dispersions of multi-walled carbon nanotube (MWNTs) in steady shear flow. Uncured epoxy was used as a viscous, Newtonian suspending medium, and samples were prepared from ‘aligned’ MWNTs using methods previously reported (Rahatekar et al., J Rheol 40:599, 2006). Flow induced structural measurements were made in the vorticity (1-3) plane of simple shear flow using in-situ wide angle x-ray scattering techniques in a rotating disc shear cell. Azimuthally-dependent diffraction from the internal layered structure of the MWNTs was used to characterize alignment. Steady state anisotropy of MWNT dispersions decrease with increasing length of the MWNTs. Surprisingly, the anisotropy is seen to increase with increasing concentration. For one of the samples, more detailed orientation dynamics are studied in steady shear and transient shear flow both in the 1-2 (flow gradient) and 1-3 (vorticity) planes of shear flow, and through comparison of wide-angle and small-angle scattering signatures of flow-induced nanotube alignment.

1:51PM Q19.00014 Polymorphism in electrospun poly(vinylidene fluoride)/nanoclay composites with prescribed morphologies

Our results indicate that the permittivity profile at interface strongly depends on the nanoscale averaging procedure. We propose an averaging model that ensures near-locality of the dielectric function. We find that: (i) the dielectric permittivity approaches the corresponding bulk value just a few atomic layers away from the interface or surface; (ii) the dielectric constant is enhanced at the surfaces of the isolated α-Al2O3 slabs, while no enhancement is observed at the iPP slab surfaces; and (iii) the dielectric transition at the α-Al2O3/iPP is mainly confined in the α-Al2O3 side.

This research was supported by the Petroleum Research Fund of the American Chemical Society, 44149-AC7.

Wednesday, March 18, 2009 11:15AM - 2:15PM –

1:27PM Q19.00002 Effect of Long-chain Branching on Surface Dynamics of Polymer Films

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1:51PM Q19.00014 Polymorphism in electrospun poly(vinylidene fluoride)/nanoclay composite nanofibers

2:03PM Q19.00015 Polymer/microrods with prescribed morphologies

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11:39AM Q20.00003 Entanglement swelling in polymer glasses, JOSHUA D. MCGRAW, KARI DALNOKI-VERESS, Department of Physics & Astronomy and the Brockhouse Institute for Materials Research, McMaster University, Hamilton, ON, Canada, L8S 4M1 — A polymer system in which the chains are much longer than the entanglement molecular weight, $M_e \gg M_c$, is well entangled. When a thin, glassy polymer film is uniaxially strained, deformations which are almost visible to the naked eye called crazes may be formed. Measuring volume fractions of deformed to undeformed regions provides a method by which entanglement densities of similar systems can be compared. We present results of deformation experiments, probing using atomic force microscopy, in which well entangled polystyrene networks have been diluted with various weight fractions of polystyrene with molecular weight in the vicinity of $M_e$. Upon dilution the system assumes an effective reduction in the entanglement density. The effective entanglement density is predicted by a conceptually simple model with $M_e$ as the only free parameter.


11:51AM Q20.00004 Microstructure Evolution during Solvent Evaporation from Thin Film Polymer Mixtures, NIGEL CLARKE, MIREILLE SOUCHE. Durham University, GAVIN BUXTON, Case Western Reserve University — We present simulations of the phase separation dynamics in a thin film polymer blend solution subject to solvent evaporation [1]. If the upper and lower surfaces are neutral with respect to the different components, we find that as the solvent diffuses through the film, and evaporates from the surface, phase separation becomes energetically favourable progressively throughout the film. This produces an ordering front which propagates through the film and leaves an ordered lateral morphology in its wake. In order to understand microstructure evolution if the surface interactions are strong enough that the film initially separates into a two layers, we have performed a linear analysis of the Marangoni instability of a deformable interface between two fluid layers of finite depths, submitted to a gradient of solvent concentration induced by the evaporation [2]. Qualitative comparison with experimental observations of spin-coating processes of solution of two immiscible polymers are then performed, yielding satisfactory agreement.


12:03PM Q20.00005 Dimension-Dependent Mechanical Properties of Pure and Antiplasticized Polymer Nanostructures, SEAN DELCAMBRE, ROBERT RIGGLEMAN, JUAN DE PABLO, PAUL NEALEY, Department of Chemical and Biological Engineering, University of Wisconsin - Madison — Dense arrays of poly(methyl methacrylate) (PMMA) grating nanostructures 80 nm to 120 nm in pitch were fabricated by electron-beam and extreme ultraviolet interferometric lithography. During development and rinse drying, the nanostructures are subjected to capillary forces that are defined by the rinse fluid properties and spacing between adjacent structures. The applied capillary forces and structure aspect ratios were varied experimentally to induce structure collapse. By coupling nanostructure collapse data with continuum cantilever beam bending models, mechanical properties such as the elastic modulus and yield stress are determined. The elastic moduli of PMMA structures at this scale are observed to decrease with structure width/length. This behavior is counteracted by the addition of a low molecular weight diluent, tris(2-chloropropyl) phosphate (TCP). At concentrations up to 5 wt%, TCPP acts as an antiplasticizing agent, decreasing the glass transition temperature while simultaneously increasing the elastic modulus. For a given applied capillary force, nanostructures containing 5 wt% TCPP are observed to remain stable at aspect ratios up to 20% higher than the pure material.

12:15PM Q20.00006 The stiffening of ultrathin polymer films in the rubbery regime—the relative contributions of bending, membrane stress and surface tension, PAUL O'CONNELL, GREGORY MCKENNA, Texas Tech University — A novel nano-bubble inflation technique has been developed which allows the determination of the absolute creep compliance of ultrathin polymer films as thin as 9 nm. Previous results have shown that the degree of reduction in Tg with film thickness is not universal, with PVAc showing no change in Tg down to 23 nm while PS shows a significant reduction at thicknesses below approximately 80 nm. Interestingly the rubbery plateau region for both materials shows a similar stiffening as the thickness is reduced. At low inflation pressures the film is dominated by the bending stiffness with PVAc showing no change in Tg down to 23 nm while PS shows a significant reduction at thicknesses below approximately 80 nm. At concentrations up to 5 wt%, TCPP acts as an antiplasticizing agent, decreasing the glass transition temperature while simultaneously increasing the elastic modulus. For a given applied capillary force, nanostructures containing 5 wt% TCPP are observed to remain stable at aspect ratios up to 20% higher than the pure material.

12:27PM Q20.00007 Molecular confinement and residual stress in ultrathin polymer films, ARNOLD YANG, National Tsing Hua University, GUNTHER REITER, University of Freiburg, Germany, YI-HSIN CHANG, YI CHIEN, National Tsing Hua University — The residual stress operative in thin films of a polymer (polystyrene) prepared by spin coating was determined from local elastic stress release induced by pinhole nucleation during dewetting instability. The measured stress was orders of magnitude greater than the capillary force and attributed to chain recoiling of the confined macromolecules. The entropy-driven stress was found to be small for thicker films but increase dramatically as film thickness became less than the unperturbed molecular dimensions. The chain conformations in these films can only be described by the Langevin, rather than Gaussian, statistic and the draw ratio was determined to be around 5, comparable to that in craze fibrils, for film thickness of 4 nm. The effects of spin speed, aging-induced relaxation, and molecular packing were investigated. The molecular processes during spin coating were proposed. In addition, conjugated polymers when squeezed into the molecular thicknesses were found to emit light with much enhanced efficiencies due to the large molecular deformation.

1 We acknowledge the financial supports of National Science Council of Taiwan, and AFOSR through its Nano-Initiatives Program with Taiwan.

12:39PM Q20.00008 Semifluorinated Polymers Confined at the Solid-Air Interface, UMESH SHRIVASTHA, Clemson University, STEPHEN CLARSON, University of Cincinnati, DVORA PERAHIA, Clemson University — Effective responsive layers should exhibit stability while retaining a dynamic mode that will allow reaction of the interface to external stimuli. Semifluorinated polymers have a potential for forming energy controlled responsive interfaces. Because of the high segregation between the fluorinated and protonated segments, well defined structures are induced at relatively short chains, retaining the capability to reassemble on short time scales. Fluorinated segments affect the interfacial energies as well as enhance thermal stability and controls the refractive index and dielectric properties. The present study investigates the interfacial response of poly trifluoro propylmethyl siloxane-polystyrene diblock copolymer (PTFPMS-PS) at volume fractions varying from 0.003 to 0.5 of fluorinated block, at the interface of oxidized silicon wafers. In all volume fractions we found that the air interface is fluorine rich and the solid surface in proton rich. Layering is detected across the films for all volume fractions. Upon annealing the layering is retained, however the interfacial compositions changes.

SOMESH PERI, MARK FOSTER, The University of Akron, JESSE ENLOW, HAO JIANG, TIMOTHY BUNNING, Wright Patterson Air Force Base, BULENT AKGUN, SUSHIL SATIJA, CHARLES MAJKRZAK, National Institute of Standards and Technology — The structures of plasma polymerized homopolymer octfluorocyclobutane (PP-OFCB) films made under different processing conditions were studied using x-ray reflectivity (XR) and neutron reflectivity (NR). The processing parameters varied were monomer feed location, plasma power, and pressure. Each dry film had a surface layer of thickness ~20 Å and a thin layer of ~10 Å thickness at the substrate in which the crosslink density was lower than in the bulk polymer film. The region of lower cross-link density at the film-air interface reflects the extent of a reaction zone that moves with the deposition and is responsible for dictating the width of interfaces that are formed when a layer of different precursor is deposited atop the first layer. Results from bilayer films support this view. Such a reaction zone is also seen for benzene and iron-containing plasma polymerized films.

1:03PM Q20.00010 Spatially Organized Polymer Films Prepared by Oblique Angle Polymerization


1:15PM Q20.00011 Rubber Friction - A Molecular Picture

ANISH KURIAN, KUMAR NANDJUNIA, ALI DHI-NOJWALA, THE UNIVERSITY OF AKRON TEAM — Understanding the relationship between adhesion, friction and the interfacial structure has been of significant interest for many years. Recent tribological experiments involve measuring friction and adhesion values to develop a molecular model to explain the macroscopic results. Here, we have used surface sensitive infrared-visible sum frequency generation spectroscopy (SFG) to study the interface between elastomer and solid surfaces. SFG is a second order nonlinear optical technique that provides information on the chemical environment, orientation and concentration of the molecules at the interface. We have designed a friction cell to probe the changes in the interfacial structure during sliding using a femtosecond laser spectroscopy. These results will be presented.

This work was supported National Science Foundation

1:27PM Q20.00012 In-situ Adhesion Measurements Utilizing Layer-by-layer Functionalized Surfaces

CHRISTOPHER M. STAFFORD, ADAM J. NOLTE, JUN YOUNG CHUNG, Polymers Division, National Institute of Standards and Technology, MARLON L. WALKER, Surface and Microanalysis Science Division, National Institute of Standards and Technology — The adhesion between poly(dimethylsiloxane) (PDMS) hemispheres coated with layer-by-layer (LbL) assemblies of poly(allylamine hydrochloride) and polyelectrolytes and rigid, planar substrates was investigated using Johnson, Kendall, and Roberts (JKR) contact mechanics. Measurements were performed against amine-functionalized glass slides both in air and in aqueous solutions of controlled pH. Despite the increased density of negatively charged carboxylate groups, LbL-functionalized PDMS exhibited lower adhesion due to the combined effects of increased surface roughness and the high Young’s modulus of the coating. Measurements of coated PDMS in aqueous solutions revealed tunable adhesion behavior dominated by pH-mediated changes in the mechanical properties of the coating. Smoothing the surface of the LbL coatings by aqueous salt annealing led to a significant increase in adhesion. Our results suggest that LbL assembly can be an effective means of surface functionalization for in-situ adhesion measurements, but understanding and predicting the adhesion behavior requires comprehensive knowledge of the chemical, mechanical, and topological properties of the coating and how such properties change in response to the ambient environment.

1:39PM Q20.00013 Tethered Lubricant Films Based On Cross-linked Polydimethylsiloxane

LUCAS LANDHERR, CLAUDE COHEN, LYNDEN ARCHER, Cornell University — We report on the interfacial friction and wear properties of surface-tethered cross-linked polydimethylsiloxane thin films. We show that thin, two-tiered films produced by covalently tethering polydimethylsiloxane (PDMS) networks to self-assembled monolayers manifest the lowest friction coefficient (mu = 0.0039) recorded for a dry lubricant film. Using a combination of lateral force microscopy, equilibrium swelling, and adhesion measurements we determined that the low friction coefficients are due to the formation of weakly hydrogen-bonded (untethered) and pendent polymer chains dispersed in thin PDMS network films on transient mechanical properties, interfacial friction, and wear characteristics.

1:51PM Q20.00014 Effect of Adsorbed Films on Nanoscale Mechanical Contacts

SHENGFENG CHENG, Department of Physics and Astronomy, Johns Hopkins University, BINQUAN LUAN, IBM T. J. Watson Research Center, MARK ROBBINS, Department of Physics and Astronomy, Johns Hopkins University — For surfaces exposed to ambient air, the presence of adsorbed molecules cannot generally be avoided. Molecular simulations are presented which show that the compliance of these adsorbed films can have a profound effect on the mechanical behavior of contacts. An adsorbed film of short chain molecules is equilibrated on a flat, elastic substrate. The film is then contacted by a non-adhesive spherical tip. The atomic scale structure of the tip is varied from amorphous to crystalline, since this has a substantial effect on contacts with clean substrates. Including adsorbed molecules reduces sensitivity to tip geometry, but introduces new effects. One is that the contact region is broadened dramatically, with measured contact radii increased from predictions of continuum theory by a constant shift. The variation of tip displacement and substrate deformation with normal load show a crossover between two regimes. At small loads, the effective elastic modulus is set by the soft adsorbed film, while at large loads the modulus is that of the substrate. Variations in friction with tip geometry are much smaller than for bare substrates and the friction rises linearly with load in almost all cases.

2:03PM Q20.00015 The Promotion of Au Adhesion on Polymer Surfaces Using Polyhedral Oligomeric Silsequioxane

CHRIS HUGHES, BRIAN AUGUSTINE, ALAN MO, JONATHAN WYRICK, BRUNO CAPUTO, ETHAN ROSENTHAL, James Madison University — The adhesion of Au on polymer surfaces is weak because of the inert nature of Au and the non-polarity of the hydrocarbon surface of the polymer films. Here, we have used oblique angle deposition (OAD) of the POSS-SA to create a molecule with both polymer and inorganic silica glass characteristics. The POSS-SA is spun cast onto the surface of PMMA creating a film which is on the order of 100 nm thick. Au dots that are 1 mm in diameter were deposited onto both the virgin PMMA surface and the POSS-SA coated surface and the samples were covered with acetone, a known solvent for PMMA. Optical microscope video images of the dots revealed their delamination from the surface and image analysis was used to determine the time that it took for the dots to be undercut -- typically in the range of seconds to minutes. An obvious increase in the time required to undercut the Au was observed for the POSS-SA treated surface. A model explaining the improved adhesion will be discussed as will future plans for device fabrication.
2:30PM T7.00001 The undulating shape of growing ribbons . HAIYI LIANG, School of Engineering and Applied Science, Harvard University — The undulating morphology of leaves and petals is now accepted as a consequence of differential growth of the underlying tissue. Various qualitative and quantitative aspects of the buckling patterns seen in both vascular and avascular leaves may thus be ascribed to the distribution of non-uniform growth in the lamina, and have been demonstrated in normal and mutant leaves, as well as in physical models thereof. To understand the different modalities that arise quantitatively, we construct a mathematical model for the stability of an initially flat or curved elastic ribbon with gradients in growth directly motivated by observations of kelp that are capable of phenotypic plasticity in different environments. Using a combination of analysis, numerical simulation, and experimental observations, we map out the phase space of possible shapes for these growing ribbons. In general, we find that as the relative growth strain is increased, the ribbon-like structure first switches to a catenoidal shape before developing undulating edges that can develop on the catenoid's edges. Our framework allows us to delineate the few macroscopic parameters that control the morphology of elongated leaves and flower petals and helps to explain the large variety of observed shapes.

3:06PM T7.00002 The Mechanics of Non-Euclidean Plates in Synthetic and Natural Sheets . ERAN SHARON, The Hebrew University of Jerusalem — Thin elastic flat plates attain non-trivial configurations when they are confined. I will show that plates with intrinsic non-Euclidean geometry attain multi scale three-dimensional configurations even when they are free of external loading. Such bodies do not have any stress-free configuration, thus current plate theories cannot properly describe their physics. I will present our recent experimental results and our theoretical model for the shaping principles of such plates. Finally, I will show how these principles are manifested during the growth of leaves.

3:42PM T7.00003 Wrinkling patterns on floating elastic films1, NARAYANAN MENON, Dept. of Physics, University of Massachusetts, Amherst — A polymer sheet floating on the surface of a fluid is an ideal arena for studying elastic instabilities in thin sheets. In our experiments we use poly styrene sheets whose typical lateral size, \( L \sim 3 \, \text{cm} \), and whose thickness, \( t \) ranges from 30 to 300 nm, yielding aspect ratios \( L/t \) of up to \( 10^3 \). In their unperturbed state, they lie on the surface of a pool of water, stretched flat by surface tension. We can then generate a rich variety of wrinkling patterns by perturbing the surface locally with capillary forces or with controlled displacements at one or more points on the surface. I will review our understanding of the length scales that characterise these localised patterns. A simple experimental setting in which a multiplicity of these length scales come into play is a situation analogous to an Euler buckling experiment performed on the surface of a fluid. We push two sides of a rectangular sheet towards each other, creating a global pattern of parallel wrinkles whose wavelength is given by a balance between gravitational potential energy of the fluid and bending energy of the sheet. These wrinkles develop a cascade of fine structure at higher wavenumbers close to the uncompressed edges of the sheet. The length scale over which this cascade occurs is the capillary length, whereas the wavenumber at the edge of the sheet reflects a balance between bending energy and surface tension. We discuss the evidence that this is a fundamentally new type of elastic cascade, which proceeds to higher wavenumbers by smooth evolution of the wrinkles, rather than by discrete, sharply localised branching. Work done in collaboration with J. Huang, E. Cerda, B. Davidovitch, W.H. de Jeu, T.P. Russell, C. D. Santangelo

1Supported by NSF DMR 0606216 and NSF MRSEC DMR-0820506.

4:18PM T7.00004 Wrinkle to fold transitions: Stress relaxation in lipid monolayers and other elastic thin films , KA YEE C. LEE, The University of Chicago — Surfactants at air/water interfaces are often subjected to mechanical stresses as the interfaces they occupy are reduced in area. The most well characterized forms of stress relaxation in these systems are first order phase transitions. However, once chemical phase transitions have been exhausted, the monolayer undergoes global mechanical relaxations termed collapse. We have previously demonstrated that for lung surfactants, a mixture of lipids and proteins that coats the alveoli to reduce the work of breathing, collapse manifests itself as protrusions of folds into the subphase. These folds remain attached to the monolayer and reversibly reincorporated upon expansion. By studying different types of monolayers, we have shown that this folding transition in monolayers is not limited to lung surfactant films, but rather represents a much more general type of stress relaxation mechanism. Our study indicates that collapse modes are found most closely linked to in-plane rigidity. We characterize the rigidity of the monolayer by analyzing in-plane morphology on numerous length scales. More rigid monolayers collapse out-of-plane via a hard elastic mode similar to an elastic membrane, with the folded state being the final collapse state, while softer monolayers relax in-plane by shearing. For the hard elastic mode of collapse, we have further demonstrated experimentally and theoretically that the folded state is preceded by a wrinkled state, and similar wrinkle to fold transitions has been observed in elastic thin films ranging from 2 nm to 10 \( \mu \text{m} \) in thickness of completely different chemical nature (lung surfactant lipid monolayers, gold nanoparticle trilayers, and polyester sheets).

4:54PM T7.00005 Nonlinear dynamics of wrinkle growth and pattern formation in stressed elastic thin films on viscoelastic substrates , RUI HUANG, University of Texas at Austin — A stressed thin film on a soft substrate can develop complex wrinkled patterns. The onset of wrinkling and initial growth is well described by a linear perturbation analysis, and the equilibrium wrinkled patterns can be analyzed based on an energy approach. In between, the wrinkle pattern undergoes a growth and coarsening process with a peculiar dynamics. By using a proper scaling along with numerical simulations, this paper develops a quantitative understanding of the wrinkling dynamics from initial growth through coarsening toward equilibrium. We discuss the evidence that this is a fundamentally new type of elastic cascade, which proceeds to higher wavenumbers by smooth evolution of the wrinkles, rather than by discrete, sharply localised branching. Work done in collaboration with J. Huang, E. Cerda, B. Davidovitch, W.H. de Jeu, T.P. Russell, C. D. Santangelo

Wednesday, March 18, 2009 2:30PM - 5:30PM – Session T18 DPOLY: Focus Session: Organic Photovoltaics and Other Photonic Devices 319

2:30PM T18.00001 Surface plasmon polariton assisted organic solar cells , P. PEUMANS, Stanford U. — No abstract available.

3:06PM T18.00002 Harvesting Lost Photons: Minimizing Sub-Bandgap Losses in Organic Photovoltaic Devices by Up-conversion , CLARA SANTATO, LORANGER SEBASTIAN, BANVILLE DAVID, Genie Physique/Polynetique Montreal, ROSEI FEDERICO, EMT-IRIS/Varennes, PEREPICKHA DMIYTO, McGill/Chemistry — We report on a novel approach to increase the efficiency of organic photovoltaic (OPV) cells in the near-infrared region of the solar spectrum by blending the organic semiconductors with rare-earth doped nanoparticles with up-converting photophysical properties. The approach consists in (i) synthesizing lanthanide-doped nanoparticles capable of efficient energy transfer of up-converted near-infrared (NIR) photon energy to conjugated polymers; (ii) assembling these nanoparticles, in blends with p-type polythiophenes and n-type fullerene, in solution-processed OPV cells capable to harvest NIR photons.
3:18PM T18.00003 In-situ X-ray characterization of thermal and solvent based annealing of thin P3HT and P3HT/PCBM films\textsuperscript{1} , TOMMY HOFMANN, Brookhaven National Laboratory, HTAY HLAING, Stony Brook University, CHANG-YONG NAM, CHARLES BLACK, BENJAMIN OCKO, Brookhaven National Laboratory, BROOKHAVEN NATIONAL LAB TEAM — We have studied the annealing of thin films of P3HT (poly(3-hexylthiophene)) and mixed P3HT and PCBM thin films using in-situ Grazing Incidence Angle x-ray scattering techniques at the National Synchrotron Light Source. The films, 50-200 nm thick, were prepared using spin coating from a volatile solution. Both thermal and solvent annealing techniques are well known to improve electrical properties yet the precise mechanism is not well understood. In our measurements, we have monitored the dependence of the diffraction peak positions and widths under a variety of different in-situ thermal and solvent conditions. A detailed comparisons between these methods provides new insight into how to improve the crystallinity beyond what can be obtained by thermal methods alone. This may eventually lead to better electrical properties in thin film organic photovoltaic devices.

\textsuperscript{1}This work is supported by the U.S. DOE Contract No. DE-AC02-98CH10886 and a Brookhaven National Laboratory LDRD Project.

3:30PM T18.00004 Excited-State Dynamics at Organic Photovoltaic Heterojunctions by Pump-Probe Photoelectron Spectroscopy . GREGORY DUTTON, DANIEL DOUGHERTY, National Institute of Standards and Technology, WEI JIN, WILLIAM CULLEN, JANICE REUTT-ROBEY, University of Maryland, STEVEN ROBEY, National Institute of Standards and Technology — The critical process of charge separation in organic photovoltaic (OPV) devices is determined directly at the organic heterojunction, but these interfaces have been less extensively studied than organic/metal interfaces. We prepare model photovoltaic heterojunctions by deposition of ultrathin films of organic semiconductors on single-crystal metal substrates. The electronic structure of the component materials and their interfaces is determined with ultraviolet photoelectron spectroscopy (UPS) and two-photon photoemission (2PPE). The systems studied in this work involve phthalocyanines and analogs as donors and C\textsubscript{60} fullerene as acceptor. Time-resolved pump-probe experiments are applied to directly measure the excited state dynamics at these OPV heterojunctions. An ultrafast visible pump pulse selectively generates excitons in one material, followed by a time-delayed UV probe to interrogate the population of the acceptor charge transport level. Analysis of cross-correlations reveals the timescales of charge separation and recombination at the interface. Additionally, comparison will be made to structural and local spectroscopic studies of similar phthalocyanine/fullerene systems made by STM/STS.

3:42PM T18.00005 The role of triplet excitons in enhancing polymer solar cell efficiency: a photo-induced absorption study\textsuperscript{1} , KAI YANG, SUCHI GUHA, Department of Physics and Astronomy, University of Missouri-Columbia, MO 65211 — Inclusion of heavy metal atoms in a polymer backbone allows transitions between the singlet and triplet manifolds. Interfacial dissociation of triplet excitons constitutes a viable mechanism for enhancing photovoltaic (PV) efficiencies in polymer heterojunction-based solar cells, which are now becoming feasible options for solar panels. The PV efficiency from polymer solar cells utilizing a ladder-type poly para phenylene polymer (PhLPFP) with trace quantity of Cd atoms and a fullerene derivative (PCBM) is almost 10 times more than its counterpart (MeLPPP) with no Pd atom. Evidence is presented for the formation of a weak ground-state charge-transfer complex (CTC) in the blended films of PhLPFP and PCBM, using photo-induced absorption (PIA) spectroscopy. Such complexes are not seen in the PIA spectrum of MeLPPP. PCBM blends. Possible mechanisms for the CTC state formation as well as the significance of this to the understanding and optimization of polymer blended solar cells will be discussed.

\textsuperscript{1}This work was supported by NSF-ECCS0823563

3:54PM T18.00006 Photophysics of charge-transfer excitons in thin films of \(\pi\)-conjugated polymers\textsuperscript{1} , DEMETRA PSIACHOS, SUMIT MAZUMDAR, University of Arizona — We develop a theory of the electronic structure and photophysics of interacting chains of \(\pi\)-conjugated polymers to understand the differences between solutions and films. While photoexcitation generates only the intrachain exciton in solutions, the optical exciton as well as weakly allowed charge-transfer excitons are generated in films. We show that a significant fraction of ultrafast photoinduced absorptions (PAs) in films originate from the lowest charge-transfer exciton. Using sophisticated many-body approaches that take into account high order configuration interaction, we have calculated the full wavelength-dependent PA spectra of pairs of interacting PPV oligomers. Good qualitative agreement is obtained with the experimental PA spectra of thin films of \(\pi\)-conjugated polymers. The origin of each individual PA is explained within our theory. Our work resolves long-standing controversies regarding the nature of the primary photoexcitations in films.

\textsuperscript{1}This work was supported by NSF-DMR-0705163.

4:06PM T18.00007 Photo-crosslinkable Polythiophenes for Efficient Thermally Stable Organic Photovoltaics , BUMJOON KIM, KAIST and UC Berkeley, YOSHI MIYAMOTO, BIWU MA, JEAN M.J. FRECHET, UC Berkeley — We report a new series of bromine-functionalized poly(3-hexylthiophene) (P3HT-Br) copolymers for use in solution processed organic photovoltaics (OPVs). P3HT-Br copolymers were synthesized from two different monomers, where the ratio of the monomers was carefully controlled to achieve a UV photo-crosslinkable layer while leaving the \(\pi - \pi\) stacking feature of conjugated polymers unchanged. Photo-crosslinkable P3HT-Br was demonstrated as effective electron donors in OPVs. The crosslinking stabilizes P3HT-Br/PCBM blend morphology preventing the macro phase separation between two components, which lead to OPVs with remarkably enhanced thermal stability. The drastic improvement in thermal stabilities is further characterized by microscopy as well as grazing incidence X-ray scattering (GIXS). The use of these copolymers for solution processed efficient bilayer PVs is also described. Benefited from the little disturbance in \(\pi - \pi\) stacking by crosslinkable units as evidenced in GIXS, P3HT-Br/PCBM bilayer device shows high power conversion efficiency at over 2.2% and excellent thermal stability.

4:18PM T18.00008 Temperature Dependence of Biexciton Decay and Intermolecular Hopping in Zinc Phthalocyanine Films . , CHRISTOPHER RYAN, Graduate Student — The femtosecond exciton dynamics of melt-pressed zinc phthalocyanine (ZnPc) films are studied in the temperature range of 90-400 K. In this range ZnPc goes through a transition from a crystalline solid to a liquid crystalline phase. For the entire temperature range, the excitons are shown to decay on the time scale of 10's of picoseconds, and these dynamics are nonlinear with respect to pump fluence. Such a behavior is well described by a biexciton recombination model under one dimensional diffusion constraints. The single exciton lifetime and the biexciton recombination crossection are extracted at all temperatures. From the latter, the exciton hopping time is calculated. The exciton hopping time decreases with temperature in the crystalline phase, but increases in the liquid crystalline phase. The role of temperature and structural order in the exciton hopping time will be discussed.
4:30PM T18.00009 White tandem OLED with carbon nanotube interlayer. ALEXIOS PAPADIMITRATOS, Solano Inc, Nanotech UT Dallas, RAQUEL OVALLE ROBLES, RAY BAUGHMAN, Nanotech UT Dallas, ANVAR ZAKHIDOV, Solano Inc, Nanotech UT Dallas — White organic light emitting diodes (OLEDs) have become well recognized as an important candidate for future lighting and display applications. An existing idea to generate white color places R, G, B pixels in a side-by-side geometry. Also, white tandem OLEDs have been developed by vertically stacking in series multiple electroluminescent layers. However, such structures require a complex interfacial layer which is usually fabricated by strong dopants to form a p+/n− interface. We have shown earlier that transparent carbon nanotubes (CNT) can be used as effective three-dimensional charge injectors in polymer light emitting diodes[1] and OLEDs[2]. Now, we show that CNT can be used as an interlayer in two cell OLEDs with complimentary colors. We show that tandem devices with CNT interlayers, together with selective barriers and PEDOT:PSS coating can control the device color. In addition, the emission intensity can be controlled by independently tuning the driving voltage and current. In the case of the over- doped p+/n− interlayers we do not have this opportunity which is a great advantage of CNT injectors. We also compare the performance of multilayer CNTs vs. that of single wall CNTs in the tandem OLEDs. [1]R.H.Baughman et al.Science, 297,787-792(2002).[2]C.D.Williams et al. Appl. Phys. Lett. 93,183506(2008).

4:42PM T18.00010 Tuning optical properties of blue-emitting polyfluorenes via hydrostatic pressure. KEISHAB PAUDEL, MEERA CHANDRASEKHAR, SUCHI GUHA, Department of Physics and Astronomy, University of Missouri-Columbia, MO 65211 — Polyfluorenes (PFs) represent a unique class of poly para-phenylene based blue-emitting polymers with intriguing structure-property relationships. Slight variations in the choice of functionalizing side chains result in dramatic differences in the inter- and intra-chain structures in PFs. Highlighting these differences are two prototypical PFs, poly-(9,9-(di n, n-octyl) fluorene) (PF8) and poly-(9,9-(di ethyl- hexyl) fluorene) (PF2/6). In addition to the nematic liquid crystal (n-LC) mesophase, PF8 is characterized by at least five structural phases. We present photoluminescence (PL) and Raman scattering studies of powder samples and thin films of PF8 under hydrostatic pressure. The powder sample was thermally annealed at 2GPa. The PL vibronics of the as-is powder sample red-shift at an average rate of 30 meV/GPa whereas the thermally annealed sample red-shifts at a higher rate of 50 meV/GPa, indicating a different crystalline line shapes for the annealed sample. The Huang-Rhys factor is found to increase with increasing pressures signaling a higher geometric relaxation of the electronic states. The Raman peaks harden with increasing pressures; the intra-ring C-C stretch frequency at 1600 cm−1/GPa and exhibits asymmetric line shapes at higher pressures.

5:44PM T18.00011 SERS Characterization of Self-Assembled Monolayers Embedded on Plasmonic Nano-structure. MASATO MAITANI, Materials Science and Engineering, Penn State University (Penn State), DOUGLAS OHLBERG, Information & Quantum Systems Laboratory, Hewlett-Packard Laboratories, Palo Alto, CA (Hewlett-Packard), PING KAO, Ee, Penn State, DEMIREL MELIK, Engineering Science and Mechanics, Penn State, ZHIYONG LI, DUNCAN STEWART, STANLEY WILLIAMS, Hewlett-Packard, THERESA MAYER, Ee, Penn State, DAVID ALLARA, Chemistry, Penn State — We discuss Raman spectroscopic analysis of self-assembled monolayers embedded in two different types of nano-structures capable of sustaining localized surface plasmon-surface plasmon polariton coupling via nanoscale gaps and curved surface features. Both structures consist of metal-molecule-metal (M3) junctions which can also allow charge transport through the molecular bridges. Our results indicate different electromagnetic and charge transport characteristics as a function of the top metal–molecule chemical interaction. We also report direct correlations between charge transport states, SERS response and inelastic vibrational scattering in selected M3 molecular electronic device junctions.

5:06PM T18.00012 Non-linear optics and local-field factors in liquid chloroform: A time-dependent density-functional theory study1. DAVID A. STRUBBE, Department of Physics, University of California, Berkeley, and Materials Sciences Division, Lawrence Berkeley National Laboratory, XAVIER ANDRADE, ANGEL RUBIO, European Theoretical Spectroscopy Facility, Universidad del Pais Vasco and Centro Mixto CSIC-UPV/EHU, San Sebastian, Spain, STEVE G. LOUIE, Department of Physics, University of California, Berkeley, and Materials Sciences Division, Lawrence Berkeley National Laboratory — Chloroform is often used as a solvent and reference when measuring non-linear optical properties of organic molecules. We calculate directly the non-linear susceptibilities of liquid chloroform at optical frequencies, using molecular dynamics and the time-dependent density-functional theory [X. Andrade et al., J. Chem. Phys. 126, 184106 (2007)]. We compare the results to those of chloroform in the gas and solid phases, and experimental values, and make an ab initio calculation of the local-field factors which are needed to extract molecular properties from liquid calculations and experimental measurements.

1Support: NSF IGERT Fellowship, NSF Grant No. DMR07-05941, US Dept. of Energy Contract No. DE-AC02-05CH11231, MEC (FIS2007-65702-C02-01), Grupos Consolidados UPV/EHU (IT-319-07) and EU e-I3 ETSF. Computational resources from NERSC.

5:18PM T18.00013 Time resolved photoluminescence studies of long lived emissive specie in F8BT:PFB blends. SIMON GELINAS, Regroupement Quebecois sur les Materiaux de Pointe, Departement de Physique de l’Universite de Montreal, IAN HOWARD, RICHARD FRIEND, Cavendish Laboratory, University of Cambridge, CARLOS SILVA, Regroupement Quebecois sur les Materiaux de Pointe, Departement de Physique de l’Universite de Montreal — Type-II heterojunctions play a crucial role in organic optoelectronic devices. We use donor-acceptor polyfluorene blends as a model system to understand excited-state dynamics at heterojunctions. These interfacial excitations are intrachain singlet and triplet excitons, geminate polaron pairs, and exciplexes (interfacial charge-transfer excitons). Time-resolved photoluminescence (PL) spectra were taken at 10 K and room temperature to investigate the interconversion dynamics of these species. We observe delayed PL with sub-linear excitation fluence dependence. This implies that delayed singlet exciton generation involves a bimolecular annihilation mechanism. By means of kinetic modeling, we propose triplet-triplet excitation annihilation as a regeneration route to singlet excitons, and subsequently to exciplexes. This points to a significant (<15%) yield of triplet excitons after interfacial charge separation, and to the central role of these species on the interfacial dynamics.

Wednesday, March 18, 2009 2:30PM - 5:30PM — Session T19 DPOLY: Theory and Simulation I

2:30PM T19.00001 Theory of polyzwitterionic solutions. RAJEEV KUMAR, GLENN FREDRICKSON, Materials Research Lab, UCSB — Conformations of polyzwitterionic molecules in aqueous solutions are investigated using the variational method. We have carried out self-consistent calculations for the degree of counterion adsorption on the zwitterionic sites and the size of a single polyzwitterionic chain. These calculations are used to analyze the solubility of these molecules in water. Results for the effect of an asymmetric counterion adsorption, electrostatic interaction strength, salt concentration, solvent quality, specificity of the zwitterionic monomeric units and the added salt on the conformations of the polyzwitterionic chain will be presented.
2:42PM T19.00002 Charge transport in conjugated polymers: a multiscale picture1. VICTOR RUEHLE, Max Planck Institute for Polymer Research, JAMES KIRKPATRICK, Imperial College London, KURT KREMER, DENIS ANDRIENKO, Max Planck Institute for Polymer Research — A framework to study charge transport in conjugated polymers using realistic morphologies is developed. First, the atomistic force field is refined using first-principles calculations. Systematic coarse graining is then performed to extend simulation times and system sizes accessible to molecular dynamics simulations. Material morphologies are generated using the coarse grained and atomistic models. Finally, the charge mobility is obtained using temperature activated hopping picture for charge transport [1]. The framework is tested on neutral and oxidized polypyrrole with different structural ordering [2].


1DPG is acknowledged for the financial support

2:54PM T19.00003 First principles electronic properties investigation of polythienoacene and its derivatives1. SIMON PESANT, PAUL BOULANGER, GUILLAUME DUMONT, MICHEL CÔTÉ, Département de physique et Regroupement québécois sur les matériaux de pointe (RQMP), Université de Montréal, Canada — The electronic properties of ladder-type polythiophene (polythienoacene) and its derivatives are studied using density functional theory. Upon an analysis of the variation of the band gap when comparing the non-ladder and the ladder-type polymers, a discrepancy is found between the thiophene and the pyrrole(nitrogen-substituted thiophene) polymer families. The polythienoacene has a larger band gap than the polythiophene whereas the opposite is found for the pyrrole polymers. Also, it is found that a simple alternation of the sulfur atom in polythienoacene structure by nitrogen or boron atoms can lead to small band gap polymers. The excitations of these polythienoacene’s derivatives are investigated using time-dependent density functional theory.

3:06PM T19.00004 Electronic structure and carrier transport in disordered conjugated polymers1. NENAD VUKMIROVIC, LIN-WANG WANG, Lawrence Berkeley National Laboratory — Thin films of realistic conjugated polymer materials contain both crystalline and amorphous regions, where the latter ones are less understood. This study was therefore focused on electronic structure and carrier transport in amorphous regions of polythiophene (PT) and poly(3-hexylthiophene) (P3HT). Atomic structures were obtained from classical molecular dynamics using a simulating annealing procedure and the charge patching method [1] was used to calculate the electronic structure. It was found that disorder in the electronic structure of P3HT comes from disorder in the conformation of individual chains, while in the case of PT there is an additional contribution due to disorder in electronic coupling among the chains [2]. The electron-phonon coupling matrix elements in P3HT were also calculated and carrier mobility due to phonon-assisted hopping was estimated.


3:18PM T19.00005 Ab initio Study of Diketo-Pyrrolo-Pyrrole Polymers for Photovoltaic Applications1. SIMON LÉVESQUE, JEAN FREDÉRIC LAPRADE, MICHEL CÔTÉ, Département de physique et Regroupement québécois sur les matériaux de pointe (RQMP), Université de Montréal, Canada — Using density functional theory with the hybrid functional B3LYP, we investigate the electrical and optical properties of polymers made with diketo-pyrrolo-pyrrole. It is found that the value of the band gap can be tuned by varying the number of thiophene units within the polymer. Band structure and time-dependent density functional theory results will also be presented.

3:30PM T19.00006 First-principles investigation of PVDF and its copolymers. V. RANJAN, LINING YU, North Carolina State University, Raleigh, NC, MARCO BUONGIORNO NARDELLI, J. BERNHOLC, North Carolina State University, Raleigh, NC and Oak Ridge National Laboratory, TN — Recently, PVDF and its copolymers have generated significant interest due to their electroactive properties [1] and potential for ultra-high energy-storage applications [2]. In this talk, we present the results of first-principles calculations of stable phases and dielectric properties of different copolymers and terpolymers of PVDF at varying concentrations. Our results show that at very high concentrations of Chloro-trifluoroethylene (CTFE), PVDF/CTFE displays sharp transitions between non-polar (α) and polar (β) phases. On the contrary, the same transitions in copolymers with trifluoroethylene (TrFE) and tetrafluoroethylene (TeFE) are not sharp and happen at lower concentrations. We discuss the interplay of copolymer admixture on the dielectric properties of PVDF and discuss the suitability of copolymers for energy storage and electroactive applications. [1] S. G. Lu et al., App. Phys. Lett. 93, 042905 (2008). [2] V. Ranjan et al., Phys. Rev. Lett. 99, 047801 (2007).

3:42PM T19.00007 Adaptive Tempering Monte Carlo Study of Dense Polypyrrole Systems1. YAFEI DAI, ESTELA BLAISTEN-BAROJAS, Computational Materials Science Center, George Mason University, Fairfax, VA 20030 — A modified rigid-ion polarizable model potential of polypyrrole is developed with parameters fitted on multiple points of the electronic energy surface of pyrrole oligomers (n-Py) of different sizes calculated with a hybrid density functional approach [1]. Using this potential, systems containing 192 chains (4-Py) and 64 chains (12-Py) were structurally optimized with the Adaptive Tempering Monte Carlo algorithm [2]. Energetics and structure of these systems were studied as a function of density. Both systems have characteristics of a liquid for densities in the range 0.66 – 1.09 g/cm³ at T=300 K. The oligomer radius of gyration is insensitive to density changes. However, an orientational order parameter shows a sharp increase as a function of density indicating a tendency of the chains to stack forming regions of aligned chains for the denser systems. [1] Y. Dai, E. Blaisten-Barojas, J. Chem. Phys. 129, 164903(2008); [2] X. Dong, E. Blaisten-Barojas, J. Comp. & Theo. Nanoscience 3, 118 (2006).

1Computational support from Teragrid grant PHY050026.
The interaction between two grafted monolayers in a good solvent is important in many applications, like nanocomposites, colloid stabilization, and polymer alloys. In our previous work [Jain et al., J. Chem. Phys. 128, 154910 (2008)], we showed that interfacial statistical associating fluid theory (iSAFT) density functional theory (DFT) successfully calculates the structure of the grafted polymer chains in the absence/presence of free polyatomic solvent. In the current work, we have applied iSAFT to calculate the force of interaction between two such grafted monolayers in implicit good solvent conditions. In particular, we have considered the case where the segment sizes of the free ($\sigma_f$) and grafted ($\sigma_g$) polymers are different. The interactions between the two monolayers in the absence of the free polymer is always repulsive. However, in the presence of free polymer, the force can be either purely repulsive or can have an attractive minimum depending upon the relative chain lengths of the free ($N_f$) and grafted polymers ($N_g$). The attractive minimum is observed only when the ratio, $N_f/N_g$, is greater than a critical value. We propose a scaling relation for this case, in agreement with self consistent field theory for ($\sigma_f = \sigma_g$).

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The authors gratefully appreciate ChemStations, Houston, TX for financial funding.

4:18PM T19.00010 ABSTRACT WITHDRAWN —

4:30PM T19.00011 Simulation of Microheterogeneous Networks and Extraction of Segment Orientation Behavior from D-NMR Spectra. BERNARDO AGUILERA-MERCADO, CLAUDE COHEN, FERNANDO ESCOBEDO, School of Chemical and Biomolecular Engineering, Cornell University — The degree of heterogeneity in the microstructure of end-linked elastomer networks has been shown to have a very strong impact on the network mechanical and elastic properties such as: ultimate strain, modulus, and toughness. Networks with crosslinks and chains inhomogeneously distributed are expected to exhibit heterogeneous segment orientation responses. The global segment orientation of systems with frozen inhomogeneities, and a significant amount of highly stretched chains at the unperturbed state, cannot be captured by measurements of the deuteron NMR spectra solely. Spectrum frequency splits quantify the segment orientation due to local excluded volume interactions only and do not account for the contributions arising from large end-to-end chain deformations. Long wings of the spectrum reflect the presence of strongly aligned segments ignored when one considers only the split. A new methodology based on the Maximum-Entropy method is proposed to find the probability density of an order parameter that describes the network segment orientation from which the global orientation behavior can be completely characterized. The methodology is validated with both molecular simulation and experimental data.

4:42PM T19.00012 Cooperative dynamics in polymer melts: a comparison of theoretical predictions with Neutron Spin Echo experiments. MARINA GUENZA, University of Oregon — We present a comparison between theoretical predictions of the Generalized Langevin Equation for Cooperative Dynamics (CDGLE) and Neutron Spin Echo data of dynamics structure factors for polyethylene melts. Experiments, performed by Zampoli and co-workers, cover an extended range of length- and time-scales providing a compelling test for the theoretical approach. Samples investigate include chains with increasing molecular weights, undergoing dynamics across the entangled to entangled transition. Measured center-of- mass mean-square displacements display a crossover from sub-diffusive to diffusive dynamics. The Generalized Langevin Equation for Cooperative Dynamics relates this anomalous diffusion to the presence of the interpolymer potential, which correlates the dynamics of a group of slowly diffusing molecules in a dynamically heterogeneous liquid. Theoretical predictions of the sub-diffusive behavior, its crossover to free diffusion, and of the number of macromolecules undergoing cooperative motion are in quantitative agreement with experiments.

4:54PM T19.00013 Equilibrium Partitioning of Polymers between Bulk Dilute Solution and Confining Pores. YANWEI WANG, FLEMMING Y. HANSEN, GUENTHER H. PETERS, OLE HASSAGER, Technical University of Denmark — We have developed a novel framework [1] for the description of the steric hindrance effect on polymers that are subject to confining geometries. The two main ingredients are (i) a new computational method, the Confinement Analysis from Bulk Structures (CABS) approach, which enables calculation of the equilibrium partition coefficient (pore-to-bulk concentration ratio) as a function of the confinement size solely based on snapshots of polymer configurations in bulk, and (ii) the definition of a new molecular size parameter, the steric exclusion radius, which permits collapsing all partition coefficient data for different polymers in the weak confinement regime onto a universal curve. Our latest development in extending the CABS method to cylindrical and spherical pores will be presented.


5:06PM T19.00014 Multivalent Nanoparticles: adsorption and organization of bidisperse polymer chains on a solid interface. FOLUSHO OYEROKUN, RICHARD VAIA, JOHN MAGUIRE, BARRY FARMER, AFRL — Multivalent nanoparticles: i.e. nanoparticles with two or more ligands attached to their surfaces, are used in a variety of scientific and technological applications. The most common protocols for synthesizing these multivalent nanoparticles involves immersion of the particles into a solution containing the various ligands or into a solution containing an excess of one ligand to drive a partial (solvent mediated) exchange reaction with a previously bound ligand. Despite intense experimental activities, the dependence of the surface coverage on free ligand concentration and solvent quality is still poorly understood. This study addresses the thermodynamics of adsorption of bidisperse end-functionalized polymer chains in a good solvent onto a flat surface. At equilibrium, the absorbed chains form a bidisperse polymer brush in contact with the solution. The role of the degree of bidispersity, adsorption energy, solvent quality on monomer concentration profile, brush height and degree of penetration of free short and long chains into the brush layer will be discussed.
5:18PM T19.00015 Molecular simulation of crystal nucleation of n-alkane melts. PENG YI, GREGORY RUTLEDGE, Massachusetts Institute of Technology — The homogeneous nucleation of a crystal phase is one of the most interesting phenomena of molecular fluids, yet the microscopic mechanism of which still remains poorly understood. It is even more a mystery in chain molecule systems because the chain connectivity could produce very different crystal nucleus conformations, which are important factors in determining the subsequent crystal growth process and the properties of the final product. In this work we report the results of molecular simulations of crystal nucleation of n-alkanes from the melt. A realistic united atom force field was employed. The crystal phase and melting behavior were first determined by ramping temperature in a set of molecular dynamics simulations. The adiabatic nucleation trajectory was then sampled using the Monte Carlo umbrella sampling technique. The surface energy of the crystal nuclei was calculated assuming a spherical nucleus model and compared with previous studies to validate our numerical definition of a crystal nucleus. We were also able to calculate the end and side surface free energies of a cylinder nucleus model from the simulation data without making further assumption. This method can be extended to study longer n-alkane molecules and the change of nucleus conformation as n increases.

Wednesday, March 18, 2009 2:30PM - 5:30PM –
Session T20 DPOLY: Focus Session: Magnetic Properties of Organic Semiconductors/ Surface Characterization of Organic Materials

2:30PM T20.00001 Magnetoresistance and magnetic-field-effects in organic semiconductor devices. MARKUS WOHLGENANNT, U. of Iowa — No abstract available.

3:06PM T20.00002 Photo-induced Magnetism and Spintronics in Organic Semiconductors1. JUNG WOO YOO1, The Ohio State University — Recent years have witnessed growing attention on manipulating spins in organic species. One of the interesting phenomena in organic-based magnets is controlling magnetic properties by optical stimulus, a property not exhibited in metallic magnets. Three classes of known phenomena and mechanism will be discussed: i) manipulation of number of spins by optically induced charge transfer in cyano-bimetallic complexes [1], ii) optical control of exchange coupling in Mn(TCNE)2 compound [2], iii) light-induced change of magnetic anisotropy in the magnetic semiconductor V(TCNE)x [3]. The second part of this talk will be devoted to ongoing research on transferring spin polarized carriers through organic semiconductors. Recently, there have been lively activities as well as controversies on the application of organic semiconductors for transporting spin information. However, the understanding of spin injection and transport in organic semiconductors is still limited. We will address detailed mechanisms for spin injection and transport in organic semiconductor film of our rubrene (C42H32)-based spin valve and potential applications of organic-based spintronics.

1This work was supported in part by the DOE, AFOSR, and NSF.

3:42PM T20.00003 Magnetic properties of TCNQF4 reacted with Ni(cod)2 , IAN TERRY, KIMBERLY QUINN, MAREK SZABLEWSKI, Department of Physics, Durham University, Durham, DH1 3LE, UK — Recently it was reported that a room temperature ferromagnetic material (Tc>400K), Ni2TCNQ, was synthesized by reacting the organic acceptor tetracyanoquinodimethane (TCNQ) with bis(1,5 cyclooctadiene) nickel (Ni(cod))2[1]. In the present work we report the magnetic properties of a material which was synthesized following the same chemical route as that of Ni2TCNQ, except tetrafluoro-tetracyanoquinodimethane (TCNQF4) was used instead of TCNQ. The new metal-organic compound shows qualitatively similar magnetic properties to Ni2TCNQ, with ferromagnetic behavior being observed at room temperature. The specific magnetic properties can be described by assuming that there is both a paramagnetic and ferromagnetic phase in the material, with the ferromagnetic phase having a measured Curie temperature of about 620K, close to that of nickel. TEM and XRD data provide evidence for the existence of nickel nanoparticles within the material. We conclude that nickel nanoparticles are produced during the synthesis and are probably responsible for ferromagnetic properties observed at room temperature. 1.R. Jain et al, Nature 445, 291, (2007).

3:54PM T20.00004 Magnetic and surface studies of transition metal complexes for molecular spintronics1, PATRICK TRUITT, RAMAN TALWAR, EZEKIEL JOHNSTON-HALPERIN, Dept. of Physics, The Ohio State University, NORBANI ABDULLAH, Dept. of Chemistry, University of Malaya, CARLY REED, NAMRATA SINGH, CHANDRANI CHATTERJEE, MALCOLM CHISHOLM, Dept. of Chemistry, The Ohio State University — We have synthesized organometallic complexes consisting of a transition metal ion chelated by amphiphilic ligands. This talk will focus on efforts to assess the suitability of these molecules for the creation of magnetically active monolayers via the Langmuir-Blodgett technique. The paramagnetic nature of the molecules is probed by SQUID magnetometry and EPR spectroscopy, demonstrating that the spin magnitude can be varied by chemical substitution of the transition metal ion. To study monolayer formation ability, the molecules are spread on a Langmuir trough and pressure-area isotherms are recorded under compression. Attempts to deposit monolayers onto substrates and to make electrical contact for transport measurements will also be discussed.

1Partial support for this research provided by the Ohio State University Institute for Materials Research under Grant No. IMR-G0010.

4:06PM T20.00005 Magneto-Transport in Polyaniline Nanofiber Network1, K. DENIZ DUMAN, N.-R CHIOU, V.N. PRIGODIN, Dept. of Physics, The Ohio State University, Columbus, Ohio; A.J. EPSTEIN, Dept. of Physics, Dept. of Chemistry, The Ohio State University, Columbus, Ohio — We report large magnetoresistance (up to 12% at 8 T and 3 K) for polyaniline nanofiber network composed of nanofibers with an average diameter of about 80 nm. The polyaniline nanofiber networks were synthesized via chemical oxidative polymerization [1] and were studied at low and high electric and magnetic fields for temperatures 2 K- 250 K for their magneto-transport behavior. A transition from positive MR (temperatures 75 K and below) to negative MR (temperatures 100K and above) is observed. The MR may be explained by possible competing mechanisms; shrinkage of the hopping wavefunction and quantum interference effect in the applied magnetic field. It is also noted that applied electric field affects MR. In the positive MR regime an increase in MR is observed as the applied electric field decreases. Detailed results of various polyaniline nanofiber samples and possible mechanisms responsible for the magneto-transport behavior will be discussed.

1Supported in part by NSF, DOE and OSU IMR.
4:06PM T20.00008 Perpendicular interaction between donor and acceptor molecules on Au (111) — U.G.E. PERERA, Department of Physics and Astronomy, Ohio University, Athens, Ohio 45701 USA, R. MISHIMA, Graduate School of Engineering Science, Osaka University, Japan, SAWAI HLA, Department of Physics and Astronomy, Ohio University, Athens, OH 45701 — The capability to modify the electronic properties of materials by the interaction between donor and acceptor molecules plays a significant role in molecular electronics. Formation of molecular charge transfer complexes have been observed for different donor acceptor system in a lateral configuration. Here, we present the structural and electronic properties of decamethylmanganocene (Mn(C5Me5)) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) molecules on a Au(111) surface at 4.6K using low temperature scanning tunneling microscopy (STM) to investigate the perpendicular interaction between the molecules. The molecular complexes were formed by depositing Mn(C5Me5) and Mn(C5Me5)2 onto predeposited TCNQ on Au(111). The TCNQ formed a well ordered self-assembled clusters on Au(111) and Mn(C5Me5)2 adsorbed either on TCNQ layer or on bare Au(111) surface. Perpendicular interaction between the Mn(C5Me5)2 and TCNQ were determined by means of conductance tunneling spectroscopy. This work provides an important step for manipulating and tuning charge state of molecules using donor-acceptor molecular systems. The research is supported by United States Department of Energy BES grant number DE-FG02-02ER46012.

5:18PM T20.00009 STM study of energy-storing photoactive organometallic molecules — JONG-WEON CHO, LUIS BERBIL-BAUTISTA, NIV LEVY, STEVE MEIER, K. PETER C. VOLLHARDT, MICHAEL F. CROMMIE, University of California at Berkeley and Lawrence Berkeley National Laboratory — (Fulvalene)tetracarbonyldiiridium (FvRu2(CO)4) molecules store light energy through photoisomerization. UV illumination of molecules in solution or in the solid state results in a conformational change to a high-energy photoisomer. Upon mild heating the molecule reverts to its original structure, liberating ∼1.3 eV. Many potential future applications of this molecule involving light energy storage requires understanding its switching behavior in a device geometry, i.e., at a surface. We have investigated self-assembly and switching behavior of FvRu2(CO)4 molecules on Au(111) using scanning tunneling microscopy at cryogenic temperatures and we will report on these studies.

9:00AM V2.00001 The low-force elasticity of single-stranded DNA — OMAR A. SALEH, Materials Dept., UCSB — Single-molecule manipulation experiments, in which a single polymer is stretched with a known force while its extension is measured, are typically described by ideal models (e.g. the worm-like chain or freely-jointed chain) that account only for the polymer’s local stiffness, but ignore long-range ‘excluded-volume’ interactions. Yet, the basic (and successful) Flory scaling theory indicates that long-range interactions must be included to describe the zero-force self-avoiding walk structure of a polymer. Here, we reconcile single-molecule force-extension data with scaling theories of polymer elasticity: measurements of denatured single-stranded DNA show a regime where the extension grows as a non-linear power law with force, in accord with previously-unproven ‘tensile blob’ models. Analysis of the salt dependence of this regime indicates that the polymer’s Kuhn length is proportional to the Debye length. This contradicts the classic Odijk-Skolnick-Fixman theory; I will discuss possible explanations for this discrepancy.


9:48AM V2.00004 Gene brushes on a chip: From crowding and the search problem to synthetic systems — ROY BAR-ZIV, Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot, 76100, Israel — We assemble DNA polymer brushes coding for entire genes on a surface by means of a new photolithographic approach. The gene density can be controlled from dilute to high density where the local concentration ~ Megabase pairs per micron cubed ~ is comparable to that in a bacterium. The gene brush, therefore, emulates the crowded medium of the cell, allowing us to study DNA transactions in vitro under native conditions. We find that transcription/translation from these gene brushes is highly sensitive to DNA density, orientation and composition. As a step towards multi-gene synthetic systems, we integrated on a chip two spatially separated gene brushes, and implemented a two-stage transcription/translation cascade.

10:24AM V2.00005 Confinement effects on folding of proteins and RNA — DEV THIRUMALAI, University of Maryland — No abstract available.
8:00AM V4.00001 Melting and Frustration in Temperature-Sensitive Colloids

ARJUN YODH, University of Pennsylvania — I will review experiments from my laboratory that employ temperature-sensitive microgel particles to induce novel phase behavior in suspension. This phenomenon offers a fantastic new variable for control of lyotropic suspensions. Recent experiments, for example, have enabled us to learn how three-dimensional crystals first begin to melt [1], to directly observe melting in 2-D wherein intermediate hexatic phases form [2], and to create geometrically frustrated colloidal “anti-ferromagnets” [3].

References:

8:36AM V4.00002 Equilibrium features in the arrested phase separation of PNIPAM microgels

VERONIQUE TRAPPE, Dept. of Physics, University of Fribourg, Switzerland — We investigate the arrested phase separation of poly-N-isopropylacrylamide (PNiPAM) microgels. At large enough concentrations we observe the formation of a macroscopic gel-body that exhibits a peculiar temperature dependence. In a temperature-range, where the volume of the individual particles no longer changes, the final dimension of the macroscopic gel body depends on the depth of the quench into the phase separation regime. Increasing the quench depth results in a decrease of the dimension of the gel-body; this is reminiscent of a thermodynamically driven phenomenon and contrasts with the fact that the formation of the gel-bodies is due to the arrest of a phase separation process.

9:12AM V4.00003 New materials with microgels

JIN-WOONG KIM, Amore-Pacific Co. R&D Center, 314-1, Bora-dong, Giheung-gu, Yongin-si, Gyeonggi-Do, 446-729, Korea — This talk introduces a flexible and straightforward method for generating responsive microgel materials with new structures by using a microfluidic technique. We demonstrate that this approach enables tight control over the size and monodispersity of droplets as well as the interfacial structures, which is essential for determining release and transport kinetics of encapsulated components. We also show that responsiveness of microgel materials is controllable by tuning their structure, thereby allowing us to overcome the limitation of length scales, since the diffusion of water molecules through the structured gel phase is much faster than through a bulk gel phase of similar dimensions. We have generated a variety of novel gel structures: microgels with complex structures, microgel shells, 3D gel network with a truly fast response, and responsive colloidosomes. The robustness and versatility of this approach are expected to generate more complex systems and create new possibilities to develop novel materials in practical applications, including drug delivery, foods, and cosmetics.

9:48AM V4.00004 Sublimation dynamics of colloidal microgel crystals

A. D. DINSMORE, University of Massachusetts Amherst Dept. of Physics — Polymer microspheres in suspension serve as a powerful model system for probing thermodynamic phase transitions. These particles are large enough to visualize using optical microscopy and the particle trajectories can be obtained with nanometer-scale resolution from the images. Equally important is the ability to tune the interactions among the particles using charge or adsorbed polymers to induce repulsion, or non-adsorbing polymers to induce attraction by the depletion effect. I will focus on short-ranged depletion attraction induced by micelles of molecular surfactants or triblock copolymers (Pluronic). Because the micellar size and concentration depend sensitively on temperature, the magnitude and range of the attraction can be tuned in situ. This approach lets us track individual microspheres as they form crystals following a quench, or as crystals sublime when superheated. We focus on systems where the particles are attracted to a flat surface by depletion and thus confined to two dimensions. We find that when crystallites are superheated, they first sublime by thermally-excited bond-breaking at the perimeter. Below a cross-over size, however, the crystallites rapidly become amorphous throughout, then evaporate very fast at an approximately diffusion-limited rate. The cross-over size varies from 20-100, depending on temperature and concentration. A similar two-stage process is followed during crystallization. During nucleation, we measure the free energy as a function of cluster size and thereby obtain interfacial tensions and chemical potentials. The results point to a thermodynamically meta- or unstable fluid phase, which is not found in equilibrium but which plays a key role in phase-separation dynamics according to Ostwald’s Rule. Results will be compared to experiments, simulations, and theory of crystallization of globular proteins.

10:24AM V4.00005 Phase behavior and rheology of ionic microgels

ALBERTO FERNANDEZ-NIEVES, Georgia Institute of Technology — Our aim is to understand and control the mechanical properties of dense microgel suspensions, where the softness of the constituent particles can have important effects over the macroscopic behavior. In particular, we are using ionic microgel particles based on poly(vinylpyridine), a monomer that ionizes with pH. When de-swollen, the particles are essentially charged hard spheres and crystallize at high enough volume fractions. By contrast, when the microgels are swollen, light and neutron scattering experiments show that the suspension does not crystallize, irrespective of particle density. But even more remarkably, these highly packed systems remain essentially liquid and do not seem to exhibit glassy behavior. This phenomenon is markedly different to that of ordinary colloids and suggests that the properties of the single particle can dramatically affect the phase behavior and mechanical properties of the packed suspension.

Thursday, March 19, 2009 8:00AM - 11:00AM — Session V18 DPoly DBP: Focus Session: Physics of Green Polymers and of Biocompatibility
8:00AM V18.00001 Spectroscopic Analyses of Microstructures Associated with Plant Based Polymers — SHAW LING HSU, Polymer Science and Engineering Department, University of Massachusetts at Amherst — Currently, less than 0.02% of polymers used are plant based with the rest originating from petroleum feedstock. The plasticification of agricultural residues is a significant opportunity to reduce the cost of the petroleum. Because of their size scale, it is most appropriate to use vibrational and NMR spectroscopy to characterize the microstructure of these plant based polymers. We present a number of examples in order to illustrate the use of these alternative polymers. Soybean is one of the most promising alternatives. Both its saturated and unsaturated components can be utilized. In various applications, the saturated component is important because the reaction pathways can be directed. The saturated component is especially significant if co-crystallization with other polymers, especially statistically random copolymers, is an important consideration. Crystallization kinetics and subsequent morphological units formed have yet to be characterized. In addition, the unsaturated component can be modified to form various polyols for use in reactive mixtures. The miscibility behavior of such polymers with other polyols or polymers strongly influences the reaction kinetics and the products formed. The extreme hydrophobic nature of soybean based polymers is reflected in that it has opposite physical properties to that of the hydrophilic polyols used in the current formulations. We also have significant interest in poly(lactic acid). We have characterized the inherent structural rigidity, correlating the changes in chain conformation to the chain conformation. We have identified the intermolecular forces which stabilized the crystalline units. In addition, we have been able to control the crystallization process resulting from addition configurational defects. These applications illustrate the opportunities we have available in a world which may embrace such a set of polymers.

8:36AM V18.00002 Toughening and Reinforcing Degradable Polymers to Extend their Properties and Applications — SUPING LYU, Medtronic Inc, JIANBIN ZHANG, ADAM BUCKALEW, JIM SCHLEY, BRYANT PUDIL, LIAN LUO, CHRIS HOBOT, MIKE BENZ, RANDY SPARER, JULIE TRUDEL — Polymer materials made from renewable feedstocks mainly are cellulose derivatives and aliphatic polyesters such as polylactide. There are two challenges in the use of these materials to replace petroleum based polymers. One is how to easily process these materials to make them into needed shapes and other is how to broaden the properties of these materials so that they can be used for applications where petroleum based polymers play major roles. Most of the renewable source based materials are brittle. This abstract presents a method of how to toughen and reinforce polylactide to make a family of polymers that cover broad ranges of toughness and strength for various applications such as biomedical device and applications. We identified the intermolecular forces which stabilized the crystalline units. In addition, we have been able to control the crystallization process resulting from addition configurational defects. These applications illustrate the opportunities we have available in a world which may embrace such a set of polymers.

8:48AM V18.00003 A QCM-D Study of the Enzymatic Degradation of Cellulose Thin Films — DAN GLICKMAN, OLEH TANCHAK, MICHAEL REID, AMANDA QUIRK, DARRELL COCKBURN, COLIN MACDOUGALL, ANTHONY CLARKE, JACEK LIPKOWSKI, JOHN DUTCHER, University of Guelph — A sophisticated surface-sensitive technique, the quartz crystal microbalance with dissipation monitoring (QCM-D), was used to study the interaction of a mixture of cellulolytic enzymes from the fungus T. reesi with cellulose thin films deposited onto polycrystalline gold surfaces. It was found that the cellulose chains can be degraded by a two processes that occur during the enzyme mixture-cellulose thin film experiment: adsorption of the enzyme to the film surface, and the subsequent degradation of the cellulose thin film. A model describing the measured frequency shift in the QCM data will be described, which gives excellent fits to the experimental data.

9:00AM V18.00004 An Atomic Force Microscopy Study of the Mechanism of Cellulose Biodegradation — AMANDA QUIRK, MAOHI CHEN, DARRELL COCKBURN, SARAH REGLI, ANTHONY CLARKE, JOHN DUTCHER, JACEK LIPKOWSKI, University of Guelph, SHARON ROSCOE, Academia University — Cellulose, a biopolymer consisting of long chain β-(1→4) linked glucose sugars, is used as structural material by plants and bacteria. Degradation of cellulose to glucose, a sugar easily fermented to ethanol, occurs by the enzymatic hydrolysis of cellulose by cellulase enzymes. The enzymes have a complex structure including carbohydrate binding modules and catalytic domains responsible for the binding and degradation of cellulose, respectively. Atomic force microscopy (AFM) was used to study native cellulose films prepared from Acetobacter xylinum using a novel application of the Langmuir-Blodgett technique. These films allowed AFM images of single fibers and their microfibril structure to be obtained. Further in situ AFM studies of single fibers were performed in solution using cellulolytic enzymes. The in situ degradation of cellulose fibers was monitored over 20-hours using AFM. These studies provided insight into the degradation timeline of a single fiber. Complementary studies of proteins adsorbed on cellulose fibers revealed information about the binding of the enzymes to the substrate. Studying the modular enzyme action separately will provide insight into the mechanism of cellulose binding and contribute to our understanding of the degradation process.

9:12AM V18.00005 Observation of Biodegradation of Cellulose Fibers Using Surface Plasmon Resonance Imaging — OLEH M. TANCHAK, SCOTT ALLEN, Department of Physics, University of Guelph, DARRELL COCKBURN, ANTHONY J. CLARKE, Department of Molecular and Cellular Biology, University of Guelph, JACEK LIPKOWSKI, Department of Chemistry, University of Guelph, JOHN R. DUTCHER, Department of Physics, University of Guelph — Cellulose is the most abundant biopolymer on Earth and can provide a renewable supply of ethanol fuel to replace fossil fuels. A fundamental understanding of the mechanisms of the biodegradation of cellulose is essential to the development novel enzyme systems that can efficiently and selectively degrade a variety of biomass substrates. A novel Surface Plasmon Resonance Imaging (SPRI) instrument was used to study the biodegradation of cellulose fibers anchored to a thiolated gold surface. The kinetics of binding of the inactive enzymes to cellulose fibers and their digestion by catalytically-active homologs will be presented.

9:24AM V18.00006 Sustainable Engineering and Improved Recycling of PET for High-Value Applications: Transforming Linear PET to Lightly Branched PET with a Novel, Scalable Process — CYNTHIA PIERRE, JOHN TORKELSON, Northwestern University — A major challenge for the most effective recycling of poly(ethylene terephthalate) concerns the fact that initial melt processing of PET into a product leads to substantial degradation of molecular weight. Thus, recycled PET has insufficient melt viscosity for use in high-value applications such as bottle blowing of PET bottles. Academic and industrial research has tried to remedy this situation by synthesis and use of “chain extenders” that can lead to branched PET (with higher melt viscosity than the linear recycled PET) via condensation reactions with functional groups on the PET. Here we show that simple processing of PET via solid-state shear pulverization (SSSP) leads to enhanced PET melt viscosity without need for chemical additives. We hypothesize that this branching results from low levels of chain scission accompanying SSSP, leading to formation of polymeric radicals that participate in chain extension and condensation reactions with other PET chains and thereby to in situ branch formation. The pulverized PET exhibits vastly enhanced crystallization kinetics, eliminating the need to employ cold crystallization to achieve maximum PET crystallinity. Results of SSSP processing of PET will be compared to results obtained with poly(butylene terephthalate).

9:36AM V18.00007 Spontaneously Formed Biocompatible Surfaces in Water by Segregation of Amphiphilic Block Copolymers — HIDEAKI YOKOYAMA, The University of Tokyo, TAKASHI ISHIZONE, Tokyo Institute of Technology, NAOYA TORIKAI, High Energy Accelerator Research Organization, JAROSLAW MAJEWSKI, Los Alamos National Laboratory, AYAKO OYANE, AIST — Reduction of hydrophobic interaction in water is important in biological interfaces. We have found that poly(styrene-b-oligo ethylene glycol methyl ether methacrylate) (PS-PENMA) segregates the PENMA block to the surface in hydrophobic environment such as in air or in a vacuum, and shows remarkable resistance against adsorption or adhesion of proteins, platelets and cells in water. We studied the interfacial structures between PS modified by the spontaneous segregation of PS-PENMA and water using neutron reflectivity and adhesion force measurement using atomic force microscope with hydrophilic probes. The interfacial structure and hydrophobic interaction depend on the number of ethylene glycol (EO) units in PENMA. PENMAs with two or more EO units show distinct swollen layers with two sharp interfaces at polymer/water interfaces, which effectively reduce hydrophobic interaction in water, while PENMA with one unit of EO displays broader single interface with unsatisfactory reduction.
9:48AM V18.00008 Electrosprun Nanofibers for Neural and Tissue Engineering, YOUNAN XIA, Washington University — Electrosprun has been exploited for almost one century to process polymers and other materials into nanofibers with controllable compositions, diameters, porosities, and porous structures for a variety of applications. Owing to its small size, high porosity, and large surface area, a nonwoven mat of electrosprun nanofibers can serve as an ideal scaffold to mimic the extra cellular matrix for cell attachment and nutrient transportation. The nanofiber itself can also be functionalized through encapsulation or attachment of bioactive species such as extracellular matrix proteins, enzymes, and growth factors. In addition, the nanofibers can be further assembled into a variety of arrays or architectures by manipulating their alignment, stacking, or folding. All these attributes make electrosprun a powerful tool for generating nanostructured materials for a range of biomedical applications that include controlled release, drug delivery, and tissue engineering. This talk will focus on the use of electrosprun nanofibers as scaffolds for neural and bone tissue engineering.

10:24AM V18.00009 Control of Protein Adsorption on Surfaces with Grafted Polymers, IGAL SZELEFFER, Northwestern University, JAN GENZER, North Carolina State University — Non-specific protein adsorption is the first process in the foreign body response. The molecular design of surface modifiers that prevent non-specific adsorption requires the understanding of the factors that determine protein adsorption. The hierarchy of time and length scales present in the adsorption requires a multiscale approach to treat the complexity of the process. We will discuss the driving forces that determine protein adsorption and how end-grafted polymers can be used to modify the ability of the proteins to reach the surface. We will show the differences between preventing protein adsorption thermodynamically and kinetically. For practical applications the relevant time scales are hours or days. We will show how a molecular approach can be used to study these time scales. In particular we will show two different levels of approximations based on a molecular understanding of the adsorption process that enables, through the proper integration of degrees of freedom, to determine the kinetics of adsorption over 16 orders of magnitude in time. This approach is applied to explain recent experimental observations carried out on orthogonal modified surfaces that suggest that protein adsorption is a universal function of the product of grafted polymer surface coverage and molecular weight.

10:36AM V18.00010 Optimization of Polymer Surfaces for Specific Targeting1, ELENA DORMIDONOVA, MATTHEW HAGY, SHIHU WANG, Department of Macromolecular Science and Engineering, Case Western Reserve University — Using Monte Carlo simulations we studied reversible binding between a polymer layer functionalized by ligands and a receptor surface. By analyzing distance-dependent profiles for the average number of ligands bound to receptors, the total free energy of polymer layer-cell surface interaction and the interaction force the influence of different design parameters of a polymer layer on the affinity and specificity of binding were investigated. We show that planar polymer layers with a smaller chain length and grafting density, larger degree of functionalization, and larger absolute binding energy exhibit higher affinity to the cell surfaces with a large density of mobile receptors. A high binding specificity can be achieved by the polymer layers with intermediate ligand-receptor binding energies or an intermediate number of ligands, as a larger binding energy or number of ligands lacks specificity while a smaller binding energy or number of ligands provides inadequate affinity. As a result, the optimal design of the polymer layers can be achieved by using several different strategies, which will be discussed.

1This work was supported by the NIH grant R21CA112436

10:48AM V18.00011 Cluster structure in urea aqueous solution and it’s effect on DNA denature1, HE CHENG, Dr., Prof., CHARLES C. HAN, BOUALEM HAMMOUDA — The existence of large cluster structure in urea aqueous solution is proved by Small Angle Neutron Scattering (SANS). Our results indicate that urea is a water-structure-breaker, and large urea cluster will be formed when its concentration is higher than 20 w%. This cluster is very stable, and almost do not change with temperature. The helix-to-coil denaturation transition of DNA was studied with various urea concentrations, to testify the solvent structure influence on this process.

1Joint Laboratory of Polymer Science and Materials, ICCAS, Beijing, China

Thursday, March 19, 2009 8:00AM - 11:00AM — Session V19 DPOLY: Focus Session: Hierarchically Ordered Systems 320

8:00AM V19.00001 Semi-crystalline PMMA Stereocomplex Fibers1, MATIJA CRNE, School of Chemistry and Biochemistry, Georgia Institute of Technology, SHIN-WOONG KANG, Department of Physics, Kent State University, JUNG OK PARK, School of Polymer, Textile and Fiber Engineering, Georgia Institute of Technology, SATYENDRA KUMAR, Department of Physics, Kent State University, MOHAN SRINIVASARAO, School of Polymer, Textile and Fiber Engineering, Georgia Institute of Technology — A mixture of isotactic and syndiotactic PMMA polymers forms a supramolecular helical structure, called “stereocomplex” PMMA, which is held together by non-covalent bonding. The helices can pack together, resulting in a semi-crystalline material with a melting point of 172°C. Furthermore, the solutions exhibit gelation behavior in appropriate solvents. We have utilized these properties to make oriented stereocomplex PMMA fibers by three different methods — wet spinning, gel spinning and electrosprun. These fibers are highly oriented and crystalline. They are resistant to high temperatures up to 160°C. They are also resistant to the PMMA polymerization conditions. We have examined the fibers using X-ray diffraction and Raman spectroscopy. The results agree with the recently proposed triple helical structure where two isotactic PMMA chains wrap around each other in a double helix and then the syndiotactic chain wraps around this double helix. The resulting structure is a triple helix with a 1:2 molar ratio of isotactic : syndiotactic PMMA.

1NSF GRANT # 0423619

8:12AM V19.00002 Hierarchically Organized Peptide Core-Silica Shell Hybrids, AYSEGUL ALTUNBAS, NIKHIL SHARMA, DARRIN J. POCHAN, University of Delaware, Department of Materials Science & Engineering, JOEL P. SCHNEIDER, UNIVERSITY OF DELAWARE, DEPARTMENT OF CHEMISTRY & BIOCHEMISTRY COLLABORATION — A biomimetic approach was applied for the fabrication of a 3D hybrid network that displays hierarchical organization of an inorganic layer around an organic self-assembled peptide fibril template. The 20 amino acid peptide used in this study consisted of alternating hydrophilic (lysine) and hydrophobic (valine) residues flanking a four amino acid turn sequence in the center. After intramolecular folding into a beta-hairpin conformation on addition of a desired solution stimulus, this peptide self-assembles into a 3D network of entangled fibrils rich in beta-sheet with a high density of lysine groups exposed on the fibril-surfaces. The lysine-rich surface chemistry was utilized to create a silica shell around the fibrils. The mineralization process of the fibrils was initiated under physiological conditions by adding the silica precursor, tetramethyl orthosilicate, to the pre-assembled hydrogel, which results in a porous silica network that retains the mesoscale structure of the peptide fibril network. Structural characterization via Transmission Electron Microscopy, cryogenic-Scanning Electron Microscopy, Small Angle Neutron and X-ray Scattering and mechanical characterization via oscillatory rheology will be presented.
8:24AM V19.00003 Hierarchically Structured Regioregular Conjugated Polymer via Evaporative Self-Assembly

MYUNGHWAN BYUN, ROBYN LASKOWSKI, Iowa State University, FENG QIU, The Key Laboratory of Molecular Engineering of Polymers at Fudan University, Shanghai, China, 200043; MALIKA JEFFRIES-EL, ZHOQUN LIN, Iowa State University — Regioregular conjugated polymers, poly (3-hexylthiophene) (P3HT) toluene solution was confined in a sphere-on-flat geometry. The geometrically constrained P3HT solution led to the formation an axially symmetric liquid capillary bridge, from which the consecutive “stick-slip” motion of the contact line of the solution due to the solvent evaporation was effectively regulated. As a result, hierarchical “snake-skin” like structures of high regularity were yielded, namely, the microscopic structures were composed of P3HT nanofibbers. This facile, one-step technique based on evaporative self-assembly opens up a new avenue for organizing semicrystalline conjugated polymers into two-dimensional patterns in a cost-effective and nondestructive manner

We acknowledge the supports from NSF (CBET-0730611), 3M, and the Key Laboratory of Molecular Engineering of Polymers at Fudan University, Ministry of Education, China.

8:36AM V19.00004 Combining Small Molecule with Block Copolymer: a Facile Approach to Direct Hierarchical Assembly of Nanoparticles, TING XU, University of California, Berkeley — Precise control over the spatial organization of nanoscopic building blocks over multiple length scales is a bottleneck in the “bottom-up” approach to generate technologically important materials. We demonstrate a new paradigm to control the hierarchical assembly of nanoparticles through the synergistic co-assembly of block copolymers (BCP), small molecules and readily available nanoparticles. Organizations of nanoparticles into one, two and three-dimensional arrays with controlled inter-particle separation and ordering were achieved without any chemical modification of either the nanoparticles or BCPs. The ordering and distribution of small molecules between different BCP blocks are temperature dependent, leading to responsive materials where the small distribution of the nanoparticles can be varied, changing the local environment and the areal density of the nanoparticles. The approach described is versatile; compatible with existing fabrication processes and enables a nondisruptive approach for the generation of functional devices.

9:12AM V19.00005 Hierarchical volume gratings by combining holographic-patterning and block copolymer self-assembly, MICHAEL BIRKRANT, RUSSELL MARRON, CHRISTOPHER LI, Department of Material Science & Engineering, Drexel University, Philadelphia, PA, LALGUDI NATARAJAN, VINCENT TONDIGLIA, TIMOTHY BUNNING, Materials Manufacturing Directorate, Wright-Patterson Airforce Base, OH — A novel hierarchical photonic crystal (HPC) was fabricated by combining top-down and bottom-up nanomanufacturing techniques. The hierarchical structure was fabricated from a volume of material by combining holographic patterning (HP) and block copolymer (BCP) self-assembly. The structure of the HPC was investigated as a function of the BCP architecture, BCP concentration and crystallization temperature. Upon heating the photonic crystal a red shift in the reflected wavelength occurs; but, an initial decrease in diffraction efficiency (DE) followed by an increase in DE indicates a non-monotonic change in the structure of the BPC. Upon cooling the reverse occurs reflecting the dynamic change in the hierarchical structure. Transmission electron microscopy, in-situ FTIR and optical spectroscopy were used to correlate the optical property change with BCP/HPC morphology. This approach could open a gateway to fabricating multifunctional hierarchical nanostructures.

9:24AM V19.00006 Heteroarm Star Block Copolyampholytes as Templates for Hierarchically-Ordered Polyelectrolyte-Surfactant Complexes, MATTHEW HAMMOND, CHAOXU LI, Univ. of Fribourg, Switzerland, CONSTANTINOS TSITSIKIANIS, Univ. of Patras, Greece, RAFFAELE MEZZENGA, Univ. of Fribourg, Switzerland — We report on the hierarchical ordering observed in dry, solid samples of polyelectrolyte surfactant complexes based upon a novel heteroarm star block terpolymer bearing short polystyrene (PS) arms and an equal number of longer poly(2-vinyllpyridine)-block-poly(acrylic acid) (PZP-b-PAAP) arms. The amphiphilic nature of the star block copolymer allowed for complexation to be carried out on either the PZV blocks (with negatively charged surfactants) or on the PAAP blocks (with positively charged surfactants), depending only on the pH at which the complexation reaction was carried out. X-ray scattering and transmission electron microscopy data reveal that the various complexes display self-organization on the length scale of the polyelectrolyte-surfactant complex (ca. 3 - 4 nm) and on that of the overall copolymer (ca. 20 - 40 nm), with the specific repeat distances and self-organized morphologies being dramatically affected by the choice of block to be complexed. This study clearly illustrates how topological design possibilities in hierarchical self-assembly of block copolymer-based supramolecular complexes can be greatly enhanced by increasing the level of complexity of the macromolecular templates used.

9:36AM V19.00007 Assembly of Organic/Nanoparticle Hybrid Systems, STEPHEN Z.D. CHENG, University of Akron, YINGFENG TU, CHUN YE, WENBIN ZHANG, XINFEI YU, RYAN M. VAN HORN, CHIEN-LUNG WANG — The structure, dispersion, and chemical functionality of particles in a material are critical to the material’s properties. We are working to build the scientific and technological foundations of using particles such as C60 and POSS to develop new, highly functional, self-assembled materials. These efforts have involved developing new synthetic techniques that are sufficiently efficient and precisely manipulate particles to control their dispersion and structure within the organic material. First, C60-polymer and POSS-polymer molecules have been synthesized. These materials are capable of crystallizing in solution, enabling the formation of highly conducting or insulating sheets on the basal surfaces of the crystals. Additionally, these molecules may form micelles in solution. Next, POSS-C60-porphyrin molecules were synthesized and were found to self-assemble into discotic columnar structures where the intimately arranged porphyrin core harvests photons and the C60 enhances charge transport, making these materials ideal for organic photovoltaic applications. Finally, C60-POSS conjugate molecules have been synthesized that crystallize into a bilayer structure with alternating conducting and insulating layers. From these investigations, we will develop how best to chemically incorporate particles into materials from a fundamental level for significant technological advancements.

9:48AM V19.00008 Quantification of the Molecular Topology for Hierarchical Macromolecules, GREGORY BEAUCAGE, University of Cincinnati — Hierarchical structures are often produced from ramified macromolecules such as comb, star, hyperbranched and dendritic polymers. We have recently derived a method for the description of complex molecular and nanostructural topologies based on a statistical analysis [1,2]. The method has been applied to a wide range of hierarchical materials from long chain branched polyelectrolytes, hyperbranched polymers [3], star polymers, H-branched polymers to cyclics, biopolymers [4], and branched nanostructured aggregates. This method, when applied to neutron scattering data, yields the mole fraction of a structure involved in branching, the number of branch sites, the average branch length, and the number if inner chain segments. Further, quantitative measures of the tortuosity or convolutions of the structure and the connectivity of the branching network can be made, opening a new window for our understanding of complex molecular topologies. This understanding has recently been applied to biological chain molecules to understand protein and RNA folding [4] for example as well as to aggregated, nanostructured, carbon soot.

10:00 AM V19.00009 Nanoparticle Assemblies via Self-Assembling Peptide Molecules, NIKHIL SHARMA, MATTHEW LAMM, JOEL SCHNEIDER, KRISTI KICK, University of Delaware. DARRIN POCHAN — The bottom up approach towards nano-scale patterning presents the possibility of creating hierarchical architectures through simple self-assembly strategies. Herein, we elucidate the self-assembly of different types of peptide molecules into unique nano-scale morphologies and demonstrate their application in the construction of linear arrays of inorganic nanoparticles. A 20 amino acid peptide, consisting of alternating hydrophilic (lysine) and hydrophobic (valine) residues flanking a central diproline turn sequence (VKVVKVKPVPTVKVKVKV-NH$_2$) was employed as a nano-scale template for the organization of 2nm gold particles. This peptide self assembles into a lamellated morphology in solution and has a periodic nanostructure consisting of alternating hydrophobic and hydrophilic layers with a lateral periodicity of 2.5 nm. Negatively charged gold nanoparticles are templated into the positively charged lysine layer through electrostatic interaction and are aligned within the template to form laterally spaced (2D) linear arrays. Also, a long chain alanine-rich polypeptide was used to create 1D nanoparticle assemblies. This peptide assemblies into fibrils with monodisperse widths and periodically along the length of the fibril. These functional groups bind nanoparticles that results in their spatially modulated linear arrangement.

10:12 AM V19.00010 Robust Three Dimensional Liquid Films through Nanoparticle Assembly, TZU-CHIA TSENG, ERIN MCGARRITY, PHILLIP DUXBURY, Michigan State University, AMALIE FRISCHKNECHT, Sandia National Laboratories, MICHAEL MACKAY, University of Delaware — We create three-dimensional thin liquid films that cover rough surfaces, typically thought to be un-wettable, by employing a nanoparticle self-assembly technique. In this technique, the nanoparticles assemble at the liquid-substrate interface during annealing and they stabilize the liquid-air interface by screening its interactions with the substrate. This results in robust liquid films capable of wetting surface protrusions that are greater than their thicknesses. In this work, blends of polystyrene and CdSe nanoparticles were spincoated onto silicon substrates containing sparsely distributed SiO$_2$ particles (circa 110 nm) and thermally annealed. Film profiles of different thicknesses (40-180 nm) were characterized using atomic force microscopy (AFM). Calculations based on a continuum theory were performed and found to be in agreement with the AFM profile data. Cross-sectional transmission electron microscopy (TEM) was performed to provide validation of the film profile contours and the 3D-assembly of the nanoparticles. This method could be used, for example, to enlarge the interfacial area for excitation dissociation in organic photovoltaic cells.

10:24 AM V19.00011 The path and motion of an electrospinning jet observed with videography and stereography, KAIYI LIU, The University of Akron, CAMDEN ERTLEY, DARRELL RENEKER, The University of Akron — An electrospinning jet illuminated with both a steady intense light and a short flash was stereoscopically recorded through a pair of prisms in a video, producing images of both traces of moving glints reflected from the surface of a jet and the instantaneous positions of the path of the jet. The relationship between the visual observation and the jet path described in the Reneker-Yarin model$^{1-2}$ was explained by analyzing the stereographic images. Computer modeling was used to elucidate the relationship between the onset of the bending instability and the bifurcation of a glint trace. The velocities and positions, in 3-dimensional space, of segments of a jet were calculated from the stereographic images. The distributions of velocities and positions of segments along the vertical direction were analyzed. A novel and facile method was used to observe the handedness of the coiled path of an electrospinning jet. 1. D.H. Reneker, A.L. Yarin, Polymer, Vol. 49, (2008) pp 2387-2425. 2. D.H. Reneker, A.L. Yarin, E. Zussman, H. Xu, Advances in Applied Mechanics, Vol. 41 (2006) pp 43-195.

10:36 AM V19.00012 Electrospinning Semicrystalline Block Copolymer Assemblies into Microfibers, KRISTEN ROSKOV, North Carolina State University, JAN MANNERS, University of Bristol, RICHARD SPONTAK, North Carolina State University — Cylindrical micelles consisting of a diblock copolymer composed of poly(ferrocenyldimethylsilane) (PFDFMS)-b-poly(2-vinylpyridine) (P2VP) develop in dimethylformamide (DMF), a P2VP-selective solvent, with lengths exceeding one micron. These self-assembled micelles are then incorporated into P2VP homopolymer solution and electrospun. Addition of the cylindrical micelles is found to improve the ability of P2VP to be electrospun and dramatically decrease the bead density that appears in the electrospun microfiber mat. Scanning and transmission electron microscopies are used to investigate both the surface and internal morphology of these fibers, along with the robustness of the micelles. The combination of self-assembled structures within a polymer matrix can lead to fascinating response behavior dependent on temperature; if the sample is heated and the melting point of PFS is surpassed, the micelles will melt and then form classical morphologies. In the case of self-assembled, conductive cylinders of PFS block copolymers, heating the sample destroys conductive pathways. The PFS-b-P2VP self-assembled cylinders have also been incorporated into other DMF-selective polymers to verify that the micelles remain intact upon electrospinning.

10:48 AM V19.00013 Electrospinning of native cellulose from nonvolatile solvent system, SHAN-SHAN XU, AIHUA HE, CHARLES C. HAN, Institute of Chemistry, CAS — Electrospinning of cellulose in a highly efficient RTIL of 1-allyl-3-methylimidazolium (AMIMCl) was investigated. It was found that the introduction of co-solvent dimethyl sulfoxide (DMSO) contributed to a continuous jet. The problems lying in nonvolatility and the high ionic strength of the RTIL were successfully resolved using a rotating copper-wire drum as a collector and solidifying the jet under high relative humidity. The water vapor played an important role in leading to “skin formation” which helped to stabilize the fibrous morphology, and finally smooth ultra-thin regenerated cellulose fibers were obtained.

Thursday, March 19, 2009 8:00 AM - 11:00 AM — Session V20 DPOLY: Thin Films and Adhesion II

8:00 AM V20.00001 ABSTRACT WITHDRAWN

8:24AM V20.0003 Physical Aging in Nanoconfined Polymer Films: Importance of 3D vs. 1D Thermal Contraction in the Resulting Physical Aging Response, CONNIE B. ROTH, ELIZABETH A. BAKER, Dept. of Physics, Emory University, Atlanta, GA 30322, PERLA RITTIGSTEIN, JOHN M. TORKELSON, Dept. of Chemical & Biological Eng., Dept. of Materials Science & Eng., Northwestern University, Evanston, IL 60208 — Studies of physical aging in confined geometries have reported conflicting observations of changes in physical aging rates with decreasing polymer film thickness. Accelerated physical aging with decreasing film thickness has been observed with gas permeation and ellipsometry in stiff backbone, so-called “high free volume,” polymers traditionally used in gas separation membranes. In contrast, no change or suppressed physical aging has been observed with fluorescence in flexible carbon-carbon backbone polymers. We have developed a new streamlined ellipsometry procedure that allows us to relatively quickly (~6 hrs) evaluate the physical aging characteristics of both stiff and flexible backbone polymers in a thin film geometry. We present measurements of physical aging rates using our new approach and compare these to existing results in the research literature. In addition, we also address the importance of 3D vs. 1D thermal contraction in the resulting physical aging response, which we believe is one of the key factors accounting for the observed qualitative differences in physical aging rate upon confinement from the existing studies.

8:36AM V20.0004 Segmental dynamics of supported and freestanding polystyrene thin films probed by dye reorientation, KEEWOOK PAENG, HAU-NAN LEE, STEPHEN SWALLEN, MARK EDIGER, University of Wisconsin-Madison — The dynamics of both freestanding and supported polystyrene thin films (down to 15 nm) were studied by measuring the reorientation of dilute dye molecules. Well below \( T_g \) dye molecules were photobleached using intense linearly polarized light creating an anisotropic distribution. The anisotropy decay was measured using circularly polarized light and probing fluorescence parallel and perpendicular to the bleaching beam during linear temperature ramping. Temperature ramping anisotropy measurements allow us to compare both dynamics and the distribution of relaxation times in thin and thick films. Both freestanding and supported thin films show faster and more broadly distributed dynamics than thick films. For 17.5 nm supported films, temperature ramping experiments show up to 14K shift in dynamics. The corresponding shift for 16.5nm freestanding films was 22K.

8:48AM V20.0005 Modeling Dielectric Relaxation in Simulations of Polymer Glasses and Thin Films, HENDRIK MEYER, Institut Charles Sadron, CNRS UPR22, Strasbourg, France, SIMONE PETER, J. BASCHNAGEL — We perform molecular dynamics simulations to study the dielectric relaxation of a bead-spring model for a polymer melt in the bulk and in supported films [1]. By assigning dipole moments parallel and perpendicular to the backbone of all chains in the completed simulation trajectories we calculate the dielectric spectra of so-called type-A polymers which exhibit relaxation processes due to the local motion of chain segments (“segmental mode”) and due to fluctuations of the end-to-end vector (“normal mode”). We find that the relaxation of both modes is enhanced in the films relative to the bulk. For the segmental mode this difference between film and bulk dynamics increases on cooling toward the glass transition. By a layer-resolved analysis of the segmental relaxation we show that the acceleration of the average film dynamics is a consequence of a smooth gradient in relaxation, originating from both interfaces where the segmental dipoles relax much faster than in the bulk.

9:00AM V20.0006 Neighboring Domains Perturb Glass Transition Temperature on Multilayer Films and Nanostructured Polymer Blend Systems, SOYOUNG KIM, CONNIE ROTH, RODNEY PRIESTLEY, JOHN TORKELSON, Northwestern University — The impact of free surface and polymer-substrate interfaces on the glass transition temperature \( (T_g) \) in nanoconfined geometries has been studied for over a decade. Free surfaces reduce the requirement for cooperative dynamics and tend to decrease \( T_g \); attractive interactions with a substrate interface reduce mobility and tend to increase \( T_g \). Employing a multilayer fluorescence technique, we show how the \( T_g \) dynamics of PS layers in nanoscale geometries has been studied for over a decade. Free surfaces reduce the requirement for cooperative dynamics and tend to decrease \( T_g \); attractive interactions with a substrate interface reduce mobility and tend to increase \( T_g \). Employing a multilayer fluorescence technique, we show how the \( T_g \) dynamics of PS layers are perturbed by immiscible polymer-polymer interfaces. We determine the length scale over which adjoining layers can perturb the \( T_g \) layer. Finally, we demonstrate the tunability of the \( T_g \) of ultrathin PS layers atop different types of polymers. Our results indicate that the cooperative segmental dynamics of an ultrathin PS layer are strongly coupled to the neighboring domains through the narrow polymer-polymer interface. These results suggest a novel route to create new material properties controlled by the type and thickness of polymers in a multilayer film geometry. Studies with nanostructured blends to monitor \( T_g \) perturbation by neighboring domain are also underway.

9:12AM V20.0007 Near Surface Dynamics of Polymers Probed with Nanoparticle Embedding, DONGPING QI, JAMES A. FORREST, Dept. of Physics and Astronomy, University of Waterloo — We use nanoparticle embedding to probe the dynamics of the near surface layer of glassy polymer films. We observe evidence for heterogeneous dynamics in the first 5-10 nm near the free surface of glassy polymers. We observe that the relaxation into the polymer immediately below the free surface is irreversible, even after a period of 1 year. On the other hand, further embedding (5-10 nm) appears to be reversible. The results are discussed in terms of possible models of near surface mechanical properties.

9:24AM V20.0008 Glass Transition of Thin Star Polymer Films, EMMANOUIL GLYNOS, University of Michigan, Ann Arbor, PETER GREEN, University of Michigan — The thickness dependence of the glass transition, \( T_g \), of thin film polystyrene (PS) star molecules, supported by SiO\(_2\) substrates, has been examined using spectroscopic ellipsometry and compared to the behavior of linear PS chains. Linear PS chains exhibit a film thickness dependence on SiO\(_2\) substrates, decreasing with decreasing film thickness, for thicknesses \( h \) less than approximately 45 nm. This thickness dependence, when normalized by the bulk \( T_g \), is observed for chains with a wide range of degrees of polymerization \( N \), from \( N < N_c \) (molecular weight between entanglements) to very large values of \( N \). The \( T_g \) of long chain star molecules, of low functionalities, \( f \), exhibit the same thickness dependence. However, as the degree of polymerization of an arm length, \( N_a \), decreases the thickness dependence undergoes a transition, wherein \( T_g \) increases with decreasing \( h \). These effects are discussed in terms of the role of architecture and entropic effects on the structure of the system. Implications on the chain dynamics will also be discussed.

9:36AM V20.0009 The Glass Transition in Ultra-Thin Polymer Films Confined between Structured Surfaces, VIKRAM KUPPA, University of Cincinnati, GREGORY RUTLEDGE, MIT — Molecular Dynamics simulations are used to probe the structure and dynamics of polymers in ultra-thin slit pores. The simulation setup follows the structure of polymer nanocomposites, depicting chains intercalated between layered inorganic silicates. The structure and dynamics of bead-spring oligomers are studied for different film thicknesses, surface-geometry interactions and temperature. In particular, we focus on the glass transition of the confined films as a function of layer thickness, interaction strength and density profiles: \( T_g \) is demonstrated to increase with confinement and attraction of the polymer with adjacent surfaces. The fragility of the polymer glasses is drastically different from the corresponding bulk system, and is shown to be dependent on the effective co-ordination number.

9:48AM V20.0010 Apparent changes in the molecular dynamics of thin polymer layers due to the impact of interfacial layers, ANATOLI SERGHEI, University of Massachusetts Amherst, MARTIN TRESS, FRIEDRICH KREMER, University of Leipzig, Germany — Possible mechanisms leading to an apparent faster glassy dynamics in thin polymer layers, as investigated by means of Broadband Dielectric Spectroscopy, are analyzed in detail. It is shown that manifold experimental findings can be traced back to the influence of interfacial sub-layers, where – due to the proximity to solid interfaces – the dielectric function of the polymer is altered and modifies, by that, the overall dielectric response of the polymer films. A large amount of experimental data is analyzed to evidence how the contribution of the interfacial dynamics combines with that of the bulk in order to give the total response of a thin polymer film. It is shown that the non-linear character of this combination could lead to apparently discrepant experimental results.
10:00AM V20.00011 Post-confinement Relaxation Behavior of Nanostructures on Polymer Surface, HUA-GEN PENG, YEN PENG KONG, ALBERT YEE, University of California, Irvine — Dimensional relaxation of nanostructures on polymer films was studied to understand dynamics at surfaces and post-confinement relaxation. Line gratings from 33 nm and up on PS surface were formed by nanoimprint lithography, and AFM was used to monitor their relaxation with time and temperature. When annealed at temperatures in the vicinity of the bulk Tg, the grating height slumps – or shrinks – as surface tension and other driving forces overcome the viscosity. The temperature for rapid slumping decreases at smaller and smaller gratings of all molecular weights, but a simple explanation based on enhanced surface mobility due to increased surface to volume ratio fails to explain the results. Analysis of viscosity shows that the stress from surface tension may cause shear thinning and thus contribute to the reduced nanostructure stability. More importantly, confinement of polymer chains to spatial dimensions comparable to or even smaller than the radius of gyration seems to enhance molecular relaxation, which may be the major factor for the surprisingly low slumping temperature.

1Acknowledgement goes to NSF (CMMI-0728352) and Zeiss Excellence Center at UC Irvine.

10:12AM V20.00012 Molecular weight and chain architecture dependence of glassy compliance of ultrathin freely standing polymer films, SHANHONG XU, GREGORY B. MCKENNA, Texas Tech University — Glassy compliance of ultrathin linear polystyrene films of different molecular weights was investigated with the novel nanobubble infiltration techniques developed in our lab. Previous work by O'Connell, Hutcheson and McKenna [1] indicates that the glassy compliance decreases as the film thickness decreases for a polystyrene sample with molecular weight of 1M g/mol. However the glassy stiffening is not nearly as dramatic as that observed in the rubbery plateau regime [2]. Preliminary results in the present work show that the glassy compliance decreases as the molecular weight increases. We are now examining a three-arm star polystyrene with branch molecular weight the same as that of the lower molecular weight linear material and eight-arm stars will also be investigated with the purpose of determining chain architecture effects on the glassy and rubbery behaviors of ultrathin polymer films.


1contact author

10:24AM V20.00013 Surface Chemistry Effects on the Reactivity and Properties of Nanoconfined Bisphenol M Dicyanate Ester in Controlled Pore Glass, SINDEE SIMON, QINGXIU LI, Department of Chemical Engineering, Texas Tech University — The influence of nanocoalnfection on the cure kinetics and glass transition temperature of a bisphenol M dicyanate ester/polycyanurate material is investigated as a function of surface chemistry and nanocoalnfection size in controlled pore glass (CPG). The glass transition temperature and conversion as a function of cure time is investigated using differential scanning calorimetry. The native CPG surface accelerates the cure of bisphenol M dicyanate to a larger extent compared to the silanized hydrophobic CPG presumably because of the catalytic nature of surface hydroxyl groups of the native pores. Two Tg’s are observed for both monomer and polycyanurate confined in the native CPGs. For the fully cured polycyanurate, the primary Tg is depressed by 60 K at 115 nm, and the secondary Tg is 10 to 33 K above the primary Tg. The length scale associated with the secondary Tg is approximately 0.8 nm. Based on the measurements of both Tg and sol content as a function of conversion, the network structure does not change upon nanocoalnfection.

2We acknowledge the American Chemical Society Petroleum Research Fund Grant 45416-AC7

10:36AM V20.00014 Relation Between Glass Transition Temperatures in Polymer Nanocomposites and Polymer Thin Films, JAMIE KROPKA, Sandia National Laboratories, VICTOR PRYAMITSYN, VENKAT GANESAN, The University of Texas at Austin — Motivated by recent experiments, we examine within a percolation model whether there is a quantitative equivalence in the glass transition temperatures of polymer thin films and polymer nanocomposites (PNCs). Our results indicate that while the qualitative behaviors of these systems are similar, a quantitative equivalence cannot be established in general. However, we propose a phenomenological scaling collapse of our results which suggests a simple framework by which the results of the thin films may be used to quantitatively predict the properties of PNCs. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under Contract DE-AC04-94AL85000.

10:48AM V20.00015 Finite Element Analysis of Nanoparticle embedding into glassy polymers, MARK ILTON, JAMES A. FORREST, Dept. of Physics and Astronomy, University of Waterloo — The embedding of rigid nanoparticles into the surface of thin film glassy polymers was modelled using a Finite Element Analysis. This method of analysis readily adapts to various material models, film thicknesses, and substrates. Moreover, it allows for modelling of the related hole relaxation process when embedded nanoparticles are removed from the film. Calculations using a viscoelastic constitutive model with depth dependent material properties are compared to recent experimental results. The results are discussed in the context of the proposed near surface enhanced dynamics in thin film glassy polymers.

Thursday, March 19, 2009 11:15AM - 2:15PM — Session W18 DPOLY: Focus Session: Mechanical Force Spectroscopy and Device Applications of Polymeric and Biological Materials

11:15AM W18.00001 ABSTRACT WITHDRAWN —

11:51AM W18.00002 Transitions of a tethered chain under tension, JUTTA LUETTMER-STRATHMANN, The University of Akron, Akron, Ohio, WOLFGANG PAUL, KURT BINDER, Johannes Gutenberg Universitaet Mainz, Germany — When the end of a polymer chain tethered to an attractive surface is pulled away from the surface, the force required to extend the chain depends on interactions with the surface as well as intrachain interactions. Similarly, when the chain is held fixed and the temperature is reduced, both adsorption and collapse transitions have a signature in the force-extension curve. In this work, we performed Monte Carlo simulations of the bond-fluctuation model with a Wang-Landau algorithm to determine the density of states in the state space of monomer-monomer contacts, monomer-surface contacts, and chain extension. We study the effect of tension on the collapse and adsorption transitions and calculate force-extension curves that may be compared with experimental data.
12:03PM W18.00003 Velocity Dependency of Dragging Force and Wetting Properties of High Viscous Liquids Using Constant Diameter Nanoneedle-Tipped AFM Probes. MEHDI YAZDANPANAH, ElectroOptics Research Institute and Nanotechnology Center, University of Louisville, MAHDI HOSSEINI, SANTOSH PABBA, CHARLES WALTER, JAYAN HEWAPARAKRAMA, ROBERT COHN, ELECTROOPTICS RESEARCH INSTITUTE AND NANOTECHNOLOGY CENTER, UNIVERSITY OF LOUISVILLE TEAM — A high aspect ratio and constant diameter Aa2Ga nanoneedle grown on an AFM cantilever was used to perform F-D experiments on four different molecular weights of PDMS surfaces. The needle is partially inserted into and retracted from the liquid surface in various scan speeds. The viscous drag force causes the cantilever to deflect and recorded as a function of vertical displacement of the needle for each scan speed. The viscosity of the liquid is calculated by fitting a model into experimental data. The results show that the viscosity has strong correlation with the scan speed. Due to simple geometry of the needles, F-D curves are also interpreted to study the wetting properties (i.e. dynamic contact angle, meniscus height) of the PDMS at different scan speeds. Also, F-D curves are interpreted for polymer fiber formation during the capillary thinning and meniscus stretching that shown a strong correlation between the fiber length and the stretching velocity.

12:15PM W18.00004 Mechanical Properties of Individual Microgel Particles, SARA HASHMI, ERIC DUFRESNE, Yale University — Microgels are important materials for both basic science and engineering and have wide applications from the study of phase transitions to the delivery of drugs. They have properties and functions that are distinct from other particulate mode of hydrogel materials, such as being responsive to various environmental conditions. The mechanical properties of microgels are environmentally sensitive, responding to temperature and pH. Our material of interest, poly(N-isopropylacrylamide) or NIPAM, undergoes a deswelling transition above a critical temperature. The deswelling behavior of this polymeric material has been thoroughly studied in ensemble microgel systems as well as in bulk hydrogel samples. We present measurements of the elastic properties of single microgel particles using atomic force microscopy. We observe a stiffening of the Young's modulus by an order of magnitude at temperatures well above the transition, where the cross-linked polymer network has fully collapsed. Interestingly, near the transition we observe a comparable softening of the material.

12:27PM W18.00005 Intrinsically Disordered Titin PEVK as a Molecular Velcro: Salt-Bridge Dynamics and Elasticity, JEFFREY FORBES, WANXIA TSAI, NIAMS/NIH, RICHARD WITTEBORT, Univ. of Louisville, KUAN WANG, NIAMS/NIH — Titin is a giant modular protein (3-4 MDa) found in the muscle sarcomere, where the intrinsically disordered and elastic PEVK segment plays a major role in the passive tension of skeletal and heart tissues. We have proposed that salt-bridges play a central role in the elasticity of PEVK. The 50 kDa engineered PEVK polyprotein shows well-resolved NMR spectra at all concentrations. From long-range NOE's, we observed stable K to E salt-bridges. Simulated annealing with NMR restraints yielded a manifold of structures for an exon 172 trimer. Steered molecular dynamics simulations were done to study how the manifold of salt-bridges evolves during the stretching experiment. Reduced SMD simulations at slow polymer stretching at 0.0005 nm/ps showed force spectra consistent with experimental AFM for a force on each of the poly(vinyl). SMD shows that salt-bridges occur even at high degrees of stretch and that these short-range interactions are in integral part of the mechanical properties of PEVK. We propose that the long-range, non-stereospecific nature of electrostatic interactions provide a facile mechanism to tether and untether the flexible chains, which in turn affect elasticity as well as control the accessibility of protein-protein interaction to these nanogel-like proteins.

12:39PM W18.00006 Mechanical Signal Filtering by Viscoelastic Properties of Cuticle in a Wandering Spider, MICHAEL E. MCCONNEY, Georgia Institute of Technology, CLEMENS SCHABER, University of Vienna, MICHAEL JULIAN, California State University Stanislaus, JOSEPH A.C. HUMPHREY, University of Virginia, FRIEDRICH BARTH, University of Vienna, VLADIMIR V. TSUKURK, Georgia Institute of Technology — As recently found, in mecha-sensors of wandering spiders (Cupinnius salei) viscoelastic materials are important in signal filtering. We used atomic force microscopy to probe the time dependent mechanical behavior of these materials in live animals. We measured Young's modulus of a rubbery material located between a vibration receptor and the stimulus source. Earlier electrophysiological studies had demonstrated that the strain needed to elicit a sensory response (action potential) increased drastically as stimulus frequencies went below 10 Hz. Our surface force spectroscopy data similarly indicated a significant decrease in stiffness of the cuticular material and therefore less efficient energy transmission due to viscoelastic effects, as the frequency dropped toward 0 Hz. The stimulus transmitting cuticular material is acting as a high-pass filter for the mechanical stimulus on its way to the strain receptors. Again our results indicate that viscoelastic mechanical signal filtering is an important tool for arthropods to specifically respond to biologically relevant stimulus patterns.

12:51PM W18.00007 Bacterial Cell Wall Peptidoglycan at Single Molecule Resolution, AHMED TOUHAMI, University of Guelph, MANFRED JERICHO, Dalhousie University, VALERIO MATIAS, Max Planck Institute, ANTHONY CLARKE, TERRY BEVERIDGE, JOHN DUTCHE, University of Guelph — The major structural component of bacterial cell walls is the peptidoglycan sacculus, which is one of nature's strongest and largest macromolecules that maintains the large internal pressure within the cell while allowing the transport of molecules into and out of the cell and cell growth. The three-dimensional structure of this unique biopolymer is controversial, and two models have been proposed: the planar model, in which the glycan strands lie in the plane of the cell surface, and the scaffold model, in which the glycan strands lie perpendicular to the cell surface. We have used atomic force microscopy to investigate the high resolution structure of isolated, intact sacculi of Escherichia coli K12 bacteria. Atomic force microscopy-single molecule force spectroscopy was performed on single sacculi exposed to the tAmiB enzyme which cleaves the peptide-glycan bonds. Surprisingly, the measurements revealed individual strands of up to 250 nm in length. This finding combined with high resolution AFM images recorded on hydrated sacculi and the stretching velocity.

1:03PM W18.00008 Unfolding polyelectrolytes in a strong DC electric field, PAI-YI HSIAO, KUN-MAO WU, Department of Engineering and System Science, National Tsing Hua University — The behavior of single polyelectrolytes in multivalent salt solutions under the action of an electric field is investigated by computer simulations. The variation of chain size against the strength of electric field displays a sigmoidal transition, which defines a critical field $E^+$ to unfold a chain. Above $E^+$, the chain is unfolded into a rodlike structure, aligned parallel to the field direction. We show that $E^+$ is a function of salt concentration and depends on the chain length via the scaling law $V^{-1/2}$ where $V$ is the ellipsoidal volume occupied by the chain. Moreover, the magnitude of the electrophoretic mobility of chain drastically increases during the unfolding. These findings provide a solid foundation to understand the fundamental properties of polyelectrolytes condensed by multivalent salt.

1:15PM W18.00009 Liquid Drop Pinning on Micro-patterned Surfaces, AHMED SOLIMAN, YEVENYI KALININ, ROBIN BAUR, ROBERT THORNE, LASSP, Cornell University — Pinning of liquid drops on surfaces is important in many areas of biotechnology. Micro-patterned surfaces provide a way to control drop pinning, and to investigate the mechanisms of pinning on real (rough) surfaces. Continuous circular rings on silicon wafers produced by etching the interior and surrounding silicon are shown to dramatically increase contact line pinning. The critical apparent contact angles and the pinning forces increase monotonically with the radius of the pattern and are predicted by a model, which is parameterized with parameters that describe the ring geometry, such as ring-wall height and width, as well as with surface energy (hydrophilicity / hydrophobicity). Micro-patterns of surfaces in this way can be used to improve droplet pinning, shape reproducibility and imaging in high-throughput protein crystallization.
1:27PM W18.00010 An Optical Biosensing Platform using Reprecipitated Polyaniline Microparticles1, LOUIS NEMZER, ARTHUR EPSTEIN, Ohio State University — A great deal of effort remains focused on the goal of developing a continuous in vivo glucose monitoring system for patients with diabetes mellitus. We report a proof-of-concept study on a reagentless optical biosensing platform that circumvents the problems usually associated with direct glucose detection by utilizing the UV-VIS absorption properties of polyaniline, a biocompatible polymer. When the enzyme glucose oxidase is entrapped within reprecipitated polyaniline microparticles, a glucose molecule readily donates two protons and two electrons to the polyaniline, reversibly altering the polymer's oxidation state. The resultant change can be monitored by measuring the absorption at wavelengths that fall within the “optical window” for skin. The micro-structured morphology also insures a high surface-area to volume ratio. Data from in vitro prototype devices indicate that in the low enzyme-loading regime, the response can be fit to the Michaelis-Menten model for enzyme kinetics, but at higher enzyme loading, diffusion effects dominate. As a biosensing platform, the system also has the potential to be adapted to detect other biologically relevant analytes, including cholesterol and ethanol.

The authors deeply appreciate the help of Nan-Rong Chiou and the support from the NSF under IGERT (0221678) and NSEC (EEC-0425626).

1:39PM W18.00011 Patternning of Ferritin Nanoparticles on Gold Posts of Silicon Substrate1, YUNXIA HU, DIAN CHEN, SOOJIN PARK, TODD EMRICK, THOMAS RUSSELL, Dept. of Polymer Science and Engineering, University of Massachusetts Amherst, HITACHI COLLABORATION — Patternning and immobilizing protein nanoparticles with nanometer-scale control has been proven integral to a range of applications in the development of biochip arrays, biosensor and electronic devices. Protein nanoparticles, such as ferritin nanoparticles, have a uniform size distribution and shape that can be used to construct well-defined patterns with nanoscale features. Here, the gold posts on silicon were produced using block copolymer PS (47.6 kg/mol)-b-P4VP (20.9 kg/mol) (PDI: 1.14) as a template and then gold chloride solution was loaded into P4VP domain. After reducing gold salt into gold and removing the block copolymer using anoxygen plasma, producing a pattern of gold posts. Thiol modified horse spleen ferritin are anchored to silicon substrate by the binding of thiol and gold. Scanning electron microscopy (SEM) shows that the feature size of gold posts decreased from 30 nm to 13 nm after attached with modified ferritin nanoparticles, which is consistent with size of modified ferritin. Also XPS result shows nitrogen and ion elements on ferritin-attached gold posts, and the signal of gold was attenuated after ferritin attached.

This work was supported by MURI, DOE and MRSEC.

1:51PM W18.00012 Rapid Hydrogel Microactuator Using Elastic Instability, HOWON LEE, CHUNGUANG XIA, NICHOLAS FANG, University of Illinois at Urbana-Champaign — Rapid Hydrogel Microactuator Using Elastic Instability Inspired by rapid movement of sensitive plants such as Venus flytrap [1], we present an innovative way to enhance actuation speed of hydrogel micro devices by exploiting elastic instability. In this work, hydrogel micro devices in doubly curved shape are designed and fabricated using projection micro-stereolithography[2], with embedded microfluidic channels on the surface. Local swelling of hydrogel around channels causes bending which subsequently induces stretching of the soft structure. Such coupling gives rise to elastic instability, the onset of which triggers rapid conversion of stored elastic energy into kinetic energy in fast motion. We further designed a set of devices with different dimensions, which leads to different coupling of elastic energy in bending and stretching [1]. Our experimental results verified the critical coupling parameter that triggers snap-buckling motion. Ongoing experiments are investigating the actuation speed as a function of coupling parameter. This novel approach promise new potential applications for hydrogel based devices in various fields of study including microfluidics, soft robotics, artificial muscle, and drug delivery. Reference [1] Forterre, Y., et al, Nature, 433, 421-425 (2005) [2] Sun, C., et al, Sensors and Actuators A, 121:1, 113-120 (2005)

2:03PM W18.00013 Effect of Single Bacterium Cell and DNA Attachment on the Electrical Properties of Chemically Modified Graphene Sheets, NIHAR MOHANTY, VIKAS BERRY, Kansas State University — Chemically modified graphene (CMG) sheets are expected to have a considerably different electrical sensitivity to molecular attachment than the pristine graphene sheets. Here we present the electrical-interfacing properties of (a) CMG’s hybrids with single bacterial cells, (b) CMG with DNA (single and double stranded) tethered on graphene-surface and (c) CMG with polyelectrolyte-layer assembled on surface. These hybrids function as: (a) single bacterium devices, (b) DNA hybridization sensor and (c) charge polarity sensitive chemical-detector, respectively. A single bacterium attachment leads to generation of ~1400 holes on a CMG while hybridization of ~4 DNA molecules on graphene-DNA-carpets lead to generation of one hole. Further explanation of the attachment-potential, system-reversibility and sensitivity will also be presented.

Thursday, March 19, 2009 11:15AM - 2:15PM — Session W19 DPOLY: The Physics of Polymer Nanocomposites: Grafting and Dispersion

11:15AM W19.00001 A theoretical study of polymer grafted nanoparticles as fillers in polymer nanocomposites, ARTHI JAYARAMAN, University of Colorado-Boulder, KENNETH SCHWEIZER, University of Illinois-Urbana — We have generalized the microscopic Polymer Reference Interaction Site Model (PRISM) theory to study the structure and phase behavior of polymer-tethered spherical nanoparticles (fillers) in a homopolymer matrix. In the absence of a polymer matrix, melts of polymer-tethered nanoparticles show strong concentration fluctuations indicative of aggregate formation and/or a tendency for microphase separation as the total packing fraction and/or nanoparticle attraction strength increase. In the presence of a polymer matrix there is competition between nanoparticle attractions, steric repulsion between grafted polymers, and polymer matrix induced depletion-like attraction. For single tethered particles, volume of the tether being equal to the volume of the nanoparticle, the apparent microphase spinodal curve exhibits both dilution-like and depletion-like features, and a non-monotonic dependence on matrix chain length. As the particle size and tether length are increased, such that the total space filling volume of the tether continues to equal the nanoparticle volume, the shape of the microphase spinodal curve remains unchanged, but the effect of matrix polymer chain length on the spinodal temperature diminishes. The effect of various parameters on the spinodal temperature will be presented.

11:27AM W19.00002 Highly-branched anisotropic hybrid nanoparticles at surfaces, VLADIMIR TSUKRUK, Georgia Tech — We present a brief overview of our recent studies on combined hybrid anisotropic structures composed of inorganic nanoparticles and highly branched molecules such as modified silsesquioxanes polyhedra cores (POSS) with mixed hydrophobic-hydrophilic tails and silver nanowires with functionalized star block copolymer with embedded gold nanoparticles (nanocobs). We demonstrate two-stage melting of that branched POSS and their ability to form monolayer and multilayered LB structures. On the other hand, we observed that silver-BCP-gold nanocobs display extremely bright Raman scattering caused by surface enhanced Raman effect with very different longitudinal and transversal optical properties as revealed by high-resolution confocal Raman microscopy. To study these hybrid nanostructures we applied combined AFM, SEM, TEM, XPS, SERS, UV-vis, and XR techniques.
11:39AM W19.00003 Particle Dynamics within Self-Assembling Polymer-Grafted Spherical Nanoparticles, PINAR AKCORA, University of Missouri, SANAT K. KUMAR, Columbia University, YU LI, BRIAN BENICEWICZ, University of South Carolina, SURESH NARAYANAN, Argonne National Laboratory, COLUMBIA UNIVERSITY COLLABORATION, UNIVERSITY OF SOUTH CAROLINA COLLABORATION — We have recently shown that the self-assembly of polymer grafted spherical nanoparticles can be achieved by varying the brush grafting density and chain length. The mechanical behavior of these nanocomposites with various states of particle dispersion has been explored using x-ray correlation spectroscopy. Nanoscale and macroscopic dynamic measurements show that mechanical reinforcement results from the percolated and also strongly entangled brushes forming strong networks. Particle dynamics within various polymeric nanostructures will be discussed.

11:51AM W19.00004 Thermally Stable Au Nanoparticles via Photo-crosslinkable Polymeric Stabilizers, JOONA BANG, MISANG YOO, Korea University, BUMJOON J. KIM, KAIST — Polymer nanocomposites consisting of polymers and inorganic nanoparticles (NPs) have attracted many interest due to their applications such as solar cell, sensors, catalysts and ferroelectric devices. To integrate NPs into polymer matrix in the controlled manner, thiol-terminated stabilizers have been used to tune the surface property of NPs such as Au, Pt, CdSe, etc. However, a practical application of such particles in the nanocomposites is very limited by thermal instability even at ~90 °C, leading to the agglomeration of NPs. To impart the thermal stability of NPs, we modified Au NPs surface using UV-crosslinkable polymeric stabilizers. After UV-crosslinking, it was found that the Au NPs exhibit the excellent stability at high temperature (~180 °C) in both solution and thin-film states. Furthermore, we demonstrate that thermally stable Au NPs can be used as compatibilizers in PS/PMMA blends. The NPs at the PS/PMMA interface produced the dramatic reduction in the droplet size after 1 day of thermal annealing at 180 °C, in which the particle size is unchanged.

12:03PM W19.00005 Design of Polymer-Grafted Particles for Biocompatibility, DAVID TROMBLY, VENKAT GANESAN, Department of Chemical Engineering, University of Texas at Austin — Drug designers often coat drug particles with grafted polymers in order to introduce a net repulsion between the particles and blood proteins. This net repulsion results from the energy cost of compressing grafted chains on approach of proteins. It thus overcomes the Van Der Waals attraction between drug and protein which would otherwise cause particle-protein agglomeration and ultimately thrombosis. This study proposes to develop a fundamental understanding of the role of different features in controlling the efficacy of the grafted layers. We address this issue by developing a framework to predict the interactions between a polymer-coated spherical particle and a bare spherical particle. In order to fully capture the two-sphere system, a numerical solution of polymer mean field theory is used in a bispHERical coordinate system. Results for protein-particle interaction energies for different design parameters will be presented. For biological applications, polyethylene glycol is often used as the grafted polymer. The unique properties of this molecule will be accounted for using the n-cluster model.

12:15PM W19.00006 Synthesis of Polystyrene-Silica Composite Particles via One-Step Nanoparticle-Stabilized Emulsion Polymerization, LENORE DAI, HUAN MA, Department of Chemical Engineering, Arizona State University — Polystyrene-silica core-shell composite particles are prepared by one-step emulsion polymerization with a nonionic initiator VA-086, solely stabilized by silica nanoparticles. The silica nanoparticles are successfully incorporated into the shell, likely due to the fact that the nanoparticles are thermodynamically favorable to self-assemble and remain at the liquid-liquid interfaces during the emulsion polymerization. The silica content, determined by thermogravimetric analysis, is approximately 20 wt% in addition, we further explore the polymerization mechanism by studying the particle growth as a function of initiator concentration and reaction time: when the silica/monomer ratio is increased from 0.83 without reaction time decreases for a fixed monomer amount, probably due to a larger number of nuclei at the initial stage of polymerization. Further increasing the initiator/monomer ratio to 4.2 wts, which may be limited by the stabilization provided by a fixed concentration of silica nanoparticles. The surface coverage also changes with initiator concentration and reaction time although the underlying mechanism is not fully understood.

12:27PM W19.00007 Effects of Grafted Chain Density on Nanoparticle and Melt Structure, JOSHUA KALB, SANAT KUMAR, Columbia University, ROBERT S. HOY, University of California, Santa Barbara, GARY S. GREST, Sandia National Laboratories — Applications of nanoparticles have increased dramatically over the last few years with uses ranging from scratch proof glass to lubricants to fighting cancer. Grafting polymer chains to these systems further increases the range of their properties, but still much remains to understand about the behavior of ‘brush grafted nanoparticle’ systems, particularly in their interaction and entanglement with a polymer melt. Previous works where polymer brushes were attached to a flat surface have demonstrated that entanglements between the attached chains and the polymer melt depend strongly on coverage and length of the attached chains. Allowing for a curved grafted nanoparticle surface allows for a wider range of interactions with the melt. Here we present molecular dynamics simulations of the structure of grafted nanoparticles and their entanglements with a highly entangled melt. Individual entanglements are identified using a modified version of primitive path analysis.

12:39PM W19.00008 Polyethylene/organically-modified layered-silicate nanocomposites with antimicrobial activity, P. SONGTIPYA, M.M. JIMENEZ-GASCO, E. MANIAns, Departments of Materials Sci & Eng and Plant Pathology, Penn State University — Despite the very intensive research on polymer nanocomposites, the opportunities for new functionalities possible by nanofillers still remain largely unexplored. Here, we present polyethylene/organic nanocomposites that exhibit strongly enhanced mechanical performance and, at the same time, also an antimicrobial activity originating from the organo-filler nature. Specifically, PE/organically-modified layered-silicate nanocomposites were prepared via melt-processing, and antimicrobial activity was designed by proper choice of their organic modification. Their antimicrobial activity was measured against several microorganisms and three reference fungi (Penicillium roqueforti and claviforme, and Fusarium graminearum) as model soilborne plant and food contaminants. Montmorillonite-based organofillers, which only differ in their organic modification, were used to exemplify how these surfactants can be designed to render antifungal activity to the nanocomposites. The comparative discussion of the growth of fungi on unfilled PE and nanocomposite PE films is used to demonstrate how the antimicrobial efficacy is dictated by the surfactant chemistry and, further, how the nanocomposites’ inhibitory activity compares to that of the organo-fillers and the surfactants.

12:51PM W19.00009 Modeling of block copolymer/nanoparticle nano-composites, MARCO PINNA, University of Central Lancashire, Preston, UK, IGNACIO PAGONABARRAGA, University of Barcelona, Spain, ANDREI ZVELINDOVSKY, University of Central Lancashire, Preston, UK — We develop a coarse grained simulation technique to study dynamics in soft nano-composites. The system consists of block copolymer melt with embedded nano-size particles. The time evolution of the system is described by a hybrid method combining a field based simulation for block copolymer component and a particle based method for nano-colloids. The block copolymer is modelled by cell dynamics simulation technique, and nano-particles are modelled as soft particles with prescribed density profile. A cross interaction term is controlling the interplay of dynamics of both components. The influence of nanofillers on block copolymer morphology is investigated.
further insight into the factors that determine the conformation of PPEs. Molecular dynamics simulations have shown that short alkyl PPEs are fully stretched out. With increasing molecular weights they assume a worm-like configuration. The current study provides additional insights into the conformational behavior of PPEs, taking into account the interplay between the polymer and the nature of the side chain, with the aim of understanding how these factors affect the behavior of PPEs in dilute solutions.

Para-polyphenyleneethylenes (PPEs) are electro-active polymers that have been studied extensively in dilute solutions. The conformation of PPEs determines the conjugation of the polymer and their assembly in the bulk. This, in turn, affects the material's properties, such as optical and electrical behavior. The current study investigates the effects of molecular weight and the nature of the side chain on the conformation of PPEs, providing a deeper understanding of their behavior in dilute solutions.

The study employs molecular dynamics simulations to investigate the conformation of highly rigid di-substituted PPEs in dilute solutions. The simulations consider the interplay between the polymer and the nature of the side chain, with the aim of understanding how these factors affect the behavior of PPEs in dilute solutions.
11:27AM W20.00002 Crystal and Rotator Phases of n-alkanes: a Molecular Dynamics Study  
NATHANIEL WENTZEL, SCOTT T. MILNER, Pennsylvania State University — The odd n-alkanes exhibit a wide variety of solid phase behavior; experimentally observed phases include an orthorhombic crystal phase, in which the molecules show long range herringbone order, and rotator phases in which the molecules do not diffuse but display various degrees of disorder. The rotator phases are of interest because they are implicated in the nucleation of n-alkane and polyethylene crystals. $C_{23}$ has been found experimentally to have two stable rotator phases, orthorhombic $R_I$ and hexagonal $R_{II}$, at temperatures between the crystal and melt. The crystal–$R_I$ and $R_I$–$R_{II}$ phase transitions are observed to be weakly first order. Simulations of $C_{23}$ to date have found the $R_I$ phase but not the $R_{II}$ phase, and have not much characterized the phases or the transitions between them. We report our results for local order and pretransitional fluctuations of rotator phases, from our all-atom molecular dynamics simulations of thin layers of $C_{23}$. We also comment on how these properties relate to the experimentally observed phase transitions.

11:39AM W20.00003 Computational Modeling of Polymers and the Influence of Molecular Level Structural Features on Mechanical Properties  
THOMAS CLANCY, SARAH-JANE FRANKLAND, National Institute of Aerospace — The role of molecular structure on the mechanical properties of polymer based materials is investigated through atomistic based molecular dynamics simulations. Models of crosslinked polymers were built with a range of moisture content in order to study the effect of environmental exposure on mechanical properties. Another key structural parameter, the degree of crosslinking, was also varied. The molecular structural features associated with these parameters are studied for their influence on the mechanical properties. The relative motion of crosslink points and the influence of penetrants such as water are investigated under deformation conditions. The mobility of penetrants within the polymer matrix is studied under equilibrium and deformation conditions in order to assess the role of these structural features on the mechanical properties as well as to assess the influence of deformation on diffusion rates.

11:51AM W20.00004 Hydrogen Bonding Structure in Hyperbranched Aliphatic Polyesters Studied by MD Simulations  
BRIAN OLSON, MUKUL KAUSHIK, SERGEI NAZARENKO, University of Southern Mississippi — Hyperbranched aliphatic polyesters based on dimethoxy propionic acid (bis-MPA) as the repeating unit and ethoxylated pentaerythritol as the tetrafunctional core gained widespread attention due to their unusual structure and properties. These globular macromolecules possess a large number of hydroxyl functional groups in particular on their periphery. These hydroxyl groups interact readily through hydrogen bonding (HB) and form clusters responsible for many physical properties of this system. The structure of these clusters however remains unclear. Therefore MD simulations have been used to elucidate the structure of these clusters. MD simulations revealed that peripheral hydroxyl groups form linear hydrogen bond clusters (strings) similar to those proposed in hydrofluoric acid (HF) but considerably shorter consisting of 4-10 hydroxyl groups per cluster. Simulations also led to prediction of WAXS pattern for these hyperbranched polyesters in the bulk with the characteristic peak at 20° = 30° due to O-O correlations similar to those in water. The predictions were in excellent agreement with the experimental WAXS data.

12:03PM W20.00005 Phases of functionalized polymer-inorganic composites in solution studied via molecular dynamics  
JOSHUA ANDERSON, RASTKO SKNEPNEK, ALEX TRAVESSET, Iowa State University and Ames Laboratory — Using self-assembling polymer systems to direct the formation of inorganic crystals, polymer-inorganic composite materials offer new opportunities in materials design. Molecular dynamics simulations allow for an exploration of the wide range of phases in these systems. Amphiphilic ABA triblocks with A hydrophilic, B hydrophobic, and functional ends with an affinity to inorganic particles are modeled to capture the minimum physics needed to describe polymer-inorganic systems currently being investigated by experiment. A number of phases are formed in solution as the attraction strength between the inorganic particles and the affinity of those particles to the functional end beads of the polymer are varied. Some of the phases found include hexagonal, square columnar, lamellar, perforated lamellar, and the gyroid. Polymer stretching plays an important role in each of the phases found, with a characteristic multi-modal behavior in the polymer end to end distance distribution. In the gyroid phase, for instance, the peaks correspond to the polymers being in two preferred conformations: v-shaped with a small end to end distance and fully extended in a line with the largest possible end to end distance. At high interaction strengths, inorganic particles are found to crystallize and form plate-like structures.

12:15PM W20.00006 The effect of chain stiffness on the structure and phase behavior of diblock copolymer melts  
G. LEUTY, MESFIN TSIGE, Southern Illinois University at Carbondale — In block copolymers the covalent bond joining the different immiscible block segments prevents the occurrence of macroscopic phase separation of the different components of a copolymer chain. Instead, the block segments give rise to well-organized periodic domain nanostructures whose size and shape mainly depend on the dimensions of the blocks and the segment-segment interaction parameters. Variations in the stiffness of the different block segments can directly affect the morphology of the system and may result in a very rich phase behavior. To the best of our knowledge, there is no theory at the atomic or molecular level that explains how variations in the stiffness of the different block segments can affect the dynamics and morphology of these systems. We have studied the microphase separation of symmetric diblock copolymers with variable block stiffness and different block chain length using coarse-grained molecular dynamics simulations. The morphology of the diblock systems we studied is found to be strongly dependent on the relative stiffness of the two block segments.

12:27PM W20.00007 Rigidity transition with increasing crosslinking of a single macromolecule  
JIWU LIU, PHILLIP DUXBURY, Michigan State University — A nano-particle can be formed by the intramolecular crosslinking of a polymer chain. In this process the rigidity of the system increases with the crosslinking density. We carried out extensive molecular dynamics simulations of the intramolecular crosslinking on six different models to study their rigidity transitions. It was found the crosslinking satisfiability of the system is greatly affected by its rigidity. A facile analysis of floppy modes of the system was employed to determine the rigidity transition threshold and a good agreement with simulation data was obtained.

12:39PM W20.00008 Spreading of Droplets on Viscous Polymer Liquids  
FLINT PIERCE, DVORA PERAHIA, Clemson University, GARY GREST, Sandia National Laboratories — Significant strides have been made in understanding the spreading of liquid droplets on solid surfaces. However from biological complexes to polymeric interfaces, the surfaces are not ideal; explicitly, the surfaces may dynamically respond as spreading takes place and the droplets may partially penetrate. Molecular dynamic simulations were carried out to investigate the spreading of liquid droplets of short chains on films of viscous polymer melts. Unlike the spreading on solid surfaces, the droplets simultaneously spread and penetrate. The degree of penetration and the magnitude of damping from the film depend on the viscosity of the underlying liquid and the relative interaction of the two constituents. At the interface with viscous films a precursor foot spreads ahead of the droplet whereas on top of less viscous interfaces, the droplets penetrate while spreading with no precursor foot. A kinetic model described the spreading of shorter chain length droplets, while a hydrodynamic model better expresses the spreading of longer chain length liquid. Supported in part under DOE contract No. ER46456.
12:51PM W20.00009 Shear rate threshold for the onset of boundary slip in dense polymer films

NIKOLAI PRIEZJEV, Michigan State University — Molecular dynamics simulations are carried out to investigate the dynamic behavior of the slip length in thin polymer films confined between atomically smooth surfaces. The polymer film is modeled as a collection of bead-spring chains of 20 Lennard-Jones monomers interacting through the FENE potential. We found that at high melt densities and low shear rates the fluid velocity profiles acquire a pronounced curvature near the walls and the slip length is approximately equal to the thickness of the immobile boundary layer. The linearity of the fluid velocity profiles is restored at higher shear rates where the slip length increases rapidly as a function of shear rate. We will show that the friction coefficient at the interface between a polymer melt and a solid wall follows power law decay as a function of the slip velocity. At large slip velocities the friction coefficient is determined by the product of the value of surface induced peak in the structure factor and the contact density of the first fluid layer near the solid wall. A relation to recent slip flow experiments is discussed.

ACS Petroleum Research Fund

1:03PM W20.00010 Direct Numerical Evaluation of Plateau Modulus of Entangled Polymer Melts via Multi-Scale Molecular Dynamics(MD)

WON BO LEE, KURT KREMER, Max-Planck Institute for Polymer Research — Plateau modulus and viscosity of entangled polymer melts can be calculated by off-diagonal elements of stress tensor, which are connected by the Green-Kubo relation and tube theory. However, direct numerical evaluation of plateau modulus via stress autocorrelation function (SAF) from MD simulation is a big challenge in a computational point of view due to the following reasons: strong fluctuations, long relaxation times and large spatial scales. In the present work, SAFs of entangled polymer melts are calculated by coarse-grained MD. We find that the use of time-averaged stress helps to reduce strong noise in SAF while capturing most local chain relaxations. Plateau values by SAF are compared with plateau values predicted from the entanglement length evaluated via primitive path analysis (PPA). The importance of well equilibrated melts for such an analysis is shortly discussed.

1:15PM W20.00011 Cole-Davidson Glassy Dynamics in Simple Chain Models

JOHN MCCOY, New Mexico Tech, JOANNE BUDZIEN, Sandia National Labs, TAYLOR DOTSON, New Mexico Tech, DOUGLAS ADOLF, Sandia National Labs, JONATHAN BROWN, New Mexico Tech — Rotational relaxation functions of the end-to-end vector of short, freely jointed and freely rotating chains were determined from molecular dynamics simulations. The associated response functions were obtained from the one-sided Fourier transform of the relaxation functions. The Cole-Davidson function was used to fit the response functions. For the systems studied, the Cole-Davidson function provided remarkably accurate fits (as compared to the transform of the Kohlrausch-Williams-Watts (KWW) function). The only appreciable deviations from the simulation results were in the high frequency limit and were due to ballistic, or free rotation, effects. The accuracy of the Cole-Davidson function appears to be the result of the transition in the time-domain from stretched exponential behavior at intermediate time to single exponential behavior at long time.

1:27PM W20.00012 Glass transition temperature of PIB, PDMS and PMMA from small-time simulations

SOLOMON DUKI, Case Western Reserve University, MESFIN TSIGE, Southern Illinois University, PHILIP TAYLOR, Case Western Reserve University — We have applied some new techniques to obtain predictions of the glass transition temperatures $T_g$ of poly(isobutylene), poly(dimethyl-siloxane), and poly(methyl methacrylate) from small-time atomistic molecular dynamics simulations. The different fragilities of these materials are reflected in the results of the simulations. One approach involved measurement of the apparent softening of the “cage” in which a monomer is bound, while another involved studying autocorrelation of a convolution of the velocity with a smoothing function in order to detect the frequency of escapes from the “cage.” To check the accuracy of the short-time methods, the $T_g$ of the polymers was also found using conventional diffusion simulations in which the rate of increase of the root mean squared displacement of an atom, monomer, or molecule is measured at very long times. The economical short-time simulations yielded results for $T_g$ that were identical to those of the computer-intensive long-time simulations.

1:39PM W20.00013 Translocation of a Polymer Through a Nanopore in the Presence of Obstacles

HENDRICK W. DE HAAN, GARY W. SLATER, University of Ottawa — The translocation of a polymer through a nanopore is interesting both as a process of fundamental biological importance and as relevant to the development of next-generation DNA sequencing technology. Due to the time and length scale of typical systems and events, computer simulations are well suited to study this problem and have been used extensively to study different aspects of the translocation process. In this work, we present results from a system in which a polymer and a membrane containing a nanopore are placed in a medium containing obstacles. Using the Espresso Molecular Dynamics simulation package, simulations are performed in which the translocation events are driven by: i) an obstacle concentration gradient and ii) a varying amount of disorder. Results indicating the establishment of a preferential direction and assessing the impact of the system configuration on details such as the translocation time will be given.

1:51PM W20.00014 Role of RNA in the self-assembly of virus: A coarse-grained Brownian Dynamics study

J.P. MAHALIK, MURUGAPPAN MUTHUKUMAR, University of Massachusetts — Assembly of a single viral capsid (icosahedral T1 type) was studied in the absence and presence of RNA. A coarse-grained rigid body model was used to represent the capsomer units and a flexible polyelectrolyte model was used to represent RNA. Brownian Dynamics simulation was used to study the assembly process. The rate of assembly was found to be enhanced in the presence of RNA. The free energy contribution of the RNA in the self-assembly process was computed using weighted histogram analysis method.

2:03PM W20.00015 Probability of adsorption of peptide (CR3-1, S2) chains on clay minerals by coarse-grained Monte Carlo simulation

RAJESH R. NAIK, Air Force Research Laboratory, WPAFB — A coarse-grained description is used to study the structure and dynamics of peptide chains (CR3-1, S2) in presence of a clay surface on a cubic lattice. A peptide chain is represented by the specific sequence of amino acids. Specificity of residues is captured via an interaction matrix based on the insight gained from the atomistic simulation, i.e., each residue interacts with surrounding residues, solvent, and the clay surface with a unique interaction potential. We use a standard LJ potential with its coefficient controlled by the interaction matrix. Simulations are performed with a number of peptide chains. Along with the global energy and dynamics of peptides, we keep track of mobility, energy (total and adsorption), and correlation with the local structure from the density profiles of each residue. Based on the analysis of local and global quantities, we are able to assess the probability of adsorption of peptides to clay surface in agreement with experiment. The probability of adsorption of S2 is found to be much higher than that of CR3-1 in which S2 is anchored by Lysine. The procedure is complementary to biopanning experiments since it allows screening a large number of peptides (more than $10^5$) on the surface to estimate their binding potential.
Global Signaling of Localized Impact in Chemo-responsive Gels

Responsive Gels might be broadly classified into two groups: those in which the material response is mediated by a phase transition involving the cooperative behavior of many molecules, or molecule moieties, together, and those in which the material response is dictated by the behavior of individual molecular components acting independently of each other. This talk will discuss the properties of supramolecular gels as a representative of the latter class of responsive materials. In the context of this talk, supramolecular gels are solvent-swollen polymer networks in which the connections between polymer chains that define the network are due to specific, directional, and reversible 1:1 interactions between molecular partners. In such cases, the properties of the network are responsive to the same stimuli that influence the reversible interaction between the molecular partners. The magnitude and sensitivity of stimulus-responsiveness in supramolecular gels is greater in the vicinity of the gel point, and the characteristics of the sol-gel phase transition will be described for a family of coordinately cross-linked poly(4-vinylpyridine) (PVP) organogels. It will be shown that the cross-linking interaction can have profound effects on the mechanical properties of similar, surface-bound networks prepared from end-grafted PVP.

Support from NSF CHE-0646670 is gratefully acknowledged.
2:42PM X18.00002 pH-Responsive Swelling of PAMAM Dendrimer-Gels. RONALD HEDDEN, BURCU UNAL, Penn State University — End-linked hydrogels containing high mass fractions of amine-terminated poly(amideamine) (PAMAM) dendrimers are prepared by reaction of dendrimers with monodisperse, epoxide-terminated linear poly(ethylene glycol) chains. PAMAM dendrimers impart pH-dependent swelling characteristics to the gels, which absorb large amounts of water due to protonation of the dendrimers’ amine groups under neutral or weakly acidic conditions. The equilibrium swelling of the gels passes through a maximum at pH of approximately 4.5, due to extensive protonation of the amine groups. Interestingly, the equilibrium swelling ratio is markedly lower at both high external pH and low external pH. We model the swelling behavior by invoking the Donnan equilibrium theory, treating the gels as phantom networks that contain a high concentration of Lewis bases having pK_a=3.5. The model captures the maximum in swelling near pH=4.5, though equilibrium swelling ratio is overpredicted in some cases. The collapse of the gels at both high and low external pH is explained in terms of the differential between the concentrations of mobile ions inside and outside the gel. We will discuss recent attempts to prepare stimuli-responsive gels based upon the remarkable swelling characteristics of PAMAM dendrimer-gels.

2:54PM X18.00003 Studies on shear-thinning and recovery properties of beta-hairpin peptide hydrogel. CONQI YAN, RADHIKA NAGARKAR, JOEL SCHNEIDER, DARRINPOCHAN, University of Delaware — In solution, freely soluble, unfolded MAX1 peptide ((VK)_6V_2PPT-(VK)_6C-NH_2) can undergo a conformation change into a folded/b-hairpin by exposure to a folding stimulus, e.g. pH change, salt addition, or temperature rise. The consequent self-assembly leads to a stiff hydrogel stabilized by physical crosslinks between fibrillar nanostructures. When a proper shear stress is applied, the hydrogel shear-thins and flows. Moreover, as soon as the stress is ceased, the gel immediately reheals into a stiff solid and recovers its original mechanical strength quickly. This shear-thinning and rehealing property makes possible hydrogel delivery via syringe injection. In this work, Rho-SANS was adopted to monitor the gel network morphology under shear flow. Also, rheological experiments were performed to measure the gel recovery after shear-thinning under various shear treatment conditions. Laser scanning confocal microscopy was used to observe the flow and velocity profile of the hydrogel through a channel. The results explain morphology changes of the gel network during shear-thinning and subsequent rehealing process. The fundamental gel shear-thinning and rehealing mechanisms will be discussed.

3:06PM X18.00004 Poly(Z-Lysine)-based Block Copolymer Organogels. SANDEEP S. NAIK, ADAM D. RICHARDSON, DANIEL A. SAVIN, School of Polymers and High Performance Materials, University of Southern Mississippi — A series of AB diblock copolymers consisting of poly(L-lysine)(Z) (A = P(Lys(Z)) and poly(propylene oxide) or poly(olefinic oligomer silsesquioxane (B = PPO, POSS) were synthesized and found to form stable, rigid organogels in THF and chloroform at room temperature. In these systems, the protecting group on the P(Lys) side-chains remains intact. As such, the secondary structure of the polypeptide chains retains helicity over a wide range of solution conditions. Gel formation in these systems results from the assembly of the solventphobic P(Lys(Z)) chains, which pack densely in an anti-parallel fashion, minimizing interfacial curvature. These gels all exhibited shear-thinning behavior, and as the temperature was heated to 350 K exhibited a gel-sol transition. The role of solvent polarity and molecular weight of the P(Lys(Z)) chains on the mechanical strength will be discussed.

3:18PM X18.00005 Anisotropic Poly(Vinyl Alcohol) Hydrogel: Connection Between Structure and Bulk Mechanical Properties1. STEPHEN HUDSON, JEFFREY HUTTER, LEONARDO MILLON, WANKEI WAN. The University of Western Ontario, Canada, MU-PING NIEH, National Research Council Canada — Poly(vinyl alcohol) (PVA) hydrogels are formed from PVA solution by creation of physical cross-links during freeze/thaw cycling. By choosing a suitable freeze/thaw protocol and applying a strain during thermal processing, gels with permanent, anisotropic bulk mechanical properties matching those of cardiovascular tissues can be made, making them useful for applications ranging from artificial heart valves to vascular grafts. We have performed small- and ultra-small-angle neutron scattering (SANS and USANS) measurements covering length scales from 2 nm to 10 µm, and modeled the structure as interconnected PVA blobs of size 20 to 50 nm arranged in fractal aggregates extending to at least 10 µm. Here, we discuss the relationship between the microstructure and bulk mechanical properties. Strength increases with the number of thermal cycles due to reinforcement of the small-scale gel phase, while anisotropy is due to elongation of the much larger fractal aggregates.

3:30PM X18.00006 Kinetics of phase separation of thermoreversible gels. FRANCISCO J. SOLIS, ASU West, CHRISTINE LEON, BRENT VERNON, Arizona State University — We study the kinetics of phase separation and thermoreversible gel formation of LCST-type polymers. A large number of NIPAM-based polymers exhibit transitions near room temperature from a liquid phase to a two-phase state. In the two-phase-region of the phase diagram, a polymer dilute phase coexists with a gel. The corresponding shrinking transition for chemically-linked gels has been extensively studied in both its thermodynamic and kinetic aspects. We show that, in the thermoreversible case, the formation of the gel phase proceeds in a similar way. Upon entrance to the two-phase region, the gel volume follows a double exponential decay. The gel undergoes a fast shrinking associated with water ejection, followed by a slower reorganization regime.

3:42PM X18.00007 Structure and Rheology of Leucine Zipper Protein Hydrogels. B.D. OLSEN, J.A. KORNFIELD, D.A. TIRRELL, California Institute of Technology — Protein hydrogels from telechelic polymers physically crosslinked by the specific association of leucine zipper domains provide fundamental insight into polymer network structures due to the unparalleled control over molecular weight and network junction multiplicity. Two different leucine zippers are used to confer either tetrameric or pentameric end block association. By varying the length of the polyelectrolyte midblock, we show that the structure and rheological properties of the hydrogels depend on both the polymer molecular weight and the aggregation state of the leucine zipper junction. Cryo-TEM and negative staining are used together to visualize the gels, revealing heterogeneous structures. The gels are strongly shear thinning, and examination of Lissajous figures of stress vs. strain suggest a yielding mechanism. Under many conditions the gels can recover nearly their full strength less than a minute after the cessation of shear. These properties combined with the ease of biofunctionalization and pH and temperature responsive gelation transitions make the materials attractive for tissue engineering.

3:54PM X18.00008 Morphology of biaxially stretched triblock copolymer gels using SAXS. ARJUN KRISHNAN, TUSHAR GHOSH, RICHARD SPONTAK, North Carolina State University — Gels of styrenic triblock copolymers swollen by a low-volatility, midblock-selective oil behave as high-strain, low-field dielectric elastomers in the design of electroactive polymeric actuators. A standard configuration of such devices involves stretching, or “prestretching,” the elastomer film biaxially. However, little is known about the effect of biaxial prestrain on copolymer morphology. In this study, small-angle X-ray scattering (SAXS) is used to probe the nanostructure of gels composed of poly(styrene-b-(ethylene-co-butylene)-b-styrene) and mineral oil by systematically changing the concentration of polymer from 5 to 30 wt% and the biaxial prestrain from 0 to 300%. In the azimuthally integrated intensity profiles, the form factor due to scattering from polystyrene microdendrons correlates strongly with polymer concentration and does not change with the applied prestrain, indicating that the polystyrene crosslinks remain as polydisperse spheres. The structure factor data correlates with prestrain, and is fitted using the Percus-Yevick approximation for interacting spheres. While a hard sphere interaction model is sufficient for unstrained gels, we resort to a square shoulder hard sphere potential for strained samples.
4:06PM X18.00009 Computer Simulation of a Switchable Metallo-Supramolecular Gel
SHIHU WANG, ELENA DORMIDONTOVA, Department of Macromolecular Science and Engineering, Case Western Reserve University — Using Monte Carlo simulation, we studied reversible metallo-supramolecular gel comprised of linear oligomers end-functionalized with ligands and metal ions that can form trans- or cis-ligand-metal complexes with a ratio up to 3:1. We found that cis-isomers exhibit a larger overall degree of association and higher average molecular weight compared to trans-isomers due to a larger fraction of 3:1 or 2:1 ligand-metal complexes. Furthermore, the metallo-supramolecular gel formed by cis-isomers occurs within a wider range of metal-to-oligomer ratios at a lower oligomer concentration and exhibits a larger elastic modulus and a smaller mesh-size compared to gel formed by trans-isomers. We found that exchanging cis- to trans-isomers leads to a monotonic change of the materials properties for most cases except for the 2:1 ligand:metal ratio at which the mesh size exhibits a minimum due to the favorable formation of intra-molecular bonds by cis-isomers. These switchable properties suggest interesting application opportunities.

3This work was supported by the NSF Career Award CHE-0348302.

4:18PM X18.00010 Cavitaton Rheology and Fracture Behavior of Polyacrylamide Hydrogels
SANTANU KUNDU, ALFRED CROSBY, University of Massachusetts-Amherst — Cavitaton rheology is a new characterization technique for the measurement of mechanical properties on small length scales, e.g. 10-1000 μm, at any arbitrary location within a soft material. The technique involves growing a cavity at the tip of a syringe needle and monitoring the pressure of the cavity at the onset of instability. This critical pressure is directly related to the local modulus of the material. We used this technique to characterize the network mechanics of polyacrylamide hydrogel materials, a common material used in many biological applications. Gels with different moduli, which were obtained by varying initial monomer to water ratio, were investigated. As monomer concentration increased, a transition from stable cavity to fracture was observed. Applying scaling theory for gels, we modify the Lake-Thomas Theory for the fracture of crosslinked networks to relate the transition from caviation to fracture to fracture in terms of molecular parameters. We anticipate this fundamental understanding of cavitation and fracture mechanism will be applicable to biological tissues, as well as the development of advanced soft materials.

4:30PM X18.00011 Dynamic display of biomolecular patterns through an elastic creasing instability of stimuli-responsive hydrogel surfaces
JUNGWOOK KIM, RYAN HAYWARD, University of Massachusetts, Amherst — Swelling a soft hydrogel film attached to a rigid substrate generates a lateral biaxial compressive stress within the gel. For sufficiently large stresses, the free surface of the gel undergoes a mechanical instability to form sharp creases on its surface. We have taken advantage of this process using temperature-responsive hydrogels to fabricate dynamic scaffolds that reversibly hide and display biomolecular patterns. Desired bioactive ligands are grafted to polyelectrolytes, which are then selectively deposited to pattern the hydrogel surface. The shapes of the patterns are directed by topographic features of the underlying substrate. At room temperature, the functionalized areas of the surface are hidden within creases, but as the temperature is raised, dehydration of the gel leads to unfolding of creases and exposure of the biomolecular patterns. By switching on and off the patterned functionalities, we could engineer dynamic interactions between our scaffolds and target objects such as microscopic beads or cells.

4:42PM X18.00012 Photo-induced locomotion of chemo-responsive polymer gels
PRATYUSH DAYAL, OLGA KUKSENOK, ANNA C. BALAZS, University of Pittsburgh — The need to translate chemical energy into a mechanical response, a characteristic of many biological processes, has motivated the study of stimuli-responsive polymer gels. Recently, it has been shown experimentally that by coupling the mechanical properties of the gel with the Belousov-Zhabotinsky (BZ) reaction it is possible to implement self-sustained oscillations in the gel. One of the means for controlling these chemical oscillations involves using light to induce changes in the gel’s mechanical properties. We present a model for the BZ reaction on a 3D gel lattice spring model (gLSM) which couples the BZ reaction kinetics to the gel dynamics. In this model, the polymer-solvent interactions were taken into account by adding a coupling term to the Flory-Huggins free energy. By virtue of this coupling term, the swelling—de-swelling behavior of the gel was captured in 3D. In order to include the effect of the polymer on the reaction kinetics, the Oreganator model for the photo-sensitive BZ reaction was also modified. Using gLSM model, we probe the effect of non-uniform light irradiation on the gel dynamics. We were able to manipulate the direction and velocity of locomotion of the gel using light as a control parameter. This ability to control the movement of the gel can be utilized in a variety of applications, ranging from bio-actuators to controlled drug release systems.

4:54PM X18.00013 Harnessing Labile Bonds between Nanogels Particles to Create Self-Healing Materials
GERMAN KOLMAKOV, CHEMICAL ENGINEERING DEPARTMENT, University of Pittsburgh, Pittsburgh, PA 15261, USA, KRYZYSZTOF MATYJASZEWSKI, Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA, 15213, USA, ANNA BALAZS, Chemical Engineering Department, University of Pittsburgh, Pittsburgh, PA 15261, USA — Using computational modeling, we demonstrate the self-healing behavior of novel materials composed of nanoscopic gel particles that are interconnected into a macroscopic network by both stable and labile bonds. Under mechanical stress, the labile bonds between the nanogels can break and readily reform with reactive groups on neighboring units. This breaking and reforming allows the units in the network to undergo a structural rearrangement that preserves the mechanical integrity of the sample. The stable bonds between the nanogels play an essential role by forming a backbone that provides a mechanical strength to the material. The simulations show that just a relatively small fraction of such labile bonds (roughly 15%) are needed to prevent the catastrophic failure of the sample. The findings provide guidelines for creating high-strength, self-healing materials.

5:06PM X18.00014 Effect of Confinement on the Dynamics of Three-Dimensional Chemo-responsive Gels
OLGA KUKSENOK, VICTOR V. YASHIN, ANNA C. BALAZS, Chemical Engineering Department, University of Pittsburgh — Chemo-responsive gels undergoing the Belousov-Zhabotinsky (BZ) reaction could be ideal candidates for creating materials that can perform sustained mechanical work. We use theory and simulation to investigate the behavior of three-dimensional samples of BZ gels that are spatially confined in various geometric arrangements and show that the spatial confinement has a dramatic effect on the samples' dynamics. We first perform a linear stability analysis in two limiting cases, where a small sample is either completely free or attached at all the boundaries to fixed, hard walls. We find the critical reaction parameters at which the gel undergoes a mechanical instability to form sharp creases on its surface. The technique involves growing a cavity at the tip of a syringe needle and monitoring the pressure of the cavity at the onset of instability. This critical pressure is directly related to the local modulus of the material. We used this technique to characterize the network mechanics of polyacrylamide hydrogel materials, a common material used in many biological applications. Gels with different moduli, which were obtained by varying initial monomer to water ratio, were investigated. As monomer concentration increased, a transition from stable cavity to fracture was observed. Applying scaling theory for gels, we modify the Lake-Thomas Theory for the fracture of crosslinked networks to relate the transition from cavitation to fracture to fracture in terms of molecular parameters. We anticipate this fundamental understanding of cavitation and fracture mechanism will be applicable to biological tissues, as well as the development of advanced soft materials.

5:18PM X18.00015 Diffusion of molecular probes and proteins in hydrogels
RICCARDO RACCIS, ROBERT ROSKAMP, ANNETTE BRUNSEN, BERNHARD MENGES, Max Planck Institute for Polymer Research, ULRICH JONAS, Max Planck Institute for Polymer Research; F. O. R. T. H. Institute of Electronic Structure and Laser Technology, WOLFGANG KNOSSL, Austrian Research Centers. GEORGE FYTAS, Max Planck Institute for Polymer Research; P. O. R. T. H. Institute of Electronic Structure and Laser Technology — We employ fluorescence correlation spectroscopy to study the diffusion of molecular probes (Cy5) and dye-tagged proteins (Cy5-AntiMouse, hydrodynamic radius 10 nm and Alexa488-Streptavidin, 4 nm) in surface-attached poly-N-isopropylacrylamide (PNIPAam) and dextran based hydrogel layers. The diffusion process depends on the crosslinking density and the presence of electrostatic and steric interactions. The protein penetration into the hydrogel layer occurs close to the isoelectric point but the local probe concentration and diffusion rate diminished with increasing penetration depth. Mesh size characterization of the hydrogels is inferred from the diffusivity and the concentration profile of fluorescent probes with different size, with the molecular free dye diffusing deeper into the gel.

Thursday, March 19, 2009 2:30PM - 5:30PM
Session X19 DPOLY: Charged and Ion-containing Polymers

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α, KIATTIKHUN MANOKRUANG, EVANGELOS MANIAS, Materials Sci & Eng; Penn State University — A series of alternating copolymers, made
LCSTs and N+. The characteristic spacing between the pseudo-cylindrical aggregates increases with the molecular weight of the PDMS segments and the size of the segments self assemble into anisotropic aggregates. This self-assembly arises from the hydrogen bonding of the urethane groups and ion sharing between Br-
induces orientation without changing the spacing in the morphology. The hard charged segments, that include DABCO, align in pseudo-cylindrical aggregates in (DABCO). X-ray scattering patterns were recorded at the small, intermediate and wide angle regions for both un-stretched and stretched films. Stretching charged entity in the backbone. Polydimethylsiloxane (PDMS) based ionenes were synthesized from 6-bromohexanoyl chloride and 1,4-diazabicyclo[2.2.2]octane (DABCO). X-ray scattering patterns were recorded at the small, intermediate and wide angle regions for both un-stretched and stretched films. Stretching induces orientation without changing the spacing in the morphology. The hard charged segments, that include DABCO, align in pseudo-cylindrical aggregates in the direction of the stretch and the PDMS soft segments remain amorphous. The orientation relative to the stretching direction suggests that the hard charged segments self assemble into anisotropic aggregates. This self-assembly arises from the hydrogen bonding of the urethane groups and ion sharing between Br- and N+. The characteristic spacing between the pseudo-cylindrical aggregates increases with the molecular weight of the PDMS segments and the size of the hard segments. Ionic conductivity measurements reveal that the through-plane conductivity increases by an order of magnitude upon stretching.

2:42PM X19.00002 PEG-based Sulphonated Ionomers Microphase Separate with Increasing Temperature, WENQIN WANG, Department of Materials Science and Engineering, University of Pennsylvania, GREGORY J. TUDRYN, RALPH H. COLBY, Department of Materials Science and Engineering, Pennsylvania State University, KAREN I. WINEY, Department of Materials Science and Engineering, University of Pennsylvania — A series of Li, Na, and Cs-neutralized sulphonated polyester ionomers with well-defined PEG spacer lengths have been investigated by in situ X-ray scattering over a wide temperature range. At room temperature, no “ionomer peak” at q=1-5 nm $^{-1}$ was observed, due to the high dielectric constant of the polymer matrix. As the length of the PEG segment increases, the crystallization of PEG segments is evidenced by multiple crystalline reflection peaks. In addition, crystallization produces period long-peak peaks, indicating a layered structure. Scanning transmission electron microscopy will be employed to facilitate the understanding of the nanoscale structures. At high temperatures, the PEG-based ionomers exhibit a new X-ray scattering peak in the angular range of 2-3 nm $^{-1}$, reminiscent of conventional ionomers. The peak intensity increases with temperature while the angular position remains fixed. A mechanism is proposed to explain the ionic association behavior as a function of temperature.

2:54PM X19.00003 Hierarchical Structures in PDMS-based Ammonium Ionomes, DAVID SALAS-DE LA CRUZ, University of Pennsylvania, SUDIPTO DAS, GARTH WILKES, Virginia Tech, KAREN WINEY, University of Pennsylvania — Ionomes are polymers with a charged entity in the backbone. Polydimethylsiloxane (PDMS) based ionenes were synthesized from 6-bromohexanoyl chloride and 1,4-diazabicyclo[2.2.2]octane (DABCO). X-ray scattering patterns were recorded at the small, intermediate and wide angle regions for both un-stretched and stretched films. Stretching induces orientation without changing the spacing in the morphology. The hard charged segments, that include DABCO, align in pseudo-cylindrical aggregates in the direction of the stretch and the PDMS soft segments remain amorphous. The orientation relative to the stretching direction suggests that the hard charged segments self assemble into anisotropic aggregates. This self-assembly arises from the hydrogen bonding of the urethane groups and ion sharing between Br- and N+. The characteristic spacing between the pseudo-cylindrical aggregates increases with the molecular weight of the PDMS segments and the size of the hard segments. Ionic conductivity measurements reveal that the through-plane conductivity increases by an order of magnitude upon stretching.

3:06PM X19.00004 Temperature and pH Responsive Chargeable Copolymers with Tunable LCSTs, KIATTHIKHUN MANOKRUANG, EVANGELOS MANIAS, Materials Sci & Eng; Penn State University — A series of alternating copolymers, made of α,ω-polyethylene glycol oligomers (M$_w$ 400 or 900) alternating with 1,6-diamino-hexane-stat (DABCO). X-ray scattering patterns were recorded at the small, intermediate and wide angle regions for both un-stretched and stretched films. Stretching induces orientation without changing the spacing in the morphology. The hard charged segments, that include DABCO, align in pseudo-cylindrical aggregates in the direction of the stretch and the PDMS soft segments remain amorphous. The orientation relative to the stretching direction suggests that the hard charged segments self assemble into anisotropic aggregates. This self-assembly arises from the hydrogen bonding of the urethane groups and ion sharing between Br- and N+. The characteristic spacing between the pseudo-cylindrical aggregates increases with the molecular weight of the PDMS segments and the size of the hard segments. Ionic conductivity measurements reveal that the through-plane conductivity increases by an order of magnitude upon stretching.

3:18PM X19.00005 Ionic Conductivity of Poly(ethylene oxide)-Containing Block Copolymers at Order-Disorder and Order-Order Transitions, NISITA WANAKULE, UC Berkeley, ASHOUTOSH PANDAY, SCOTT MULLIN, NITASH BALSARA, UC Berkeley, Lawrence Berkeley National Labs — The order-disorder transition (ODT) and order-order transition (OOT) of block copolymers with lithium bis[(trifluoromethanesulfonyl)imide (LiTFSI) salts are measured with a combination of small-angle x-ray scattering (SAXS) and birefringence. The terpolymers are uncharged at low pH while they become charged (containing lysine anions) when the solution pH increases; the phase diagrams in the temperature and pH space are drawn, and the tunability of the critical points in water as it is controlled by the copolymer composition is discussed. These copolymers, due to their hydrophilic polyelectrolyte-oxide comonomers, exhibit a genuine LCST, i.e., a bona fide first order thermodynamic transition, rather than the usual micellization related LCST of copolymers that contain hydrophobic blocks or grafts. This last point is demonstrated by comparisons against micelle-forming copolymers, consisting of hydrophobic and chargeable comonomers.

3:30PM X19.00006 Origin of Lateral Nanoscale Heterogeneities in Weak Polyelectrolyte Brushes, YOU-YEON WON, KEVIN WITTE, JAEHYUN HUR, Purdue University — In this talk, we will first discuss experimental evidence of lateral nanoscale heterogeneities in a single-component weak polyelectrolyte brush system under zero to low salt conditions. Using an amphiphilic diblock copolymer, poly(2-(dimethylamino)ethyl methacrylate-b-butyl acrylate) (PDMAEMA-PnBA), for Langmuir film compression and Langmuir-Blodgett deposition on a hydrophobic substrate followed by fluid AFM imaging, we show the existence of regions of different brush heights, indicative of the thermodynamic instability (and resultant local clustering) of the PDMAEMA chains in the low-salt limit. Using SCF and scaling theories, we will also show that the lateral heterogeneities occur due to the combined effects of (i) the osmotic instability regulated by charge equilibrium and (ii) the hydrophobicity of the chains.

3:42PM X19.00007 In situ Neutron Reflectivity study of alcohols into ultra-thin ionomer films, THUSITHA ETAMPAWALA, DVORA PERAHIA, LILIN HE, Clemson University, CHRISTOPHER CORNELIUS, Virginia Polytechnic Institute — For many applications a polymeric membrane with selective well-controlled transport is desired. A new class of materials that consist of rigid hydrophobic polyphenylene-decorated by sulfonic acid functionalized phenylene side chains has shown a potential as controlled transport membranes for energy applications. The nature of the diffusion depends on the polymer structure and the interaction of its different segments with the solvent. In addition, the interfacial layer plays a critical role in the transport characteristics. The current work introduces an in situ neutron reflectivity study of penetration of long-chain alcohols into ultrathin films. The time dependence of the penetration of deuterated n-hexanol into films of 20nm thick ultra-thin films was determined and compared with that of less hydrophobic solvents. The process consists of two stages, a relatively fast stage in which the film thickness increases linearly with time followed by a slow phase in which structural changes take place.

4:06PM X19.00009 Counter-ion fluctuations in the presence of a spherical macromolecule. — LEANDRO BOONZAIEER, KRISTIAN K. MUELLER-NEDEBOCK, Institute of Theoretical Physics, University of Stellenbosch, 7602 Matieland, South Africa; FREDERIK G. SCHOLTZ, National Institute for Theoretical Physics, Stellenbosch Institute for Advanced Study, 7600 Stellenbosch, South Africa — The effective interactions of charged macromolecules (e.g. polyelectrolytes) are still not fully understood. The role of counter-ion fluctuations, in the presence of these macromolecules, seems to be crucial in understanding these effective interactions. We consider a single charged spherical macromolecule, enclosed in a finite volume, in the presence of point-like counter-ions in an electrically neutral solution. Writing the partition function as a functional integral and only keeping terms up to quadratic order, we calculate the free energy in this approximation exactly.

4:18PM X19.00010 Counterion Condensation and Collapse of Sodium Polystyrene Sulfonate in Water: A Molecular Dynamics Study. — JAN-MICHAEL CARRILLO, ANDREY DOBRYNIN, University of Connecticut — Hydrophobic polyelectrolytes are known to form necklace-like structures of dense beads connected by strings of monomers. This structure appears as a result of optimization of electrostatic and short-range interactions. To elucidate the effect of counterion condensation on polyelectrolyte conformations we performed two sets of molecular dynamics simulations of sodium polystyrene sulfonate (NaPSS) chains with degree of polymerizations $\mathcal{N}=16, 32$ and 64 and fraction of charged monomers $f=0.25, 0.33, 0.5$ and 1.0 in aqueous solutions. (1) water molecules were considered explicitly using TIP3P model and (2) water molecules were modeled as a dielectric continuum with dielectric constant 77.73. Our simulations showed that with increasing $f$ a polyelectrolyte chain adopts an elongated conformation. The transition between collapsed and elongated states does not show any features of abrupt transition due to the fact that only relatively short chains were considered. Furthermore, even for our longest chains ($\mathcal{N}=64$) the necklace-like globule was not observed. Effect of the water-ion interactions on counterion condensation was analyzed by comparing the radial distribution function between the sulfonate groups and sodium counterions for chains with different $f$. It was found that in simulations with explicit water ionized groups are located at the globular surface.

4:30PM X19.00011 ABSTRACT WITHDRAWN —

4:42PM X19.00012 Computational titrations of linear and branched polyethyleneimine. — JESSE ZIEBARTH, YONGMEI WANG, University of Memphis — Despite a great deal of interest in polyethyleneimine (PEI) for its potential use as a gene therapy vector, the protonation state of this polycation is currently not well understood. PEI is rare among polyelectrolytes as every third atom along the backbone of the polymer is a protonable nitrogen. The closeness of these potentially charged sites can lead to high electrostatic repulsion and a large shift in the effective pKa of the amine groups as the degree of protonation increases. Previous experimental and theoretical estimates of the degree of protonation of PEI under physiological conditions have ranged from 0.15 to 0.80. Here, we perform computational titrations on coarse-grained models of both branched and linear PEI under various conditions. Chain length, degree of branching, salt concentration, and the solvent dielectric constant are varied to determine how these factors influence the protonation of PEI.

4:54PM X19.00013 Phase diagrams of effective charge and size of an isolated polyelectrolyte chain and gels[1]. — ARINDAM KUNDAGRAMI, MURUGAPPAN MUTHUKUMAR, Polymer Science and Engineering, University of Massachusetts, Amherst — We consider an isolated polyelectrolyte chain and charged gels under poor solvent conditions and calculate the phase diagrams for the effective charge and size of the respective systems as functions of physical parameters such as temperature and salt concentration. Phase boundaries and the critical point for the first order collapse transition - induced cooperatively by counterion adsorption and solvent quality - are calculated self-consistently in terms of both the effective charge and the size of the chain with arbitrary ionizability.

1 NSF, NIH

5:06PM X19.00014 Single chain contraction and re-expansion by counterions of polyelectrolytes[1]. — PENGXIAN JIA, JIANG ZHAO, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China — We have studied the re-entry transition of polyelectrolytes at single chain level. Diffusion rate of single chains of polystyrene sulfonate (PSSNa) has been investigated by fluorescence correlation spectroscopy under different counterion condition. Upon the addition of external salts, the hydrodynamic radius of PSSNa was found to decrease with the increase of salt concentration, i.e., the chain contracts due to electrostatic screening and ion bridging effect. When the salt concentration increased beyond a certain value, the chains were observed to increase their dimension for a few mono-, double- and triple-valent counterions. The experimental evidence shows the single chain behavior of re-entrant transition of polyelectrolytes.

1 Project supported by National Natural Science Foundation of China (NSFC).

5:18PM X19.00015 Conformation and Dielectrophoresis of Single Weak Polyelectrolyte under AC Electric Field. — SHENQIN WANG, YINXI ZHU, Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556, USA — The application of AC-electric fields, when integrated with current microarray and ”lab-on-chip” platforms, has emerged as a useful tool to manipulate and assemble supramolecular aggregates, such as AC-field induced protein crystallization and DNA hybridization, yet the detailed mechanism remains unclear. To understand the AC-polarization mechanism of biomacromolecules, we examine the conformational and dielectrophoretic behavior of polyelectrolytes under AC-electric field using fluorescence correlation spectroscopy (FCS) at single molecular level. We focus on poly (vinyl pyridine) (PVP) as a model polyelectrolyte whose conformation can be tuned by adjusting the pH and ionic strength. We observe that in the non-uniform AC electric field, PVP in a coil conformation experiences the positive DEP force at applied frequency below 500 kHz; it is also intriguing to observe the elongation of PVP coils at a characteristic AC-frequency of ~ 200 kHz. In sharp contrast, PVP in a globule conformation shows insensitive to imposed AC-fields. We also examine the conformational change in a uniform AC-field where the DEP force is absent; the result suggests a redistribution of counterions with an induced dipole of polyelectrolyte. The behavior is further investigated with varied medium conductivity and microelectrode geometry.
2:30PM X20.00001 Long range ordering in block copolymer thin films. CAROLINE ROSS, MIT — Thin films of microphase separated block copolymers, which can form patterns consisting of dense arrays of lines or dots, are attractive materials for self-assembled nanolithography. The long range order of the block copolymer microdomains can be controlled by the use of chemical or topographical patterns. In this work, we discuss how Si-containing block copolymers, polystyrene-b-polyferrocenylidimethylsilane (PS-PFS) and polystyrene-b-polydimethylsiloxane (PS-PDMS), can be templated on substrates patterned with posts or steps. In the case of 40 nm period spherical morphology PS-PDMS, < 20 nm diameter posts, which are coated with a grafted layer of PDMs homopolymer, define the locations of surrounding PDMs microdomains. The lattice spacing and orientation of the templated PDMs microdomain can be predicted from the ratio between the post spacing and the self-assembly microdomain spacing. PFS spheres, formed from spherical-morphology PS-PFS, can be aligned within shallow trenches to form a close-packed array with row spacing determined by the trench width. We also show how 32 nm period cylindrical morphology PS-PDMS can be templated using topographical features. Templating using posts or linear substrate features gives arrays of straight parallel cylinders with controllable period and orientation, while templating in circular pits creates sharply curved, concentric toroidal structures. The overall morphology and period of the block copolymer microdomain arrays can be varied by annealing in mixed solvent vapors. For example cylindrical-morphology PS-PDMS can form perforated lamellae by annealing in toluene plus heptane. These results will be discussed in the context of nanolithography, including examples of pattern transfer to form metal, oxide and polymer functional nanostructures. Bita et al, Science 321 939 (2008); Jung et al, Nano Letts. 7 2046 (2007); 8 2975 (2008).

3:06PM X20.00002 Surface Morphology Diagram for Cylinder-Forming Block Copolymer Thin Films. ALAMGIR KARIM, University of Akron, XIAOHUA ZHANG, JACK DOUGLAS, RONALD JONES, Polymers Division, NIST — We investigate the effect of annealing temperature (T) and film thickness (hf) on the surface morphology of flow coated films of a cylinder forming block copolymer, poly (styrene-block-methyl methacrylate) (PS-b-PMMA). A transition from a perpendicular to a parallel cylinder orientation with respect to the substrate is observed upon increasing hf when the substrate interaction is highly selective for one of the blocks (PMMA) and the polymer-air interface has a nearly neutral interaction with both blocks. Surface morphology transitions with increasing hf are observed in these model ‘frustrated-orientation’ films: (a) first, a transition occurs from cylinders oriented parallel to the substrate to a mixed or ‘hybrid’ state where the two orientations coexist (b) this hybrid morphology transforms to cylinders oriented perpendicularly to the polymer-air interface for larger hf. The characteristic values of hf defining these surface morphological transitions depend on T and we construct a surface morphology diagram as a function of hf and T. The surface morphology diagram is found to depend on the method of film formation (flow coated versus spun cast films) so non-equilibrium effects evidently have a large effect on the surface pattern morphology. In particular, the residual solvent within the film (quantified by neutron reflectivity measurements) can have a large effect on the surface morphology diagram and the physics of glass-formation is also apparently important.

3:18PM X20.00003 Practical Implementation of Order Parameter Calculation for Directed Assembly of Block Copolymer Thin Films. CHI-CHUN LIU, GORDON CRAIG, PAUL NEALEY, Dept of Chem and Bio Engineering, Univ of Wisconsin-Madison, RICARDO RUIZ, Hitachi Global Storage Technologies, San Jose Research Center, NICOLA FERRIER, Dept of Mech Engineering, Univ of Wisconsin-Madison — The assembled morphologies in thin films of block copolymers are gaining interest for potential applications in advanced lithography and template fabrication due to their low defect density, pattern rectification, and resolution enhancement. For such applications, the ability to quantitatively analyze the extent of order achieved with different assembly methods and materials is crucial. Previous studies analyzed the translational order parameter (\textit{V}\textit{T}) based on reciprocal lattice vectors obtained from Fourier Transforms, but discussed neither the accuracy of these vectors nor the effect of domain positioning on the calculation results. In both simulations and real systems we have shown the inaccuracy of these parameters can lead to huge difference in \textit{V}\textit{T}. Here we present a computational procedure to delineate the importance of these parameters and analyze with a high level of accuracy the translational and orientational parameters of the guiding pattern, the domains of a block copolymer directed to assemble on this pattern, as well as the underlying structure after lift-off. We observe that order can be preserved over a large area and can be retained in subsequent processing.

3:30PM X20.00004 Controlling the self-assembly of block copolymer materials in thin-films. EUNGNAY HAN, Department of Materials Science & Engineering, University of Wisconsin-Madison, KARL STUEN, PAUL NEALEY, Department of Chemical & Biological Engineering, University of Wisconsin-Madison, PADMA GOPALAN, Department of Materials Science & Engineering, University of Wisconsin-Madison — We present a simple and efficient strategy toward surface control and self-assembly of (styrene-b-methylmethacrylate) diblock copolymer (BCP) in thin films. Photo-patternable, substrate-independent neutral surface was created to achieve vertical orientation of block copolymer (BCP) microdomains. A random copolymer of styrene (f= 0.580-0.63), methylmethacrylate (f= 0.41-0.46) and glycidyl methacrylate (f= 0.01-0.02) was synthesized. The copolymer uses photo-crosslinking reaction of epoxy groups by photacid generator to formulate the neutral surface. Ultra-thin (2-6 nm) crosslinked film was created as a neutral interfacial layer between the block copolymer and the substrate. The composition of the copolymer was fine tuned to tailor the wetting behavior and hence the domain orientation (parallel or perpendicular to the substrate) in the top self-assembled block copolymer film. The effectiveness of the new neutral polymer on a range of substrates such as glass and gold coated silicon wafer and for both symmetric and asymmetric BCPs is demonstrated.

3:42PM X20.00005 Shear Alignment and Realignment of Cylinder-Forming Block Copolymer Thin Films. ANDREW MARENCIC, RICHARD REGISTER, Princeton University, PAUL CHAIKIN, New York University — The microdomains in cylinder-forming block copolymer thin films can be oriented by applying a sufficient shear stress to the film; the cylinders lie in-plane and align with the shear direction, as shown by atomic force microscopy (AFM) post-shear. To understand the alignment process, we applied a stress gradient to the film, and focused on the structure in the transition region from unaligned to aligned. To sample a statistically useful number of grains, we used the moiré patterns formed by the AFM scanning grid with the microdomain lattice to determine the cylinder orientation. The results are compared with a simple melting-recrystallization model, in which grains misaligned with the shear direction are eliminated as the shear stress is increased. In addition, we have applied two shear gradients to the sample in different directions, to directly probe how ordered cylinders can be realigned by a subsequent shear. We again find qualitative agreement with the simple model, but the stress required is a factor of 1.7 larger than required for single shear. We also observed grain boundary generation within the area between alignment with the first shear direction and alignment with the second shear direction.

3:54PM X20.00006 Structural transition with thickness in films of poly-(styrene-b-2vinylpyridine) (PS-b-P2VP) diblock copolymer/homopolymer blends. VINDHYA MISHRA, Materials Research Laboratory, University of California, Santa Barbara, EDWARD KRAMER, Department of Materials and Chemical Engineering, University of California Santa Barbara, SU-MI HUR, GLENN FREDRICKSON, Materials Research Laboratory, University of California, Santa Barbara, MICHAEL SPRUNG, Argonne National Lab, IL — In multilayer thin films of spherical morphology block copolymers, the surface layers prefer hexagonal symmetry while the inner layers prefer BCC. Thin films with spherical morphology of PS-b-P2VP blends with short homopolymer polystyrene (hPS) chains have an HCP structure up to a thickness \textit{n*} at which there is a transition to a face centered orthorhombic structure. Using grazing incidence small angle X-ray scattering and transmission electron microscopy we show that that \textit{n*} increases from 5 to 9 with increase in hPS from 0 to 12 \textit{vol\%}. For thicknesses just below \textit{n*} the HCP and FCO structures coexist, but on long annealing HCP prevails. We hypothesize that the PS segregates to the interstices in the HCP structure reducing the stretching of the PS blocks and the free energy penalty of HCP versus BCC layers. Self consistent field theoretic simulations are being carried out to see if this idea is correct.
4:06PM X20.00007 A Modular and Hierarchical Supramolecular Block Copolymer Self-assembling Strategy Towards Square Arrays, CHUANBING TANG, ERIN LENNON, MICHAEL DIMITRIOU, GLENN FREDRICKSON, EDWARD KRAMER, CRAIG HAWKER, Materials Research Laboratory, University of California, Santa Barbara — We present a modular and hierarchical self-assembling strategy for the generation of novel nanoscale patterns suitable for block copolymer lithography. Supramolecular block copolymers consisting of poly(ethylene oxide)-b-poly(styrene-4-hydroxystyrene) and poly(styrene-4-vinylpyridine)-b-poly(methyl methacrylate) diblock copolymers blends with hydrogen-bonding interactions between the polystyrene majority segments were prepared by living free radical polymerization. By combining supramolecular assembly of H-bonding phenolic and pyridyl units with controlled phase separation of diblock copolymers, highly ordered square arrays were obtained. The co-assembly of hydrogen-bonding units for generating long range order and for controlling the spatial arrangement of ordered arrays. The utilization of these materials as lithographic masks was successful and allowed transfer of the polymeric template with high fidelity to silicon oxide substrates, leading to a highly ordered array of 20 nm cylindrical pores with a spacing of 50 nm. This modular blending approach to block copolymer resists demonstrates a new and powerful strategy for the fabrication of unique patterns for nano lithographic applications.

4:18PM X20.00008 Macroscopic Addressable Arrays of Block Copolymer Microdomains1, SOOJIN PARK, DONG HYUN LEE, BOKYUNG KIM, SUNG WOO HONG, JI XU, Dept. of Polymer Science and Engineering, University of Massachusetts Amherst, UNYONG JEONG, Dept. of Metallurgical Engineering, Yonsei University, TING XU, Dept. of Materials Science and Engineering, University of California, Berkeley, THOMAS P. RUSSELL, Dept. of Polymer Science and Engineering, University of Massachusetts Amherst — Generating addressable, macroscopic arrays of nanoscopic elements with perfect lateral order has the potential to revolutionize the micro electronic and storage industries. A novel approach is shown using faceted surfaces of commercially available sapphire wafers to guide the self-assembly of block copolymer (BCP) microdomains into arrays with single crystal textures over the entire wafer surface. Perfectly ordered arrays of BCP microdomains, with areal densities in excess of 10 Terabit/inch\(^4\), have been produced. The saw toothed substrate topography provides registered, directional guidance of the BCP self-assembly that is tolerant of surface defects, maintaining the lateral registry and ordering of the microdomains over the entire surface. The approach provides unprecedented areal densities, and opens simple, yet versatile routes to ultra high density, addressable systems.

1This work was supported by the U.S. Department of Energy (DOE), the NSF supported MRSEC and NSEC at the University of Massachusetts Amherst. Use of the Advanced Light Source, Berkeley National Laboratory, supported by the U.S. Department of Energy, Office

4:30PM X20.00009 Self-Extinguishing Crystallization: Copolymer Behavior under Flow, DIANA SMIRNOVA, MEISAM HAJIMORAD, JULIA KORNFIELD, California Institute of Technology — It is known that short chain branches in copolymers act as crystal defects, resulting in materials with low crystallinity and poorly-defined morphology. We are interested in the behavior of copolymers under flow in the presence of species that readily form well-defined shish-kebab morphologies. Bimodal blends containing small concentrations of high molecular weight, high density polyethylene (HDPE, Mw = 526 kg/mol, Mw/Mn = 3) in an ethylene-co-hexane matrix (Mw = 50 kg/mol, Mw/Mn = 2.5, 5 mol % hexene) were studied via rheo-optical and rheo-xray techniques. HDPE concentrations were selected above and below the overlap concentration of 0.6%, but maintained below 1% such that the rheology of the blends was not significantly altered from that of the copolymer matrix. DSC traces were collected to ensure that co-crystallization between the two blend components occurs. Crystallization after shear quickly leveled off revealing a self-extinguishing behavior. The time frame for this extinction is coupled with a loss of anisotropy in scattering patterns indicating random crystallization uncorrelated with existing oriented structures.

4:42PM X20.00010 Quasicrystalline long-range order in an ABC star block copolymer, TOMONARI DOTERA, Department of Polymer Chemistry, Kyoto University, Japan — We report the formation of a dodecagonal quasicrystal (DDQC) in a lattice Monte Carlo simulation of a star-shaped three component polymeric alloy. We have observed a series of Archimedean and quasicrystalline phases \((4.6^2) \rightarrow (37.4.3.4) \rightarrow DDQC \rightarrow (4.6.12)\) with increase of one component of ABC star polymers. This phase behavior can be regarded as a transition from square tiling to triangle tiling via square-triangle tiling. The simulation is associated with the recent striking experimental manifestation of quasicrystalline order: A mesoscopic tiling pattern with twelvefold symmetry in a three-component star polymer system composed of polyisoprene, polystyrene, and poly (2-vinylpyridine). Since, the same kind of quasicrystalline structures have been found for metal alloys, chalcogenides, and liquid crystals, the present result confirms the universal nature of quasicrystalline long-range order over several hierarchical length scales.


4:54PM X20.00011 Effect of chain extender on the phase behavior and morphology of high hard block content polyurethanes, ALBERTO SAIANI, ACHILLES TSIOTAS, The University of Manchester — Thermoplastic Polyurethanes (TPU) are linear block copolymers typically constructed of statistically alternating soft (SS) and hard (HS) segments. Due to their numerous industrial applications these materials have received considerable attention. We have investigated the phase behavior and morphology of a set of high hard block content polyurethanes and varied the chain extender used. Using mainly calorimetry, scattering and microscopy techniques we were able to elucidate the origins of all the thermal events observed through differential scanning calorimetry. Correlating our thermodynamic work with our structural work we were able to propose a new morphological model of the structure and the phase behavior of high hard block content polyurethanes. We have shown that above 65% hard segment content the melt-quenched samples present a two-phase morphology one pure hard segment phase co-existing with a mixed phase with the same hard segment content of 65% for all samples. When annealed at high temperature the mixed phase undergoes phase separation resulting in the same phase-separated mesophase. Changing the chain extender has a significant impact of the phase behavior and morphology of these systems.

5:06PM X20.00012 Ligand-induced order in Spotted vesicles and Striped micelles, DAVID CHRISTIAN, WOUTER ELENBROEK, ANDREA LÍU, DENNIS DISCHER, MRSEC, University of Pennsylvania — Mixtures of amphiphiles are ubiquitous and assemble

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Peaks during the collapse follows very closely the amount of water in the layer and can be related to the local dielectric environment within the network. The transition of tethered poly(NIPAAm) networks coincides with the miscibility gap of linear poly(NIPAAm) solutions. Whether or not the poly(NIPAAm) network undergoes a continuous or discontinuous collapse depends on its degree of cross-linking. At cross-link densities above 5 mole% the network remains in the single-phase region of the linear solution phase diagram and shows only a continuous transition between the swollen and collapsed states. Moreover, in the collapsed state, 30-35% by volume of water remains in the network, which is independent of cross-link density with both neutron reflection and ATR-FTIR. Neutron reflection reveals that the volume-phase transition in thin, mechanically anchored responsive polymer networks is bimodal and confirms Monte Carlo simulation results.

Friday, March 20, 2009 8:00AM - 11:00AM
Session Y16 DPOLY: Elastomers and Gels II

8:00AM Y16.00001 Deuterium NMR studies of segment orientation in PDMS unimodal and bimodal endlinked networks.1, CLAUDE COHEN, GEOFFREY GENESKY, T. MICHAEL DUNCAN, Cornell University — Polymer segment orientation in elastomers is revealed by solid state deuterium NMR spectra: earlier work has focused on the frequency split between the peaks of the spectra from stretched elastomers rather than the details of the lineshape. The split has classically been interpreted as a measure of polymer segment order parameter S caused by excluded volume interactions between neighboring segments. We synthesized deuterated PDMS chains of about 5000 g/mol and 50,000 g/mol to probe the segmental orientation of each component separately in bimodal networks. Even in the unstretched state, the spectra for the labeled short chain component show an evolving lineshape with varying short chain content. We compute the average absolute value of the frequency shift of the entire spectrum to better account for the highly aligned segments. This method allows us to probe the chain segment alignment with increasing strain in both unimodal and bimodal networks and confirms Monte Carlo simulation results.

1 NSF Polymers Program DMR-0705655

8:12AM Y16.00002 Volume-phase Transitions and Confined Water in Surface-tethered Poly(N-isopropylacrylamide) Networks, AJAY VIDYASAGAR, RYAN TOOMEY, University of South Florida — We present a simple approach for studying volume-phase transitions in thin, mechanically anchored responsive polymer networks. The approach is based on the photo-cross-linking of copolymers synthesized from N-isopropylacrylamide (NIPAAm) and methacryloyloxybenzophenone (MaBP). We monitored the swelling of poly(NIPAAm-co-MaBP) networks in contact with aqueous solution as a function of cross-link density with both neutron reflection and ATR-FTIR. Neutron reflection reveals that the volume-phase transition of tethered poly(NIPAAm) networks coincides with the miscibility gap of linear poly(NIPAAm) solutions. Whether or not the poly(NIPAAm) network undergoes a continuous or discontinuous collapse depends on its degree of cross-linking. At cross-link densities above 5 mole%, the network remains in the single-phase region of the linear solution phase diagram and shows only a continuous transition between the swollen and collapsed states. Moreover, in the collapsed state, 30-35% by volume of water remains in the network, which is independent of cross-link density. The relative position of the FTIR absorption peaks during the collapse follows very closely the amount of water in the layer and can be related to the local dielectric environment within the network.

8:24AM Y16.00003 Strain induced alignment of particles in an elastomer host1, BEN SPOTT, JEREMY NEAL, PETER PALFFY-MUHORAY, Liquid Crystal Institute, Kent State University — The properties of composite materials consisting of anisometric nanoparticles dispersed in a host depend on the orientation of the nanoparticles. It is interesting to ask how mechanical strain of the composite affects their orientation. We have carried out experiments stretching both two- and three-dimensional rubber samples containing rigid rod-like particles and measured their orientational order parameter as a function strain. We discuss these results, and make connections with theoretical models.

1 This work was supported by the AFOSR under the MURI grant FA9550-06-1-0337

8:36AM Y16.00004 Dynamics of uniaxially oriented elastomers using dielectric spectroscopy2, HYUNGKI LEE, DANIEL FRAGIADAKIS, Penn State University, DARREN MARTIN, University of Queensland, JAMES RUNT, Penn State University — We summarize our initial dielectric spectroscopy investigation of the dynamics of oriented segmented polyurethanes and crosslinked polyisoprene elastomers. A specially designed uniaxial stretching rig is used to control the draw ratio, and the electric field is applied normal to the draw direction. For the segmented PUs, we observe a dramatic reduction in relaxation strength of the soft phase segmental process with increasing extension ratio, accompanied by a modest decrease in relaxation frequency. Crosslinking of the polyisoprene was accomplished with dicumyl peroxide and the dynamics of uncrosslinked and crosslinked versions are investigated in the undrawn state and at different extension ratios. Complimentary analysis of the crosslinked PI is conducted with wide angle X-ray diffraction to examine possible strain-induced crystallization, DSC, and swelling experiments. Quantitative analysis of relaxation strengths and shapes as a function of draw ratio will be discussed.

2 Supported by the NSF Polymers Program, DMR-0605627

8:48AM Y16.00005 Shape-Memory Polymers Based on Fatty Acid-Filled Elastomeric Ionomers, ELISE IZZO, ROBERT WEISS, University of Connecticut — Shape memory polymers (SMPs) have applications as medical devices, actuators, sensors, artificial muscles, switches, smart textiles, and self-deployable structures. All previous design of SMPs has involved synthesizing new polymers or modifying existing polymers. This paper describes a new type of SMP based on blends of an elastomeric ionomer and low molar mass fatty acids or their salts (FAS). Shape memory elastomers were prepared from mixtures of a sulfonated EPDM ionomer and various amounts of a FAS (e.g., zinc stearate, zinc oleate, and various aliphatic acids). Nanophase separation of the metal sulfonate groups provided the “permanent” crosslinks, while sub-microscopic crystals of the low molecular weight FAS provided a physical crosslink needed for the temporary shape. The material was deformed above the melting point of the FAS and the new shape was fixed by cooling the material while under stress to below the melting point of the FAS. Polar interactions between the ionomer and the FAS stabilized the dispersion of the FAS in the polymer and provided the continuity between the phases that allowed the crystals of the FAS to provide a second network of physical crosslinks. The temporary shape was erased and the material returned to the primary shape by heating above the melting point of the FAS.
9:00AM Y16.00006 Dynamics of Segmented Polyurethane Elastomers Using Dielectric Spectroscopy\textsuperscript{1}, JAMES RUNT, The Pennsylvania State University, DANIEL FRAGIADAKIS, ALICIA CASTAGNA, TAEYI CHOI — This investigation focuses on the molecular dynamics of segmented polyurethane copolymers with different hard segment contents (30 to 52 wt percent) and soft segment chemistries. Methylene bis(p-phenyl isocyanate) and 1,4-butanediol constitute the hard segments in all materials under investigation, while soft segments include poly(tetramethylene oxide) and a 80-20 mixture of poly(dimethylsiloxane) and poly(hexamethylene oxide). The dynamics of these materials were explored over a wide temperature and frequency range using dielectric spectroscopy. In addition to investigating the details of segmental and local processes, three dielectric relaxations above Tg were observed for the first time in segmented polyurethanes, and their origin discussed in the presentation. For example, the highest temperature process is assigned to Maxwell-Wagner-Sillars interfacial polarization. The strength of the MWS process is a sensitive indicator of the change in microphase-separated character. It disappears at a temperature similar to that at which the small-angle X-ray scattering maximum disappears, indicating the transformation to the single phase state.

\textsuperscript{1}Supported by the NSF Polymers Program, DMR-0605627.

9:12AM Y16.00007 Polydomain to monodomain transition in nematic liquid crystal elastomers\textsuperscript{1}, BADEL MBANGA, FANGFU YE, JONATHAN SELINGER, ROBIN SELINGER, Liquid Crystal Institute / Kent State University — Liquid crystal elastomers are crosslinked polymer networks covalently bonded with liquid crystal mesogens. In the nematic phase, due to strong coupling between mechanical strain and orientational order, these materials display strain-induced instabilities associated with formation and evolution of orientational domains. Deformation of an initially polydomain nematic elastomer film induces a transition to the monodomain configuration. We model this phenomenon using a recently developed finite element elastodynamics simulation method. We study the rate-dependent material response upon uniaxial extension and resolve the textures that form along with the associated stress-strain behavior. Our simulations yield qualitative agreement with experimental observations. This model allows us to explore the fundamental physics governing dynamic mechanical response of nematic elastomers and also provides a potentially useful computational tool for engineering device applications.

\textsuperscript{1}Supported by U.S. National Science Foundation DMR-0605889

9:24AM Y16.00008 Liquid crystal elastomers: Bent core flexo-electricity\textsuperscript{1}, MARTIN CHAMBERS, Liquid Crystal Institute and Physics Department, Kent State University, Kent OH44240, USA, RAFAEL VERDUZZCO, Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge TN37831, USA, SAMUEL SPRUNT, JAMES T. GLEASON, Physics Department, Kent State University, ANTAL JAKLI, Liquid Crystal Institute, Kent State University — We report on the swelling of calamatic liquid crystal elastomers (LCE) with bent-core mesogens (BCM); this swelling took place at a temperature where both materials were in their isotropic phase. The BCM used varied in the degree of saturation of their hydrocarbon tails, which affects both viscosity and phase behaviour. We determined both swelling magnitude and dynamics. The host LCE systems homogeneously imbibes BCM up to 30-40 % mol. Based on differential scanning calorimetry, shape change anisotropy, and optical birefringence measurements, the swollen elastomers are all found to exhibit nematic phases, with some possessing a lower temperature smectic phase. Bent-core liquid crystal elastomers and swollen calamitic LCE in BCM were investigated for the flexoelectric properties by inducing a mechanical deformation. The value of the bend flexoelectric constant, $e_3^\text{SW}$, of the swollen BCM containing LCE systems is comparable of that of the neat bent-core liquid crystal.

\textsuperscript{1}This work was supported by the ONR (N00014-07-1-140).

9:36AM Y16.00009 Photoinduced distortions of polydomain liquid crystal elastomer samples\textsuperscript{1}, WILDER IGLESIAS, PETER PALFFY-MUHORAY, Liquid Crystal Institute, Kent State University — We have studied the effects of illumination of a dye doped polydomain nematic elastomer. The sample was on a glass substrate, and its free surface was illuminated by polarized light from an Ar+ laser. The intensity of the reflected light in the far field was studied to probe photoinduced deformations. Above a threshold intensity, a target pattern appeared in the far field, indicating sample deformation. We discuss the experimental observations, and relate these to the processes such as photoinduced surface relief. Experimental results are compared with the predictions of simple theory.

\textsuperscript{1}This work was supported by the NSF under grant DMR 0606357.

9:48AM Y16.00010 Dynamic Aspect of Electro-Opto-Mechanical Effects in Swollen Nematic Elastomers\textsuperscript{1}, KENJI URAYAMA, ATSUSHI FUKUNAGA, TOSHIKAZU TAKIGAWA, Dept. Mater. Chem., Kyoto Univ., ANTONIO DESIMONE, SISSA, LUCIANO TERESI, SMFM, Univ. Roma III, KYOTO UNIV. TEAM, SISSA COLLABORATION, UNIV. ROMA III COLLABORATION — The nematic elastomers swollen by low molecular mass liquid crystals exhibit a macroscopic deformation with a significant change in birefringence in fast response to electric fields. We experimentally characterize the dynamics of this “electro-opto-mechanical effect.” The optical and mechanical rise times (in response to field-on) decrease in nearly proportion to the square of field strength, while the corresponding decay times (in response to field-off) are almost independent of field strength. The optical rise and decay times are about one order of magnitude smaller than the mechanical ones. We also propose a minimal model to describe the main features of both static and dynamic characteristics of this phenomenon observed experimentally. 1) Urayama, K., Honda, S., Takigawa, T., Macromolecules, 2006, 39, 1943. 2) Fukunaga, A., Urayama, K., Takigawa, T., DeSimone, A., Teresi, L., Macromolecules, in press.

10:00AM Y16.00011 Analysis of Diffusion through Dynamic Network Polymers using Multi-photon Fluorescence Recovery after Photobleaching\textsuperscript{1}, JIAHUI LI, Department of Chemical Engineering, University of Rochester, KELLEY SULLIVAN, EDWARD BROWN, Department of Biomedical Engineering, University of Rochester, MITCHELL ANTHAMATTEN, Department of Chemical Engineering, University of Rochester — Multi-Photon Fluorescence Recovery after Photobleaching (FRAP) techniques are utilized to study small molecule transport through polymer networks containing multiple hydrogen-bonding functional groups. Experiments involve uniformly dispersing small dye molecules (fluorophores) into functionalized polymers and networks. Polymer samples are then locally bleached, and the recovery of fluorescence is studied using 2-photon fluorescence microscopy. By curve-fitting fluorescence recovery curves to a model, diffusion coefficients are obtained. We have investigated series of polymer networks containing H-bonding interactions with different compositions at different temperatures. The diffusion coefficient through these polymer networks shows an expected Arrhenius-like temperature dependence. Our results are compared with the predictions of simple theory.

10:12AM Y16.00012 Gelling Mechanism of Aluminum Di-Soaps in Oils\textsuperscript{1}, XIAORONG WANG, Bridgestone Americas, Center for Research and Technology, 1200 Firestone Parkway, Akron, OH 44317, MINDAUGAS RACKAITIS — This work demonstrates that aluminum di-soaps form nano-sized colloidal micelles in the oil, and that the aggregation of these micelles forms a network that gives rise to a gel formation — thereby refuting a long-held belief that the gel formation was the result of linear polymeric chains of aluminum association. The discovery of such aluminum nano-particles could expand application of these materials to new technologies because these materials are chemically inert, odorless and nontoxic, and have been widely used in greases, paints, gels, cosmetics, drugs and foods.

\textsuperscript{1}Supported by the ONR (N00014-07-1-140).
optoelectronics, and biotechnology, among other areas. The controlled, evaporative self-assembly of polymer or nanocrystal solutions yields a variety of complex, intriguing, and well-ordered structures over large confined in a simple geometry comprised of a curved surface placed upon a flat substrate. By changing the shape of the upper surface of the imposed geometry, over the evaporation process of the drop, the challenge remains to use evaporative self-assembly to rationally “synthesize” “coffee rings” of different shapes and self-assembles into a number of concentric “coffee rings” by repetitive “stick-slip” motion of the three-phase contact line. However, due mainly to lack of control from Polymers to Nanoparticles

demonstrate that the lateral instability can be controlled by the imprinting conditions, and can be greatly enhanced by the additions of surfactants. The characteristics of the lateral instability were successfully carried out by annealing the patterns under a temperature gradient. We certain patterning conditions, lateral instability of the surface patterns, driven by surface fluctuations, can also become an effective mechanism for reducing patterns with relatively high aspect ratios can be created using NIL. Upon thermal annealing, the as-imprinted polymer patterns will smooth out due to the characteristic of an isotropic surface stress, while buckles initiated at the edges align radially, indicating a theta-dominated state of compressive stress. Here, we present experimentally-observed buckling morphologies resulting from a variety of surface geometries, as well as Finite Element Modeling results which provide insight into the specific evolution of stresses which led to the formation of these morphologies.

From Polymers to Nanoparticles

8:36AM Y18.00002 Morphology of Osmotically-Driven Surface Buckles, DEREK BREID, ALFRED CROSBY, University of Massachusetts — The ordering of osmotically-driven surface buckles on an elastomically-supported stiff plate depends strongly upon the dominant stresses acting on the surface during formation. For example, conditions which lead to buckle initiation at the center of the plate yield hexagonal dimple arrays characteristic of an isotropic surface stress, while buckles initiated at the edges align radially, indicating a theta-dominated state of compressive stress. Here, we present experimentally-observed buckling morphologies resulting from the variety of surface geometries, as well as Finite Element Modeling results which provide insight into the specific evolution of stresses which led to the formation of these morphologies.

8:48AM Y18.00003 Lateral Instability of Nanoimprinted Polymer Patterns during Thermal Annealing, YIFU DING, University of Colorado, KYLIE ALVINE, Pacific Northwest National Laboratory, HYUNWOOK RO, MANISH KULKARNI, JACK DOUGLAS, CHRISTOPHER SOLES, NIST — Nanoimprint Lithography (NIL) is a promising candidate for next generation lithography. Dense polymer patterns with relatively high aspect ratios can be created using NIL. Upon thermal annealing, the as-imprinted polymer patterns will smooth out due to the surface energy and sometimes residual stress within the patterns. Both effects will predominately drive the pattern decay vertically. Here, we present that under certain patterning conditions, lateral instability of the surface patterns, driven by surface fluctuations, can also become an effective mechanism for reducing the total surface area. The characteristics of the lateral instability were successfully carried out by annealing the patterns under a temperature gradient. We demonstrate that the lateral instability can be controlled by the imprinting conditions, and can be greatly enhanced by the additions of surfactants.

9:00AM Y18.00004 Mechanical instabilities in periodic porous elastomer solids, SRIKANTH SINGAMANENI, Georgia Institute of Technology, KATIA BERTOLDI, MIT, SEHOON CHANG, Georgia Institute of Technology, JI-HYUN JANG, MIT, SETH YOUNG, Georgia Institute of Technology, EDWIN THOMAS, MARY BOYCE, MIT, VLADIMIR TSUKURK, Georgia Insitute of Technology, GIT/MIT COLLABORATION — We describe the transformation of the periodic microporous structures fabricated by interference lithography followed by their freezing below glass transition. Periodic porous microstructures subjected to internal compressive stresses can undergo sudden structural transformation at a critical strain. The pattern transformation of collapsed pores is caused by the stresses originated during the polymerization of acrylic acid (rubbery component) inside of cylindrical pores and the subsequent solvent evaporation in the organized microporous structure. The results of a non-linear numerical investigation confirm the critical role of the bifurcation of the periodic solid under compressive stresses. In striking contrast to the earlier observations of elastic instabilities in porous elastomeric solids, the elastic-plastic nature of the crosslinked periodic microstructure studied here provides for the ability to lock in the transformed pattern with complete relaxation of the internal stresses. By confining the polymerization of acrylic acid to localized porous areas complex microscopic periodic structures are obtained.
9:12AM Y18.00005 Peculiarities in liquid phase of Styrene Butadiene rubber surface induced by Atomic Force Microscopy-assisted electrostatic nanolithography . MINDAUGAS RACKAITIS, Bridgeston Americas, SERGEI LYUKSYUTOV, The University of Akron, DMYTRO KASHYN, PAVEL PARAMONOV, ROBERT MALLIK — Nanoscale surface changes are reported for styrene butadiene rubber (SBR) films (10-100 nm) using protocol derived from Atomic Force Microscopy (AFM) electrostatic nanolithography. Under appropriate tip bias conditions, the electric field magnitude induced in SBR films is of the order of 10^{-10} V m^{-1}, which is sufficient large to initiate cross-linking in the rubber. Peaklike surface features, surrounded by a circular trough and a raised ring, are observed after completing AFMEN-based protocol. The nanostructure dimensions vary from 0.5-20 nm high and 200-500 nm in diameter. The topology of the nanostructures is attributed to the interplay between film thickness, the rate of the modulating surface potential, and the rate of the protein adsorption. The unique properties of the electric field based on the numerical solution of Laplace equation for cylindrical geometry suggests that non-uniformity of electric field plays an important role in nanostructure formation. The stability of the features which remain stable for days suggests cross-linking between macromolecules at the nanoscale.

9:24AM Y18.00006 Diffusion-Controlled, Self-Organized Growth of Symmetric Wrinkling Patterns . CHRISTOPHER M. STAFFORD, JUN YOUNG CHUNG, ADAM J. NOLTE, Polymers Division, National Institute of Standards and Technology, POLYMERS DIVISION, NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY TEAM — The formation of self-organized wrinkling patterns is a potential route for generating such tunable ordered patterns on surfaces across many length scales. Here, we demonstrate that surface wrinkling of ultraviolet/ozone (UVO) treated polymer films through osmotically driven swelling by solvent vapor sorption leads to unique and intriguing patterns, some of which have not been previously reported. The type of pattern and speed of its growth is coupled to the degree of UVO crosslinking and the rate of solvent diffusion into the film from a localized defect. This simple yet novel approach could serve as a test-bed for studying topography-driven phenomena such as wettability and adhesion and diffusion related processes, as well as facilitate a better understanding of dynamic self-assembly.

9:36AM Y18.00007 Transition from Non-interacting to Interacting Regime of Tethered Polymer Chains . RYAN VAN HORN, JOSEPH X. ZHENG, MING-SIAO HSIAO, BERNARD LOTZ, EDWIN L. THOMAS, JUTTA LUETTMER-STRAITHMANN, STEPHEN Z.D. CHENG, University of Akron — Tethered polymer chains have become an important area of research over the last few decades. Their unique properties make them appealing for various applications. The tethering density of the chains determines the state of the chains as well as the resulting properties, as shown by various theoretical and experimental work. Our group uses single crystals of crystalline-amorphous diblock copolymers to study tethered polymer chains. This system provides better control of tethering density and molecular weight as compared to previous methods. Previous work on PS-b-PEO and PS-b-PLLA shows, for the first time, the reduced tethering density value of the interacting regime transition regardless of molecular weight or solvent quality. Other factors that were not addressed included adhesion and chain stiffness effects. The work presented here will look at the role of chain adsorption using miscible polymers, namely PMMA-b-PLLA, and chain stiffness with PEO-b-PCL where PEO is the amorphous block. In addition to experimental results, Monte Carlo simulations were used to estimate the chain conformation of adsorbed PMMA.

9:48AM Y18.00008 Internal Structure of Diblock Copolymer Brushes . BULENT AKGUN, CHARLES F. MAJKRZAK, SUSHIL SATIJA, Center for Neutron Research, National Institutes of Standards and Technology, Gaithersburg, MD 20899, GOKCE UGUR, WILLIAM J. BRITTA, MARK D. PETER, Department of Polymer Science, The University of Akron, Akron, OH 44325-3909, XUEFA LI, JIN WANG, Experimental Facilities Division, Argonne National Laboratory, Argonne, IL 60439 — Although diblock copolymer brushes (DCBs) have been studied due to their stimuli-responsive behavior, their internal structure has been unknown. We have resolved the internal structure of DCBs using neutron reflectivity and grazing incidence x-ray scattering (GIXS). The DCB is a composite with PMMA(A) and polystyrene(B) as the outer shells, and the core is the diblock copolymer in the center. The thickness of each shell depends on the length of the diblock copolymer, which is called the brush thickness. The measured reflectivities were modeled using Monte Carlo simulations that include both the core and shells, as well as the solvent. The reflectivity data show that the diblock copolymer backbone is aligned with the dipole moment of the solvent, that is, the diblock copolymer backbone is aligned perpendicular to the meniscus of the liquid. The height of the diblock copolymer backbone increases with the length of the diblock copolymer, while the thickness of the diblock copolymer backbone decreases with the length of the diblock copolymer.

10:00AM Y18.00009 Steric effects on the phase behavior of end-tethered temperature-responsive polymers . CHARLES HOGSHEAD, EVANGELOS MANIAS, Materials Sci & Eng; Penn State University — End-tethering polymers from a planar surface at high grafting density results in an apparent spatial confinement originating from interchain steric repulsion. This effective confinement can alter the phase behavior of temperature-responsive polymers in solution, relative to their bulk solution behavior. Here we report on experiments where we synthesized tethered polymer layers with a gradient in grafting density. The systems studied were temperature-responsive alternating copolymers in aqueous solutions. Underwater AFM was used to directly observe the tethered chain collapse upon heating through the bulk LCST, and the resulting reversible adhesion switch. The transition of the tethered layers occurs at temperatures that are similar to the binodal points of the respective solution, but over a much broader temperature range. This behavior is consistent with the collapse being a cooperative conformational transition, reflecting the effects of chain confinement, rather than a first-order thermodynamic LCST transition (as these same polymers exhibit in bulk aqueous solutions). The onset-temperature of the transition, of both the tethered layers and the LCST, was tailored by varying the copolymer composition, i.e., by tuning the hydrophilic/hydrophobic balance within the chain.

10:12AM Y18.00010 Self-Assembling Pi-conjugated Monolayer on Silicon . J.-C. LIN, J. KELLAR, J.-H. KIM, S. NGUYEN, M. HERSAM, M. BEDZYK, Northwestern University, K. BEVAN, Purdue University — Pi-conjugated molecules play an important role in molecular electronic applications. For conductivity, the intrinsic ordering of the structure strongly influences its efficiency but is difficult to characterize by conventional scanning probe and IR spectroscopy techniques. In the present study, we combine a complement of techniques, including XSW(X-ray standing waves), AFM, XPS, XRR(X-ray reflectivity), XRF(X-ray fluorescence), and DFT(Density functional theory) to determine the atomic scale molecular configurations and packing densities of two self-assembled aromatic monolayers (SAMs) grown on H-passivated silicon. P-4-bromophenyl-ethylphenyl-acetylene, which has two phenyl rings, is directly bonded to the p-4-bromophenyl and its results with p-4-bromophenyl-ethylphenyl-acetylene SAM are different than the results with the p-4-bromophenyl-acetylene SAM. The packing of the p-4-bromophenyl-ethylphenyl-acetylene SAM suggests the average spacing between molecules is within the pi-pi interaction range, which will contribute to the charge transport. The detailed atomic structure of SAMs are also constructed using our characterization package. The result suggests the possibility of the application of self-assembling method on the growth of molecular electronics.

10:24AM Y18.00011 The Dynamic Reinforcement of Polyvinyl Alcohol (PVA) as a Result of Non-equilibrium State of Polymer Supermolecular Structures and their Confinement in Nanofibers . EYAL ZUSSMAN, EMIL SHAKED, ARKADI ARNSTEIN, Technion — The results of mechanical testing of PVA-based electrospun nanofibers and bulk in static and dynamic modes are presented. An increase in the elastic moduli resulting from sample deformation was observed in both the bulk and as-spun fibers. This increase occurs when the deformation rate exceeds a critical value and can be attributed to the non-equilibrium dynamics of the supermolecular structures of the polymer matrix. That is, the evolution of these supermolecular structures results in an observable extended relaxation time. It is noted that the rate of the modulus increase is the confinement effect on the confinement influence on the polymer matrix of the nanofibers. In addition, the tests revealed that the Tg of the nanofiber is noticeably higher than that of bulk specimen. Reinforcing the nanofibers by cellulose whiskers showing that the dependence of the effective modulus on the whisker concentration has an initial increase that changes to a decrease when the whisker concentration exceeds 2 %. Such behavior can be explained in the framework of an aggregation concept – when the cluster size reaches that of the fiber diameter (cluster confinement), the whisker distribution becomes inhomogeneous and results in a measurable weakening of the composite.
10:36AM Y18.00012 Phenomenology of Polymer Thin Film Dewetting during Vapor Deposition Polymerization1, MITCHELL ANTHAMATTEN, XICHONG CHEN, University of Rochester, DEPARTMENT OF CHEMICAL ENGINEERING TEAM — Initiated chemical vapor deposition (iCVD) is a solventless technique to grow polymer thin films directly from gas phase feeds. The free radical technique involves the dissociation of gaseous initiator followed by adsorption onto a surface and subsequent polymerization with monomer to produce linear or crosslinked polymer films. We have designed and built an axisymmetric hot-zone iCVD vacuum reactor. Using this reactor, smooth poly (methyl methacrylate) films are grown from methyl methacrylate and t-butyl peroxide gas feeds. When solvent vapors are added to the process, we observe dewetting of vapor deposited polymer films. The objective of the current study is to understand the phenomenology of the observed solvent-induced dewetting. White light interferometry was used to investigate the surface topography of dewetted structures. The observed length scale depends on several process parameters including the deposition rate, the type of solvent used, and the surface free energy. Higher deposition rates suppress dewetting, and higher solvent content leads to dewetted structures with larger length scales. A dynamic model is applied to explain how droplet size and droplet aerial density depend on time and process parameters.

3This study was supported by the National Science Foundation (NSF-0828437).

10:48AM Y18.00013 Nano-adsorbents control surface properties of polyurethane, SUPING LYU, DARREL UNTEREKER, JIM SCHLEY, TOM GRAILER, ANNA BELU, CHRIS HOBOT, TERRI BARTLETT, RANDY SPÄRER — Additives are minor but critical components that polymers need for processing and applications. However, these additives may also have adverse effects, e.g. for polymeric biomaterials, leaching additives can change surface properties, and may lead to poor biocompatibility. How to use additives yet keep them from detrimental behaviors is challenging. Diffusion barriers may be used to slow down the additive migration but it is difficult to stop it. In this paper, we introduced the concept of “nano-adsorbents” in polymers. These nano-adsorbents confined the additives within the polymers via thermodynamically interacting with them. While the additives are still present in polymers to provide intended functions, they are thermodynamically constrained from freely migrating to the surface. Nano sized-fillers were selected due to their high surface-to-volume ratio. This new use of nano-fillers for polymers was demonstrated with a biomedical polyurethane and a surface coated nano-clay that thermodynamically attracts the additive in the polyurethane.

Friday, March 20, 2009 8:00AM - 11:00AM –
Session Y19 DPOLY: Surfaces and Adsorption I

8:00AM Y19.00001 Sequence-directed organization in self-assembled monolayers of beta-peptides on solid surfaces: A Monte Carlo simulation study1, JAGANNATH MONDAL, University of Wisconsin Madison, BONG JUNE SUNG, Sogang University, ARUN YETHIRAJ, University of Wisconsin Madison — The sequence-directed organization of self-assembled monolayers (SAM) of amphiphilic β-peptides adsorbed on gold surfaces is studied using Monte Carlo simulations. A phenomenological model is considered where each (helical) molecule is represented by a rigid nano-rod with the side groups at appropriate locations. This model effectively distinguishes between two, namely globally amphiphilic (GA) and non-globally amphiphilic(non-GA), sequence-isomers of an amphiphilic β peptide Y-(ACHC-ACHC-K)3. The simulations show that the GA isomers have a high degree of orientational order that is not exhibited by the non-GA isomers, consistent with experiment. The simulations quantify a subtle balance between electrostatic, hydrophilic, and hydrophobic interactions on the self-assembly of β-peptides on surfaces.

1NSF grant DMR-0425880

8:12AM Y19.00002 Thermal Response of PNIPAM Brushes Studied by Numerical Self-Consistent Field Calculations, DONG MENG, QIANG WANG, Department of Chemical and Biological Engineering, Colorado State University — Unlike most polymers, poly(N-isopropyl acrylamide) (PNIPAM) exhibits a lower critical solution temperature in water, i.e., PNIPAM chains are soluble (expand) at low temperatures and insoluble (collapse) at high temperatures. This property has been used to create “smart” surfaces of PNIPAM brushes that can switch wettability, porosity and cell-adhesion properties as temperature is changed. Such thermal response of PNIPAM brushes are strongly affected by both chain length and grafting density. In this study we use numerical self-consistent field calculations with a composition-dependent Flory-Huggins parameter obtained from experiments to study the thermal response of PNIPAM brushes. The effects of chain length and grafting density are systematically investigated to provide guidance to experimental design of PNIPAM brushes for targeted applications.

8:24AM Y19.00003 Time evolution of the structure of fluorinated alkanes near solid surfaces1, MESFIN TSIGE, Southern Illinois University at Carbondale — The study of thin films of physisorbed molecules has attracted much experimental and theoretical interest in the past few decades. This is mainly due to numerous reports of anomalous behavior in the structural and dynamical properties of polymer thin films at interfaces and the expected consequences in their wide range of practical applications. Although great advances have been made in our understanding of the physics and chemistry of polymer melt/solid and polymer melt/vapor interfaces, there remain a number of fundamental as well as practical issues that need to be addressed regarding the influence of interfaces on a polymer film. One of the issues, which I think no systematic study has been yet conducted on, is the stability and/or time evolution of the molecular layering in a film next to a solid substrate. The main focus of my presentation will be on our recent computer simulation study result that shows that the extent of layering in an alkane film next to a solid substrate may oscillate in time with an amplitude and period that strongly depends on temperature.

1Work supported by the Donors of the American Chemical Society Petroleum Research Fund.

8:36AM Y19.00004 Activation of CO2 on transition metal surfaces and oxide supported metal thin films, SUJATA PAUL, MARCO BUONGIORNO NARDELLI, NC State Univ — Using first principles simulations based on Density Functional Theory, we have investigated the adsorption and activation properties of CO2 on a variety of transition metal surfaces and oxide supported metal thin films. We intend to focus on the chemical conversion of CO2 through heterogeneous catalysis using surfaces and interfaces where there is nanoscale control over charge density at the reactive sites. The activation of CO2 on clean metal surfaces is possible at very high temperatures and the situations changes drastically when reaction happens on oxide supported metal thin film. The chemical reactivity of the molecule on the surface depends on the charge rearrangement at the metal-alkaline earth oxide interface. We want to understand the possible catalytic systems and characterize the relevant geometrical and electronic parameters related to the reaction mechanisms, rates and yield.
8:48AM Y19.00005 Dynamics of an Adsorbed Polymer Chain , JOSHUA KALB, SANAT KUMAR, Columbia University — Because of the current precision in fluorescent labeling, it is possible to label single polymers such as DNA or PEG and track their dynamical and equilibrium properties in the bulk as well as near attractive surfaces [Maier et. al., Macro. 2000][Sukhishvili et. al., Macro. 2002]. Recent evidence from these experiments and related simulations has shown that the dynamics of a single polymer near an attractive surface appear diffusive, however further evidence coming from the ‘diffusion coefficient’ implies a different process other than diffusion is at work such as reptation, ‘hover crafting’, or ‘hopping’ [Sukhishvili et. al., Macro. 2002]. In general, these possible dynamical behaviors are determined by the length of the polymer itself as well as the microscopic details of the attractive surface which include the density, strength, and distribution of attractive surface sites[Desai et. al., PRL 2007][Qian et. al. PRL 2007]. In this presentation, we investigate the effects of microscopic surface sites on single polymer dynamics through DMD simulations and compare these results to the properties of the chain in the bulk and near a flat attractive surface.

9:00AM Y19.00006 Investigation of Carboxymethyl cellulose Adsorption onto Regenerated Cellulose Surfaces via Quartz Crystal Microbalance with Dissipation Monitoring and Surface Plasmon Resonance Spectroscopy , ZELIN LIU, Department of Chemistry (0212), Virginia Tech, Blacksburg, VA 24061, PAUL GATEN-HOLM, Department of Materials Science and Engineering (0237), Virginia Tech, Blacksburg, VA 24061, ALAN ESKER, Department of Chemistry (0212), Virginia Tech, Blacksburg, VA 24061 — The adsorption of anionic polyelectrolytes, sodium salts of carboxymethyl celluloses (CMC), with different degrees of substitution (DS = 0.9 and 1.2) from aqueous electrolyte solutions onto regenerated cellulose surface was studied via quartz microbalance with dissipation monitoring (QCM-D) and surface plasmon resonance (SPR). The influence of both calcium chloride (CaCl2) and sodium chloride (NaCl) was examined. Both QCM-D and SPR results indicate that CMC adsorption onto regenerated cellulose surfaces increases with increasing electrolyte concentration and CaCl2 (divalent cation) showed a significant effect on CMC adsorption compared to NaCl (monovalent cation) at the same ionic strength. Voigt-based viscoelastic modeling of the QCM-D data and analysis of the SPR data are consistent with the existence of a swollen CMC layer on the cellulose surface with a viscosity of ~1.310-3 kg m-1 s-1 and an elastic shear modulus of ~105 kg m-1 s-2.

9:12AM Y19.00007 Theory of Polymer Adsorption Onto Selected Chemically Patterned Substrates , ALEXANDER CHERVANYOV, GERT HEINRICH, Leibniz Institute of Polymer Research Dresden — We theoretically studied the reversible adsorption of polymers onto selected rigid and soft chemically non-uniform substrates with an emphasis on the polymer adsorption onto the selective binary mixed brushes. In the course of our study, we developed two independent theoretical methods, the self-consistent perturbation expansion and the transfer operator formalism, which made it possible to thoroughly investigate the density structure of polymers adsorbed onto chemically non-uniform substrates. As successive stages of our research, we applied the above theoretical methods to the study of the polymer adsorption onto the selected substrates, as follows: (i) periodically patterned rigid surface; (ii) randomly patterned rigid surface; (iii) surface that bears an array of periodically distributed adsorption centers; (iv) ripple, random and dipole morphologies of the binary mixed brush. By comparing the results obtained for the above listed systems we derived the qualitative trends that are common for the polymer adsorption onto the investigated chemically non-uniform substrates. In this talk, we discuss what are the main factors that influence the polymer adsorption onto the patterned substrates and how to reduce/enhance the polymer adsorption by way of manipulating these competitive factors.

9:24AM Y19.00008 Cationic xylan adsorption onto self-assembled monolayers and model cellulose surfaces , ALAN ESKER, ABDULAZIZ KAYA, DANIEL DRAZENOVICH, WOLFGANG GLASSER, Virginia Tech, KATRIN SCHWIKAL, THOMAS HEINZE, University of Jena — Self-assembly of cationic hydroxypropyltrimethylammonium xylans (HPMAs) with different degrees of substitution (DS) onto self-assembled monolayers (SAMs) and model cellulose surfaces has been investigated by surface plasmon resonance (SPR). Maximal adsorption of HPMAs onto COOH-terminated SAMs occurs at an intermediate DS=0.10. Ionic strength effects on adsorbed amount follow different trends at low and high DS values which qualitatively agree with predictions of scaling theory for polyelectrolyte adsorption. For adsorption on model cellulose surfaces and OH-terminated SAMs, surface excess values are relatively low compared to COOH-terminated SAMs. For adsorption on CH3-terminated SAMs, solubility of the HPMAs plays an important role as HPMA adsorption decreases with increasing DS values.

9:36AM Y19.00009 Introduction of a novel surface plasmon resonance imaging method for use in the study of quantitative kinetic surface interactions , SCOTT ALLEN, OLEH TANCHAK, JOHN DUTCHER, University of Guelph — The surface plasmon resonance (SPR) phenomenon is widely used as a surface sensitive probe of biomolecular surface interactions. SPR imaging (SPRI) is an experimental mode that takes advantage of the SPR phenomenon to directly visualize nanoscopic changes to surfaces using simple optics and a CCD camera. SPRI, performed at a fixed angle of incidence, enables one to study association, dissociation and degradation processes in a multi-arrayed format without the need for fluorescent tags. A discussion of specific challenges associated with performing kinetic measurements at a fixed angle of incidence will be presented. A novel SPRI method that enables one to perform reproducible quantitative kinetic measurements will be introduced, along with experimental examples of the use of this technique.

9:48AM Y19.00010 Pentacene on Cu(911): A Density Functional Theory study , ABDELLKADER KARA, University of Central Florida — I use density functional theory to calculate the adsorption energies, geometric and electronic structures of pentacene (C22H14) on the Cu(911) vicinal surface. The pentacene molecule is found to adsorb nearly flat (slightly arched at the edges) on top of the terrace but close to the step with an adsorption energy of 1.3 eV. The adsorption geometry on Cu(911) is found to differ from that on Cu(110); but there is a strong bonding between the center carbon atoms of the molecule and Cu atoms near the step. In accord with experimental observations, the arched geometry induces brightness at the edges of the molecule in the STM images. The alignments of the energy levels at the interface induce a change in the work function of about -0.4 eV, in qualitative agreement with the observed -0.9 eV, which is an indication of charge transfer from the molecule to the surface. The details of the electronic structure at the interface will be presented.

10:00AM Y19.00011 Dynamics within alkylsiloxane SAMs studied by sensitive dielectric spectroscopy1, MARY SCOTT, DERRICK STEVENS, JASON BOCHINSKI, LAURA CLARKE, North Carolina State University, Raleigh, NC 27695 — Self-assembled monolayers (SAMs) are a ubiquitous tool in modern research and their static structure has been extensively studied. Fewer investigations have addressed dynamics within these systems; however, such motions within SAMs will affect surface properties such as friction and blocking ability (permeability). In this study, sensitive, dielectric spectroscopy over a broad temperature range (4-400 K) has been employed to study relaxations within planar alkylsiloxane SAMs[1]. Highly disordered SAMs of varying density were grown by vapor deposition. Two dielectric relaxations were observed. The first, a polyethylene-like relaxation similar to that previously reported in phase-segregated alkyl side-chain polymers, is observed for all films with alkyl chains containing four or more carbons. This is an interacting or glassy relaxation. The second motion, which is observable only at high film densities, is a local mode, which follows an Arrhenius dependence on temperature, and has been previously assigned to a sub-chain rotation. [1] M.C. Scott, D.R. Stevens, J.R. Bochinski, L.I. Clarke, ACS Nano. DOI: 10.1021/n800543j.

1 NSF grant 04-03871
and recovery behavior makes them interesting candidates for injectable delivery in vivo. Once formed into a solid, the self-supporting gel network can be disrupted, allowing encapsulated payloads to diffuse. This process is dictated by pinning the spinodal decomposition process. The surfaces exhibit high water contact angles greater than 150 degrees, making them candidates for applications requiring super-hydrophobicity.

In collaboration with Joel Schneider, University of Delaware.

1 Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China

Friday, March 20, 2009 8:00AM - 10:36AM – Session Y20 DPOLY: Biological-Synthetic Hybrid Materials 321

8:00AM Y20.00001 Peptide Folding and Consequent Self-assembly for Sheep Thinning Hydrogels with Immediate Recovery1. DARRIN POCHAN, University of Delaware — The local nano- and overall network structure, and resultant viscoelastic properties, of hydrogels that are formed via beta-hairpin self-assembly will be presented. The 20 amino acid peptides have been shown to intramolecularly fold and intermolecularly self-assemble into a rigid hydrogel based on environmental cues such as pH, salt, and temperature including physiochemical conditions, super-hydrophobic polymeric surfaces (contact angle higher than 150°) with tunable sliding angles (from less than 1° to higher than 90°) can be prepared from isotactic polypropylene (iPP)/ polypropylene chloride (PPC) blend under ambient atmosphere. No further modification with low-surface-energy component is needed. The formed surfaces have good thermal property, chemical and moisture resistance and potentially low manufacturing cost.

1 In collaboration with Joel Schneider, University of Delaware.

8:36AM Y20.00002 Designing ‘smart’ hydrogels using peptide-responsive conjugates. ALBERTO SAIANI, JEAN-BAPTISTE GUIBAUD, ALINE MILLER, The University of Manchester — Polymers displaying phase transitions in aqueous solution from a hydrophilic to hydrophobic state are of widespread interest as ‘smart’ biomedical materials. Hydrogels formed from self-assembling peptides have also attracted considerable attention in the past decade. These hydrogels are based on the self-assembly of short peptides into supra-molecular fibres that entangle or associate to form three dimensional networks and, ultimately, self-supporting hydrogels. In order to create a new generation of hydrogel based on self-assembling peptides but possessing an internal transition that can be used as a trigger to release a drug molecule or a specific biological signal, we have synthesized a new family of peptide-polymer conjugates using free radical polymerization. We were able to create a new generation of ‘smart’ hydrogel in which gelation is driven by the peptide while the polymer phase transition can be used to release in a controlled fashion a specific signal or drug molecules. These materials are though to be of prime interest for tissue culture applications where they can be used to deliver specific signals stimulating a specific cell response.
8:48 AM Y20.00003 “Backpack” Functionalized Living Immune Cells1, ALBERT SWISTON, MIT Dept of Materials Science and Engr., SOONG HO UM, DARRELL IRVINE, MIT Dept of Biological Engr., ROBERT COHEN, MIT Dept of Chemical Engr., MICHAEL RUBNER, MIT Dept of Materials Science and Engr. — We demonstrate that functional polymeric “backpacks” built from polyelectrolyte multilayers (PEMs) can be attached to a fraction of the surface area of living, individual lymphocytes. Backpacks containing fluorescent polymers, superparamagnetic nanoparticles, and commercially available quantum dots have been attached to B and T-cells, which may be spatially manipulated using a magnetic field. Since the backpack does not occlude the entire cellular surface from the environment, this technique allows functional synthetic payloads to be attached to a cell that is free to perform its native functions, thereby synergistically utilizing both biological and synthetic functionalities. For instance, we have shown that backpack-modified T-cells are able to migrate on surfaces for several hours following backpack attachment. Possible payloads within the PEM backpack include drugs, vaccine antigens, thermally responsive polymers, nanoparticles, and imaging agents. We will discuss how this approach has broad potential for applications in bioimaging, single-cell functionalization, immune system and tissue engineering, and cell-based therapeutics where cell-environment interactions are critical. 

1This work was supported primarily by the MRSEC Program of the NSF under award number DMR - 0819762, and is based upon work supported by a NSF Graduate Research Fellowship.

9:00 AM Y20.00004 Reversible Structural Transition of a DNA Lipid Film. MATTHEW TIRRELL, SUREKHA GAJRIA, THORSTEN NEUMANN, LUC JAEGER, University of California, Santa Barbara, MATERIALS RESEARCH LABORATORY COLLABORATION — Polyanions such as nucleic acids (RNA and DNA) can self-assemble with cationic lipids via electrostatic complexation, driven thermodynamically by the release of counterions. The structures of these complexes in water have been studied extensively and are recognized as potentially useful in the field of gene delivery. The structure of films in water is dominated by the nature of the lipid. Within these lamellar complexes in aqueous solution the lipid assumes a bilayer formation and the DNA is a double helix. It is possible to obtain dry nucleic acid-lipid films when the dissolved cationic lipid complex of DDAB and nucleic acid is cast on a solid. These self-standing films have been characterized by tensile and nucleic acid intercalation experiments. The tensile properties of these films are adjustable by mixing different molecular weights. It was expected that these films would have the same characteristic structure as these complexes in water. However, our work shows that the film undergoes a transition from double stranded helical DNA complexed with a bilayer of DDAB in the wet state, while in the dry state we observed a repeat unit of single stranded DNA complexed with a monolayer of DDAB.

9:12 AM Y20.00005 Gecko-Inspired Carbon Nanotube-Based Adhesives1, LIEHUI GE, SUNNY SETHI, ANUBHA GOYAL, LIJIE CI, PULICKEL AJAYAN, ALI DHINOJWALA, THE UNIVERSITY OF AKRON COLLABORATION, RICE UNIVERSITY COLLABORATION — Nature has developed hierarchical hairy structure on the wall-climbing gecko’s foot, consisting of microscopic hairs called setae, which further split into hundreds of smaller structures called spatulas. In the last five years, numerous attempts to mimic gecko foot-hair using polymer soft molding and photolithography methods have been reported. However, most of these polymer-based synthetic gecko hairs fall short of the clinging ability of geckos. Vertically aligned carbon nanotubes (CNT) have shown strong adhesion at nanometer scale. Here, we present our work on developing CNT-based macroscopic flexible tape mimicking the hierarchical structure found on gecko’s foot. The synthetic gecko tape is made by transferring aligned CNT array onto flexible polymer tape. The unpatterned CNT-gecko tape can support a shear force stress similar to gecko foot (10 N/cm²). The supported shear stress increase by a factor of four, when we use micro-patterned CNT patches (50 to 500 μm). We find that both setae (replicated by CNT bundles) and spatulas (individual CNT) are necessary to achieve large macroscopic shear adhesion. The carbon nanotube-based tape offers an excellent synthetic option as a dry conductive reversible adhesive in microelectronics, robotics, and space applications.

1Research Supported by National Science Foundation

9:24 AM Y20.00006 Sensing Structures Inspired by Blind Cave Fish. MICHAEL E. MCCONNEY, Georgia Institute of Technology, NANNAN CHEN, University of Illinois at Urbana-Champaign, DAVID LU, KYLIE D. ANDERSON, Georgia Institute of Technology, HUAN HU, Northwestern University, CHANG LIU, Northwestern University, VLADIMIR V. TSUKRUK, Georgia Institute of Technology — Blind cave fish, with degenerate visionless eyes, have evolved to “see” their hydrodynamic environment by using the flow receptors of the lateral line system. The hair-cell receptors are encapsulated in a hydrogel-like material, called a cupula, which increases the sensitivity of the hair-cell receptors by coupling their motion to the surrounding flowing media. We characterize the viscoelastic properties and of blind cave fish cupulae by using colloidal-probe spectroscopy in fluid. A photo-patternable hydrogel with similar properties was developed to mimic the fish receptor coupling structure. Flow-based measurements indicated that the hydrogels enhance drag through increased surface area, but also inherent material properties. These bio-inspired structures endowed micro-fabricated flow sensors with sensitivities rivaling that of fish.

9:36 AM Y20.00007 Giant super-helix formation from aqueous bioinspired block copolymers. H.K. MURNEN, A.M. ROSEALS, Dept. of Chemical Engineering, University of California-Berkeley, R.N. ZUCKERMANN, The Molecular Foundry. Lawrence Berkeley National Laboratory, R.A. SEGALMAN, Dept. of Chemical Engineering, University of California-Berkeley — Polypeptides are a class of bioinspired polymers based on N-substituted glycines with the side group bonded to the backbone nitrogen rather than the alpha carbon as in natural polypeptides. Due to the lack of backbone hydrogen bonding and the sequence specific synthesis of these materials, side chain interactions can be designed to induce the formation of macromolecular structures in aqueous solution. An amphiphilic block copoly peptide consisting of a hydrophobic block, poly[N-(2-phenylethyl)glycine] and a hydrophilic block, poly[N-[2-carboxyethyl]glycine] is found to form giant superhelices in aqueous solution by scanning and transmission electron microscopy and atomic force microscopy. With a diameter greater than 600nm, these helices are much larger than the fully extended length of the molecules (7 nm). Furthermore, while the molecules are completely achiral, the helices are all left handed and remarkably regular (pitch 670nm, length greater than 2 microns). We will discuss possible preferential chain conformations that may provide the driving force for the superstructure.

9:48 AM Y20.00008 The effects of supramolecular network topology on hapten-receptor avidity. JASON BENKOSKI, ANDREW MASON, JILL LA FAVORS, JOSHUA WOLFE, The Johns Hopkins University Applied Physics Laboratory — Antibodies produced in the early stages of the immune response have much lower affinities for a given antigen than those produced later on. Nature compensates for the initial weakness of these associative bonds by synthesizing multivalent antibodies. The total binding strength, represented by the avidity constant, is equal to the product of the affinity constants for the individual hapten/receptor sites. However, under realistic conditions the individual binding sites do not act independently. Factors such as steric hindrance, intramolecular stresses, and competitive binding can significantly alter the relationship between affinity and avidity. We investigate the influence of these factors on a model system consisting of synthetic multifunctional nanoparticles and polymers. Each polymer or nanoparticle is decorated with either multiple, antigens (thromboxane B2) or multiple antibodies. We then measure the association and dissociation in real time using Surface Plasmon Resonance Spectroscopy (SPR). By using synthetic polymers and nanoparticles, we are able to systematically control the degree of functionality, flexibility, and distance between receptor and hapten sites.
10:00AM Y20.00009 Dynamic DNA Interactions with Functionalized Colloids, LU ZHANG, YINGXI ELAINE ZHU, Department of Chemical and Biomolecular Engineering, University of Notre Dame — Many biomedical processes, such as protein adsorption, DNA hybridization and enzyme reactivity, are intimately related to their interactions with surfaces and complex ionic environments, yet the details of biomacromolecular interaction remain insufficiently understood. In this work, we use confocal laser scanning microscopy to examine the interaction between DNA molecules and functionalized colloidal particles in aqueous suspension. We observe an intriguing attractive interaction between DNAs and carboxyl-functionalized silica particles of varied sizes from 50 nm to 3 um, resulting in complex DNA-colloid aggregation with a strong dependence on DNA/colloid size ratio and ionic strength. As colloidal size becomes larger than DNA dimensions, colloidal doublets and triplets with adsorbed DNAs are observed at high DNA concentration and ionic strength. The intriguing DNA-colloid complex structures are further confirmed by SEM and appear stable for at least 2 weeks.

10:12AM Y20.00010 Growth of well-defined metal and oxide nanoparticles on biological surfaces, VLADIMIR TSUKRUK, Georgia Tech — We present a brief overview of our recent studies in the field of bio-enabled surface-mediated growth of inorganic nanoparticles at room temperature and ambient conditions. We demonstrate that all titania, gold, and silver nanoparticles can be grown with relatively monodisperse diameter within 4-6 nm surrounded by biological shells of 1-2 nm thick. As biological templates we utilized ultrathin, molecular uniform and micropatterned surface layers of two different proteins: silk fibroin (for growth of gold and silver nanoparticles) and silalbin (for growth of titania nanoparticles). To identify the grown nanophases and chemical composition/secondary structure of biological templates we applied combined AFM, SEM, TEM, XPS, SERS, UV-vis, and ATR-FTIR techniques.

10:24AM Y20.00011 Fluorescent DNA-bound Ag nanoclusters, PATRICK O’NEILL, LOURDES VELAZQUEZ, KIM WEVERICH, DEBORAh FYGENSON, University of California Santa Barbara — Few-atom fluorescent Ag nanoclusters self-assemble on short, synthetic DNA strands, and exhibit sequence and structure dependent fluorescence ranging from the blue to the near infrared. Here we report UV excitation as a ubiquitous feature of these emitters. Each emitter thus has two excitation peaks: a visible peak which is cluster-dependent, and a UV peak which has the same wavelength for all DNA-bound Ag clusters. This UV peak corresponds to resonant absorbance by the DNA bases, and produces the same emission spectra as visible excitation, suggesting energy transfer from the DNA bases to the Ag cluster. We make use of this UV excitation to image the emitters in unstained polynucleotide gels, and show that electrophoresis can be used to create a pure solution of green DNA:Ag11 clusters from an inhomogeneous red solution of DNA:Ag>12 clusters.

Friday, March 20, 2009 8:00AM - 10:36AM
Session Y36 DMP DPOLY: Organic and Hybrid Surfaces and Interfaces 408

8:00AM Y36.00001 Diffusivity control in molecule-on-metal systems using electric fields, Y.Y. ZHANG, N. JIANG, S.X. DU, H.-J. GAO, Institute of Physics, Chinese Academy of Sciences, MATTHEW J. BECK, SOKRATES T. PANTELIDES, Department of Physics and Astronomy, Vanderbilt University — Electronic devices constructed from molecule-on-metal systems are actively being explored for applications in logic and memory devices, sensors, fuel cells, and solar cells. The implementation of practical molecular electronic devices requires molecule-on-metal systems in which the arrangement of active molecules is fixed or can be controlled and the contact-molecule-contact system exhibits desirable electronic properties. Fe(II) Phthalocyanine (FePc) on Au (111) exhibits a number of promising electronic properties, but diffuses rapidly at room temperature. Using scanning tunneling microscopy and density functional theory calculations we show that applied electric fields can be employed to enhance or retard the diffusivity of FePc molecules on Au (111) independent of temperature. These results demonstrate the possibility of dynamic field-guided patterning of molecule-on-metal systems.

8:12AM Y36.00002 Oxygen-related traps in pentacene thin films: Energetic position and implications for transistor performance, WOLFGANG KALB, Laboratory for Solid State Physics, ETH Zurich, Switzerland, KURT MATTENBERGER, BERTRAM BATLOGG — We studied the influence of oxygen on the electronic trap states in a pentacene thin film kept under highly controlled conditions. This was done by temperature-dependent gated four-terminal measurements on pentacene thin-film transistors prior to and after controlled oxygen exposure. We developed and used a scheme that allows for the calculation of the essential transport parameters, such as the trap DOS, in an unambiguous way. The results are free from parasitic contact artifacts. Oxidation of pentacene in light leads to a peak of trap states centered at 0.28 eV from the mobility edge, with trap densities of the order of 10^13 cm^-3. The measurements reveal how these traps affect the key device parameters, i.e. subthreshold performance and field-effect mobility. The study supports the assumption of a mobility edge for charge transport, and contributes to a detailed understanding of an important degradation mechanism of organic field-effect transistors.

8:24AM Y36.00003 Grazing-incidence X-ray Diffraction of Tetracene Thin Films on Hydrogenated Si(001) Substrate, DE-TONG JIANG, ANDREW TERSIGNI, Dept. of Physics, University of Guelph, CHANG-YONG KIM, Canadian Light Source, JUN SHI, Dept. of Physics, University of Guelph, ROBERT GORDON, Physics Dept., Simon Fraser University, NING CHEN, Canadian Light Source, XIAORONG QIN, Dept. of Physics, University of Guelph — Ex situ grazing-incidence X-ray diffraction (GIXD) and wide angle Bragg diffraction have been performed on UHV epitaxially grown tetracene thin films on H/Si(001)-2x1 substrates. The in-plane lattices of the crystalline films were characterized by 2D reciprocal space imaging of the in-plane (11), (12) and (20) GIXD diffraction spots and the out-place lattices were characterized by the wide angle Bragg diffraction. The thickness of the tetracene films ranged from 1.2 monolayer (ML) to 15 ML. H/Si(001)-2x1 substrates with different surface roughness were used. The results indicate that the film structure characteristics are strongly influenced by the substrate conditions and under favorable conditions the homogeneous thin-film phase could dominate the growth up to about 8 ML. The implications of the results to the growth mechanisms and to thin film electronics applications will be discussed.

8:36AM Y36.00004 Nanoscale conductivity measurements on organic thin films and interfaces, JUSTIN WELLS, NTNU, Trondheim, Norway, FEI SONG, PHILIP HOFMANN, iNANO and ISA, Aarhus Univ., Denmark. — Despite the importance of conductance measurements to bulk solid state physics, there is poor understanding of surface and nano-scale conductance - despite the relevance to smaller devices and the development of novel concepts for electronics. Of particular interest in this respect are self-organized organic nano-structures, which offer a virtually unlimited design freedom. Electron delocalization and transport in such systems is of great current interest. In this work, we utilise a recently developed nanoscale multi-contact mono-cantilever probe with a minimum spacing of 250 nm. We measure the conductivity of the Si(111) (√3 × √3)Ag surface, and the corresponding changes in the conductivity which occur when organic absorbates are present. By increasing the coverage from sub-monolayer to multilayer, it is possible to see doping of the underlying Ag layer, as well as conduction through the organic film. These measurements are supported by PES and NEXAFS studies, and thus can be interpreted in terms of charge transfer and geometric structure.
HOMO is incomplete for AlPc-Cl thickness of 200 ˚A, leading to a great reduction of the hole injection barrier compared to the case without MoO$_3$ spectroscopy (PES and IPES). We have investigated the electronic structure of the interfaces formed by inserting thin layer of MoO$_3$, HUANJUN DING, IRFAN IRFAN, YONGLI GAO, Department of Physics and Astronomy, University of Rochester, MIRKO CINCHETTI, MARINA SANCHEZ-ALBANEDA, JAN-PETER WUSTENBERG, OLEKSII ANDREYEV, MICHAEL BAUER, MARTIN AESCHLIMANN, Department of Physics, University of Kaiserslautern — We have investigated the spin dynamics in organic semiconductor, copper phthalocyanine (CuPc), with spin and time resolved two photon photoemission spectroscopy (STP-TPPS). The computed electron are detected optically from GaAs substrate, and injected into the unoccupied states of CuPc film. The apparent spin relaxation time is observed to have strong energy dependence. The spin polarization at high energy levels decreases much faster than that of the low energy levels. The experimental results are then explained by a cascade model. The calculation suggests that the spin information of the hot electrons can be well preserved during the energy relaxation process.

We have employed electronic structure methods to describe substitution effects on the reorganization energy. The substitutions on the internal nitrogen in phthalocyanine have strong influence on reorganization energy. The detailed relation between reorganization energy and substitution in reorganization energy leads to a large change of charge mobility. We have employed electronic structure methods to describe substitution effects on the various discotic materials has been studied using the Marcus formalism. In the Marcus formalism, charge mobility is depends on two parameters, reorganization energy and fractionation of P3AT. Both solvent composition and temperature have been manipulated to tune the solvent quality on both hydrophobic and hydrophilic type stationary phases in order to obtain more well-defined samples of these electrically conducting polymers. In addition to HPLC separations on an analytical scale, semi-prep scale LC separations in the regime of 10mg to 100mg has also been carried out as proof of concept. Finally the interplay between solvent quality and the surface energy has been investigated using HPLC stationary phases consisting of either bare silica or C18 bonded silica.

The substitution effect on the reorganization energy of metal free phthalocyanine, HOONGKEUN LEE, KARL SOHLBERG, Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104-2875 — Many discotic (disk-like) materials such as phthalocyanine are of interest for use in organic electronic devices because of their high charge mobility. The mobility of various discotic materials has been studied using the Marcus formalism. In the Marcus formalism, charge mobility is depends on two parameters, reorganization energy and coupling matrix constant. Of these two parameters the reorganization energy has more influence on the charge hopping rate. A small change in reorganization energy leads to a large change of charge mobility. We have employed electronic structure methods to describe substitution effects on the reorganization energy of phthalocyanine. The substitutions on the external phenyl rings have almost no influence on reorganization energy, but the substitutions on the internal nitrogen in phthalocyanine have strong influence on reorganization energy. The detailed relation between reorganization energy and substitution will be presented.
10:12AM Y36.00012 Anisotropic phases in ferromagnetic ultrathin films from multipolar interactions\textsuperscript{1}. DANIEL BARCI, University of the State of Rio de Janeiro, Brazil, DANIEL STARIOLO, Federal University of Rio Grande do Sul, Brazil — We present a model to describe complex phases observed at mesoscopic scales in ultrathin magnetic films with perpendicular anisotropy. The model is based on the interaction between magnetic dipolar as well as quadrupolar moments. This model has a very rich phase diagram. In the special case of films with strong perpendicular anisotropy, a nematic phase, characterized by orientational (stripe-like) but not translational order, is predicted. The isotropic-nematic transition belongs to the Kosterliz-Thouless type in the thermodynamic limit. However, we find that in actual experimental scales the fluctuations of the nematic order parameter are regularized by the sample size, and real orientational order, as predicted by mean field, should be observable. The transition may be characterized experimentally from measurements of the magnetic structure factor, from which the nematic order parameter is derived.

\textsuperscript{1}Partially supported by the Brazilian agencies CNPq and FAPERJ.

10:24AM Y36.00013 ABSTRACT WITHDRAWN —

Friday, March 20, 2009 11:15AM - 2:15PM –
Session Z3 DPOLY DBP: Non-viral Based Gene Delivery Systems: Opportunities, Obstacles and Challenges 301/302

11:15AM Z3.00001 Small Bioactive Lipoplex (SBL) Nanoparticles Self-Assembled at Elevated Temperature and Pressure\textsuperscript{1}. LEAF HUANG, University of North Carolina at Chapel Hill — Conventional lipoplex (cationic liposome/DNA complex) serves well for gene transfer in cultured cells. However, their in vivo gene delivery activity is limited due to its relatively large size (>100 nm). This is due to incomplete charge neutralization as a result of the steric hindrance during the complexation between DNA and liposomes. Behr et al hypothesized that monomolecular DNA condensate can be prepared if the DNA sees the cationic lipid as monomers. Indeed, small nanoparticles (∼30 nm) were prepared by using a single-chain cationic amphiphile which has a high solubility at the physiological condition. To stabilize the monomolecular condensate, Behr has included a SH group in the cationic amphiphile which could be oxidized to form a dimer. Unfortunately, the stabilized nanoparticles showed no transfection activity when delivered into cells. We hypothesized that similar small lipoplex can be prepared by using a double-chain cationic amphiphile if both DNA and the amphiphile can be soluble in the same solvent. A hydrofluorocarbon HFC-152a is an excellent solvent for the cationic lipid DOTAP at an elevated temperature (∼35 °C) and pressure (∼300 atm). Since the solvent can accommodate small amounts of water, DNA or siRNA could be introduced into the system to allow lipoplex formation. The resulting Small Bioactive Lipoplex (SBL) is 30-50 nm in diameter and can transfect cultured cells. Freeze-fracture electron microscopy showed that SBL are solid nanoparticles without any lipid bilayer structure. Since plasmid DNA is fragile at elevated temperature and pressure, we have concentrated our effort in siRNA which is stable under the same conditions. The new formulation shows great promise as an in vivo delivery vector when small particles are required for efficient penetration into the tissues.

\textsuperscript{1}Work supported by Eshelman Distinguished Professorship.

11:51AM Z3.00002 New Developments in Non Viral Gene Delivery. RAM MAHATO, University of Tennessee Health Science Center — No abstract available.

12:27PM Z3.00003 Image-Guided Hydrodynamic Gene Delivery. DEXI LIU, University of Pittsburgh — Gene delivery by rapid injection of a large volume of DNA solution into a blood vessel, commonly called hydrodynamic gene delivery, has become a common method for gene therapy studies in rodents. In this presentation, I will focus on our recent work aiming at establishment of an image-guided hydrodynamic procedure for gene delivery in humans. Our study employed swine as an animal model and the procedure developed includes image-guided insertion of a balloon catheter into the selected blood vessel of the targeted organ from the jugular vein and hydrodynamic injection of plasmid DNA in saline. The talk will cover the rationale of our approach, the effectiveness of procedure for gene delivery to liver and muscle, and the impact of the procedure on physiological functions and serum chemistry of the animals. The results will be discussed with respect to potential applications of the hydrodynamic gene delivery to human gene therapy.

1:03PM Z3.00004 Revisit an old problem – Complexation between DNA and PEI. CHI WU, Department of Chemistry, The Chinese University of Hong Kong — After revisiting the captioned problem by using a combination of chemical synthesis and physical methods, we studied the dynamics of the complexation between branched polyethyleneimine (iPEI) and plasmid DNA (pDNA) and characterized the structure, size and surface charge of the resultant DNA/PEI complexes (polyplexes). As expected, in order to reach a high efficiency in gene transfection into cells it is necessary to use a higher N:P ratio and make the polyplexes positively charged. Our results reveal that it is those uncomplexed iPEI chains free in the solution mixture that plays a vitaly important role in enhancing the transfection efficiency, inspiring new thinking of how to correlate in vitro and in vivo studies so that we can improve the in vivo transfection efficiency. Increasing the N:P ratio normally results in a higher cytotoxicity, which is a catch-22 problem. Recently, we found that a proper modification of iPEI can greatly reduce its cytotoxicity without any suffering in the transfection efficiency. In this lecture, we will show that our properly modified iPEI is even much more effective and less cytotoxic in the gene transfection than those commercially available lipoflexes. Our recent breakthrough leads to a complete new direction in the development of non-viral vectors for molecular medicines, including gene transfection.

1:39PM Z3.00005 Recent Developments in Non-Viral Gene Delivery. ALEXANDER KABANOV, University of Nebraska Medical Center — No abstract available.

Friday, March 20, 2009 11:15AM - 2:15PM –
Session Z4 DPOLY DBP: Biological Polyelectrolytes 306/307

11:15AM Z4.00001 How mechanical properties of DNA relate to chromosome structure. KERRY BLOOM, University of North Carolina at Chapel Hill — No abstract available.
11:51AM Z4.00002 Electrostatic Rigidity of Biological Polyelectrolytes1, ANDREY DOBRYNNIN. University of Connecticut — Electrostatic persistence length is one of the most controversial subjects in polymer physics. In this talk I will present an overview of the history of the problem and a new results showing that the bending rigidity of the biological polyelectrolytes (semiflexible charged polymers) is a multiscale process. The existence of the different length scales in the bending process is manifested in change of the form of the correlation function, describing bond-bond orientational correlations, with salt concentration. At high salt concentrations when the electrostatic interactions are significantly screened these correlations may be approximated by a single exponential function indicating the existence of a dominant length scale. However, when the Debye screening length exceeds a critical value the orientational correlations between chain’s bond vectors undergo a qualitative change resulting in appearance of two different bending rigidities (persistence lengths). One increases quadratically and the other changes logarithmically with the Debye screening length. This transition occurs when the chain’s bare persistence length becomes on the order of so-called OSF electrostatic persistence length. Simulation results and theoretical model demonstrate good qualitative agreement.

1This work was done in collaboration with A. Gubarev and J.-M. Carrillo. This work was supported by the ACS Petroleum Research Fund and the Fulbright Fellowship Program.

12:27PM Z4.00003 Deafness and espin-actin self-organization in stereocilia , GERARD C.L. WONG1, University of Illinois at Urbana-Champaign — Espins are F-actin-bundling proteins associated with large parallel actin bundles found in hair cell stereocilia in the ear, as well as brush border microvilli and Sertoli cell functions. We examine actin bundle structures formed by different wild-type espin isoforms, fragments, and naturally-occurring human espin mutants linked to deafness and/or vestibular dysfunction. The espin-actin bundle structure consisted of a hexagonal arrangement of parallel actin filaments in a non-native twist state. We delineate the structural consequences caused by mutations in espin’s actin-bundling module. For espin mutation with a severely damaged actin-bundling module, which are implicated in deafness in mice and humans, oriented nematic-like actin filament structures, which strongly impinges on bundle mechanical stiffness. Finally, we examine what makes espin different, via a comparative study of bundle formed by espin and those formed by fascin, a prototypical bundling protein found in functionally different regions of the cell, such as filopodia.

1In collaboration with: Kirstin Purdy-Drew; Lori Sanders; James Bartles, University of Illinois, Department of Materials Science and Engineering; Department of Physics; Department of Bioengineering

1:03PM Z4.00004 Mesoscale Modeling of Chromatin Folding1, TAMAR SCHLICK, New York University — Eukaryotic chromatin is the fundamental protein/nucleic acid unit that stores the genetic material. Understanding how chromatin fibers fold and unfold in physiological conditions is important for interpreting fundamental biological processes like DNA replication and transcription regulation. Using a mesoscopic model of oligonucleosome chains and tailored sampling protocols, we elucidate the energetics of oligonucleosome folding/unfolding and the role of each histone tail, linker histones, and divalent ions in regulating chromatin structure. The resulting compact topologies reconcile features of the zigzag model with straight linker DNAs with the solenoid model with bent linker DNAs for optimal fiber organization and reveal dynamic and energetic aspects involved.

1In collaboration with: Gaurav Arya, S. Grigoryev, S. Correll, and C. Woodcock.

1:39PM Z4.00005 Complexation of oppositely charged polyelectrolytes in gene delivery and biology, BORIS SHKLOVSKI, University of Minnesota — Charge inversion of a DNA double helix by a positively charged flexible polymer (polyelectrolyte) is widely used to facilitate DNA contact with negative cell membranes for gene delivery. Motivated by this application in the first part of the talk I study the phase diagram a solution of long polyanions (PA) with a shorter polycations (PC) as a function the ratio of total charges of PC and PA in the solution, x, and the concentration of monovalent salt. Each PA attracts many PC to form a complex. When x = 1, the complexes are neutral and condense in a macroscopic drop. When x is far away from 1, complexes are strongly charged and stable. PA are overcharged by PC at x > 1 and undercharged by PC at x < 1. As x approaches 1, complexes attached to PA disproportionate between complexes. Some complexes become neutral and condensed in a macroscopic drop while others become even stronger charged and stay free. The second part of the talk deals with biological example of PA-PC complexes namely self-assembly of vegetable viruses from long ss-RNA molecule paying role of scaffold and identical capsid proteins with long positive tails. I show that optimization Coulomb energy of the virus leads to the charge of RNA twice larger than the total charge of the capsid, in agreement with the experimental data. Then I discuss kinetics of the Coulomb complexation driven virus self-assembly. Capsid proteins stick to unassociated chain of ss RNA (which we call “antenna”) and slide on it towards the assembly site. I show that at excess of capsid proteins such one-dimensional diffusion accelerates self-assembly more than ten times. On the other hand at excess of ss-RNA, antenna slows self-assembly down. Several experiments are proposed to test the role of ss-RNA antenna in self-assembly.

Friday, March 20, 2009 11:15AM - 2:15PM — Session Z18 DPOLY: Surfaces and Adsorption II 319

11:15AM Z18.00001 Dynamics of six-member molecular rings adsorbed onto graphite and MgO(100)1, JOHN Z. LAREOE, Oak Ridge National Laboratory and University of Tennessee, PETER YARON, University of Tennessee — Molecular dynamic studies of adsorption of six-member molecular rings (cyclohexane and benzene) onto various substrates (like MgO(100) and graphite) have been undertaken using a commercial modeling package (Materials Studio by Accelrys Software Inc.) that employs central force field potentials. These studies indicate that such systems exhibit rotational translational coupling and strong signs that the translational diffusion is lattice-like on graphite. The cyclohexane rotational motion has a distinct out of plane component coupled to the translational diffusion much like the rolling motion of a wobbly wheel with three hydrogen atoms in “contact” with the substrate plane, while the benzene is more planar. These studies will be compared to results of neutron scattering investigations of the temperature dependence of the dynamics.

1Supported by the U.S. Department of Energy, Materials Science Division under contract No. DE-AC05-00OR22725 with Oak Ridge National Laboratory managed and operated by UT-Battelle, LLC, and the National Science Foundation under grant DMR-0412281.

11:27AM Z18.00002 Heterogeneity of nitrogen multilayers adsorbed on graphite, M. GOLEBIOWSKA, L. FIRLEJ, University of Missouri Columbia, Department of Physics and Astronomy; LCVN, Université Montpellier. B. KUCHTA, University of Missouri Columbia, Department of Physics and Astronomy, Laboratoire Chimie Provence, M.W. ROTH, University of Northern Iowa — The low temperature structures and their relative packing (hexagonal or cubic) are analyzed. The nitrogen molecules are simulated as rigid, interacting via site-site potential (Etters model). The interaction with graphite includes atomic corrugation (Steele’s potential). We show that the temperature and the mechanism of both orientational and melting phase transitions vary with the surface coverage and change from layer to layer. In particular, melting of the bilayer is preceded by compression of the first layer, which has not been observed before. The results are compared with simulations of two similar systems: (i) three nitrogen layers confined in slit graphite pore, and (ii) an adsorbed incommensurate structure that mimics low temperature alpha phase of bulk nitrogen.
11:39 AM Z18.00003 Surface Hopping and Sliding of Single DNA Chains under Electric Field

BENXIN JING, JIANG ZHAO, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China — The motion of non-adsorbing DNA chains under electric field at solid-liquid interfaces was investigated by single molecule fluorescence microscopy at the total internal reflection geometry (TIRF). In situ observation discovered that the motion of single non-adsorbing lambda-DNA chains was hopping-and-sliding-like along the surface. By varying the surface chemistry of the solid substrates, from the negative-charged hydroxyl group-rich surface to positive-charged amino group-rich surface, as well as hydrophobic surfaces, the dependence of DNA mobility on the surface-DNA interaction was studied. The results show that a well-defined dependence of the mobility of DNA on the surface polarity with respect to DNA itself. The study on different surfaces such as hydroxyl, amide, amino, and methyl-group rich surface show a sequence of DNA mobility of hydroxyl > amide > amino. The mobility of DNA on methyl terminated surface was found to be similar to that in amino surface.

1Project supported by National Natural Science Foundation of China (NSFC)

11:51 AM Z18.00004 First Principles study of the formation of molecular junctions: benzenethiolate on Au (111)

YONGDUO LIU, VIDVUDS OZOLINS — We perform density functional calculations to study the formation mechanism of benzenethiolate molecular junctions on the Au (111) surface. Specifically, we investigate the geometry change and the mechanical properties of the metal-molecule contact when it is under stretching. It is found that by pulling up the thiolate molecule from Au (111), one Au surface atom can be converted to an adatom. And moreover, if the stretching is enough, another Au atom would successively be pulled up to form a two-atom bridge between the Au (111) and the sulfur end group. Based on these findings, we propose a mechanism to the formation of pyramidal molecular junctions: benzenethiolate on Au (111).

12:03 PM Z18.00005 Molecular Dynamics Simulation of friction in contact-mode Atomic Force Microscopy of alkane films and nanoparticles

F.Y. HANSEN, Tech. U. of Denmark. P. SOZA, P.U. Catolica Chile, H. TAUB, U. Mo-Columbia, U. VOLKMANN, P.U. Catolica Chile — In addition to sample topography, contact-mode Atomic Force Microscopy (AFM) can yield the lateral frictional force experienced by the AFM tip as it moves across a surface. This frictional force is measured by the torsional angle of the microscope’s cantilever arm, which, in the case of a surface composed of highly anisotropic alkane molecules, can depend on the molecular orientation. We have conducted molecular dynamics simulations of an AFM tip moving over films and nanoparticles of C12H26 (C24) in the contact mode. For films in which the long axis of the C24 molecules is oriented parallel to the surface, we find a smaller frictional force in a scan direction perpendicular to the long axis than parallel to it. On surfaces where the alkane molecules are oriented perpendicular to the interface, we find that in all scan directions the frictional force is less than when the long molecular axis is parallel to the interface. All of these findings are consistent with experimental observations.


STEPHEN HUTCHESON, GREGORY MCKENNA, Texas Tech University — In previous work, we used particle embedment data to determine the rheological response of the surfaces of a polystyrene film, a phase separated copolymer and a commercially available polydimethylsiloxane (PDMS) rubber through the application of a viscoelastic contact mechanics model. The goal of the current research is to build off this analysis and use micro- and nano-sphere embedment experiments to probe the surface rheological behavior of PDMS in the rubbery state. The work includes measurements made with different particle diameters and chemistries. An atomic force microscope (AFM) is used to measure the embedment depth as nanoparticles are pulled into the surface by the thermodynamic work of adhesion. Present results show that silica probes of different sizes (500 nm and 300 nm) give different results for the surface adhesion properties and the surface rheological properties determined from the particle embedment data and at scales much larger than the nanometer size scale where one might expect such deviations. Possible water entrapment and effects of particle surface composition on the results will be discussed.

12:27 PM Z18.00007 Test of the universality of the scaling energy in alkanes based on the melting transition of monolayers adsorbed on graphite

L. FIRLEJ, Université Montpellier 2, B. KUCHTA, Université de Provence, M. ROTH, University of Northern Iowa, C. WEXLER, University of Missouri — The quality of the results of computational treatment of complex systems depends crucially on the quality of the interaction potentials used. When modeling non-rigid molecules an essential difficulty resides in the correct accounting for all energies related to internal degrees of freedom. Of particular importance is to avoid over- or under-counting non-bonded intramolecular van der Waals and electrostatic interactions between close neighbors that are chemically bonded. In many force fields (e.g. CHARMM) 1-4 non-bonded interactions are scaled down by the use of the “scaling factor” (SF). Typically, this SF is assumed to be universal (and ~ 1.0). In this talk, we study this universality hypothesis by comparing computational and experimental melting temperatures of alkane monolayers adsorbed on a solid graphite surface. Three alkanes (C6, C12, C24) of different lengths (7-30 Å) have been analyzed using an all-atom representation, standard CHARMM parameters, and various SF’s. We show that the scaling parameter has no universal value but depends on the molecular length.

1Support: U.S. DOE (DE-FG02-07ER46411), ACS-PRF (PRF43277-B5), and Univ. of Missouri Bioinformatics Consortium.

12:39 PM Z18.00008 The role of local domain formation in the melting of hexane adlayers on graphite

M.W. ROTH, Univ. of Northern Iowa, L. FIRLEJ, B. KUCHTA, C. WEXLER, Univ. of Missouri — Hexane is the shortest alkane [CH3–(CH2)n−2–CH3] whose flexibility has any considerable impact on its dynamics. When adsorbed on graphite, a monolayer of hexane melts at a temperature of approximately 175 K. To understand the mechanisms of this transition we have performed large scale molecular dynamics simulations (several runs over 100 ns, total computation time ~ 10 cpu-years), using the most realistic model of the system (a fully atomistic representation of hexane, explicit site-by-site interaction with graphite carbons and CHARMM force field with carefully chosen adjustable parameters of interactions). We show that the melting of the low temperature herringbone solid phase starts with the formation of gauche defects at the ends of neighboring molecules, followed by molecular reorientation within a lamellae, without perturbing the overall structure of the adsorbed film. The melted phase has a domain-type structure with domains’ orientation that reflects the 6-fold symmetry of graphite. The size of domains decreases progressively when the temperature increases and the deformation of molecules to quasi globular shape is driven by progressive formation of gauche defects.

1Support: US-DOE (DE-FG02-07ER46411), ACS-PRF (PRF43277-B5), and Univ. of Missouri Bioinformatics Consortium.
12:51PM Z18.00009 Chain-length dependence in surface stresses of alkanethiolate-covered Au(111)\textsuperscript{1}

V. SRINIVASAN, Berkeley NanoScience and Nanoengineering Institute, UC Berkeley, CA 94720, G. CICERO, Materials Science and Chemical Engineering Department, Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129, Torino, Italy, J. C. GROSSMAN, Berkeley NanoScience and Nanoengineering Institute, UC Berkeley, CA 94720 — We have recently shown that adsorption-induced stresses in alkanethiolate-covered Au(111) contribute significantly to the stress-response in nano-mechanical cantilever sensors. In particular, we proposed a local stress relief (LSR) mechanism whereby charge removal by the Au-S bond from the Au surface promotes a stress reducing rearrangement of surface Au atoms. Since LSR depends on the nature of the Au-S bond it was unclear how the contribution to the stress-response would depend on the alkanethiolate structure. We present a first-principles study of the chain-length dependence in surface stresses of alkanethiolate-covered Au(111). We find that the surface stress upon adsorption is anisotropic and tensile, in increasing in magnitude with the chain-length. We analyze this trend in the context of the LSR mechanism and inter-adsorbate interactions.

\textsuperscript{1}Supported by LDRD/Lawrence Livermore National Laboratory and UC Berkeley/NSF Grant No. 0425914

1:03PM Z18.00010 All-atom Molecular Dynamics simulations of partial pentane and hexane films on graphite\textsuperscript{2}

M. KASPAR, M.W. ROTH, University of Northern Iowa, CARLOS WEXLER, University of Missouri, L. FIRLEJ, Université Montpellier, B. KUCHTA, Université de Provence — We compare the self-assembly patterns of pentane (C\textsubscript{5}H\textsubscript{12}) and hexane (C\textsubscript{6}H\textsubscript{14}) adlayers physisorbed onto graphite at various coverages using the results of molecular dynamics simulations. Near monolayer coverage, the solid low temperature structure of the pentane film is nematic-like, and that of hexane-herringbone-like. At submonolayer coverages both systems exhibit three distinct topological regimes: vacancy patches at higher densities, percolating networks at intermediate densities and ultimately individual patches. The systems’ orientational behavior and melting dynamics is discussed with respect to its unique density-dependent topology. The simulations explicitly include hydrogens of pentane and hexane and the graphite is modeled as a six-layer all atom structure.

\textsuperscript{2}Work supported by the U.S. Department of Energy (DE-FG02-07ER46411) and the American Chemical Society Petroleum Research Fund (PRF43277-B5). Computational resources were provided by the University of Missouri Bioinformatics Consortium.

1:15PM Z18.00011 Temperature Dependent Adsorption Dynamics of Binary Mixtures of Halomethanes on Graphite and α-quartz Surfaces\textsuperscript{1}

JONATHAN NEHRING, North Park University, G. LEUTY, MESFIN TSIGE, Southern Illinois University at Carbondale — Using atomic molecular dynamics simulations, we have investigated the structure and dynamics of binary mixtures of halomethanes (CF\textsubscript{3}Cl, CF\textsubscript{3}Br, and CF\textsubscript{3}I) as a function of temperature on two structurally and chemically different surfaces. The initial distribution of the binary mixtures is either they are uniformly mixed or a layer or layers of one component is placed on top of a layer or layers of the other component. As a function of temperature (below and above the melting temperature of CF\textsubscript{3}I) and the two surface types, we observed a marked change on the concentration, dynamics, orientation, and structure of each of the components in the first layer of the binary mixtures next to the surfaces.

\textsuperscript{1}Work supported by the Donors of the American Chemical Society Petroleum Research Fund.

1:27PM Z18.00012 Liquid Chromatography at Critical Conditions: Balancing size exclusion and adsorption in nanopores

ASEM ABDULAHAD, JEFFREY AMOS, CHANG RYU, Rensselaer Polytechnic Institute — Liquid chromatography at critical condition (LCCC) is a measure to identify thermodynamic conditions, in which polymers elute independently of molar mass during high performance liquid chromatography. Under these critical conditions the entropic exclusions that dominate size exclusion chromatography (SEC) and the enthalpic adsorption that governs adsorption-based interaction chromatography (IC) are said to negate one another resulting in simultaneous elution of the polymer of different molecular weights. Using multiple C18-bonded silica columns with different average nanopore sizes (from 5 nm to 30 nm), we will study the LCCC conditions of PS in methylene chloride/acetone solvent mixture at different temperature. In addition, we will show that the separation of polystyrene can be fine tuned using a refined temperature gradient interaction chromatography (TGIC) that employs multiple columns of varying pore size in sequence.

1:39PM Z18.00013 Using Amphiphilic Copolymers and Nanoparticles to Organize Charged Biopolymers\textsuperscript{1}

JUNG HYUN PARK, MARLA MCCONNEELL, YUIJE SUN, YALE GOLDMAN, RUSSELL COMPOSTO, University of Pennsylvania — Nanoparticles (NPs) on amphiphilic random copolymers control filamentous actin (F-actin) attachment. 3-aminopropytriethoxysilane (APTES) coated silica NPs are selectively bonded to acrylic acid groups on the surface of a poly(styrene-r-acrylic acid) (PS-r-PAAM) film. By changing the concentration of NPs in the medium, the surface density of positively charged anchors is tuned. Using total internal reflection fluorescence (TIRF) microscopy, immobilization of F-actin is observed via electrostatic interaction with NPs at high NP coverages. Below a critical coverage, F-actin is weakly attached and undergoes thermal fluctuations near the surface. Another method to tune F-actin attachment is to use APTES to cross-link and create positive charge in PAA films. Here, the surface coverage of F-actin decreases as APTES concentration increases. This observation is attributed to an increase in surface roughness and hydrophobicity that reduces the effective surface sites that attract F-actin. In addition, in-situ G-actin polymerization to F-actin is observed on both the NP and cross-linked PAA templates.

\textsuperscript{1}This work is supported by the Nano / Bio Interface Center at the University of Pennsylvania and the U.S. National Science Foundation under grant number DMR-0425780.

1:51PM Z18.00014 Non-translational Molecular Diffusive Motion on Two Different Time Scales in Alkane Nanoparticles\textsuperscript{1}

S.-K. WANG, M. BAI, H. TAUB, U. Mo.-Columbia, E. MAMONTOV, K.W. HERWIG, ORNL, F.Y. HANSEN, Tech. U. Denmark, J.R.D. COPLEY, T. JENKINS, M. TYAGI, NIST, U.G. VOLKMANN, P. U. Catolica Chile — Using quasielastic neutron scattering, we have investigated molecular diffusive motion in n-alkane nanoparticle whose structure and phase transitions have been studied previously.\textsuperscript{2} The spectra reveal non-translational (dispersionless) diffusive motion occurring simultaneously on time scales of ~1 ns and ~40 ps. The onset of the faster motion occurs in the crystalline phase at least 15 K below the melting point and is tentatively identified with rotation about the long molecular axis. Similarly, we suggest that slower motion involves molecular conformational changes whose onset appears to coincide with the abrupt transition to the bulk rotator phase about 3 K below melting. These two types of diffusive motion bear a strong resemblance to those observed previously in C24 monolayers adsorbed on a graphite surface.\textsuperscript{3} 4\textsuperscript{th} F. Y. Hansen et al., Phys. Rev. Lett. 92, 046103 (2004).

\textsuperscript{1}Supported by Grant Nos. U.S. NSF DMR-0705974, DMR-0454672, and FONDECYT 1060628 and 7070248.

\textsuperscript{2}Supported by LDRD/Lawrence Livermore National Laboratory and UC Berkeley/NSF Grant No. 0425914

Aliphatic polyesters are surface nucleation on polymer droplet, high molecular weight of UHMWPE as well as the soft confinement of supercritical fluid. The 2.5 dimensional growth makes it possible to observe both the nucleation site and sheaf-like structure on the surface of a spherulite and to obtain (UHMWPE) have been successfully prepared from supercritical ethanol. The spherulite grows to 2.5 but not 3 dimensions with only one nucleation site on the mer spherulite from both solution and melt has been a challengeable subject. In this letter, micro-sized spherulites of ultrahigh molecular weight polyethylene (UHMWPE) were attempted, but one (the Gambler’s Ruin model) did not properly account for the constraint of melt density, and the other (heuristic configuration counting of Flory et al.) did not account for chain connectivity. These shortcomings are resolved by a new “pseudobrush” theory of the amorphous interphase, which represents the reentrant chains as a polydisperse brush of loops in a self-consistent hydrostatic pressure field. This theory predicts the fraction of adjacent reentry, shows how the anisotropy of the interphase dies away with distance, and how the Gambler’s Ruin model is recovered far from the interface. Extension to the case of a finite slab between two crystal-melt interfaces predicts the frequency of tie chains, a key parameter for nonlinear deformation and ductile failure of semicrystalline polymers.

The impact of chain folding on the structure and morphology of polymer lamellae. The major structure and morphology features of polymer lamellae (and single crystals) are usually defined by the characteristics of the crystal lattice (cell geometry and symmetry, stem length). However, the fold surfaces that sandwich the crystalline core may have an impact on that crystalline core. In isotactic polyolefins, restrictions on the relative (up/down) orientation of stems linked by a fold may result in lowered unit-cell symmetry. Also, surface stresses linked with the presence of folds determine to a large extent the non-planar shape of polymer crystals. In bulk crystallization, they may induce twisted and/or scrolled lamellae. However, this impact can be inferred only for specific polymers and/or crystal structures and/or unit-cell symmetries. (Work performed with Dr. A. Thierry and J. Ruan.)

Unexpected Observation of 2.5 Dimensional Growth of Polymer Spherulite

Structural evolution under uniaxial drawing of Poly(D, L-lactide) Films

Vitrification and Devitrification of Rigid Amorphous Fraction of PET during Quasi-isothermal Cooling and Heating

Research supported by the National Science Foundation, Polymers Program of the Division of Materials Research, through grant DMR-0602473 and MRI Program under DMR-0520655.
12:15PM Z19.00006 Crystallization of Model Long Chain Branched Polyethylenes with Different Branching Architectures, M. VADLAMUDI, R. G. ALAMO, FAMU-FSU College of Engineering — While the impact of long chain branching (LCB) of different architectures (stars, α-ω H type, pom-pom, combs) on rheology has been studied extensively, the effect on crystallization is less known. This work analyses the influence of LCB architecture on crystallization from quiescent melts using models based on hydrogenated polybutadienes, all with a constant 2.1 mol% of ethyl branches (LCB PE). Crystallization rates measured by DCS, the phase structure, and morphology of the LCB PE are studied in reference to the linear chain. At a fixed undercooling the crystallization rates of all LCB PE are 30 to 40% lower than the rate of the linear as expected from transport limitations to the nucleation rate of the LCB systems. Smaller differences in the rate are found within the various LCB architectures. The components of the phase structure are controlled by the content of short chain branching with a negligible effect from the LCB architecture. For all LCB PE the crystalline component is ~30% and the interphase region ~15% as determined by WAXD, RAMAN and DSC. A major impact of LCB is found in the supermolecular morphology. Restrictions from the LCB melt topology to propagate long organized arrays bring about a change from spherulites (linear) to poorly organized crystallites (LCB PE). Long range dynamics (NMR T2f) and lamellar structures (AFM) are presently investigated.

12:27PM Z19.00007 An anomaly in the crystallisation rate of bimodal poly(ethylene oxide) weight distributions, JESSICA L. CARVALHO, SARA L. CORMIER, KARI DALNOKI-VERESS, Department of Physics & Astronomy and the Brockhouse Institute for Materials Research, McMaster University, Hamilton, ON, Canada, L8S 4M1 — We present results on the crystallisation of blends of poly(ethylene oxide) (PEO) of differing molecular weight, Mw. Previous studies probing PEO blends have mainly focused on blends of low Mw, for which integral chain folding is important, with very high Mw. The PEO samples used in this study consist of a blend with both Mw’s well above the integral chain folding limit. In general, one would expect that such blends should show a monotonic decrease in spherulite growth rate, G, as the blend contains more high-Mw component. Our results however show a clear non-monotonic G, with a minimum in a plot of G as a function of the volume fraction. In short, blending a small amount of the low-Mw into the high-Mw PEO slows the growth kinetics. These results along with a possible mechanism will be discussed.

12:39PM Z19.00008 Effect of ppm Levels of Long Chain Branishing on the Crystallization of Isotactic Poly(propylenes) from the Melt and from Solution, RUFINA G. ALAMO, JUAN P. FERNANDEZ-BLAZQUEZ, SYED A. ABDULLAH, MADHAVI VADLAMUDI, FAMU-FSU College of Engineering — Small concentrations of long chain branching (LCB) added via copolymerization with a diene to a linear poly(propylene) chain have a dramatic effect on crystallization. LCB IPPs with diene levels between 100 and 400 ppm show greatly enhanced nucleation density, increasing with diene content. The increased nucleation observed in optical micrographs, is also evident in the crystallization half-time observed by DSC in isothermal crystallization as a function of crystallization temperature. Isothermal crystallization studies from dilute solution measured by light scattering gave the same trend with diene content and rule out any effect of gel structures affecting the nucleation rate. The linear growth rates are unchanged. The increase in nucleation rate is not linear with the increase of diene as revealed from studies of blends of LCB IPPs with the linear matrix, suggesting that length of molecules and connectivity of the LCB structure are more important than the chemical nature of the junction. The enhanced nucleation levels off at concentrations of diene that approach the critical concentration for coil overlapping (c*) as calculated for chains generated by a Monte Carlo simulation of the LCB molecules having the experimental molecular weight distribution.

12:51PM Z19.00009 Melting, Recrystallization and Superheating of Polymer Crystals Studied by Fast Calorimetry (1 MK/s)¹, CHRISTOPH SCHICK, ALEXANDER MINAKOV, ANDREAS WURM, EVGENY ZHURAVLEV, University of Rostock — For polymers the origin of the multiple melting peaks observed in DSC curves is still controversially discussed. This is due to the difficulty to investigate the melting of the originally formed crystals exclusively. Recrystallization is a fast process and most experimental techniques applied so far do not allow fast heating in order to prevent recrystallization totally. We developed a thin-film (chip) calorimeter allowing scanning rates as high as one million Kelvin per second. The calorimeter was used to study the melting of isothermally crystallized polymers like isotactic polystyrene (iPS), isotactic polypropylene (iPP), poly(ethylene terephthalate) (PET) and others. Our results on melting at rates as high as 1,000,000 K/s support the validity of a melting-recrystallization remelting process at low scanning rates (DSC) for all studied polymers. At isothermal conditions they form crystals, which all melt within a few dozens of K slightly above the isothermal crystallization temperature. There is no evidence for the formation of different populations of crystals with significantly different stability (melting temperatures) under isothermal conditions.

¹We gratefully acknowledge the support of DFG.

1:03PM Z19.00010 Nano-Scale Confinement Effects on Poly(–caprolactone) Crystallization at the Air/Water Interface, QIONGAN XIE, BINGBING LI, TOMONORI SAITO, WEN YIN, TIMOTHY LONG, RICHARD GANDEUR, ALAN ESKER, Department of Chemistry (0212), Virginia Tech, Blacksburg, VA 24061 — Poly(–caprolactone) (PCL) with different mole mass were synthesized by using tri-ester primary amine as an initiator, tin(II) 2-ethylhexanoate as the catalyst, anhydrous tetrahydrofuran as a solvent at 80 °C. The three triester groups were further hydrolyzed to render PCL linear polymers with triacid end groups (PCL Triacid). The as-synthesized PCL triacids were attached to 9 nm magnetic nanoparticles (MNP) by ligand exchange with oleic acid in refluxing chloroform for 24 h. The crystallization behavior of PCL triacid and PCL MNPs at the air/water interface were compared with reported linear PCL crystallization. Regular crystalline morphologies observed for linear PCL are not observed for PCL-triacid and PCL-MNPs.

1:15PM Z19.00011 Microphase Separation Controlled Beta Sheet Crystallization Kinetics in Silk Fibroin Protein,¹ JIAO HU, QIANG LU, DAVID KAPLAN, PEGGY CEBE, Tufts University — We investigate the mechanism of isothermal crystallization kinetics of beta-sheet crystals in silk multiblock fibrous proteins. The Avrami analysis kinetic theory, for studies of synthetic polymer crystal growth, is for the first time extended to investigate protein self-assembly in beta-sheet rich Bombyx mori silk fibroin samples, using time-resolved Fourier transform infrared spectroscopy, differential scanning calorimetry and synchrotron real-time wide-angle X-ray scattering. Results indicate formation of beta sheet crystals in silk proteins is different from the 3-D spherulitic crystal growth found in synthetic homopolymers. Observations by scanning electron microscopy support the view that the protein structures vary during the different stages of crystal growth, and show a microphase separation pattern after chymotrypsin enzyme biodegradation. We present a model to explain the crystallization of the multiblock silk fibroin protein and analogy to synthetic block copolymers. This model could be widely applicable in other proteins with multiblock (i.e., crystallizable and non-crystallizable) domains.

¹Research supported by the National Science Foundation, Polymers Program of the Division of Materials Research, through grant DMR-0402849.
Polymers: One Dimensional Nano-Swelling Measured using iVSANS, MAN-HO KIM, Materials Science & Technology Research Division, Korea Institute of Science and Technology (KIST), GLINKA J. CHARLES, NIST Center for Neutron Research, National Institute of Standards and Technology — Changes in the nanoscale structure of semi-crystalline polyethylene (PE) resulting from the sorption/diffusion of n-hexane vapor have been observed and quantified by the in-situ Vapor Sorption Small-Angle Neutron Scattering (iVSANS). We found a linear correlation between vapor sorption/diffusion and nano-expansion of the amorphous phase within the lamellae confined in the spherulite domains. The diffusion coefficient measurements using (iVASNS) revealed that the molecular packing in amorphous phase is different between low and high crystalline PE. Furthermore, the one dimensional expansion is reversible during cyclic sorption and desorption processes, suggesting that the crystals were not destroyed unlike the inference of a previous study. These results are relevant to processing methods for tailoring the barrier and sorptive properties of semicrystalline polymer films. * This work utilized facilities supported in part by the National Science Foundation under Agreement No. DMR-0454672. The author, MHK, acknowledges support by the KIST (2E20844).

Friday, March 20, 2009 11:15AM - 2:03PM – Session Z20 DPOLY: Polymer Blends 321

11:15AM Z20.00001 Microemulsions in Asymmetric Polymer Blends, ALISYN NEDOMA, Univ. of California, Berkeley, MEGAN ROBERTSON, Univ. of Minnesota, NITASH BALSARA, Univ. of California, Berkeley — Microemulsions and lamellar phases have been observed in previous experiments wherein block copolymers are added to blends of immiscible homopolymers. To our knowledge, all of the previous studies are restricted to homopolymers of nearly identical chain lengths with critical volume fractions in the vicinity of 0.5 (symmetric systems). The present study concerns the formation of microemulsions and lamellar phases phases in blends of immiscible polymers with substantial differences in chain lengths and critical volume fractions far removed from 0.5 (asymmetric systems). The characteristics of the block copolymers that enable the creation of these phases will be discussed in the presentation.

11:27AM Z20.00002 Nanostructured polymer blends by addition of gradient copolymer during melt mixing: Effects of copolymer sequence distribution on morphology and crystallization behavior, ROBERT SANDOVAL, JUNGKI KIM, JOHN TORKELSON, Northwestern University — Nanostructured blends of polystyrene and poly(ethylene oxide) (PEO) are produced via the addition of styrene/methyl methacrylate (S/MMA) gradient copolymer during conventional melt mixing, introducing dipole-dipole interactions between PEO and MMA repeat units. Upon addition of S/MMA gradient copolymer, stable PEO domains with diameters of ~ 100 nm are formed in optimized cases. This results in PEO domains homogenously crystallizing at ~ 20 °C, well below the crystallization temperature of bulk PEO (~ 50 °C). Additionally, nanostructured blends annealed at room temperature for 40 days resulted in no melting behavior upon heating, showing that the nanoconfined PEO domains remain in a rubbery state at room temperature, while bulk PEO typically remains in a crystalline state. This demonstrates that the blend properties can be easily tuned by adjusting the copolymer characteristics. This study is the first to lead to nanostructured polymer blends from non-reactive, simple melt mixing of two homopolymers and a compatibilizer.

11:39AM Z20.00003 A Morphological Study of Poly(Butylene Succinate)/Poly(Butylene Adipate) Blends with Different Blend Ratios and Crystallization Processes, JEROILD SCHULTZ, University of Delaware, HAIJUN WANG, ZHIGUA GAN, SHOUKE YAN, Chinese Academy of Sciences — Morphologies of blends of poly(butylene succinate) (PBS, m.p. 114 °C) with poly(butylene adipate) (PBA, m.p. 60 °C) varying in blend ratio and in crystallization temperature of the PBS component were studied using optical and atomic force microscopies. When PBS is crystallized at 75 °C, subsequent PBA crystallization occurs only within PBS spherulites. When PBS is crystallized at 100 °C, a portion of the PBA is rejected from the growing PBS. The morphological difference is also reflected in the time-dependence of the crystallization kinetics. The difference in behavior at these two temperatures reflects a large change in the diffusion length. Further, the location of PBA crystals within PBS spherulites depends on PBA concentration and on PBS crystallization temperature. Lower PBA concentrations lead to interlamellar segregation, while when PBA is the majority phase, interbiblar crystallization crystallization dominates. Replace this text with your abstract body.

11:51AM Z20.00004 Phase equilibria and crystallization in mixtures of azobenzene chromophore and triacrylate1, GARRETT O'MALLEY, Bucknell University, KENNETH MILAM, NAMIL KIM, THEIN KYU, University of Akron — A temperature versus composition phase diagram of azobenzene chromophore/triacrylate system was established by means of differential scanning calorimetry (DSC). The isotropic liquid (I) and crystal solid + liquid (Cr + I) coexistence regions bound by liquidus and solidus lines were tested with the theoretical curves obtained by self consistently solving the combined free energies of Flory-Huggins (FH) theory for isotropic mixing and phase field (PF) theory for crystal solidification pertaining to the compositional order parameter ($\phi_1$) and the crystal order parameter ($\psi_1$), respectively. With the aid of phase diagram, various phase morphologies were mapped through thermal quenching into various coexistence gaps. Azobenzene in the blend produced multiple crystal structures, including gigantic single crystals. Real time images demonstrating the nucleation and growth of the crystallization process were captured under polarized optical microscopy. The spatiotemporal growth of such single crystal has been elucidated theoretically using the time-dependant Ginzburg Landau (TDGL) dynamics.

12:03PM Z20.00005 Miscibility Studies on Polymer Blends Modified with Phytochemicals, NEELAKANDAN CHANDRASEKARAN, THEIN KYU, The University of Akron — The miscibility studies related to an amorphous poly(amide)/poly(vinyl pyrrolidone) [PA/PVP] blend with a crystalline phytochemical called “Mangiferin” is presented. Phytochemicals are plant derived chemicals which intrinsically possess multiple salubrious properties that are associated with prevention of diseases such as cancer, diabetes, cardiovascular disease, and hypertension. Incorporation of phytochemicals into polymers has shown to have very promising applications in wound healing, drug delivery, etc. The morphology of these materials is crucial to applications like hemodialysis, which is governed by thermodynamics and kinetics of the phase separation process. Hence, miscibility studies of PA/PVP blends with and without mangiferin have been carried out using dimethyl sulfoxide as a common solvent. Differential scanning calorimetry studies revealed that the binary PA/PVP blends were completely miscible at all compositions. However, the addition of mangiferin has led to liquid-liquid phase separation and liquid-solid phase transition in a composition dependent manner. Fourier transformed infrared spectroscopy was undertaken to determine specific interaction between the polymer constituents and the role of possible hydrogen bonding among three constituents will be discussed.

*Supported by NSF-DMR 0514942, REU DMR 0648318, and the Air Force Office of Scientific Research through the Collaborative Center for Polymer Photonics.
12:15PM Z20.00006 Phase Separation Mechanism of Polybutadiene/Polyisoprene Blends Under Oscillatory Shear Flow\textsuperscript{1}, CHARLES C. HAN, Dr.,Prof., RUOYU ZHANG, HE CHENG, XIA DONG, Dr., Prof. — Viscoelastic polymer blends of polybutadiene (PB)/low vinyl content polyisoprene (LPI), with a lower critical solution temperature (LCST) has been studied under oscillatory flow conditions. The phase separation mechanism has been investigated with the consideration of the nucleation mechanism, spinodal fluctuations, and also the shear induced mixing. Frequency and temperature ramping rate dependence of the apparent binodal and spinodal points will be discussed.

\textsuperscript{1}Joint Laboratory of Polymer Science and Materials, ICCAS, Beijing, China.

12:27PM Z20.00007 Impact of Deuterium Substitution on the Physical Properties of Polymer Melts and Blends\textsuperscript{1}, RONALD WHITE, JANE LIPSON, Dartmouth College — We examine the effects on blend properties when one of the polymeric components is deuterated. Here we use SANS-fitted model calculations to explore the underlying physical behavior, and relate our findings to subtle effects in molecular size and energetics. A special emphasis is given to the prediction and analysis of phase behavior for polymeric mixtures (e.g. liquid-liquid partial miscibility), including a comparison of phase diagrams for several related systems. We discuss effects such as pressure and molecular weight dependence and also include an analysis of calculations in which we probe the influence of key model parameters on blend miscibility. As with our earlier studies, the results featured here involve the application of a microscopically parameterized equation of state derived from an integral equation theory for lattice-based chain molecule fluids.

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12:39PM Z20.00008 Mapping Mechanical Properties and Glass Transition Temperature in Polymer Materials with sub-100 nm Resolution\textsuperscript{1}, MAXIM NIKIFOROV, Oak Ridge National Laboratory, STEPHEN JESSE, SANGAM GAM, RUSSELL COMPOSTO, LOUIS GERMARINO, SERGEI KALININ, OAK RIDGE NATIONAL LABORATORY TEAM, UNIVERSITY OF PENNSYLVANIA TEAM, EASTMAN CHEMICAL CO. TEAM — Thermomechanical properties at the nanoscale are extremely important for understanding fundamental as well as technological problems. To date, Local Thermal Analysis (LTA) provides information about glass transition and melting temperature with about 1-2 \textmu m spatial resolution. We developed LTA technique based on Scanning Probe Microscopy that allows probing not only melting and glass transition temperatures, but also elastic and loss moduli on a 100 nanometer length scale. This universal method for quantitative thermomechanical analysis was used to study the kinetics of phase separation in PMMA/SAN system. The maps of mechanical properties as function of temperature were obtained with sub-100 nm resolution. The difference of mechanical properties for two materials was determined.

\textsuperscript{1}This Research at Oak Ridge National Laboratory's Center for Nanophase Materials Sciences was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

12:51PM Z20.00009 Understanding Dynamics of Multicomponent Polymer Systems Using Homopolymer/Copolymer Blends, CALEB DYER, Department of Chemistry, Univ. of TN, DIAS LINTON, Dept. of Chemistry, Univ. of TN, MARK DADMUN, Oak Ridge National Lab, Oak Ridge TN and Dept. of Chemistry, Univ. of TN — Blending two polymers is a cost-effective method to produce new materials with tailored properties, although the effect of the presence of one component on the dynamics of the second component is not well understood. Recent studies on miscible polymer blends show that the local environment in a polymer blend has a critical impact on the dynamics of each component in the blend. To this end we have utilized neutron reflectivity (NR), quasi-elastic neutron scattering (QENS), and rheology to study the dynamics of a polystyrene-ran-poly(methyl methacrylate) (PS-ran-PMMAn) copolymer in a PMMA matrix. The system consists of a miscible blend that is 90% PMMA/10% random copolymer. The copolymer composition varies from 60% to 90% MMA in the blend, effectively tuning the thermodynamic interactions in the system. We will present these results to provide insight into the role of thermodynamic interactions on the dynamics of this miscible polymer blend.

1:03PM Z20.00010 Influence of polymer chain connectivity on local composition distribution in miscible polymer blends, DMITRY BEDROV, University of Utah, WENJUAN LIU, RALPH COLBY, Pennsylvania State University — Molecular dynamics simulations using bead-necklace model have been utilized to investigate concentration distribution of local environments in model polymer blends. Distribution of effective composition around polymer segments has been investigated for different blend scenarios and bulk concentrations. Inter- and intramolecular contributions to the effective composition have been analyzed. Our analysis indicates that chains connectivity has a significant and nontrivial effect on distribution of effective composition around polymer segment. The results of this work are compared with assumptions of several theoretical models that commonly used to describe structural and dynamical correlations in miscible polymer blends.

1:15PM Z20.00011 Origins of Deviations from the RPA in Polymer Blends: Simulations and Theory, JUN KYUNG CHUNG, School of Physics and Astronomy, University of Minnesota, DAVID MORSE, Department of Chemical Engineering and Materials Science, University of Minnesota — We performed continuum Monte Carlo simulations of symmetric binary polymer blends to precisely quantify deviations from RPA predictions for composition fluctuations, including critical phenomena. This comparison is made possible by an unambiguous procedure for determining the self-consistent field (SCF) \( \chi \) parameter by extrapolating thermodynamic perturbation theory to the limit of infinite chain length \( N \). Corrections to the RPA are shown to be proportional to \( N^{-1/2} \), and to be accurately predicted outside of the critical region by a renormalized one-loop theory. The difference between the apparent (i.e., measured) interaction parameter and the SCF value is positive (destabilizing) far from the spinodal.

1:27PM Z20.00012 Two DSC Transitions in Miscible Blends of Polypolysisoprene / Poly(4-tet-butyl styrene), JUNSHU ZHAO, YE SUN, LIAN YU, MARK EDIGER, University of Wisconsin-Madison — Conventional and temperature modulated differential scanning calorimetry experiments have been carried out on miscible blends of polypolyisoprene (PI) and poly(4-tet-butyl styrene) (P4tBS) over a broad composition range. This system is characterized by an extraordinarily large component \( T_g \) difference (~215 K) between the two homopolymers. Two distinct calorimetric \( T_g \)s were observed in blends with an intermediate composition range (25%~50% PI) by both conventional and temperature modulated DSC. Good agreement was found between the \( T_g \) values measured by the two methods. Fitting of the measured \( T_g \)s to the Lodge-McLeish model gives a \( \phi_{eff} \) of about 0.6 for this blend and 0.02~0.05 for P4tBS. The extracted \( \phi_{eff} \) is larger than those reported for PI blends with smaller component \( T_g \) differences. This observation suggests the presence of a confinement effect in PI/P4tBS blends, which results in enhanced fast component dynamics below the effective \( T_g \) of the slow component.
Segmental dynamics in polymer blends: adapting the Long-Lequeux model. GARETH ROYSTON, PAUL SOTTA, DIDIER LONG, Laboratoire Polymères et Materiaux Avances (FRE2911) — In recent years several models have been proposed which attempt to describe the distribution of relaxation times observed in glass forming systems as they approach vitrification. We have adapted the Long-Lequeux model, initially proposed for van der Waals liquids, for application to polymer blends. Considering thermally induced density fluctuations, the glass transition is considered to be controlled by percolation of small domains of slow dynamics. Here we present a comparison of the model with experimental data including recently acquired data on miscible blends of poly(alpha-methylstyrene) and poly(cyclohexyl methacrylate). The model is shown to provide a good fit to the data over a range of conditions.

The Viscoelastic Behavior of Polymer/Oligomer Blends, WEI ZHENG, GREGORY MCKENNA, SINDEE SIMON, Texas Tech University — The dynamics in athermal blends of poly(alpha-methyl styrene) (PaMS) and its short chain oligomer are investigated using rheometry and differential scanning calorimetry (DSC). Master curves for the dynamic shear responses, $G'$ and $G''$, are successfully constructed for both the pure materials and the blends, indicating the validity of the time-temperature superposition principle. The temperature dependence of the shift factor follows the WLF (Williams-Landel-Ferry) behavior over the temperature range studied, and for the blends, the dependence is dominated by the high mobility oligomer. The discrete relaxation spectra of the materials are calculated and are found to be broader for the blends than for the pure materials. A similar domination of the dynamics by the oligomer is observed in DSC enthalpy recovery studies and in the broadened glass transition from DSC. The ability to predict the dynamic responses of the blends from the responses of the neat materials is examined, and whether this prediction needs to incorporate the self-concentration idea as described in Colmenero’s model will be discussed.