

SYMPOSIUM BB

Multicomponent Polymer Systems—Phase Behavior, Dynamics, and Applications

November 29 - December 3, 2004

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* Invited paper

8:30 AM *BB1.1

Self-organizing polymer nanofiltration membranes with sub-nanometer size selectivity. Anne M. Mayes¹, Ariya

Akthakul¹, Ayse Asatekin¹, Allon I. Hochbaum¹, Francesco Stellacci¹ and Richard F. Salinaro²; ¹Materials Science and Engineering, M.I.T., Cambridge, Massachusetts; ²Pall Corporation, Port Washington, New York.

Membranes that deliver nanoscale size selectivity are desirable for applications ranging from water treatment to molecular separations. Here we describe polymer nanofiltration membranes incorporating amphiphilic graft copolymers consisting of a poly(vinylidene fluoride) (PVDF) backbone and polyoxyethylene methacrylate (POEM) side chains, PVDF-g-POEM. These materials molecularly self-assemble into bicontinuous nanophase domains of semicrystalline PVDF, providing structural integrity, and poly(ethylene oxide) (PEO), providing selective transport channels of well-defined size. PVDF ultrafiltration membranes coated with PVDF-g-POEM wet instantaneously and reject > 99.9 % of the oil from a 1000 ppm stabilized oil/water emulsion feed at 66 psi without fouling. Their molecular sieving capability is demonstrated through separation of like-charged organic dyes varying in molecular dimensions by several Ångströms. Thicker films of PVDF-g-POEM also act as a chromatograph, exhibiting time-dependent permeation of vitamins B₂ and B₁₂. Finally, we demonstrate the fractionation of monolayer protected gold nanoparticles to achieve a well-defined cutoff diameter and reduced particle size dispersity. These new nanochannel membranes hold potential utility for both high volume and high end value liquid-based separations.

9:00 AM *BB1.2

Block Copolymers with Precisely Tuned Crystal Thicknesses and Melting Points. Li-Bong Lee, John Hatjopoulos and Richard Register; Chemical Engineering, Princeton University, Princeton, New Jersey.

In semicrystalline homopolymers of even moderate molecular weight, crystal thickness and melting point are kinetically set; the predominant crystal stem length, and the extent of chain folding, are determined through the processing history of the material. Statistical copolymers have a broad distribution of crystal thicknesses and melting points, reflecting both kinetic constraints and the broad distribution of crystallizable sequence lengths within the ensemble. For block copolymers of uniform chain length, however, there is a longstanding theoretical prediction that the crystalline domains should be of an essentially uniform thickness, with a crystal stem length set via equilibrium considerations, as a compromise between the extended-chain conformation favored by the crystalline block at equilibrium, and the random coil conformation favored by the amorphous block. The longer the amorphous block, the more folded the crystalline block should become. Well-defined diblocks of highly-crystalline hydrogenated polynorbornene, hPN, and amorphous hydrogenated poly(ethylene norbornene), hPEN, were synthesized by ring-opening metathesis polymerization (ROMP) to probe this idea. ROMP hPN is a highly crystalline polymer at room temperature, while hPEN is an amorphous rubber. The small Flory interaction parameter between hPN and hPEN permits the diblocks to crystallize from single-phase melts at all the molecular weights explored to date. At 6 kg/mol, hPN homopolymers readily form extended-chain crystals. Attachment of the hPEN block induces folding of the hPN block to maintain equal area per chain on both sides of the lamellar interface; up to four folds per block were achieved for hPN of 6 kg/mol, producing a crystal only one-fifth the thickness in the homopolymer. The scaling of crystal thickness and domain spacing are in good accord with theoretical predictions, and also show discrete steps corresponding to integral chain folding. As crystal thickness is reduced, melting temperature T_m is lowered concomitantly, though T_m is also modulated by the crystallites' surface energy, through the block copolymer composition. The living nature of ROMP, catalyzed with suitable homogeneous Mo- or Ru-based initiators, and the high ring strain of norbornene-type monomers, allows the synthesis of polymers of more complex architecture than simple diblocks. Currently, we are synthesizing hPN-hPaN-hPN triblocks, where hPaN represents hydrogenated poly(5-alkylnorbornene). Monomers bearing hexyl and decyl substituents produce polymers with glass transition temperatures below -20°C, while the hPN endblocks form crystalline "hard domains". Further results on these materials will be presented at the meeting. Support for this work through the National Science Foundation, Polymers Program (DMR-0220236) is gratefully acknowledged.

9:30 AM *BB1.3

Rich Dynamics in Diblock Copolymers. George Fytas,¹FORTH, IESL, Heraklion, Crete, Greece; ²University of Crete, Department of Materials Science and Technology, Heraklion, Crete,, Greece; ³Max-Planck Institute for Polymer Research, Mainz, Germany.

The dynamic structure factor of ultra-high molecular mass diblock copolymers in the two different regimes of their phase diagram was systematically investigated by photon correlation spectroscopy. By probing the dynamics of the order parameter fluctuations at the relevant length scales of the system the different relaxation mechanisms were identified and the influence of the disorder-to-order transition was assessed. In the ordered state, the phonon dispersion relations obtained from the inelastic (Brillouin) light scattering can sensitively index the geometrical, morphological characteristics of the structure and reveal its micromechanical properties.

10:30 AM *BB1.4

Multicompartment Micelles and the Superstrong Segregation Regime in ABC Triblock Copolymers. Timothy Lodge¹, Marc Hillmyer¹, Zhibo Li¹, Zhilian Zhou¹ and Ishi Talmon²; ¹Chemistry, U. Minnesota, Minneapolis, Minnesota; ²Chemical Engineering, Technion, Haifa, Israel.

The ability of block copolymers, lipids and low molar mass surfactants to form micellar aggregates is well-known. By tuning variables such as composition a variety of micellar architectures are accessible. Addition of a third block, i.e., an ABC triblock copolymer, opens the door to multicompartment micelles, where the hydrophobic interior is subdivided into two or more nanodomains. We have prepared a series of ABC systems containing water-soluble, hydrocarbon, and fluorocarbon blocks by controlled polymerization methods, and characterized the resulting micellar assemblies by dynamic light scattering, small angle scattering, and cryogenic transmission electron microscopy. A variety of novel structures are observed, especially when ABC mikto-arm stars are employed. The results are interpreted in part by recognizing that the strong mutual repulsion among the three blocks places these polymers in the previously hypothesized superstrong segregation regime, whereby interfacial tension contributions overwhelm the conformational entropy of the smaller blocks.

11:00 AM *BB1.5

Characterization and Properties of Epoxy Thermosets with Self-Assembled Nanoscale Morphologies. Stephen F. Hahn¹, Dan J. Murray², Theresa J. Hermel², Brian G. Landes⁴, Houxiang Tang⁴, Nikhil E. Verghese³ and Ha Pham³; ¹Plastics, The Dow Chemical Company, Freeport, Texas; ²Corporate R&D, The Dow Chemical Company, Midland, Michigan; ³Performance Chemicals and Thermosets, The Dow Chemical Company, Freeport, Texas; ⁴Analytical Sciences, The Dow Chemical Company, Midland, Michigan.

Epoxy thermoset systems that contain amphiphilic diblock copolymers can self-assemble into micellar morphologies that persist through the curing cycle, providing thermosets with relatively well-defined 10-20 nm scale morphologies. A series of block copolymers derived from hydrogenated polyisoprene and polyethylene oxide were prepared and used to template epoxy thermosets. The observed morphologies were found to be sensitive to the molecular weight and composition of the block copolymer, and to the manner in which the block was dispersed prior to cure. SAXS studies were performed as the systems were being cured that allowed for characterization of morphology through the curing process. For these materials, the morphology that was observed in the uncured epoxy monomer mixture persisted through to the cure without modification of the morphology. These systems are particularly attractive for a variety of applications due to the profound changes in toughness brought about by the addition of low levels of block copolymer. Bulk mechanical analysis showed that, although the glass transition temperature and modulus of the system were not modified appreciably by the templating process, consistent improvements in fracture toughness were observed.

11:30 AM BB1.6

Surface Assembly and 2D Micelle-Chaining in Star-Block Copolymers. Randy S. Duran¹, Rachid Matmour², Yves Gnanou², Daniel Taton², Jennifer Logan¹ and Raju Francis³; ¹Chemistry, Univ of Florida, Gainesville, Florida; ²Laboratoire de Chimie des Polymères Organiques, ENSCPB-CNRS-Université Bordeaux, Bordeaux, France; ³Chemistry, St. Joseph's College, University of Calicut, Calicut, India.

This contribution will describe the surface assembly and surface morphology of well-defined star-block copolymer monolayers at the air/water interface. In particular, a new set of Poly(butadiene)-block-PEO stars with well-defined molecular weights, block volume fractions and architecture will be compared with

analogous Poly(styrene)-block-PEO amphiphilic star block copolymers. Isotherm experiments showed the following three characteristic regions : a compact brush region, a pseudoplateau at a pressure of ca 10 mN/m and a pancake region where the observed surface area depended on the amount of PEO present. AFM measurements showed significant differences in the surface morphology, including micelle chaining in both systems.

11:45 AM **BB1.7**

Molecular Asymmetry and Interface Structure in Miktoarm Star Block Copolymer Melts. Gregory Michael Grason and Randall D. Kamien; Physics and Astronomy, University of Pennsylvania, Philadelphia, Pennsylvania.

Using both strong-segregation theory (SST) and self-consistent field theory (SCFT) techniques we investigate the phase behavior of AB_n miktoarm copolymer melts. In particular, we examine how the molecular asymmetry stabilizes morphologies with highly curved interfaces. Previous SST calculations adopt the unit-cell approximation (UCA) and ignore the effect of lattice packing, treating the micelle shape a perfectly cylindrical (in two dimensions) or spherical (in three dimensions). Our SST calculation considers two-dimensional micelles constrained to fill the Voronoi of the hexagonal lattice. In particular, we parameterize a large class of micelle configurations by allowing the AB interface to adopt non-circular shapes. We find that the interface separating unlike monomer domain is highly distorted towards the hexagonal shape of the lattice Voronoi cell for large molecular asymmetries (large n) and large volume fractions of the inner domain. While SST calculations adopting the UCA tend to overestimate the effect of increased stability of micellar phases for asymmetric molecules, the SCFT and SST results are in strong agreement with experiments on PI-PS miktoarm copolymer melts. In addition, we report the stability of a new cubic phase of one-component block copolymer melts, with $Pm\bar{3}n$ symmetry. This phase, the A15 phase of spherical micelles, is a stable phase for melts of AB_n copolymers for $n \geq 2$. The stability of this phase is attributed to the polyhedral distortion of the AB interface since the area of A15 Voronoi polyhedral is known to be minimal among three-dimensional periodic structures.

SESSION BB2: Copolymers: Patterning, Morphology, and Properties

Chairs: George Fytas and Stephen Hahn
Monday Afternoon, November 29, 2004
Room 309 (Hynes)

1:30 PM **BB2.1**

Long Range Order in Cylindrical Diblock Copolymer Thin Films using Graphoepitaxy. Scott M. Fontana¹, Mark Dadmun¹ and Douglas H. Lowndes²; ¹Chemistry, University of Tennessee, Knoxville, Tennessee; ²Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Controlling the interfacial energies and wetting behavior of asymmetric diblock copolymers of polystyrene (PS) and polymethylmethacrylate (PMMA) in contact with a silicon surface, enables control over the orientation of its micro-phases. Micro-phases of a diblock copolymer that are placed onto a neutral surface will align perpendicularly to the surface. Neutrality is obtained by a variety of methods, including passivation of the surface of the silicon wafer. Removing the silicon oxide layer from the wafer with a washing in hydrofluoric acid solution does this. Neutrality can also be obtained by depositing a random copolymer brush of PS-r-PMMA with a mole fraction of styrene at 58%. A diblock copolymer thin film, of a controlled thickness, that is cast onto a neutral surface will micro-phase separate and align perpendicular to the surface. The film must have a thickness that is L_0 and be annealed above its T_g for a period of time allowing the micro-phases to align. By controlling the composition of PS and PMMA the micro-phase morphology can be controlled. When the PMMA phase of a diblock copolymer is 22%, vertically aligned hexagonally close packed PMMA cylinders will form. The PMMA cylinders can easily be degraded with 254 nm UV radiation and removed from the polymer matrix by washing with acetic acid leaving a nanoporous template. Published work has shown that graphoepitaxy provides a method for achieving long-range order of spherical domain block copolymers. This ordering is obtained by confining the micro-phases on mesas and in troughs of a patterned substrate to achieve long range alignment over the whole sample. This talk will discuss results that combine the work being done on vertically aligned diblock copolymer systems and graphoepitaxy to achieve long-range order of vertically aligned diblock copolymer films. This work will examine the effect of trough depth and width on the long range order of the polymer film. The dependence of the amount of long-range order present in the film on annealing time will also be presented. In order to provide a quantitative means for describing the

order, fast Fourier transform is used to determine an order parameter for these systems. This allows for the quantification of the evolution of order as annealing time increases.

1:45 PM **BB2.2**

Controlling Local Self-Assembly of Block Copolymers using Topographical Substrates. Joy Y. Cheng¹, Marianna

Shnayderman¹, Anne M. Mayes¹, Edwin L. Thomas¹, Henry I. Smith², G. Julius Vancso³ and Caroline A. Ross¹; ¹Materials Science & Engineering, MIT, Cambridge, Massachusetts; ²Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts; ³Materials Science and Technology of Polymers, University of Twente, AE Enschede, Netherlands.

The self-assembly process is a simple and low cost method to produce large-area nanostructures. However, phase-separated block copolymer thin films typically contain a population of uncontrolled defects and therefore lack long-range order. Here we investigate the formation and control of local defects in a self-assembled 2D array of polystyrene (PS) -b-polyferrocenyldimethylsilane (PFS) spherical block copolymer microdomains, formed within electron-beam-written topographical substrate features. The features consist of shallow grooves of various widths in an oxidized silicon substrate. The self-assembly of PS-PFS block copolymers with a range of different molecular weights within these grooves will be described. Perfect ordered sphere arrays of polymers can form in both constant-width templates and width-modulated templates. For modulated templates, the transition between configurations having a constant number of rows of spheres, and configurations of stable arrays with varying numbers of rows, is shown to be analogous to dislocation formation in an epitaxial thin film system. A row of block copolymer spheres will be added or annihilated only if the strain energy reduction is large enough to create the necessary distortions of the array. Based on the configuration transition energy and fluctuation energy, templates designed with a high tolerance for lithographical imperfections can direct the formation of precisely modulated block copolymer nanostructures. This study provides insights into the design of hybrid systems combining top-down and bottom-up fabrication. Ref: Cheng et al, Advanced Materials 19, 1599 (2003).

2:00 PM **BB2.3**

Epitaxial Phase Transformation in Cylindrical and Double Gyroid Mesophases in Diblock Copolymers. Lei Zhu¹, Lu Sun¹,

Qing Ge², Roderic P. Quirk², Stephen Z. D. Cheng², Benjamin S. Hsiao³, Carlos A. Avila-Orta³ and Igors Sics³; ¹Institute of Materials Science and Department of Chemical Engineering, University of Connecticut, Storrs, Connecticut; ²Department of Polymer Science, University of Akron, Storrs, Ohio; ³Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York.

Block copolymers are "smart" materials that self-assemble on a length scale of a few tens of nanometers. Conventional equilibrium morphology are lamellae, hexagonal cylinders (Hex), and body-centered cubic (Bcc) spheres, and complex phase morphology includes double gyroid (G) and hexagonally perforated layers (HPL). The G phase is considered as an equilibrium phase, while the HPL phase, which is controlled by edge dislocations under mechanical shear, is metastable. Phase transformations among these ordered mesophases, including the order-to-disorder and order-to-order transitions, have received research attention, especially the ones between complex phase morphologies. In this work, multiple phase morphologies were observed in a semi-crystalline polystyrene-b-poly(ethylene oxide) (PS-b-PEO) diblock copolymer with a PEO volume fraction of 37%. The PS and PEO had number-average molecular weights of 11.6k g/mol and 18.5k g/mol, respectively. The molecular weight distribution determined by size exclusion chromatography is 1.09. From differential scanning calorimetry, the glass transition temperature of the PS blocks was 72 °C, and the PEO crystals melted around 51 °C. The sample exhibited a G phase as cast from chloroform solution and annealed in vacuum at 120 °C for 24 hrs. After it was subjected to a large amplitude-reciprocating shear at 120 °C, a "single-crystal"-like Hex phase was obtained. This Hex phase was metastable, and a Hex-to-G transformation was observed at 145 °C in a low frequency rheology study. This transformation was also confirmed by polarized optical microscopy. Upon annealing at 150 °C for 40 min, the oriented Hex phase partially transformed back to the G phase with a retention of orientation. High-resolution small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) techniques were used to study the phase transformation from Hex to G. Epitaxial transformation relationships were revealed by SAXS and visualized by TEM: Hex[001] - G[111], Hex[100] - G[121], and Hex[120] - G[202]. The mechanism of the Hex-to-G transformation was confirmed by TEM observations: One cylinder was surrounded by six neighbors, where three of them (every other ones) evolved into left-handed helices and the other three formed right-handed helices. An intermediate five-fold junction was speculated to facilitate the phase

transformation. The phase transformation was observed to follow the nucleation and growth mechanism, where the transition took place within a transition zone of less than one unit-cell width. Acknowledgements. This work was supported by the University of Connecticut Research Foundation, ACS Petroleum Research Fund, and NSF CAREER award (DMR-0348724). The synchrotron X-ray experiments were carried out at Advanced Polymer Beamline X27C in the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the Department of Energy.

2:15 PM **BB2.4**

Block Copolymers under Cylindrical Confinement.

Hongqi Xiang, Kyusoon Shin, Sung In Moon, Taehyung Kim, Thomas J. McCarthy and Thomas P. Russell, Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts.

Block copolymers were introduced as melts into nanoscopic cylindrical pores in alumina membranes via capillary force. The influence of geometric confinement on the block copolymer morphology was investigated by transmission electron microscopy. It was found that well-developed microphase-separated structures formed. Polymers that exhibit bulk lamellar morphology take a concentric multi-layer cylinder morphology under the cylindrical confinement. The concentric cylinders were oriented along the nanorod axis due to preferential wetting of the high-energy pore surface with one block of the copolymers. The number of concentric cylinders depends on the ratio of the nanorod diameter to the equilibrium period of the copolymer. With styrene-butadiene diblock copolymers with lamellar microdomains, due to the preferential segregation of polybutadiene block at the alumina surface, either polybutadiene or polystyrene block can form the central core. By varying the ratio of the pore diameter to fundamental repeat period of the copolymer, conditions of frustration were encountered where the morphology of the copolymer was changed. These results indicate a method by which copolymer microdomains can be manipulated in a simple manner for the fabrication of isolated nanostructures.

2:30 PM **BB2.5**

Templated Growth of Sub-20nm GaN Nanostructures Using Block Copolymer Lithography. Azar Alizadeh¹, Christopher Keimel¹, Seth T. Taylor¹, Surya Ganti¹, Steven F. LeBoeuf¹, Fatemeh Shahedipour-Sandvik² and James Grandusky²; ¹General Electric Global Research, Niskayuna, New York; ²School of Nano-Science and Nano-engineering, SUNY-Albany, Albany, New York.

With the advent of nanotechnology, there is a growing consensus in the technical community regarding the enormous application potential of wide bandgap (WBG) semiconductor nanostructures. Presently, it appears that the templated growth method is perhaps one of the more promising avenues for fabrication of tailored WBG nanostructures. Templated growth of WBG nanostructures (which involves the use of a selective mask) allows for a precise control over quantum dot size and location, and avoids the nonradiative defects associated with the direct writing techniques. Selective growth of III-nitride structures, particularly gallium nitride, using a dielectric mask with micron size openings has been numerous reported in the literature. In comparison, to the best of our knowledge, there appears to be only one report on the selective growth of gallium nitride nano-pillars inside sub 100 nm SiO₂ windows via molecular beam epitaxy. Recent theoretical and modeling framework developed in our lab suggests that (unlike the case for thin epitaxial films) for WBG nanostructures below critical lateral dimension (<100 nm), dislocation free structures of any thickness can be grown [1]. Such nanostructures have the potential to revolutionize a variety of technologies such as in field emission, optoelectronics as well as high temperature sensing. Here, we will report on the templated growth of gallium nitride nanostructures inside sub 20 nm SiO₂ windows using metal organic chemical vapor deposition (MOCVD). We have used block copolymer (BCP) lithography [2] and reactive ion etching as a nano-patterning technology to produce SiO₂ templates. The nanostructured templates are then used to selectively control the MOCVD growth of both homo and heteroepitaxially grown GaN pillars with diameters less than 30nm. The morphology of these GaN nanostructures was characterized by SEM. In addition, cathodoluminescence, photoluminescence and TEM were used to examine the defect densities of the GaN nanostructures. 1 A. Alizadeh, P. Sharma, S. Ganti, S. F. LeBoeuf, and L. Tsakalakos, J. Appl. Phys. (2004) 2Thurn-Albrecht, T., Schotter, J., Kastle, G.A., Emby, Shibauchi, N.T., Krusin-Elbaum, L., Guarini, K., Black, C.T., Tuominen, M.T., Russell, T.P.;(2000); Science, 290, p. 2126; Harrison, C., Adamson, D.H., Cheng, Z., Sebastian, J.M., Sethuraman, S., Huse, D.A., Register, R.A., Chaikin, P.M.; (2000); Science, 290, p. 1558

2:45 PM **BB2.6**

Self-Assembly of Rod-Coil Block Copolymers. Venkat Ganesan, Chemical Engineering, The University of Texas at Austin, Austin, Texas.

In the context of polymers for electronics applications, there is a recent surge of interest in understanding the phase behavior and self-assembly of rod-coil block copolymers as simple models of self-assembly in block copolymers possessing conjugated units. In this talk, we present a self-consistent field theory based model for the self-assembly behavior of rod-coil block copolymers. The orientational interactions between the rods were modeled through a Maier-Saupe interaction, while the enthalpic interactions between rods and coils were modeled through a standard Flory Huggins approach. We outline a "real space" numerical approach to solve the self-consistent field equations for such rod-coil block copolymers. A major focus of our work is upon the non-lamellar phases observed in the experiments on such polymers. To develop a physical understanding of these phases and their regimes of occurrence, we compute the phase diagram for our model which shows significant departures from results of some of the earlier researches, but matches qualitatively with the existing experimental results. We also present scaling arguments that rationalize the numerical results for the self-assembly behavior, and suggest rational strategies to experimentally access novel self-assembled phases of rod-coil block copolymers.

3:30 PM **BB2.7**

Structural Characterization of Mesomorphic Phases in a PP/PE Copolymer. Hristo A. Hristov, Katrina Werpetski and Denise Taylor; Analytical, Kimberly Clark Corp., Roswell, Georgia.

Rapid quenching and mechanical deformation of polypropylene (PP) can generate peculiar structures (dubbed //mesomorphic// phase [1]), exhibiting a specific WAXS pattern. The structure is modeled [2] by bundles of helical chains arranged similarly to the chains in the PP α -crystal, with partial order extending to 3-4 nm. Recent SAXS and Electron Microscopy (EM) studies indicate that the meso-phase is organized in domains extending up to 20-30 nm [1,3]. These discrepancies necessitate further studies of the mesophase. The starting material for our studies is a PP/PE copolymer fiber. The fiber was ground for 10 min. with freezer mill, using liquid nitrogen as a cryogenic agent. The structures of the initial material and the cryo-produced powder were studied by using WAXS and SAXS. The WAXS curve of the powder is typical for a PP material containing amorphous and mesomorphic phases [1,2]. To evaluate the extent of the interatomic correlation, the radial distribution function (RDF) method [4] was employed. The results indicate that the interatomic correlation extends to 2 nm. The SAXS curve of the powder is of a //single particle// scattering type [4], with particle diameters in the range of 12 nm. A comparison of WAXS and SAXS results shows significant differences in the characteristic size of the mesophase. In an attempt to clarify the source of this discrepancy, the WAXS curves were modeled by using the atomic coordinates of the monoclinic α -crystal [2]. The results show a good match between the experimental curve and the scattering from randomly oriented crystals with dimensions 5aX2bX4c (3X4X3 nm; a, b, c are the unit cell parameters). The coincidence between the experimental and the model curves is further improved if the WAXS curve is modeled as scattering from two crystals with sizes 5aX1bX4c having a misalignment in the order of 4-5°. Increasing the angle of misalignment to 10° produces scattering curve similar to the scattering curve from two independent crystals with sizes 5aX1bX4c. The last two results are a key to understand the peculiarities of the structure of the PP meso-phase. Large mosaic crystals made of small blocks with angle of misalignment between the nearest neighbor blocks approximately 5°, and misalignment 10° or more for the higher order neighbors will show different coherence lengths depending on the experimental method. WAXS measurements will give the average size of the small block, EM and SAXS will measure the large dimensions. Similar results can be obtained from a system containing large bent crystals, with appropriate radius of curvature. It is proposed that the PP mesomorphic phase is a combination of both: mosaic and bent α -crystals. 1. Phillips R. A. at al., Polypropylene Handbook 1996, Chpt. 3, 113. 2. Corradini P. at al., Macromolecules 1986, 19, 2699. 3. Wang Z. at al., Polymer 2001, 42, 7561. 4. Balta-Calleja F.J.; Vonk C. G. X-ray Scattering of Synthetic Polymers 1989.

3:45 PM **BB2.8**

Azobenzene-Containing Triblock Copolymers for use as Photoactive Thermoplastic Elastomers. Li Cui¹, Xia Tong¹, Xiaohu Yan², Guojun Liu² and Yue Zhao¹; ¹Chemistry, University of Sherbrooke, Sherbrooke, Quebec, Canada; ²Chemistry, University of Calgary, Calgary, Alberta, Canada.

A series of ABA triblock copolymers were synthesized and designed to behave like photoactive thermoplastic elastomers. The samples have the same rubbery midblock of poly(n-butyl acrylate) (PnBA) but differ in the degree of polymerization of the endblocks of a methacrylate-based azobenzene-containing side-chain liquid crystalline polymer (Azo-SCLCP). The coupling between elasticity, liquid crystallinity and photoactivity imparts interesting features to

this type of thermoplastic elastomers. When the solution-cast film is stretched at $T \gg T_g$ of the Azo-SCLCP whose microdomains act as physical crosslinks, in contrast to conventional thermoplastic elastomers (such as styrene-butadiene-styrene triblock copolymer) that lose the elasticity, liquid crystalline microdomains can support part of the elastic extension of PnBA chains and, in the same time, deform to result in a long-range orientation of azobenzene mesogens. The liquid crystal orientation is retained in the relaxed film at $T < T_g$, which creates a thermoplastic elastomer whose glassy microdomains contain oriented azobenzene mesogens. The reversible trans-cis photoisomerization of the azobenzene chromophore can be used to modulate the molecular orientation, and mechanically tunable diffraction gratings can be recorded using these photoactive triblock copolymers.

4:00 PM **BB2.9**

On The Origin of Color Degradation in Polyfluorenes - Block Copolymer Approach for Stable Blue Emission.

Vasilis Gregoriou, Christos L. Chochos, Georgia Kandilioti and Joannis Kallitsis; FORTH-ICEHT, Patras, Greece.

Spectroscopic studies on a series of rod-coil block copolymers with oligofluorenes as the rigid segment demonstrate that the main cause of color instability in fluorene oligomers and polymers is aggregate formation and not the presence of keto defects along the molecular chain. Polyfluorenes are considered as the most promising materials for blue light emission, however they suffer from the appearance of a low-energy emission band occurring at 520 nm which converts the blue color to an undesirable blue-green shade. In this study, we have examined the influence of structural parameters on the color degradation. In order to achieve this, we have performed a detailed spectroscopic study under various aging conditions (temperature, UV exposure). These conditions resemble operational conditions in polymeric light emitting diodes (PLEDs). In particular, using spectroscopic techniques (FT-IR, photoluminescence), we have tried to correlate the observed optical behavior to the spectral characteristics and in the infrared we have followed the presence of the carbonyl stretching mode of the fluorenone moiety. Therefore, the synthesis of materials where aggregation is inhibited is the key approach for the production of stable polymeric light-emitting devices (PLEDs). The potential of this method is demonstrated by the synthesis of thermally stable and photooxidative stable diblock fluorene/styrene and triblock fluorene/styrene/C60 copolymer blue emitters. Finally, voltage-induced infrared spectra of oligofluorene PLEDs have been measured using reflection-absorption Fourier-transform infrared spectroscopy. These voltage-induced infrared spectra have been measured using the difference spectrum method. These spectroscopic studies allow the investigation of the role that molecular orientation plays on the performance of these devices as well as to probe the interaction of the polymeric layer with the metal electrodes.

4:15 PM **BB2.10**

The Effect of Molecular Architecture on the Ordering Kinetics of AnBn Star Block Copolymers in Supercritical Carbon Dioxide. Xiaochuan Hu¹, Samuel P. Gido¹, Thomas P. Russell¹, Ferass M. Abuzaina² and Bruce A. Garetz²; ¹Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts; ²Chemical and Biological Sciences and Engineering, Polytechnic University, Brooklyn, New York.

The effect of the number of arms on the grain growth kinetics of a series of lamellae-forming AnBn ($n = 1, 2, 4,$ and 16) star block copolymers annealed in supercritical carbon dioxide (SC CO₂) has been investigated via transmission electron microscopy (TEM) image analysis. Across this series all materials have the same A and B block molecular weight and all have the equal number (n) of each type of arm. It is found that SC CO₂ can be used to promote the grain growth of these AnBn star block copolymers at relatively low temperatures. Also, the ordering kinetics is found to be dependent on the number of arms. Initial results suggest the existence of an optimum number of arms for grain growth dynamics. This is similar to results obtained previously for the same series when thermally annealed. However, the optimal topological conditions and the ordering kinetics in SC CO₂ are found to be different from that of their thermally annealed counterparts. This may be attributed to dilation of the AnBn star block copolymers in SC CO₂.

4:30 PM **BB2.11**

Morphological Characteristics of Core-Shell Nanogels in Block Copolymer and Homopolymer Blends and Their Dewetting Efficacy. Bin Wei¹, Paul A. Gurr², Jan Genzer¹, Greg G. Qiao² and Richard John Spontak¹; ¹Chem. Eng. and Mater. Sci. & Eng., NC State University, Raleigh, North Carolina; ²Chem. & Biomol. Eng., University of Melbourne, Melbourne, Victoria, Australia.

Most studies of block copolymer and homopolymer blends employ

linear macromolecules that can adapt to their local environment and undergo some level of structural reorganization to minimize enthalpic and entropic penalties. Core-shell nanogels are permanent particles that closely resemble block copolymer micelles. Model nanogels have been synthesized in this study by the "arms-first" procedure wherein poly(methyl methacrylate) (PMMA) arms are synthesized first by atom transfer radical polymerization (ATRP) and then cross-linked with divinyl benzene (DVB) to form discrete particles with dangling arms and cross-linked cores. According to GPC analysis, the number-average molecular weight of each PMMA arm is about 11 kDa, with a polydispersity of less than 1.1. Details of the synthesis and subsequent characterization of the nanogel particles will be provided. These particles have been incorporated at different concentrations into thin films of both polystyrene (PS) and PMMA homopolymer, as well as a microphase-ordered PS-*b*-PMMA diblock copolymer, to discern their aggregation behavior in one- and two-dimensionally confined environments. Transmission electron microscopy is employed to discern the resultant blend morphologies. The nanogel particles are also incorporated into thin PS films, each of which is then placed on top of a thin PMMA substrate to form a double-layer, which is subsequently heated to 180 C to promote dewetting of the top layer. Dewetting kinetics are measured by time-resolved optical microscopy. The dewetting rates of PS/nanogel blends varying in nanogel concentration are compared to those of corresponding PS/PS-*b*-PMMA blends with low copolymer concentrations to ensure the formation of copolymer micelles to deduce the mechanism by which dewetting occurs in each system and the extent of interfacial restructuring, as discerned by atomic force microscopy.

4:45 PM **BB2.12**

Influence of Grain Boundaries and Clay Particles on the Deformation Behavior of Block Copolymers.

Panitarn Wanakamol¹, Mary C. Boyce² and Edwin L. Thomas¹;

¹Materials Science and Engineering, MIT, Cambridge, Massachusetts;

²Mechanical Engineering, MIT, Cambridge, Massachusetts.

The evolution of the microdomain structure of block copolymers (BCP) during tensile deformation has been extensively studied using a variety of experimental techniques. Transmission electron microscopy (TEM) and small angle x-ray scattering (SAXS) can provide detailed information on the changes taking place at the microdomain level and above. In situ synchrotron SAXS is especially useful for dynamic monitoring of the deformation. Most previous studies are on isotropic, polygranular materials, where the role of grain boundaries on the deformation is largely unknown. In order to develop a fundamental understanding of the defects on the deformation, we have utilized model bicrystals made by first producing a near-single crystal BCP sample using the roll casting process and then cutting appropriate pieces and adhering these together to yield bicrystal BCP specimens with various types of pure tilt boundaries. The deformation behavior of these samples was then monitored dynamically in reciprocal space using SAXS and step scanning the small beam across the boundary region after each increment of applied strain. This approach gives precise information on changes in domain spacings and domain reorientation from the sequence of 2D SAXS patterns, which can be compared with the deformation of well oriented single crystal BCP grain deformed at the corresponding angles. Additional real space information affording direct examination of the heterogeneous nature of the deformation process is available from a specially built deformation apparatus working with an atomic force microscope (AFM). In addition, polygranular BCP materials were also employed to the study the influence of grain boundaries on deformation. Clay particles act as a nucleating agent in clay filled BCP and grain density increases strongly with clay concentration. The microstructure of clay filled BCP solidified via quiescent solvent evaporation was examined via TEM and the mechanical behavior of these nanocomposites was explored via tensile deformation experiments.

SESSION BB3: Poster Session: Block Copolymers,
Nanocomposites and More

Chair: Richard Register

Monday Evening, November 29, 2004

8:00 PM

Exhibition Hall D (Hynes)

BB3.1

Self Assembled Structures of

Poly(styrene-*b*-ferrocenyldimethylsilane) (PS-*b*-FS) Blended With Other Block Copolymers. Arielle Jolan Galambos¹,

Young-Soo Seo², Miriam Rafailovich², Jonathan Sokolov², Rob G. H. Lammertink³ and G. J. Vancso³; ¹Wellesley College, Wellesley, Massachusetts; ²Mat. Sci. Eng., Stony Brook University, Stony Brook, New York; ³Faculty of Chemical Engineering, University of Twente, AE Enschede, Netherlands.

The Polymer, Poly(styrene-*b*-ferrocenyldimethylsilane) (PS-*b*-FS) can be self-assembled, building iron-containing nanostructures from the molecular level. Such structures can be utilized for a variety of purposes such as templates for lithography.[1] PS-*b*-FS was spread onto Si wafers using a Langmuir Blodgett trough, and the resulting structures were determined to be dependent on the ratio of PS and PFS, as well as surface pressure. Novel structures can also be achieved through blending with other copolymers. These blends have been shown to create very regular features which are easily oriented in external electromagnetic fields.[2] The resulting features can be used as a template for creating nanoscale structures which will be used to study magnetic properties in confined geometries. [1] R.G.H. Lammertink, et al., *Macromolecules* 1998, 31, 795. [2] Young-Soo Seo, et al., *Nano Letters* 2004, 4, 483-486. Work supported by the NSF-MRSEC program

BB3.2

Forced Polymer Chain Folding in Amphiphilic Unimolecular Micelles. Jianjun Miao¹, Lei Zhu¹, Lu Tian², Kathryn E. Uhrich², Carlos A. Avila-Orta³ and Benjamin S. Hsiao³, ¹Institute of Materials Science and Department of Chemical Engineering, University of Connecticut, Storrs, Connecticut; ²Department of Chemistry and Chemical Biology, Rutgers, the State University of New Jersey, Piscataway, New Jersey; ³Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York.

It is known that chain-folded crystalline lamellae are the basic morphological building blocks of larger superstructures such as spherulites. Unlike the folding in proteins, which is thought to be thermodynamically stable, polymer chain-folding is kinetics driven and a necessary step to form lamellar morphology. However, monodisperse oligomers show unique chain folding pathways in the solid state, namely, integer folds (IF). The number of folds depends on the molecular weight; short oligomers can only form extended (E) chain crystals. It is generally accepted that the chain-ends are rejected from the crystalline region to both basal planes to minimize the overall free energy. Nevertheless, non-integer folding (NIF) has been observed as a kinetically favorable process in oligomer crystallization. The NIF crystals can transform into IF crystals through a thinning and/or a thickening process. In this work, the crystallization and self-assembly behavior of an amphiphilic star-like macromolecule (ASM) with an aliphatic core and four PEO (Mn = 2,000 g/mole) were studied. Note that PEO homopolymers with 2,000 g/mol molecular weight crystallize into only extended chain crystal under all conditions. Computer simulation indicated that the core size was ca. 2.3 nm. Conventional negative spherulites were observed under polarized light microscopy, proving the growth of lamellar PEO crystals inside the spherulite. The samples were also characterized by synchrotron small angle X-ray scattering (SAXS) at different crystallization temperatures (Tcs). The overall d-spacing increased from 10.1 nm for samples quenched into liquid nitrogen to 20.1 nm for Tc = 42 °C, as observed in SAXS experiments. From correlation function analysis of the SAXS scattering profiles using a three-phase model assumption, individual layer thickness for the core, amorphous PEO, and crystalline PEO was obtained. Once-folded to extended chain crystal transition was observed with increasing the Tc, and this was further confirmed by differential scanning calorimetry. For once-folded PEO crystalline morphology, the aliphatic cores were not much deformed, while they were deformed into an ellipsoid shape as the PEO chains had extended chain conformation in the crystals. The forced chain folding was considered to be a consequence of insufficient arm-to-core ratio in the ASM molecules for the PEO-arm crystallization. Acknowledgements. This work was supported by the University of Connecticut Research Foundation, ACS Petroleum Research Fund, and NSF CAREER award (DMR-0348724). The synchrotron X-ray experiments were carried out at Advanced Polymer Beamline X27C in the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the Department of Energy.

BB3.3

Emission Properties of Block Copolymer Photonic Crystal Nanocomposite Doped with Optically Active Gain Materials. Jongseung Yoon¹, Wonmok Lee¹, Steven Kooi² and Edwin L.

Thomas^{1,2}, ¹Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Institute for Soldier Nanotechnologies, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Recently, block copolymers have been successfully utilized to develop one-, two- and three-dimensional photonic bandgap structures for optical frequencies. In this investigation, optically active gain materials are added into one-dimensional photonic crystal of lamellar-forming poly(styrene-*b*-isoprene) block copolymer for achieving photonic band edge lasing, in which the radiative transition of gain materials lies in the frequency range of photonic band gap of

block copolymer. Thin films of the nanocomposite are fabricated by solvent evaporation technique between sub-/superstrates with a thin film spacer in order to achieve sharper photonic bandgap with a minimum defect formation during self-assembly. Emission characteristics of the doped gain materials in the block copolymer photonic bandgap structure will be discussed.

BB3.4

Thermo-mechanical properties of semicrystalline syndiotactic polypropylene diblock and triblock copolymers. Atsushi Hotta¹, Vikram Khanna¹, Glenn H. Fredrickson¹, Ed J. Kramer¹, Geoff W. Coates² and Fumihiko Shimizu³, ¹Mitsubishi Chemical Center for Advanced Materials and the Department of Materials and Chemical Engineering, Univ of California, Santa Barbara, Santa Barbara, California; ²Department of Chemistry and Chemical Biology Baker Laboratory, Cornell University, Ithaca, New York; ³Mitsubishi Chemical Corporation, Tokyo, Japan.

Polyolefin copolymers of diblock (poly)(syndio-)propylene-*b*-ethylene-propylene and triblock (poly)(syndio-)propylene-*b*-ethylene-propylene-(syndio-)propylene were synthesized using new living single site titanium catalyst. The phase diagram was established and interesting morphology was observed in the microphase-separated domains where both polypropylene (PP) and ethylene-polypropylene (EP) layers were semicrystalline. Crystallinity of the copolymers was determined and mechanical properties such as stress-strain and stress relaxation behaviors were examined to observe fracture stress and strain, Young modulus and mechanical hysteresis at different temperatures. It was found that molecular structures strongly affect the mechanical properties of the copolymers. Increasing molecular weight improves the ductility of the copolymers and increasing PP content increases Young modulus and the plastic strain after deformation. Higher ethylene content in EP block produces a higher fracture stress even in the weak diblock copolymers. We will discuss these interesting mechanical characteristics in terms of the semicrystalline microstructures of the copolymers.

BB3.5

Nanoscale Glassy Dynamics in Gradient Copolymers and Polymer Nanocomposites: Novel Studies of Nanophase Separation and the Impact of Free Surfaces and Polymer-Nanofiller Interactions on Glass Transition and Physical Aging Behavior. Christopher J. Ellison¹, Maisha K. Gray², Jungki Kim¹, Perla Rittigstein¹, Rodney D. Priestley¹, Hongying Zhou³, SonBinh T. Nguyen³, Linda J. Broadbelt¹ and John M. Torkelson^{1,2}, ¹Chemical & Biological Engineering, Northwestern University, Evanston, Illinois; ²Materials Science & Eng., Northwestern University, Evanston, Illinois; ³Chemistry, Northwestern University, Evanston, Illinois.

Gradient copolymers, in which composition varies along the chain length, and polymer nanocomposites have been characterized by methods sensitive to glass transition, physical aging, and enthalpy relaxation behavior. These studies reveal that gradient copolymers have substantially different nanoscale phase behavior as compared with random and block copolymers. These studies also show that gradients in glass transition dynamics occur over several tens of nanometers at free surfaces and polymer-substrate interfaces within polymer nanocomposites. Styrene (S)/acetoxystyrene, S/hydroxystyrene, S/4-methyl styrene, S/*n*-butyl methacrylate, and S/*n*-butyl acrylate gradient copolymers made by controlled radical polymerization were compared to random and block copolymers using differential scanning calorimetry (DSC) and other methods. In limited cases, gradient copolymers exhibit two glass transition temperatures (Tgs) although more commonly only a single, broad Tg is discernable. The presence of two Tgs is apparently limited to the following circumstances: a somewhat blocky structure and/or a strong repulsive interaction of the comonomers. In some cases enthalpy relaxation studies (physical aging followed by enthalpy recovery upon heating through Tg) reveal that nanophase separation is present even when only one Tg is apparent. This is evidenced by the presence of two enthalpy recovery peaks at different temperatures. It has been hypothesized that enthalpy relaxation behavior may be sensitive to characteristic length scales smaller than those associated with Tg and thus reveals the presence of nanoscale heterogeneity when Tg measurements cannot, a condition that may apply in some gradient copolymers. Novel fluorescence and DSC methods have been used to characterize glass transition dynamics and physical aging behavior in model and real polymer nanocomposites. The distribution of Tgs across silica-substrate-supported polymer films, serving as model polymer nanocomposites, has been obtained by a fluorescence/multilayer method, revealing that the enhancement of dynamics at a free surface affects Tg several tens of nanometers into the film. The extent to which the dynamics smoothly transition from enhanced to bulk states depends strongly on nanoconfinement. When films are sufficiently thin that a reduction in thickness leads to a

reduction in overall T_g, the surface-layer T_g actually increases with a reduction in overall thickness, whereas the substrate-layer T_g decreases. When attractive polymer-substrate/nanofiller interactions are present, e.g. via hydrogen bonding between hydroxyl groups as the substrate/nanofiller surface and the polymer, the dynamics at the interface slow dramatically resulting in a major rise in polymer T_g. Similar rises in T_g have been observed in real nanocomposites made from polyvinylpyridine and silica nanospheres. Related studies of the impact of nanofillers on physical aging of polymers will also be discussed.

BB3.6

Effects of Chain Extension and Branching on the Properties of Poly (Ethylene-Terephthalate)-Organoclay Nanocomposites. Ali Emrah Keyfoglu and Ulku Yilmazer; Chemical Engineering, Middle East Technical University, Ankara, Turkey.

The effects of chain extension and branching on the properties of nanocomposites produced from recycled poly (ethylene-terephthalate) and organically modified clay were investigated. As the chain extension/branching agent, maleic anhydride (MA) and pyromellitic dianhydride (PMDA) were used. The nanocomposites were prepared by twin-screw extrusion, followed by injection molding. Recycled poly (ethylene-terephthalate), was mixed with 2, 3 or 4 weight % of organically modified montmorillonite. During the second extrusion step, 0.5, 0.75 or 1 weight % of MA or PMDA was added to the products of the first extrusion. As the second extrusion step is reactive extrusion, the anhydrides were added at three different screw speeds of 75, 150, 350 rpm, in order to observe the change of properties with the screw speed. The effects of the sequence of addition of the ingredients on the final properties of the nanocomposites were also investigated. X-Ray Diffraction analysis showed that, the interlayer spacing of Cloisite 25A expanded from 19.21 Angstrom to about 28-34 Angstrom after processing with polymer indicating an intercalated structure. PMDA content, MA content and screw speed did not have a significant effect on the expanded interlayer distance. Mechanical tests (tensile, flexural and impact) were used to characterize the nanocomposites. In the first extrusion step, nanocomposites containing 3% organoclay content gave significant increase in tensile modulus and decrease in elongation at break values indicating good interfacial adhesion. After the addition of chain extenders, it was observed that both MA and PMDA improved the mechanical properties of the nanocomposite owing to the branching and chain extending effects that increase the molecular weight. However, PMDA gave better results at lower content which makes it a more effective chain extender. The addition of clay followed by the addition of MA displayed better results owing to the initial low molecular weight of recycled poly (ethylene-terephthalate). DSC analysis showed that MA was more effective in increasing the glass transition temperature and melting temperature in comparison to PMDA.

BB3.7

Abstract Withdrawn

BB3.8

Synthesis of Polymer Brushes Grafted Silica Nanoparticles via Surface Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization. Chunzhao Li^{1,3}, Amitabh Bansal², Quan Chen², Sarah L. Lewis², Linda S. Schadler² and Brian C. Benicewicz^{1,3}; ¹Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York; ²Department of Materials Science & Engineering, Rensselaer Polytechnic Institute, Troy, New York; ³NYS Center for Polymer Synthesis, Rensselaer Polytechnic Institute, Troy, New York.

Reversible Addition-Fragmentation chain Transfer polymerization (RAFT) was used to prepare silica nanoparticles coated with polymer brushes. RAFT agents anchored silica nanoparticles were synthesized by the functionalization of silica nanoparticles with a RAFT-silane agent. RAFT polymerization was then conducted from the nanoparticle surfaces to attach polymer brushes to the particles. Kinetics of St, n-BuA surface RAFT polymerizations were investigated. It was found that the surface graft polymerization proceeded in a controlled way, the first-order kinetics evolved in a linear fashion with time and molecular weights increased linearly with conversions. The well-defined polymer brushes attached silica particles and the PSt-g-SiO₂ / pure PSt nanocomposites were then characterized by TEM. Preliminary mechanical testing results of the nanocomposites will be presented.

BB3.9

Hypothesis of Composite Filler Particles Interaction with Polymeric Matrix. Viktor Makaryan, State Engineering University Armenia, Yerevan, Armenia.

In order to determine the adhesion of filler particles to polymeric matrix a set of tests on the tensile strength of composite materials

based on CFD and PPS has been performed. The best results were observed for composites with nanosized amorphous fillers Mo and MoO₂. The strength of composites filled with such fillers increased up to 2 times compared to the pure polymer value. The effect of using fine-ground mineral fillers is less about 1.5 times. Coarse fractions of mineral fillers (50 μ m) do not have positive effect on the composite tensile strength. Thus, the effect of fillers on the mechanical properties of polymer-based composites depends heavily on the nature and dispersivity of the filler and is apparently determined by the behavior of chemical and mechanical bonds occurring on the phase boundaries. The large number of bonds for nanosized fillers is promoted by the high specific (to surface area) number of radicals on their surface, which results in strong bounding of particle to matrix, besides the polymeric material close to the phase boundary gains additional properties. Since the size of nanoparticles is proportional to the thickness of interphase boundary layer, the considerable portion of the composite material transforms to a boundary interphase state, which properties, being different from both filler and polymer properties, determine the new characteristics of the composite material

BB3.10

Layered Structures of Shear-Oriented and Multilayered PEO/Montmorillonite Nanocomposite Films.

Avinash Dundigalla¹, Matthew M. Malwitz¹, Vincent Ferreiro², Paul D. Butler³ and Gudrun Schmidt¹; ¹Chemistry, Louisiana State University, Baton Rouge, Louisiana; ²CNRS, University des Science et Technologie de Lille, Villeneuve d Ascq, France; ³ORNL, Oak Ridge, Tennessee.

The structure and orientation of polymer and clay platelets in multilayered, micrometer-thick nanocomposite films was investigated by means of scanning electron microscopy (SEM), atomic force microscopy (AFM), optical microscopy and small-angle neutron scattering (SANS). Microscopic and scattering methods complementarily measured the morphology and shear-induced orientation of polymer and platelets in films when spread layer by layer from a network-like polymer clay solution. During the drying process, the polymer clay network collapsed and clay platelets oriented inside the network with the clay surface normal perpendicular to the spread direction (x-z plane). On nanometer length scales, SANS and AFM yielded structure and orientation of platelets and polymer in and perpendicular to the spread direction of the film. SEM investigations led to the observation of unexpected morphology on the micron length scale. SEM did not detect boundaries between single spread, micron-thick film layers, but surprisingly showed a highly ordered and layered structure of the film. Polarized light microscopy showed differences in birefringence in each plane.

BB3.11

Multilayered PEO/Laponite Nanocomposite Films.

Matthew M. Malwitz¹, Avinash Dundigalla¹, Sheng Lin-Gibson², Vincent Ferreiro³ and Gudrun Schmidt¹; ¹Chemistry, Louisiana State University, Baton Rouge, Louisiana; ²NIST, Gaithersburg, Maryland; ³CNRS, Universite des Science et Technologie de Lille, Villeneuve d Ascq, France.

The structure and orientation of polymer and Laponite clay platelets in transparent and multilayered, micrometer-thick nanocomposite films was measured using scanning electron microscopy (SEM), atomic force microscopy (AFM), optical microscopy and scattering techniques; SAXS, WAXS (small angle and wide angle X-ray scattering). Each method is sensitive to different aspects of structure and all complementarily measured the morphology and shear-induced orientation of polymer and platelets in films when spread layer by layer from a network-like polymer clay gel. During the drying process, the polymer clay network collapsed and clay platelets oriented inside the network with most of the clay surface-normal perpendicular to the spread direction (x-z plane). On nanometer length scales, SAXS, WAXS and AFM yielded structure and orientation of platelets and polymer in and perpendicular to the spread direction of the film. SEM investigations led to the observation of highly oriented unexpected morphology on the micron length scale. SEM did not detect boundaries between single spread, micron-thick film layers, but surprisingly showed an ordered and layered structure of the film. Polarized light microscopy showed differences in birefringence in each plane.

BB3.12

Toward Real-Time Process Monitoring of Thermoset-Layered Silicate Nanocomposite Systems Using Dielectric Spectroscopy. John David Jacobs^{1,3}, Richard A. Vaia³, Hilmar Koerner², Peter Mirau³ and Patrick H. Garrett¹; ¹Electrical Engineering, University of Cincinnati, Cincinnati, Ohio; ²University of Dayton Research Institute, Dayton, Ohio; ³Materials and Manufacturing Directorate, Airforce Research Laboratory, Wright-Patterson AFB, Ohio.

The development of innovative process monitoring techniques for multi-component polymeric materials with nano-particulate fillers is a necessity for robust manufacturing of these specialty engineered materials. Wideband dielectric sensing has proven to be a valuable tool for extracting a broad range of material properties, simultaneously across a continuum of length scales. In contrast to real and reciprocal space techniques, which are equipment, time and expertise intensive, morphology monitoring based on characteristics that reflect the internal surface area between constituents are amenable to fast, reliable process control schemes. Since, dielectric measurements reflect interfacial polarization, charge carrier density and mobility, morphological attributes relating to the degree of layered silicate dispersion, the state of intercalation/exfoliation, and evolving changes in surface area during thermoset resin cure may be monitored directly. Dielectric and impedance spectroscopy of thermoset systems consisting of organically modified montmorillonite dispersed in an epoxy matrix are considered. Spectra of modified montmorillonite, cured and uncured epoxy resin, and the corresponding nanocomposite are compared to deduce the unique, synergistic characteristics associated with the layered silicate-epoxy interface. Polarization of the mobile surfactant on the silicate surface, such as Maxwell/Wagner/Sillers, influences the complex dielectric function of the nanocomposites and provides a local probe of the interfacial environment. Cure monitoring methods and techniques for evaluating material morphology are investigated and discussed. Adaptation of existing process-monitoring schemes based on dielectric/impedance spectroscopy of macroscopic composite systems may be extended to provide an elegant solution for the process control of thermoset nanocomposites in real-time.

BB3.13

Nanoparticles of Tin(IV) Sulfide Dispersed in Polymeric Hosts. Thomas A. Baker^{2,1}, Brian D. Pate¹ and Edwin L. Thomas¹; ¹Institute for Soldier Nanotechnologies, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Chemistry, Indiana University of Pennsylvania, Indiana, Pennsylvania.

Tin(IV) sulfide possesses a high refractive index with low loss in the visible region, making it an interesting candidate material for photonic applications. Nanoparticles of tin(IV) sulfide have been prepared using a variety of methods, including surfactant templating of molecular precursors. Control of the dimensionality of the nanoparticles will be discussed, as will the effect of aspect ratio on physical properties. In particular, we will highlight the dispersion of these inorganic fillers in polymeric hosts to form multifunctional hybrid materials.

BB3.14

Generation of Polymer / Carbon-Nanotube Composites with Highly Dispersed Single-Walled Carbon Nanotubes. Jong Dae Kim¹, Enrique V. Barrera² and Constantine D. Armeniades¹; ¹Chemical Engineering Department, Rice University, Houston, Texas; ²Mechanical Engineering and Materials Science Department, Rice University, Houston, Texas.

Composites with Single-Walled Carbon Nanotubes (SWNTs), dispersed uniformly in a polymer matrix are generated by atomization and continuous deposition of dilute solutions of the prepolymer components and SWNTs in mutual solvents. Buildup of coherent and solvent-free composites is achieved by simultaneous solvent flashing and polymerization reactions while the solution droplets are in flight. Epoxy resin composites with 1 wt % SWNTs showed a highly uniform dispersion of SWNTs and an increase in electrical conductivity by 5 orders of magnitude.

BB3.15

Spherical Nanoparticle Ordering in Block Copolymer Systems. John M. Papalia and Mary E. Galvin; Materials Science & Engineering, University of Delaware, Newark, Delaware.

In recent years, both self-assembling systems and nanoparticles have been areas of extensive research. The current work investigates the ordering of nanoparticles in block copolymers (BCPs) thus combining the unique properties associated with the individual components into a single composite system. Balazs et al. put forth an expansive set of theories to explain and predict the behaviors of hard nanoparticle inclusions in block copolymer systems. These composites combine the natural drive of the BCPs to self-assemble with the physical and optical properties of the nanoparticles, yielding complex and interesting systems. Our goal is to develop model experimental systems to methodically investigate the theoretical predictions. Silica (≤ 22 nm) and gold (≤ 15 nm) particles have been incorporated into the styrene phase of a polystyrene-*b*-poly(ethylene-co-propylene) diblock copolymer. Parameters such as particle size, BCP molecular weight, surfactant length, and surfactant coverage are varied in a controlled fashion with the corresponding effects on the ordering of the particles studied. Preliminary results indicate the use of surfactant is almost mandatory to provide the particles with the

energetic advantage needed to integrate them into the BCPs. Surfactant modified particles of two different sizes (7nm, 12nm) showed definitive particle ordering within discrete BCP domains. Current systems seek to further investigate these results, as well as the trends in systems with other particle sizes and surfactant lengths. Preliminary contraindications to the theories are also being investigated. The impact of block swelling via homopolymer inclusion on particle location will also be studied. The combination of these result sets, along with experimentation related to domain size, will aid the design of multi-size particle systems potentially suited for improved photonic devices or nano-scale waveguides.

BB3.16

Coarse-grained, Dynamic Simulation of Nanocomposites Composed of Nanoparticles and Homopolymer Blends. Gang He and Anna Balazs; Chemical and Petroleum Engineering Dept., University of Pittsburgh, Pittsburgh, Pennsylvania.

Nanocomposites that involve homopolymer blends and nanoscopic particles combine the ductility and processability of the polymers and the mechanical, electromagnetic and optical properties of the particles. These nanocomposites form the optimal materials for a wide range of industrial applications. Adding the nanoparticles to a blend of incompatible homopolymers has a significant impact on the phase separation dynamics of the system. In particular, the nanoscopic particles can arrest the domain growth of the phase-separating homopolymers. Thus, the particles can be used to control the structural evolution and final morphology of the mixture; this, in turn, permits control over the macroscopic properties of the material. In this study, we develop a dynamic mean field theory to model the time-dependent behavior of the system. Using this model, we investigate how the characteristics of the particles (size, volume fraction and interaction energies) and polymers (length and incompatibility) affect the phase separation process. We show how these results can potentially be utilized to create various multifunctional materials.

BB3.17

Structure and properties of Nylon6/ Montmorillonite nanocomposite fibers. Kadhira Shanmuganathan, Sarang V. Deodhar, Prabir K. Patra, Qinguo Fan, Yong K. Kim and Steven B. Warner; Textile Sciences, University Of Massachusetts, Dartmouth, North Dartmouth, Massachusetts.

The flame retardancy of Nylon6/montmorillonite nanocomposites has been widely investigated over the years. However, much of the work has been confined to the synthesis and characterization of nanocomposite films with less investigation on nanocomposite fibers. The morphology and dispersion of the fillers is a critical factor in determining the properties of the nanocomposites and hence the behavior of the nanocomposite fibers will be different depending on the extrusion conditions. Our goal is to investigate the rheological behavior of nanocomposites in the fiber formation process and the influence of extrusion and drawing on the morphology and dispersion of fillers in the fibers. Further we will investigate the effect of these conditions on the thermal stability and flame retardant behavior of nanocomposite fibers. In this study we synthesized Nylon6/ montmorillonite (modified with dihydrogenated tallow ammonium) nanocomposite by twin screw melt mixer followed by extrusion of fibers in a Brabender single screw extruder. Differential Scanning Calorimetry studies indicate that the peak crystallization temperature of nanocomposites has increased by $8-10^{\circ}$ C. The % crystallinity has not increased significantly. Thermal gravimetric analysis results show no significant improvement in thermal stability of nanocomposites over neat nylon 6. Comparative investigation of the morphology and dispersion of fillers in the nanocomposite films and the nanocomposite fibers with Wide angle X ray diffraction and Transmission Electron Microscopy and Cone calorimeter investigations on flame retardancy is in progress.

BB3.18

Polypropylene/silica nanocomposite fibers. Sarang Vishnu Deodhar, Kadhira Shanmuganathan, Sandeep Razdan, Qinguo Fan, Prabir Patra, Yong Kim and Steven Warner; Textile sciences, UMass Dartmouth, north dartmouth, Massachusetts.

Inorganic particles with nano scale dimensions have recently emerged as alternative flame-retardants for polymers. Silica in its various forms e.g. fumed silica, silica gel, has proved as a potential flame retardant additive for polypropylene. Earlier, research groups worked on char formation of PP/silica composites, with less stress on fiber formation and resultant thermal and morphological properties of the composite fibers. Our work involves preparation of i-polypropylene and maleic anhydride grafted polypropylene / nano fumed silica composite fibers with 5 wt % and 10 wt % loading of filler. Solution and melt mixing methods were used to prepare the composites before extruding fibers from them. These techniques were expected to give good dispersion of

nano particles in the polymer matrix. Thermogravimetric analysis of the nanocomposites showed an increase in thermal stability of polypropylene. There was almost a 30 °C rise in decomposition temperature at 10% mass loss. For maleic anhydride grafted polypropylene composites there was 5% increase in the amount of char formed. Nanocomposites fibers were prepared using Brabender single screw extruder. The effect of fumed silica on the thermal properties and morphology of the nanocomposite fibers is being investigated using Differential Scanning Calorimeter, Thermogravimetric Analyzer, X-ray Diffraction and Transmission Electron Microscopy. Flammability characterization of the synthesized fibers will be investigated via Cone calorimetry. Due to enhanced interaction between grafted polypropylene and silica, we expect to see an enhancement in thermal and flame retardant properties of the synthesized composite fibers.

SESSION BB4: Polymer Nanocomposites: Carbon Nanotubes and Clays

Chairs: Andrew Burgess and Wesley Burghardt
Tuesday Morning, November 30, 2004
Room 309 (Hynes)

8:30 AM **BB4.1**

Mobile Nanoparticles Retard Phase Separation in Polymer Blend Films. Russell J. Composto, Hyun-joong Chung and Jena D. Deng; Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania.

In materials science, the combination of dissimilar, yet complementary components are used to create materials with unique properties. Despite their utility, the impact of nanoparticles (NP) on phase behavior of polymer blends has not been systematically investigated. We have studied phase separation dynamics in polymer blend films containing mobile NP (0, 2, and 5wt%). Films (650nm) of PMMA:SAN (50:50) containing methyl-terminated silica NP (22nm) were chosen as a model system. Initially, the particles are homogeneously dispersed, as confirmed by TEM and RBS. Upon annealing, films with NP undergo three-stages of morphology development (early, intermediate, and late), similar to the pure polymer blends (See eg. Wang & Composto, JCP (2000)). A partitioning of the NP into PMMA-rich phase is also confirmed by TEM, RBS, and AFM. During the intermediate stage, the in-plane PMMA-rich domains grow via coalescence and follow a correlation length ξ that scales as $\xi \propto (\sigma/\eta)^{1/3}d^{2/3}t^{1/3}$, where σ is the PMMA:SAN interfacial energy and η is the viscosity of PMMA (Chung & Composto, PRL (2004)). Because NP partition into the PMMA phase rather than decorate the interface, σ is taken as constant. Rather, the slowing down of phase separation is attributed to an increase in the effective viscosity of the PMMA phase, which increases with NP loading. This model is supported by rheology measurement of bulk PMMA/SAN/NP. Here, the NP are mixed with PMMA ($M_v = 100,000$ [Da], $PDI = 3$) from co-solvent using a coagulation method (Du et al., J. Polym. Sci. Pol. Phys. (2003)). The addition of NP increases the effective PMMA viscosity, especially at lower shear-rates. For example, 10wt% of NP increases the zero-shear viscosity by a factor of ca. 10 with respect to the pure PMMA. This measurement is in agreement with the phase separation coalescence model, which predicts a viscosity increase of 12.6 for 5wt% NP in the PMMA/SAN film (or 10wt% in PMMA after complete partitioning). In conclusion, low concentration of mobile, preferentially wetting NP in polymer blend films retards phase separation by the effective viscosity of the partitioning component.

8:45 AM **BB4.2**

HREM Imaging of Layered-Silicate/Epoxy Nanocomposites. Lawrence F. Drummy¹, Hilmar Koerner², Ashley Tan¹, Karen Farmer¹, Barry L. Farmer¹ and Richard A. Vaia¹; ¹Materials and Manufacturing Directorate, Air Force Research Labs, Wright Patterson AFB, Ohio; ²University of Dayton Research Institute, Dayton, Ohio.

While transmission electron microscopy has been used extensively in the past to examine the microstructure of polymer/layered silicate nanocomposite materials, several experimental difficulties have limited the usefulness of the technique. These difficulties include the relation of a two-dimensional image projection to the three-dimensional sample structure, as well as imaging large sample areas while maintaining high resolution. Montmorillonite (MMT)/epoxy nanocomposites are studied here with the goal of improving understanding of microstructure and how it relates to properties. Using High Resolution Electron Microscopy (HREM), the local variations in order present in intercalated and exfoliated nanocomposites at the molecular/atomic length scale were directly imaged. Using relatively low magnifications, it was possible to image several square microns of material while maintaining sub-nanometer

spatial resolution. This data allowed for quantification of macroscopic orientation of the MMT sheets over large areas of sample, for comparison with orientation information generated by x-ray scattering techniques. The data is also sufficient for measurement of various length scale dependent order parameters, from the analysis of bulk scale aggregation of clay tactoids to atomic-level structural defects in the MMT sheets. The 0.45 nm hexagonal lattice spacings in the MMT [001] crystallographic zone were directly imaged in the bare MMT, MMT intercalated with surfactant, and MMT dispersed in an epoxy matrix. Multi-slice calculations of HREM image contrast gave insight into the experimental range of focus needed to successfully image both the inter-sheet and intra-sheet MMT lattice spacings. The intra-sheet MMT spacings were found to be sensitive to electron beam exposure, with measurable damage beginning to occur at an electron dose of approximately 20 C/cm². Imaging of the sheets oriented both perpendicular and parallel to electron beam allowed for significant information about the 3D structure of the nanocomposites to be extracted from the experimental images.

9:00 AM **BB4.3**

Understanding the Role of Intermolecular Interactions in the Dispersion of Polymer Nanocomposites. Mark D. Dadmun and Deepali Kumar; Chemistry, University of Tennessee, Knoxville, Tennessee.

The addition of a small amount of layered silicate to a polymer matrix can result in a non-linear improvement in properties such as gas permeability and impact strength. However, the optimum improvement in properties is only realized if the layered silicate is uniformly dispersed in the polymer matrix, i.e. exfoliated. Unfortunately, most polymers do not readily exfoliate these clays, and thus most polymer-clay nanocomposites do not exhibit dramatic property improvements. In this talk, results of a study that correlates the extent of hydrogen bonding between a polymer matrix and layered silicates to the extent of dispersion that is found in the polymer nanocomposites will be presented. The extent of hydrogen bonding is controlled by mixing various layered silicates with poly(styrene-*r*-vinyl phenol) with varying amounts of vinyl phenol. The hydrogen bonding is quantified using infrared spectroscopy, while the extent of silicate dispersion is monitored by small angle x-ray scattering and transmission electron microscopy. Thermal properties of the resultant nanocomposites are also measured. Initial results show that for 5% clay loadings, the copolymer with 40% vinyl phenol most effectively exfoliates the layered silicate, which agrees with recent work in our group that suggests this amount (and spacing) of hydroxyl group in the styrenic copolymer will result in an optimum amount of intermolecular hydrogen bonding. Moreover, the glass transition temperature of these exfoliated nanocomposites were significantly higher than those of similar, but more poorly mixed nanocomposites.

9:15 AM **BB4.4**

Influence of the Particle Morphology on the Micro-and Macromechanics of Nano-Reinforced Materials.

Hartmut Rudolf Fischer^{1,3}, Alexander Sarkisov^{2,3} and Han E.H. Meijer^{2,3}; ¹Innovative Materials, TNO TPD, Eindhoven, Netherlands; ²Mechanical Engineering, TU Eindhoven, Eindhoven, Netherlands; ³Engineering Plastics, Dutch Polymer Institute, Eindhoven, Netherlands.

Nanocomposites composed from polymer matrix materials and nanoscopically dispersed inorganic particles have gained a considerable attraction due to the possibility to design materials with new and/or improved properties. Many studies report an increase of the elastic modulus as well as an enhancement of other properties. The objective of this contribution is to discuss experimentally results concerning the mechanical behavior of polymer material reinforced homogeneously on a nano-level. Generally, the properties of composite materials depend strongly on the interaction between the reinforcing elements and the matrix, the intrinsic properties and on their aspect ratio and on the perfection of the constituents and morphological characteristics of the composite. It is well recognized that addition of a small weight percent of clay particles can have a pronounced effect on mechanical properties, crystallization behaviour and morphology of the polymer matrix. This is a result of the nano-scale dimensions, the huge surface area and aspect ratios, and the shape and morphology of the clay minerals. In this study, nanocomposites based on semi-crystalline matrices have been prepared. Two different types of clay were used: layered platelet shaped silicates and fibrous clay minerals. The platelet clay used (Montmorillonite) has a thickness of 1 nm and lateral dimensions of 400 nm, while the fibrous clay (Sepiolite) has a shape of a tube with diameter of 30 nm and length of 600 nm. HDPE was used as a matrix material. The nanocomposite materials were prepared by extrusion melt mixing using PE-g-MA as a coupling agent. The mechanical characterisation of these nanocomposite materials is linked to an identification of their morphology on different length scales, starting at the level of polymer crystals up to few hundreds microns, and to

follow its evolution during tensile deformation in attempt to relate the microscopic deformation processes to the macroscopic response of the material. The main techniques used are X-ray diffraction and ESEM combined with a tensile testing apparatus that makes possible to perform in-situ experiments during deformation and thus to identify the changes in morphology at the different regions of the tensile curve. The results obtained so far indicate that both types of clay act as a nucleation agent at the initial stage of crystallization but at later stage the crystallization is delayed in the case of platelets while no such effect is observed for the materials filled with fibrous clay. This suggests that a difference in the size crystallites, number of tie molecules and trapped entanglements. Theoretical work is underway to specify the dependency of the principle fracture behaviour on to different particle shapes with a focus on the identification of local stress concentrations and energy dissipation.

9:30 AM **BB4.5**

Nonlinear Viscoelastic Behavior of Polymeric Nanocomposites: The Role of Nanoparticle Structure, Shape, and Surface Chemistry. Meisha L. Shofner, Rahmi Ozisik, Linda S. Schadler and Sanford S. Sternstein; Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Previous work by this laboratory has demonstrated unequivocally the individual characteristics of storage modulus and loss modulus are directly related to filler surface-polymer interfacial interactions in nanocomposites. The properties of polymeric nanocomposites are significantly affected by the interfacial region due in part to the excess surface area of the filler and the degree of compatibility between the filler surface and the matrix. Control of the interface has been used to tailor multifunctional properties such as electrical resistivity, thermal transitions, and mechanical properties. However, many properties are not well understood, for example, the decidedly nonlinear viscoelastic behavior above the glass transition temperature. In this research, issues of nanoparticle structure, shape and surface chemistry are examined to further elucidate rheological phenomena in nanoscale silica/poly(vinyl acetate) composites. The effect of nanoparticle structure on nonlinear viscoelastic properties above the glass transition temperature is examined by comparing the behavior of fumed and colloidal silica nanoparticle fillers. Composites prepared with equiaxed and anisotropic particles are compared to examine reinforcement mechanisms as a function of surface area and aspect ratio. Nanoparticle composites having different filler surface treatments are compared to those made with untreated particles as well as a nanoscale fluoropolymer particle composite. Special attention is directed to the nonlinear behavior of these composites as manifested in the shape of the loss factor and reinforcement curves with strain amplitude, temperature and frequency. The glass transition region is also explored in the same composite systems using a combination of dynamic mechanical analysis and differential scanning calorimetry. Master curves and superposed loss moduli are used to investigate the issue of relaxation time distribution in the nanofilled polymers. Interfacial interactions and filler agglomeration are further explored using infrared spectroscopy and electron microscopy, respectively.

9:45 AM **BB4.6**

Nanoparticle Surface Segregation in Polymer Thin Films. Amalie L. Frischknecht¹, R. S. Krishnan², M. A. Holmes² and M. E. Mackay²; ¹Sandia National Laboratories, Albuquerque, New Mexico; ²Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, Michigan.

Recently it has been shown that nanoparticles can suppress dewetting in thin polymer films, a counterintuitive result since particles usually induce dewetting. The mechanism for this dewetting suppression is not yet known. Because of the small size of the nanoparticles, the interactions are qualitatively different than the well-understood interactions between colloidal particles and polymers. One proposed mechanism for the inhibition of dewetting is that the nanoparticles segregate to the substrate surface where they confine the polymers and change the surface energies and thus the spreading coefficient. We explore this segregation by calculating the density profiles for dilute nanoparticles in polymer melts near a substrate using classical density functional theory (DFT). The DFT requires as input bulk liquid state information, which we obtain from the polymer reference interaction site model (PRISM) theory. The polymers are modeled as freely-jointed chains of spherical interaction sites and the nanoparticles as simple spheres. The use of PRISM with DFT allows the inclusion of local packing effects due to the finite size of the monomers, which should be important in the presence of the nanoparticles since the nanoparticles are significantly smaller than the linear polymer. The DFT shows that the particles do segregate to the surface. We investigate the effect of interactions, concentration, and nanoparticle size on the density profiles and surface free energies. We also calculate the expected neutron reflectivity from the theoretical density profiles in order to compare with experiments on polystyrene nanoparticles in polystyrene thin films. Sandia is a multiprogram

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.

10:30 AM **BB4.7**

NMR Characterization of Polymer Interfaces in Clay Nanocomposites. Peter A. Mirau, Jennifer Garber and Rich Vaia; Polymer, Air Force Research Labs, Wright-Patterson AFB, Ohio.

High-resolution solid-state ¹³C, ³¹P and ¹H NMR has been used to study the interface in synthetic clay nanocomposites. NMR-active nuclei were introduced into the interface in Laponite and Fluoromica composites using hexadecyltributyl phosphonium and dodecyltriphenyl phosphonium surfactants. The synthetic clays have a low iron content and the NMR signals at the organic/inorganic interface can be easily observed. The ³¹P signals have a good sensitivity and can be used to monitor the dynamics over a wide range of time scales (nanoseconds to seconds) by using a variety of relaxation rate measurements and the line shapes measured by 2D NMR. The solid-state ³¹P and ¹³C relaxation rates show that the dynamics depend strongly on the chemical structure of the surfactant, and that large differences in the proton lineshapes are observed using 2D wideline correlation spectroscopy. Molecular motions on a kHz time scale lead to narrowing of the proton lineshapes for the tributyl but not the triphenyl composites. Two dimensional spin exchange experiments of the phosphorus chemical shifts in static samples can be used to probe the dynamics on a much longer time (milliseconds to seconds) scale. The results show that the triphenyl surfactants remain relatively rigid on the time scale of one second. The results and implications for polymer nanocomposites will also be presented.

10:45 AM **BB4.8**

Infiltration: A Fabrication Method for Single-Walled Carbon Nanotube/Epoxy Nanocomposites. Fangming Du¹, Csaba Guthy², John E. Fischer² and Karen I. Winey²; ¹Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; ²Material Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania.

Due to their superior properties, single-walled carbon nanotubes (SWNTs) have been proposed as fillers for multifunctional nanocomposites. Although extremely low thresholds (0.01 wt%) for electrical conductivity percolation have been reported for nanotube polymer nanocomposites, the improvement in thermal conductivity is relatively moderate (2 times) even with high nanotube loading (10 wt%). High interfacial thermal resistance between the nanotubes and polymer chains or among the nanotube themselves limits the improvement in the thermal conductivity of the nanocomposites. We use infiltration to produce SWNT/epoxy nanocomposites with intimate tube-tube contacts. Results show that the 2 wt% nanocomposite has a thermal conductivity of 1.6 W/m-K, more than 7 times higher than that of the pure epoxy, 0.22 W/m-K. The morphologies of the nanocomposites and the nanotube framework inside them will be studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to understand the relationship between the morphology and the thermal conductivity of the materials.

11:00 AM **BB4.9**

Enhanced Properties of Single-Walled Carbon Nanotube-Poly(styrene-co-vinylphenol) Nanocomposite by Hydrogen Bonding. Asif Rasheed¹, Mark D. Dadmun¹, Phillip F. Britt² and David B. Geoghegan³; ¹Department of Chemistry, University of Tennessee, Knoxville, Tennessee; ²Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ³Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Carbon nanotubes are known for their excellent mechanical and electrical properties. Dispersing nanotubes in a polymer matrix provides an effective way to exploit their extraordinary properties. However nanotube dispersion in a polymer matrix is very difficult due to strong inter-tube interaction. We will present results that demonstrate that optimal favorable interactions between the nanotubes and polymer can improve mechanical properties of the resulting nanocomposite. Specifically, single walled-carbon nanotubes (SWNT) are oxidized to provide carboxylic acid groups on the tube that are capable of forming hydrogen bonds with a copolymer of styrene and vinyl phenol (PSVPh). Previous work in our lab has shown that controlling the amount of vinyl phenol in the copolymer provides a mechanism to optimize the intermolecular interactions between components. This protocol is applied to the polymer/nanotubes composites. Composites are characterized using dynamic mechanical measurements for mechanical properties, thermogravimetric analysis and differential scanning calorimetry for thermal properties. The interaction between polymer and nanotube

are studied by Raman spectroscopy.

11:15 AM **BB4.10**

Raman Study on Electronic Property of Single-walled Carbon Nanotubes Composite. Bin Chen, NASA Ames Research Center, Moffett Field, California.

The chromophoric Raman scattering signal of C-C bonds in both carbon nanotubes and polymers, combining with the characteristic response for semiconducting or metallic single wall carbon nanotubes (SWNTs), enables the Raman spectroscopy an ideal technique to study variety of composites. This technique probes the electronic density of states (DOS) of SWNTs and related vibration symmetries in the composites simultaneously, providing a direct correlation of the electronic property with its microscopic structures. In the first part of the talk, we will focus on the results of electronic properties of SWNTs dispersed in a polymer matrix of polymethyl methacrylate (PMMA). Two different procedures were used to prepare the composites: by melt blending and by in-situ UV polymerization. We demonstrated the anisotropic interaction between SWNTs and PMMA caused significant changes in its electronic property in a composite. In the melt-blended sample, the SWNTs ? originally semiconducting ? become predominantly metallic. In contrast, the DOS of the UV polymerized composite remain unchanged as that of the pristine SWNTs. Raman studies relate the vibration symmetry changes in PMMA backbone, SWNT sidewall and radial breathing modes with the corresponding changes in the electronic DOS of the SWNTs. This electronic property changes are also confirmed by dielectric constant measurements of the composites. In the second part of the talk, we will briefly discuss the Raman results of the structure as well as the electronic properties of several other carbon nanotube composites. High throughput Raman analysis is very powerful to monitor the composite film homogeneity, charge-carrier type and polymer chain conjugation in the composite.

11:30 AM **BB4.11**

Thermal Conductivity in Semicrystalline Polyethylene - Single Walled Carbon Nanotube Composites.

Reto Haggenueller¹, Csaba Guthy¹, Jesse J. Cugliotta², Jennifer R.

Lukes², John E. Fischer¹ and Karen I. Winey¹; ¹Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; ²Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, Pennsylvania.

Nanocomposites with single walled carbon nanotubes (SWNTs) are being investigated to take advantage of the superior properties of SWNTs. While notable successes have been reported for the electrical properties, particularly low percolation thresholds, the remarkable thermal conductivity of SWNTs is proving more difficult to impart to a nanocomposite. To date, attempts to raise the thermal conductivity in SWNT-amorphous polymer composites have been only marginally successful. In this work, we use semi-crystalline polymers, namely polyethylenes (PE), as the composite matrices, because the crystallinity of PE might create an interface favorable for phonon transfer and support phonon conduction throughout the nanocomposite. Preliminary results show an increase of 300% in thermal conductivity for a 10 wt% SWNT/PE composite. This work explores the effects of the percent crystallinity by using different grades of PE, the orientation of PE crystallites, and the orientation of SWNT relative to the PE crystallites. Melt fiber spinning of the composites is used to align both the SWNT and PE crystallites. Characterization methods include the comparative method and modulated thermorefectance to measure thermal conductivity, x-ray scattering to quantify SWNT and PE alignment, and Raman spectroscopy, SEM and AFM to determine SWNT dispersion.

11:45 AM **BB4.12**

Structure and Properties of Polycarbonate / Carbon Nanotube Fibers. Timothy D. Fornes^{1,2}, Yizhak Sabba^{1,2}, Jeffrey

W. Baur¹ and Edwin L. Thomas^{1,2}; ¹Institute for Soldier Nanotechnologies, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Two important steps in fully utilizing the mechanical benefits of carbon nanotubes (CNTs) is obtaining a good dispersion of the filler within the polymer matrix and invoking high degrees of alignment of the nanotubes with respect to the applied load. By using a combination of solution blending and melt processing techniques we have fabricated polycarbonate fibers containing well dispersed and highly aligned single (SWNT) and multiwall (MWNT) nanotubes. Morphological investigations using transmission electron microscopy, Raman spectroscopy, and X-ray diffraction indicate aligned nanotubes parallel to the fiber axis, while mechanical property investigations demonstrate exceptional reinforcement at very low filler loadings. Discussion is made on morphological and property differences between the various SWNT and MWNT nanocomposites.

SESSION BB5: Polymer Nanocomposites:
Morphologies, Processing, and Thermodynamics
Chair: Cora Leibig
Tuesday Afternoon, November 30, 2004
Room 309 (Hynes)

1:30 PM ***BB5.1**

Probing Self-Organization of Single Conjugated Polymer Chains and Polymer-Blend Nanoparticles Under 3-D

Confinement. Michael D. Barnes¹, Pradeep Kumar², Adosh Mehta², Bobby Sumpter² and Mark Dadmun²; ¹Department of Chemistry, University of Massachusetts, Amherst, Massachusetts; ²Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Semiconducting polymers are widely used in so-called "plastic opto-electronic" devices and luminescent display technologies. However, a number of issues related to poor control over inter- and intra-chain organization of these materials in conventional thin-films limit many aspects of device performance. This problem is especially critical at smaller length scales where conjugated polymers are envisioned to play an important role in the emerging field of nanoscale optoelectronics. Recent work in our laboratory has explored the effects of 3-dimensional confinement on the self-organization of single chains of conjugated polymers used commonly in polymer LEDs. Isolated in tiny droplets of dilute polymer solution and allowed to dry en route to a glass substrate, these nanoscale species (roughly the size of a biological protein) adopt structural, spectroscopic, and photophysical properties that are markedly different than those of their (well-studied) thin-film counterparts. In this talk, we describe recent work probing the self-organization and orientation mechanism of these interesting species and the effect of forming nanoscale blends of single molecules of conducting polymers with other (non-luminescent) co-dissolved polymers or oligomers.

2:00 PM ***BB5.2**

Structure and Thermodynamics of Nanofilled Polymers.

Sanat Kumar, Amitabh Bansal and Linda Scadler; RPI, Troy, New York.

We unequivocally show that the physics of polymers filled with nanoparticles are quantitatively equivalent to the well studied behavior of thin polymer films confined between two parallel impenetrable flat walls. To provide the underpinnings for this unifying picture we have measured the glass transition temperature of polystyrene (PS) when it is blended with 15 nm diameter SiO₂ particles over a range of silica loadings. The T_g of the polymer is found to decrease with increases in silica loading, qualitatively consistent with decreases found with decreasing thickness of polymer films sandwiched between planar silica walls. This analogy is quantified using electron micrograph images of the nanocomposites which yield an appropriate average ligament thickness, the nanocomposite analog for the wall-to-wall distance in thin films. In combination with recent results on polymer blend phase transitions, where both filled systems and thin films provide similar results, we conclude that the proposed analogy between nanofilled polymers and thin polymer films helps to provide a unified quantitative understanding of these two apparently disparate physical situations.

2:30 PM ***BB5.3**

X-ray Studies of Orientation in Polymer/Clay Nano-

composites Under Shear Flow. Wesley Burghardt and Laura Dykes; Chemical and Biological Engineering, Northwestern University, Evanston, Illinois.

Nanometer-scale dispersal of inorganic clay sheets in a polymer matrix has been found to lead to enhancements in many properties, such as stiffness, heat resistance and barrier properties. As in any composite material, it is expected that the properties of interest will depend on the orientation distribution of the dispersed phase, which in turn will be affected by flow fields during processing. At a more basic level, some basic understanding of nanocomposite rheology will be necessary to rationally design operations to process these materials. As in most complex polymer fluids, the rheology of nanocomposite samples is strongly affected by flow-induced changes in fluid structure. While many rheological phenomena have been interpreted in terms of flow-induced particle orientation, there are relatively few in situ studies of particle orientation in nanocomposite materials during flow. For this reason, we have initiated research using in situ synchrotron x-ray scattering to probe the structural response of polymer nanocomposites in shear flow. Two types of samples have been studied. The first are model dispersions of organically modified clay in a low molecular weight, low viscosity PDMS melt, which may be conveniently studied at room temperature. These materials are intercalated so that the layered clay structure,

though swollen with polymer, remains intact. We have studied these materials in an annular cone & plate x-ray shear cell which provides access to the flow-gradient plane in reciprocal space. Two-dimensional x-ray diffraction patterns allow determination of the degree and direction of average particle orientation relative to the flow direction, while high flux synchrotron radiation allows for time-dependent studies of the orientation dynamics in transient shear flows. The orientation behavior is interpreted in the context of hydrodynamic models for plate-like particles under flow. Studies have also been conducted on polypropylene-based materials. Dispersions of organically modified montmorillonite lead to an intercalated structure when prepared via melt blending, but exhibit higher levels of exfoliation when processed using a solid-state pulverization technique. The intercalated melt-blended sample shows orientation behavior in shear flow that somewhat resembles that observed in the 'model' intercalated PDMS materials. Conversely, the more highly exfoliated PP/clay sample shows lower degrees of particle orientation in shear. In addition to studies in homogeneous shear, the polypropylene samples have also been studied in pressure-driven channel flows. These experiments reinforce the hypothesis that shear flow studies in the flow-gradient plane are most informative, due to tendency of plate-like particles to 'lie down' in shear flow.

3:30 PM *BB5.4

Hierarchically Ordered Block Copolymer-Nanoparticle Composites. Edwin L. Thomas, Materials Science and Engineering, MIT, Cambridge, Massachusetts.

Polymer systems containing nanoscale fillers have recently attracted much attention and seen a flurry of research activity. The unique characteristics of these fillers when married with a polymer matrix yield materials with novel mechanical, optical, barrier, thermal, or electronic properties, not associated with the pure material. In the past, much of the effort has been directed at homopolymers, but the distinct features of block copolymers provide fertile ground for exceptional new materials. The incorporation of nanoparticles in a block copolymer matrix allows for an unprecedented level of control over the morphology of the material due to the self assembly of the polymer into ordered domains. The aim is to achieve multifunctional materials by inclusion of the nanoparticles to augment the properties of the block copolymers beyond those available with the neat polymer on its own. The block copolymer is used as a template to sequester the particles in a particular region of the matrix as well as to orient them in accordance with the desired application. The detailed behavior of the particles depends on many factors such as particle size, surface chemistry, size of the corona region, interaction (?) with the polymer host, and size of the surface ligands with respect to the size of the block copolymer domains. The chemistry of the block copolymers themselves can also be varied to include domains with diverse properties (glassy, rubbery, crystalline, liquid crystalline) and a range of processing methods can be used to influence the morphology of the composites. Furthermore, the properties of the composite materials could be tuned by exposure to external fields (stress, electric, magnetic). With such a broad parameter space, understanding and optimizing the properties of these nanoscale composites presents an interesting challenge. Selected examples of recent research will be used to emphasize some of the many aspects outlined above and highlight the rich and myriad possibilities available to the polymer scientist to make tailored and functional materials.

4:00 PM *BB5.5

A Study of Compatibility in Organoclay Nanocomposites. Andrew N. Burgess, Darwin Kint, Fouad Salhi, Gordon Seeley and Steve Rogers; Strategic Technology Group, ICI, Redcar, United Kingdom.

In order to produce organoclay composites that exhibit high degrees of intercalation or exfoliation, it is imperative that good thermodynamic compatibility is achieved between the organic modification on the clay and the host matrix material. We have established simple procedures for assessing compatibility and have made a systematic study of a range of solvent and monomer systems with the commercially available organically modified clays. We will describe the various compatibility results obtained with reference to the properties of the composites produced and an assessment of some theoretical approaches to understanding compatibility in these systems.

4:30 PM *BB5.6

Dispersion of Single Wall Carbon Nanotube in Poly (ε-caprolactone). Cynthia A. Mitchell and Ramanan Krishnamoorti; Department of Chemical Engineering, University of Texas, Houston, Texas.

Development of single walled carbon nanotube (SWNT) based polymer nanocomposites is attractive because of the combining of the extraordinary properties of SWNTs with the lightweight character of polymers. Optimizing such nanocomposites requires homogeneity of

dispersion, good interfacial compatibility and exfoliation of the nanotubes. Here we demonstrate the development of dispersed SWNT nanocomposites with poly(ε-caprolactone) (PCL) using a zwitterionic surfactant as a compatibilizer. Nanocomposite structure was characterized using spectroscopy, microscopy, X-ray scattering, calorimetry, melt rheology and electrical conductivity. A nanoparticle network structure with a hydrodynamic percolation at a volume fraction of SWNT of 0.0005 suggests efficient dispersion of the SWNTs and an effective anisotropy of > 1000 for the nanotubes. This result is further corroborated by an electrical percolation threshold of 0.0006 volume fraction of SWNT. The SWNTs were found to be strong nucleators for polymer crystallization with the effect of the nanoparticles on crystallization saturating at volume fractions of 0.0005 with a pronounced decrease in crystalline grain sizes. This talk will focus on the characterization of the dispersion, the interactions between the polymer, surfactant and nanotube, crystallization process and the crystalline morphology.

MRS TURNBULL LECTURER AWARD TALK PRESENTATION

5:00 PM *BB5.7

Network Phases in Block Copolymer Melts. Frank S. Bates, Chemical Engineering and Materials Science Department, University of Minnesota, Minneapolis, Minnesota.

Linear block copolymers containing two block types, including AB diblocks and ABA triblocks self-assemble into four equilibrium morphologies, including the triply periodic and triply continuous double gyroid. Increasing the number of chemically distinct blocks expands this portfolio of ordered structures - at least two-dozen morphologies have been documented in linear ABC triblock copolymers. This lecture will outline a strategy that led to the discovery of three triply periodic and multiply continuous network phases in poly(isoprene-*b*-styrene-*b*-ethylene oxide) (ISO) triblock copolymers. Two cubic phases (Q^{230} and Q^{214}) and an orthorhombic phase (O^{70}) were identified using a combination of experimental and modeling techniques, including small-angle x-ray scattering, transmission electron microscopy, birefringence measurements, and dynamic mechanical spectroscopy. Lattice symmetry, identified by powder and single crystal SAXS, was modeled using a level set method, which provided real space structures that were projected into two dimensional images for comparison with TEM. Birefringence experiments discriminated between isotropic (cubic and disordered) and anisotropic (orthorhombic) states. These results revealed a channel of contiguous network phases over a wide range of compositions, nested between those associated with two- and three-domain lamellae. All three network structures belong to the (10,3) class of uniform nets, where a closed loop of ten nodes with three-fold connectivity forms the basic structural unit. Q^{230} , a pentacontinuous core-shell version of the familiar double gyroid, and Q^{214} , a triply continuous, single gyroid both conform to the (10,3) net topology. The O^{70} phase contains a single (10,3)c net, the first non-cubic network phase identified in self-assembling soft materials. Reversible phase transitions have been documented between Q^{214} and O^{70} , indicative of equilibrium behavior. These findings establish a concrete strategy for locating potentially valuable network morphologies in ABC triblock copolymer melts. * Research collaborators: Thomas H. Epps, III, Eric W. Cochran, Travis S. Bailey, Ryan S. Waletzko, Cordell M Hardy.

SESSION BB6: Associating Polymers: Solutions, Gels and Membranes
Chair: Karen I. Winey
Wednesday Morning, December 1, 2004
Room 309 (Hynes)

8:30 AM *BB6.1

Equilibrium Polymerization in the Stockmayer Fluid as a Model of Self-Organization. Jack F. Douglas¹, Kevin Van Workum¹, Jacek Dudowicz² and Karl F. Freed²; ¹Polymers Division, NIST, Gaithersburg, Maryland; ²The James Franck Institute, University of Chicago, Chicago, Maryland.

A diverse range of molecular self-organization processes arise from a competition between directional intermolecular interactions and isotropic van der Waals interactions. The objects that form through this interaction interplay often have a highly specific structure, while maintaining a dynamic nature in which monomeric elements enter and leave at dynamic equilibrium. The geometry of the aggregates can be network-like, string-like, or globular [as found in thermoreversible gels, linear 'equilibrium' polymers, and spherical micelles, respectively], depending on the geometrical form of the molecules, the symmetry and the range of inter-particle interactions. The extent of

clustering varies with the initial concentration of associating particles, temperature, ion or polymer additive concentration or other control parameters that alter the strength and nature of the interactions responsible for the dynamic clustering. There are evidently a large number of physical systems in materials science and biology exhibiting this phenomenon and we seek to understand organizing principles through the intensive study of specific models using a combination of analytic modeling and simulation. We focus on the Stockmayer fluid (SF) since it is one of the simplest molecular fluid models involving a combination of both directional (dipolar) and isotropic van der Waals interactions. First, we calculate the polymerization transition curves for the SF from MC simulation of the maximum in the specific heat and the inflection point of the extent of polymerization. Good agreement with the analytic model of equilibrium polymerization is found where the enthalpy of association is fixed by the minimum of the intermolecular potential between two SF particles in a head-to-tail configuration. The second virial coefficient and the Boyle (or theta) temperature are determined exactly for the SF model over a wide range of dimensionless dipolar energy and these results are used to test the accuracy of the MC simulations. This again leads to excellent agreement between simulation and previously developed analytic theory. However, the scaling of the average degree of polymerization L with temperature and concentration exhibits deviations from simple unrestricted equilibrium polymerization of linear chains, the concentration and temperature dependence instead behaving like a polymerization model subject to strong kinetic constraints, as found in living polymerization with a low initiator concentration and activated equilibrium polymerization with a small activation rate constant. These discrepancies are traced to a topological transition between linear chains and ring polymers upon cooling that was not originally anticipated in the analytic modeling of polymerization in the SF.

9:00 AM *BB6.2

Electrophoretic Dynamics of Polyelectrolytes in Polymer Solutions and Gels. Lynden A. Archer, Daniel M. Heuer and Sourav Saha; School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York.

We have developed a procedure for synthesizing large stable star-branched DNA structures that enables visualization via fluorescence microscopy. Using this procedure we have synthesized DNA stars with variable numbers of arms and arm lengths and observed their electrophoretic behavior in model polymer solutions and gels. In dilute polymer solutions, both star-branched and linear DNA drift in their native random coil configurations and the electrophoretic mobility is set primarily by the bulk (Zimm) viscosities of the polymer solution. At solution concentrations above the overlap threshold, c^* , electrophoretic dynamics of linear and star-branched DNA manifest profound differences. Star arms extend in the direction of the field and drag the core through the matrix during electrophoresis, while linear DNA migrates in either a U-shaped or I-shaped configuration depending on the field strength and solution concentration. Despite these differences, the electrophoretic mobility at fixed electric field and polymer concentration is nearly identical for equal-sized linear and branched molecules. We show that both observations are a result of non-Newtonian flow of polymer in the electric double layer around charged DNA segments, and that the local flow environment near the charged DNA segments controls mobility. In entangled polymer solutions and gels, star-branched DNA is retarded much more than linear molecules due to coupled dragging of the surrounding polymer chains for stars and the possibility of reptile motion of linear DNA.

9:30 AM *BB6.3

Phase Behavior of Polyelectrolyte Solutions.

Murugappan Muthukumar, University of Massachusetts, Amherst, Massachusetts.

Results of a recently developed theory of phase behavior of polyelectrolyte solutions will be presented. The theory [M. Muthukumar, *Macromolecules*, 35, 9142, 2002] bridges the Flory-Huggins theory for solutions of uncharged polymers and the Restricted Primitive Model of unpolymers strong electrolytes. For binary solutions of the salt-free polyelectrolyte solutions, the critical point, coexistence curve, and spinodal curve (corresponding to an upper critical solution behavior) have been calculated. The presence of added salt is dealt with by computing ternary phase diagrams, with novel results unexpected from the quasi-two-component approximation. First, the critical temperatures for the salt-free solution and polymer-free salty solution are depressed by the third component until the approach of a bicritical point. For temperatures above the bicritical point, it is possible to solubilize the precipitate by adding the third component. For temperatures below the bicritical point, the precipitate phase is always stable. These results and effects of valencies and sizes of various ions [B. K. Fischer, C-L. Lee, and M. Muthukumar, *J. Chem. Phys.* preprint] on the ternary phase diagrams will be presented. One of the parameters of the theory is the degree of

ionization of the polyelectrolyte. Although the Manning condensation devised for infinitely long line charges is used ad hoc for flexible polyelectrolytes, a new model for counterion condensation for flexible polyelectrolytes will be discussed (M. Muthukumar, *J. Chem. Phys.* 120, 9343, 2004). This model considers (i) free energy of the polyelectrolyte chain, (ii) translational entropy of adsorbed counterions, (iii) adsorption energy, (iv) translational entropy of unadsorbed counterions, (v) fluctuations of dissociated ions, and (vi) correlation among ion-pairs formed by adsorbed counterions on the polymer. The effective charge and size of the polymer are calculated self-consistently, by stipulating equivalence of chemical potential between adsorbed and unadsorbed counterions. The effective charge of the polymer depends sensitively on local dielectric heterogeneity. The predictions of the new model are consistent with all trends observed in simulations and are distinctly different from the Manning argument for rodlike chains.

10:30 AM *BB6.4

Influence of Electrostatic Interactions on Chain Dynamics and Morphological Development Perfluorosulfonate Ionomer Membranes. Robert B. Moore and Kirt A. Page; Polymer Science, Univ. Southern Miss, Hattiesburg, Mississippi.

Several high temperature methods of processing Nafion[®] have been developed using various alkylammonium ion forms of the ionomer, and the choice of counterion has been shown to have a significant effect on the thermal and mechanical properties of this material. In particular, it has been shown that neutralization gives rise to two high-temperature mechanical relaxations as observed in dynamic mechanical analysis (DMA). While several studies in the literature have attempted to explain the molecular origins of these mechanical relaxations, the assignments were based primarily on limited DMA results and have at times been contradictory. The study presented here is a fundamental investigation into the molecular origins of the thermally induced morphological relaxations and dynamics of alkylammonium forms of Nafion[®] membranes as studied by variable temperature small-angle x-ray scattering (SAXS) and solid-state ¹⁹F NMR spectroscopy. The intensity of the small-angle ionomer peak at ca. $q = 2 \text{ nm}^{-1}$ was monitored as a function of temperature for each alkylammonium neutralized sample in unoriented and oriented states. In the case of the oriented samples, the degree of anisotropic scattering from the oriented ionomer morphology was quantified using the Hermans orientation function and monitored as a function of temperature. Changes in intensity of the ionomer peak and the Hermans parameter as a function of temperature were shown to correlate well with relaxations observed in DMA. Several variable temperature solid-state ¹⁹F NMR techniques (including spin diffusion, side-band analysis and $T_{1\rho}$ experiments) were used to investigate the dynamics of the Nafion[®] chains. Side band analysis indicated that the side-chain is more mobile than the main chain and that the mobility is greatly affected by the size of the counterion. Changes in side-band intensity as a function of temperature were shown to correlate well with DMA data. Results from $T_{1\rho}$ experiments show strong counterion dependence and suggest coupled main- and side-chain motions. A two-component relaxation process was also observed for the main-chain fluorines. The results of the NMR investigations, along with the SAXS data, have led to the development of a more detailed description of the dynamics of Nafion[®] and the molecular origins of the mechanical relaxations. With this information, the continuing goal to determine how the strength of the electrostatic interactions in perfluorosulfonate ionomers affects the chain dynamics and developing morphology may be realized for the purpose of controlling the morphology to create more efficient ionomeric membrane materials.

11:00 AM *BB6.5

Responsive Brushes, Gels and Block Copolymers for Soft Nanotechnology. Anthony J. Ryan¹, Colin J. Crook¹, Jonathon R. Howse¹, Paul Topham¹, Richard A. L. Jones², Mark Geoghegan², Lorena Ruiz-Perez² and Simon J. Martin²; ¹Department of Chemistry, The University of Sheffield, Sheffield, United Kingdom; ²Department of Physics & Astronomy, The University of Sheffield, Sheffield, United Kingdom.

Progress in the development of generic molecular devices based on responsive polymers is discussed. Characterisation of specially synthesised polyelectrolyte gels, grafted from brushes and triblock copolymers is reported. A Landolt pH-oscillator, based on bromate/sulfite/ferrocyanide, with a room temperature period of 20 min and a range of $3.1 < \text{pH} < 7.0$, has been used to drive periodic oscillations in volume in a pH responsive hydrogel. The gel is coupled to the reaction and changes volume by a factor of at least 6. A continuously stirred, constant volume, tank reactor was set-up on an optical microscope and the reaction pH and gel size monitored. The cyclic force generation of this system has been measured directly in a modified JKR experiment. The responsive nature of polyelectrolyte brushes, grown by surface initiated ATRP, have been characterised by

scanning force microscopy, neutron reflectometry and single molecule force measurements. Triblock copolymers, based on hydrophobic end-blocks and either polyacid or polybase mid-block, have been used to produce polymer gels where the deformation of the molecules can be followed directly by SAXS and a correlation between molecular shape change and macroscopic deformation has been established. The three systems studied allow both the macroscopic and a molecular response to be investigated independently for the crosslinked gels and the brushes. The triblock copolymers demonstrate that the individual response of the polyelectrolyte molecules scale-up to give the macroscopic response of the system in an oscillating chemical reaction.

11:30 AM ***BB6.6**

Dynamics of Ion-Containing Polymer Systems. James Runt and Shihai Zhang; Materials Science and Engineering, Penn State University, University Park, Pennsylvania.

In an extension of our research on segmental and local dynamics of polymer blends and solutions exhibiting strong intermolecular hydrogen bonding, we have investigated the dynamics of model ion-containing polymer systems by dielectric relaxation spectroscopy. These include complexes of poly(vinylmethylether) [PVME] with LiClO_4 , and ionic single ion conductors based on poly(ethylene oxide). Although no microphase separation was observed in DSC experiments of the former system, dielectric (particularly derivative) spectra reveal two segmental relaxations and one localized ion motion process. The fastest process is attributed to relaxation of segments in ion-depleted domains and it slows down with increasing salt content. The process with intermediate rate is proposed to originate from ion motion in ion-rich domains, and it is also retarded in complexes with higher LiClO_4 content. The segmental relaxation of PVME chains in ion-rich domains is even slower than the ion motion process. This process becomes faster with increasing LiClO_4 content, despite the concurrent increase in the bulk T_g . Maximum molar conductivity is obtained for a 2/100 LiClO_4 /PVME complex and the ionic conductivity is about 10^{-9} S/cm at 30 °C. By using a dynamic bond percolation model, it was estimated that ions move about 1 nm in the 0.5/100 complex at 0 °C at the time scale of the slow segmental relaxation, assuming that structural renewal is realized by the latter. This size, together with the strong correlation between ionic conduction and the slow segmental relaxation, supports the view that hopping from one segment to another is likely the effective fundamental step in the macroscopic conduction of these complexes.

SESSION BB7: Nanocomposites: Properties, Structure, and Phase Separation

Chairs: Russell Composto and Anne Mayes
Wednesday Afternoon, December 1, 2004
Room 309 (Hynes)

1:30 PM **BB7.1**

Spectroscopic and Mechanical Characterization of Nanocomposites of Syndiotactic Polypropylene and Polyethylene. Vasilis Gregoriou, Stavros Bollas, Spyros Tzavalas and Georgia Kandilioti; FORTH-ICEHT, Patras, Greece.

In this study, polymeric type nanocomposites of syndiotactic polypropylene (sPP) as well as high-density polyethylene (HDPE) were prepared and studied. Organically modified montmorillonite and multi-walled carbon nanotubes were used as nanoadditives in these systems. The samples were prepared via melt mixing at temperatures 20 to 40°C above the melting point of the polymeric matrix. The mechanical properties of the samples were examined by tensile measurements that showed an increase of the stress at yield with increased clay content for both polymeric matrices. Furthermore, the stress at break was increased up to a certain percentage of clay in the matrix, above which it declined. Differential scanning calorimetry (DSC) studies showed an elevation in the glass transition temperature (T_g) of sPP, which was more profound at low concentrations of clay. The crystallinity in both polymeric matrices sPP and HDPE was reduced as the clay content increased. Finally, FT-IR spectroscopy was employed in an attempt to correlate the conformational changes in the polymeric matrices to amount of the nanoadditive. In the case of sPP polymer, FT-IR analysis showed an increase in the amount of chains which adopt the helical conformation with increased clay content. During the mechanical elongation of the samples, the FT-IR spectra revealed that a conformational transformation took place from the helical form I to the trans-planar form III. However, the addition of clay hindered the chains from achieving full transformation into the trans-planar conformation. Concurrently, infrared linear dichroism experiments were performed in order to monitor the orientation of the chains. Furthermore, both the neat sPP and sPP/nanoclay samples were left to relax after extended elongation. A tendency of all the samples to return to their initial helical conformation was observed. However, this reversal was not

complete and the polymer chains exhibited a mixture of helical and trans-planar conformation. It was interesting to note that the samples where nanoclay was added showed a higher inclination to return to the helical conformation. Finally, the phase transformation behavior of sPP and sPP-nanocomposites was studied upon thermal treatment. Highly stretched samples of sPP with and without clay were heated up to 120 °C and the infrared spectra of the samples were recorded. It was evident that the transformation from the trans-planar to the helical conformation was affected from the presence of nanoclay in the matrix. HDPE samples with various contents of clay were subjected to mechanical stretching. The FT-IR spectra showed a transformation from orthorhombic to monoclinic crystallinity. In the case of the IR spectra of the HDPE-nanotube samples, no evident difference was observed between the pure sample and the blends. It could be claimed that the polymeric matrix was not affected by the presence of nanotubes.

1:45 PM **BB7.2**

Nanoscale interaction and its influence in polypropylene silica nanocomposites. Sandeep Razdan, Scott Paquin, Prabir Patra, Yong Kim and Steven Warner; Textile Sciences, University of Massachusetts Dartmouth, North Dartmouth, Massachusetts.

Inclusion of nanometer size inorganic particles in polymer matrices has shown remarkable improvements in thermal and flame retardant properties of the polymer. This has generally been attributed to the higher specific surface area of these particles. In our work, we are trying to investigate the effect of chemical interactions, at nanometer dimensions, of the nanoparticles with the polymer matrix on the thermal stability of the polymer. For this purpose, we chose polypropylene, a versatile commodity polymer, which has an organic non-polar molecular structure with no affinity or interaction with inorganic polar molecules such as silica. Fumed silica was chosen as filler due to its nanometer size as well as its ability to form hydrogen bonds with polypropylene grafted with maleic anhydride. This enabled us to study the interactions between g-polypropylene and silica at nanoscale level and to observe the resultant effect on the thermal stability of the polymer. We prepared polypropylene and g-polypropylene nanocomposites via melt mixing method carried out using three different rpm viz., 10, 50 and 100 rpm. Fillers were added at a loading of 5 wt% and 10 wt%. We also prepared polypropylene/silica nanocomposites containing 50 wt% of g-polypropylene added. Differential scanning calorimetry results showed a slight increase (2-3 degrees) in peak melting temperature of the nanocomposites, with the largest increase showed in the case of PP/g-PP/silica nanocomposites. Addition of silica increased the peak crystallization temperature of polypropylene by 7 degrees in case of both 5 wt% and 10 wt% loading, whereas the enhancement for g-PP was less than a degree. Thermogravimetric analysis showed enhancement in decomposition temperature by almost 50 degrees for 10 wt% filler addition for both polypropylene and g-polypropylene. However, the largest enhancement in decomposition temperature (about 60 degrees) was shown by PP/g-PP/silica nanocomposites. Visual observation of the char obtained from thermogravimetric analysis showed the formation of a porous fluffy char in case of g-PP nanocomposites whereas no char was formed in case of polypropylene composites. Interestingly in the case of PP/g-PP/silica nanocomposites, the char formed was hard, non-porous, contiguous, and almost retained the shape of the original sample used for combustion. The char thus obtained from PP/g-PP/silica is expected to be highly thermally protective. Further cone calorimetry experiments are being performed to corroborate this theory. Investigations are also underway to determine the type of chemical bonds present in the char formed using Fourier Transform Infra-Red analysis. This would provide us information regarding the functional groups present in the char obtained from the g-PP nanocomposites enabling us to theorize the protective char formation phenomenon on the basis of chemical reactions occurring during combustion.

2:00 PM **BB7.3**

Plasticization and reinforcement in polyhedral oligomeric silsesquioxane (POSS)-PMMA nanocomposites.

Edward T. Kopesky¹, Gareth H. McKinley² and Robert E. Cohen¹;

¹Chemical Engineering, MIT, Cambridge, Massachusetts; ²Mechanical Engineering, MIT, Cambridge, Massachusetts.

Hybrid organic-inorganic materials such as polyhedral oligomeric silsesquioxanes (POSS) have drawn considerable interest for their potential applications in fields ranging from polymer toughening to hydrophobic surface modification. An interesting characteristic of POSS nanoparticles is their ability to be incorporated into a polymer matrix in two distinct ways: as discrete, nonreactive nanoparticles ($\text{R}_8\text{Si}_8\text{O}_{12}$) and as covalently tethered groups along the polymer chain ($\text{R}_7\text{XSi}_8\text{O}_{12}$, where X takes part in the polymerization). POSS particles disperse in a polymer matrix on a range of length scales, including as molecularly dispersed particles ($d \approx 1.5$ nm), two-dimensional nanoscopic 'rafts', and as three-dimensional

crystalline aggregates which can range in size from $10 \text{ nm} < d < 10 \text{ }\mu\text{m}$. In order to study the effects of POSS on the rheological properties of poly(methyl methacrylate) (PMMA) homopolymer with and without crystallites present, both an amorphous POSS (R = methacryl) and two crystalline POSS species (R = isobutyl and R = cyclohexyl) were blended with the homopolymer and tested in small amplitude oscillatory shear-flow. Addition of the amorphous POSS species leads to a monotonic decrease in both the glass transition temperature (T_g) and the zero shear-rate viscosity (η_0) due to increased free volume as determined from fits to the WLF/Doolittle equation. The crystalline-POSS/PMMA blends exhibit a minimum in viscosity at low loadings ($\phi < 5 \text{ vol}\%$) before increasing at high loadings. No change in the T_g or free volume is observed in these blends. Isobutyl-POSS was also blended with a POSS-PMMA copolymer containing 25 wt% isobutyl-POSS tethered randomly along the chain. Blends of POSS filler with copolymer show a significant increase in η_0 for all loadings, much greater than that expected for traditional hard-sphere fillers. The filled copolymer system exhibits both an upward shift (reinforcement) and a horizontal shift to lower frequencies (retardation) in the storage modulus G' and the loss modulus G'' . The reinforcement effect is observed in the filled homopolymer also, but the retardation effect is not. Thus, in the filled copolymer system, associations between untethered-POSS and tethered-POSS cages in the blend retard chain relaxation processes in a way that can be understood in light of the "sticky reptation" model. Time-temperature superposition also holds for the filled copolymer system and fits to the WLF/Doolittle equation show a substantial increase in free volume at low POSS filler loadings. This indicates that both viscosity and free volume increase, a counterintuitive result made possible by the affinity of the tethered-POSS groups on the copolymer for the POSS filler particles.

2:15 PM BB7.4

Degree of Clay Exfoliation and the Crystallization Behavior of Poly(L-Lactic Acid). Vahik Krikorian^{1,2} and Darrin J.

Pochan^{1,2}, ¹Materials Science and Engineering, University of Delaware, Newark, Delaware; ²Delaware Biotechnology Institute, University of Delaware, Newark, Delaware.

We have investigated the crystallization behavior of semicrystalline poly (L-lactic acid) (PLLA) upon addition of organically modified montmorillonite clay. Two types of commercially available organoclays were employed to study the effect of extent of miscibility and/or dispersion of silicate layers on the overall crystallinity of the matrix. The exfoliation-adsorption technique was employed to fabricate the nanocomposites from solution. Crystallization studies were performed on cast nanocomposite films which were isothermally recrystallized at different temperatures from the quiescent melt. The radial spherulite growth rate measurements and isothermal bulk crystallization kinetics indicate that the silicate layers, in the case of the fully miscible organic modifier, did not act as a nucleating agent. However, the less miscible clay acted as a good nucleating agent and significantly decreased the spherulite sizes. Interestingly, spherulite growth rates were significantly increased by the addition of organoclays, being the highest in the fully exfoliated case. Moreover the overall bulk crystallization rate was increased in the intercalated case and retarded in the exfoliated.

2:30 PM BB7.5

Theoretical Model for the Dynamics of Entangled Polymer Melts Reinforced with Nanoparticles. Catalin Picu and Alireza Sarvestani; Department of Mechanical, Aerospace, and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York.

The dynamics of entangled polymer melts reinforced with nanosize rigid spherical particles is studied theoretically. Nanocomposites with low filler volume fraction (10%) and strong polymer-filler interactions are considered. The effect of entanglements is included in the model by requiring that the macromolecules diffuse at different rates in the directions along and perpendicular to the chain axis. The effect of the filler particles is to reduce the polymer mobility by increasing the average friction coefficient associated with the reptation. Some significant viscoelastic characteristics of polymer nanocomposites such as rubber like behavior at low frequency oscillations are described by the model.

3:15 PM BB7.6

In situ Synthesis and Characterization of Silver (Ag) Nanoparticles, by Thermal Decomposition Method in Thin Films of PMMA and Blends of PMMA and SAN to Study Ag Nanoparticle Distribution and Dynamics of Spinodal Phase Separation. Ranjan D. Deshmukh and Russell J. Composto; Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania.

Silver nanoparticles were synthesized in situ by thermal decomposition of silver hexafluoro-acetylacetonate (AgHFA) precursor

at 185°C in thin films of PMMA and thin film blends of PMMA and SAN. The Ag nanoparticles (average size 4.4 nm) were characterized by TEM, XRD and AFM imaging. Rutherford backward scattering (RBS) was used to observe strong surface segregation to the polymer/air surface and weakly to the substrate in PMMA thin films. UV/Vis spectroscopy on the PMMA/Ag composite films show plasmon resonance due to the presence of Ag nanoparticles. RBS was also used to study the nanoparticle distribution in the phase separated critical blends of PMMA and SAN. The dynamics of the spinodal phase separation morphology was studied in presence of Ag nanoparticles by AFM. Correlation length (ξ) vs time (t) studies, obtained via fast fourier transform (FFT) of the AFM images, show slowing down of the dynamics of phase separation as compared to blends without Ag nanoparticles in the initial as well as the intermediate growth regimes. The scaling law in the intermediate regime was found out to be $\xi t^{-1/3}$. This scaling law is not affected by the presence or absence of the nanoparticles. A novel necklike structure due to self assembly of nanoparticles on the polymer blend surface was also observed by AFM.

3:30 PM BB7.7

Effect of Nanoscale Filler Particles on the Kinetics of Phase-Separating Multi-Component Fluids. Mohamed Laradji and Michael J.A. Hore; Physics, The University of Memphis, Memphis, Tennessee.

Using large scale dissipative particle dynamics simulations, we investigated the effect of nanoscale spheres and rods on the dynamics of phase separation of three-dimensional multicomponent fluids. We considered both cases of three-dimensional bulk systems and thin films. We found that spherical nanoparticles, which interact more attractively with one of the two segregating components, lead to a reduction of domain growth rate during the phase separation process, and that this reduction is intensified as the nanoparticles volume fraction is increased or as their radius is decreased. The qualitative features of the dynamics, however, as illustrated by the growth law for example, are found to be identical to that of pure binary fluids. Nanorods, on the other hand are found to have a much more pronounced effect on the dynamics as opposed to nanospheres. In particular, we found a more dramatic reduction of phase separation growth rate as the aspect ratio of the nanoparticles is increased. We will show that the nature of the dynamics, in this case, is strongly correlated with the isotropic-nematic transition of the nanorods within the preferred component. We will also present results pertaining to the effect of nanospheres and nanorods on the dynamics of thin-film multicomponent polymers.

3:45 PM BB7.8

Polymer-Grafted Nanoparticles Affect Wetting and Phase Separation in Polymer Blend Films. Hyun-joong Chung¹, Russell J. Composto¹, Kohji Ohno² and Takeshi Fukuda²; ¹Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; ²Institute for Chemical Research, Kyoto University, Kyoto, Japan.

Wetting and phase separation are inseparable phenomena in complex liquid systems. Especially, for nanoparticle (NP) containing systems, the importance of wetting is crucial because nanoparticles introduce a large interfacial area. So far, most studies of polymer nanocomposites has focused on their rheological properties, which typically show a viscosity increase with NP loading. This increase has been attributed to attractive interactions between polymer and NP, as well as chain confinement near the nanoparticle surfaces. Here, we study the impact of surface grafted NP on phase separation and wetting behavior of polymer blend films. Thin and thick films (100 nm to several microns) with a 50:50 ratio of deuterated poly(methylmethacrylate) (dPMMA) and poly(styrene-ran-acrylonitrile) (SAN) were chosen as a model system that undergoes phase separation and preferential wetting at interfaces. The polymer-NP interaction was varied using different grafting species (alkanes or PMMA) on silica particles. Both type of particles partition into the dPMMA-rich phase upon phase separation. The polymer-NP interaction can be controlled by varying the molecular weight (Mn) of grafted PMMA chains from 1.8K to 160K. Using the combination of Rutherford backscattering spectrometry (RBS) and elastic recoil detection (ERD) to depth profile nanoparticles and dPMMA, respectively, the wetting of NP and dPMMA is simultaneously followed during early stage growth. Surface force microscopy (SFM) of the free surface and the buried dPMMA-rich/SAN-rich interfaces is used to investigate the morphological development.

4:00 PM BB7.9

Core-Shell Nanoparticle Baroplastics as Thermoplastic Elastomer Substitutes. Juan Gonzalez, Sang-Woog Ryu, Sheldon Hewlett and Anne M. Mayes; DMSE, MIT, Cambridge, Massachusetts.

The processing and mechanical properties of nanophase polymer mixtures are intimately linked with their thermodynamic compatibility. Here we describe core-shell nanoparticle systems comprised of a low glass transition (T_g) core component, such as poly(butyl acrylate), and a high T_g shell component, such as polystyrene, that can be processed into solid objects at reduced temperatures with the application of pressure. Narrowly distributed core-shell nanoparticles were synthesized by standard miniemulsion polymerization and processed by compression molding and simple extrusion at temperatures as low as 250°C and pressures of 5000 psi. Characterization of these baroplastic materials by DSC, TEM and SANS reveals the formation of a mixed interphase when pressure is applied, due to pressure-enhanced miscibility of the nanoparticle components. However, distinct domains of each component remain even after multiple reprocessing steps, providing materials with mechanical properties sufficient for application. Tensile tests carried out on the processed core-shell nanoparticle baroplastics show that a wide range of mechanical properties are possible upon changing their size and composition. Materials rich in the low T_g component present properties comparable to commercial block copolymer thermoplastic elastomers, demonstrating the possible application of core-shell baroplastics as thermoplastic elastomer substitutes.

4:15 PM BB7.10

Classical Atomistic Study of Interactions between Clay Sheets. Hendrik Heinz^{1,2} and Barry Farmer¹; ¹Materials and Manufacturing Directorate, Air Force Research Laboratory, WPAFB, Ohio; ²Department of Mechanical and Materials Engineering, Wright State University, Dayton, Ohio.

We investigate the interaction energy between two clay lamellae when they are separated apart from each other as a function of distance. As common model systems in clay-polymer nanocomposites, we consider montmorillonite and mica, both in the natural form and with exchange of the alkali ions for trimethyloctadecylammonium ions (C18), using an extended polymer consistent force field [1, 2]. Electrostatic energy and van-der-Waals energy constitute the main attractive forces between the clay sheets. In the natural (unmodified) minerals, the electrostatic attraction is of primary importance next to van-der-Waals attractive forces, while in the organically modified minerals electrostatic interactions are effectively shielded. In montmorillonite, the interaction energy between the sheets is negligible for more than 2 nm separation. Presence of an organic layer (with a thickness of >1 nm) on the surface reduces the range of interactions to approximately 1 nm separation (predominantly van-der-Waals forces). The absence of long-range electrostatic forces may be explained with short dipole (multipole) lengths in the minerals on the order of 0.1 nm, which limit polar effects to the vicinity of the surface. The results help to explain exfoliation behaviour in polymer-clay nanocomposites and to parametrize coarse-grained models for clays. [1] H. Heinz, H. J. Castelijns, U. W. Suter, J. Am. Chem. Soc. 125, 9500 (2003). [2] H. Heinz, U. W. Suter, Angew. Chem. Int. Ed. 43, 2239 (2004).

4:30 PM BB7.11

Ordered High Temperature Ceramics from Block Copolymer Mesophases. Marleen Kamperman, Carlos Garcia, Phong Du, Hooisweng Ow and Ulrich Wiesner; Materials Science & Engineering, Cornell University, Ithaca, New York.

Structuring ceramics on the nanoscale is a promising research field, because of their potential novel properties. While for oxide ceramics it has been demonstrated, nanostructuring of non-oxide high temperature ceramics remains a challenge. Non-oxide ceramics are of special interest because of their excellent thermal stability and mechanical properties. Here we demonstrate an easily controlled bottom-up approach for the preparation of nanostructured high temperature ceramic materials stable up to 1500 C. An amphiphilic block copolymer is used as a structure directing agent for a polysilazane, commercially known as Ceraset. By blending it with the block copolymer, the Ceraset is expected to selectively swell the hydrophilic block. Different mesophases similar to those in block copolymer/ homopolymer mixtures are observed by systematically increasing the polysilazane to block copolymer weight fraction. The nanocomposites are cast into films and the structure is permanently set by crosslinking the Ceraset with a radical initiator. Heat treatment under nitrogen up to temperatures as high as 1500 C converts the composites into high-temperature ceramics. The materials are characterized by small angle X-ray scattering (SAXS), transmission electron microscopy (TEM) and nitrogen adsorption-desorption measurements showing that mesoporous ceramics with open and accessible pores can be obtained. Implications of these findings for various application fields will be discussed.

4:45 PM BB7.12

Dynamics of Nanocomposite Formation and Impact Modification of Polyethyleneterephthalate. Elif Alyamac and

Ulku Yilmazer; Chemical Engineering, Middle East Technical University, Ankara, Turkey.

This study was conducted to investigate the effects of component concentrations and addition order of the components, on the final properties of nanocomposites composed of amorphous Polyethyleneterephthalate (PET) matrix, organically modified clay (Cloisite 25A-Southern Clay Products), and an ethylene/methyl acrylate/glycidyl methacrylate (E-MA-GMA) terpolymer as the impact modifier for PET. A 16 mm co-rotating, fully intermeshing twin-screw extruder, barrel length 384 mm (Thermoprism TSE 16 TC) was used for compounding. The addition orders investigated can be summarized as follows: P, I and C stand for PET, Impact Modifier (Lotader), and Clay respectively. The first two letters indicate the materials mixed in the first run. This mixture was compounded with the third ingredient in the subsequent run. The following sequences were prepared: Sequence 1 (PI-C), Sequence 2 (PC-I), Sequence 3 (CI-P), Sequence 4 (All-S) all simultaneous feeding. The compounds were subsequently injection molded and analyzed by XRD, SEM and mechanical tests. In the first step, the mechanical properties of impact modifier-PET binary blends were analyzed. The tensile modulus and the tensile strength decreased, however, the strain at break significantly increased with the impact modifier content. Thus, the impact modifier content was chosen as 5 wt. %, in order to have balanced mechanical properties. In the next step, 5 wt. % impact modifier-PET-clay nanocomposites were prepared and analyzed. In these nanocomposites, tensile modulus was significantly influenced by the clay content and the addition sequence of the three components. For PI-C; there was a sharp increase of tensile modulus for very small clay loadings (1 wt. %) followed by a much slower increase beyond 1 wt. % loading. Tensile modulus of pure PET increased by 166 % in samples with 5 wt. % E-MA-GMA plus 5 wt % clay loading. Addition of 5 wt % impact modifier did not significantly change the impact strength of pure PET, whereas the impact strength drastically increased when the impact modifier was added as a third component to the PET/clay nanocomposites. Strain at break increased significantly with the addition of the impact modifier plus clay. For example, it increased from 5% for pure PET to nearly 300% for PI-C with 1 wt % clay content. X-ray diffraction indicated that extensive layer separation associated with delamination of the original clay structure occurred in PI-C and CI-P compounds with both 1 and 3 wt. % clay contents. These compositions also gave the most tortuous crack propagation paths as observed by SEM. Thus, the best sequence of component addition was determined to be (PI-C). In this mixing order, the polymer matrix mixture prepared in the first run (PI) has higher melt viscosity than pure PET, thus this matrix can apply high shear stresses on the clay particles and delaminate the clay layers resulting in best mechanical properties.

SESSION BB8: Associating Polymers: Ionomers and Membranes

Chairs: Jack Douglas and Robert Moore
Thursday Morning, December 2, 2004
Room 309 (Hynes)

8:30 AM BB8.1

Morphology and Dynamics of Self-Associating Ionomers. Aniket Bhattacharya¹, Monojoy Goswami² and Sanat K. Kumar²;

¹Physics, University of Central Florida, Orlando, Florida; ²Chemical Engineering, Rensselaer Polytechnic Institute, Troy, New York.

We present molecular dynamics simulation results for polymers with charged end groups in a solution containing equal number of neutralizing counterions. We study the morphology and dynamics of the self-assembled structures, size distribution of the micelles, and relevant time dependent quantities. The response of the system against shear is also studied using nonequilibrium molecular dynamics (NEMD). We compare our results with recent experiments, with those simulation results obtained for telechelics with sticky ends, and those obtained using Monte Carlo methods for lattice ionomers.

8:45 AM BB8.2

Application of Analytical Electron Microscopy Methods in Ionomer Systems. Nicholas M. Benetatos, Hansoo Kim and Karen I. Winey; Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania.

Our research explores the effects of chemistry and processing on the morphology and properties of ionomers and the use of analytical electron microscopy methods to elucidate the morphologies of these materials. We have previously demonstrated the use of scanning transmission electron microscopy (STEM) in characterizing the cation-rich nanoaggregates of ionomers. This paper will focus on the influence of specimen thickness (20 to 100 nm) and electron probe size (FWHM is 0.3 to 0.7 nm) on the detection of ionic aggregates in

STEM. For this purpose, STEM has been used to image a model system containing functionalized undecagold nanoparticles (gold core is 0.8 nm diameter) deposited on spin-coated polystyrene films of known thickness. STEM imaging of the sub-nanometer gold particles improves substantially as the polymer thickness decreases below 50 nm, while the influence of the STEM probe size is negligible. X-ray scattering provides complimentary data from these undecagold particles, so that we can establish reliable image analysis protocols for aggregate size and shape. We are also probing the local chemical composition of ionomers using x-ray energy dispersive spectroscopy (XEDS) and especially energy filtered TEM, where the undecagold specimens again provide a model system for analysis. These analytical electron microscopy experiments involving model nanoparticles have improved our experimental protocols for studying ionomer morphologies.

9:00 AM **BB8.3**

Probing Molecular-Level Functionality and Mesoscale Architecture of Segmented Poly(ester urethanes) using Solid-State Two-Dimensional Homo- and Heteronuclear Correlation NMR Spectroscopies. James Howard Small, David Langlois, Douglas Anson Loy, Debra Wroblewski and Edward Bruce Orler; Polymers and Coatings Group, Los Alamos National Laboratory, Los Alamos, New Mexico.

For the past few years we have been extremely interested in probing multi-length scale phenomena (10-10 to 10-3 m) using solid-state nuclear magnetic resonance (NMR) spectroscopy. More specifically, we wish to further understand the fundamental chemical interactions occurring at the molecular-level that lead to mesoscale architectures and ultimately bulk macromolecular properties in segmented poly(ester urethanes). While traditional characterization techniques such as single crystal x-ray diffraction as well as small angle scattering have allowed for the structural determination of crystalline solids, this task can be quite daunting for an amorphous material. To bridge the gap between small-scale structures and macromolecular morphology of amorphous structures, we have employed the synthesis of model dicarbamate compounds coupled with conformational analysis and multidimensional solid-state NMR. We are employing multidimensional solid-state NMR techniques to confirm the chemical functionalities involved in the important hard-hard domain interactions as well as probe the subtle hard-soft domain interfacial regions. We wish to present here 2D 1H-13C FSLG-HETCOR and 2D 1H-1H LG-CRAMPS results which confirm the presence of hard-hard domain structure as speculated in the literature. In particular, interchain hydrogen-bonding between adjacent carbamates within a repeat unit in both orthogonal planes was clearly evidenced. This offset 3D structure is definitively confirmed by the appearance of hard segment aromatic protons significantly shifted upfield due to diamagnetic anisotropy. These results, in conjunction with both mechanical and thermal properties of these materials, affords a much broader understanding of multi-length scale phenomena in segmented poly(ester urethanes). In addition, this general approach should prove as a case study for the application of multidimensional solid-state NMR spectroscopy as a viable tool for the systematic analysis of structure of amorphous solids spanning many length scales.

9:15 AM **BB8.4**

Viscoelastic Behavior of Low Molecular Weight Sulfonated Polystyrene Ionomers. Hongying Zhao and R. A. Weiss; Polymer, Institute of Materials Science, Storrs, Connecticut.

The rheology of sulfonated polystyrene ionomers (SPS) was characterized using a series of ionomers prepared from a low molecular weight (4,000) narrow molecular weight distribution (1.06) polystyrene. The molecular weight of the PS was far below the entanglement molecular weight of polystyrene. Two sulfonation levels were examined, 2.50 and 4.78 mol%, and the metal counterions was varied across the alkali metal series of the periodic table. Dynamic and steady shear experiments were performed. Time-temperature superposition was obeyed by the dynamic data for the higher sulfonation level, but failed for the lower sulfonation level. The steady shear viscosity increased with sulfonation level and as the size of counterion decreased for the alkali metal salts, whereas the parent polystyrene exhibited no elasticity. The ionomers had first normal stress difference that increased with sulfonation level and with decreasing size of the counterion. The microstructure of the SPS ionomers was also studied using small-angle X-ray scattering (SAXS). The scattering peak and the upturn near zero angle confirmed the existence of the ion clusters.

9:30 AM **BB8.5**

Miscibility of Polystyrene/Sulfonated Polystyrene and Sulfonated Polystyrene/Sulfonated Polystyrene Blends. Nancy C. Zhou¹, Chen Xu², Wesley R. Burghardt³, Russell J.

Composto^{2,1} and Karen I. Winey^{2,1}; ¹Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia,

Pennsylvania; ²Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; ³Department of Chemical Engineering, Northwestern University, Evanston, Illinois.

Sulfonated polystyrene is a commercially important ionomer that has been widely studied, but recent experimental and theoretical findings suggest that the morphology and phase behavior in sulfonated polystyrene systems require renewed research efforts. Our approach is to study the miscibility of polystyrene (PS) and sulfonated polystyrene (P(S-SSx)) (homopolymer/copolymer blends) and the miscibility of sulfonated polystyrenes with other sulfonated polystyrenes of differing sulfonation level (x) (copolymer/copolymer blends) using the ion beam technique of forward recoil spectrometry (FRES). FRES requires that one component of the blend pair be deuterated and determines the coexistence compositions in polymer bilayers by detecting the deuterium level as a function of depth. Blend miscibility has been studied as a function of temperature and sulfonation level. FRES results for the homopolymer/copolymer blend indicate fully miscibility at $x < 0.2\%$, partial miscibility at $x = 0.7$ to 1.6% , and complete immiscibility at $x > 2.7\%$ at 170°C . The data is comparable at 190°C . In addition, the miscibility between P(S-SSx)/P(S-SSy), a copolymer/copolymer blend, will also be examined at low, medium, and high sulfonation levels. In the fully miscible systems, FRES has been applied to study the diffusion of deuterated PS into P(S-SSx) and preliminary data indicates that diffusion slows as the level of sulfonation increases. This miscibility information about PS/P(S-SSx) and P(S-SSx)/P(S-SSy) blends serves as a foundation for future ionomer morphology studies of neutralized P(S-SS).

9:45 AM **BB8.6**

Association Behavior of Multiblock Copolymers in Selective Solvents: Brownian Dynamics and SANS Study. Rama Bansil, Huifen Nie and Yongsheng Liu; Boston University, Boston, Massachusetts.

It is well known that multi-block copolymers in selective solvents associate forming bridged or isolated micelles arranged in liquid-like or ordered states. The association behavior can be tuned by varying the number of component polymers and the number of blocks, the chemical composition and length of the blocks, and the interactions with solvents. The insoluble blocks tend to aggregate into micro-domains on the nanometer scale, and the soluble blocks can either form loops, with both ends landing on the same micro-domain, or form bridges between neighboring domains. In this talk we will present results of Brownian dynamics simulation on triblock (ABA, BAB), penta-block (ABABA, BABAB) and hepta-blocks in selective solvents for either A or B blocks to study the effect of varying the number of blocks, solvent selectivity, concentration and temperature on the association behavior of multi-blocks. The size of the micro-domains and the distance between neighboring micro-domains are calculated and compared with the fitting results from small-angle neutron scattering (SANS) experiments. The ratio of the loops to bridges is obtained from the equilibrium configuration in simulation.

10:30 AM **BB8.7**

Kinetics of Polymeric Membrane Morphology Formation and Evolution during Immersion-Precipitation Process. Bo Zhou and Adam Clayton Powell; Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Most commercial polymeric membranes are made from nonsolvent/solvent/polymer ternary systems by immersion precipitation. In this work, a ternary Cahn-Hilliard formulation incorporating a Flory-Huggins homogeneous free energy function is used to study the kinetics and phase behavior of the immersion precipitation process, which determines much of the final morphology of membranes. The Water/DMF/PVDF ternary system with a two-layer polymer-solvent/nonsolvent initial condition is used to simulate actual membrane fabrication conditions. 2D and 3D simulation results show the membrane morphology evolution of liquid-liquid demixing during the immersion precipitation process. The simulated final morphologies in both 2D and 3D represent an asymmetric structure of membrane morphology, which strongly agrees with the experimental observation. Simulations with different initial compositions show membrane morphology changes from isolated droplets to bicontinuous patterns. Furthermore, the effects of concentration-dependent mobilities are studied. In addition, the Navier-Stokes equations are coupled with this ternary system to model hydrodynamics in 2D and 3D. The results show that fluid flow destabilizes the top layer of membrane, with larger surface tension and smaller viscosity making the top layer more unstable. Concentration-dependent viscosity is then used in the simulations.

10:45 AM BB8.8

Chemical Polymerization of Aniline on Commercial Cation-Exchange Membranes Using Different Oxidants and Their Effect on the Membrane Properties. Sophie Tan, Jacqueline H. Tieu and Daniel Belanger; Chimie, Université du Québec a Montreal, Montreal, Quebec, Canada.

Cation exchange membranes (CEMs) allow selective transport of cations and are used in several electrochemical technologies such as electrolysis, electrosynthesis, electro dialysis and fuel cells. However, one of the CEMs limitations is its lack of permselectivity for different types of cations. For example, direct methanol fuel cells require CEMs that allow transport of protons without methanol cross-over. Some applications of electro dialysis processes require a CEM permselective to monovalent cations against bi- or multivalent cations. One approach used to improve the CEMs permselectivity for monovalent cations is to create a positively charged layer within or on a commercial CEM.[1-3] We have previously demonstrated that the presence of polyaniline (PANI) chemically polymerized on a Neosepta[®] CMX membrane, a commercial CEM bearing sulfonate groups, decreased the Zn²⁺ transport by a factor of over ten times less than for the unmodified CMX membrane after electro dialysis in acidic media.[1-2] Here, we will demonstrate that the permselectivity behavior of the composite membranes depends on the location and/or the type of PANI layer present within the membrane. Several chemical oxidants including (NH₄)₂S₂O₈, FeCl₃, KIO₃, H₂O₂ were used to polymerize aniline within the commercial membranes. These membranes were characterized by electro dialysis of Zn²⁺ in acidic solutions, ionic conductivity measurements, scanning electron microscopy, X-ray photoelectron microscopy and ion exchange capacity. 1. Tan, S.; Viau, V.; Cugnod, D.; Belanger, D., *Electrochem. and Solid-State Lett.*, 2002, 5, E55. 2. Tan, S.; Laforgue, A.; Belanger, D., *Langmuir*, 2003, 19, 744. 3. Chamoulaud, G.; Belanger, D., *Langmuir*, 2004, 20, 4989.

11:00 AM BB8.9

Molecular Simulation of the Structure and Glass Transition of Sulfonated Copolyimides for Fuel Cell Application. Naiping Hu and Andrew Hsu; Mechanical Engineering, Indiana University -Purdue University Indianapolis, Indianapolis, Indiana.

The use of atomic modeling techniques to predict the structure-property relationship of sulfonated polyimides affords the opportunity to provide a guideline for the development of novel copolyimides as PEM fuel cell membranes. Of particular interest of this study is to simulate the structure and glass transition temperatures (T_g) of several potential sulfonated polyimides. Molecular dynamics simulation has been used to obtain specific volume as a function of temperature for two dry and four hydrated polyimides synthesized from Naphthalene-1,4,5,8-tetracarboxylic dianhydride (NTDA), 2,2'-benzidinedisulfonic acid (BDSA), 4,4'-diaminodiphenylether-2,2'-disulfonic acid (ODADS), and non-sulfonated diamine monomers. The volumetric glass transition temperature T_g has been determined from plots of specific volume versus temperatures above and below T_g. The simulation results suggest that ODADS-based polyimide membranes display lower T_gs thus better stability than BDSA-based polyimides, which may be attributed to high mobility of ODADS as supported by the vectorial autocorrelation function (VACF) results of this study. In addition, comparison of the simulated T_gs for dry and hydrated polyimides indicates an increased T_g for polyimide with lower hydration. The relationship between the conformation and chain flexibility of these polyimides, and their properties including T_gs and water uptake is explored on the basis of these and other simulations in progress.

11:15 AM BB8.10

Dynamical Models for the Transport of Macromolecules through Polymeric Membranes. Mihail Mihailescu and Anna Christina Balazs; Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

One of the most important properties of biological membranes is their ability to control the passage of species with various structures and functionalities in and out of the interior of a system. To gain insight into this process, we model membranes formed from homopolymers and investigate the motion of chains and nanoparticles through these synthetic membranes. In particular, we use a dynamic mean-field theory to monitor the structural evolution of the system as these species penetrate the membrane. Within this computational model, we vary the mobility and size of the transported specie, as well as those of the polymers that form the membrane, to isolate conditions when the synthetic system mimics biological activities. Specifically, we locate the parameters that lead either to formation of a hole in the membrane, to allow for transport, followed by membrane reformation, or to permanent disruption of the membrane by the penetrating specie. These studies allow us to identify cooperative phenomena that govern hole formation and closure in the membrane and to potentially develop a better understanding of the factors that control the

transport of molecules through biological membranes.

11:30 AM BB8.11

Morphological Manipulation and Plasticization of the Electrostatic Network in Perfluorosulfonate Ionomers. Alan K. Phillips and Robert B Moore; Department of Polymer Science, The University of Southern Mississippi, Hattiesburg, Mississippi.

The addition of small molecule fluorosurfactants to perfluorosulfonate ionomers has been found to have a profound effect on the morphology and mechanical properties of solution processed membranes. Past research has shown the use of both alkali metal and alkylammonium counterions to be an effective means of altering the morphology and properties of the perfluorosulfonate ionomer Nafion[®]. The work presented extends the concept of counterion modification to an eight carbon fluorosurfactant which can be incorporated into Nafion[®] during solution processing. As noted in literature, increasing counterion radius can cause the fluorosurfactant to transition from a crystalline solid to a viscous fluid. Neutralization of a sulfonate terminated eight-carbon fluorosurfactant with sodium, tetramethylammonium and tetrapropylammonium counterions results in a crystalline powder easily recovered by solvent evaporation. Neutralization of the fluorosurfactant with tetrabutylammonium generates a viscous fluid after solvent evaporation that is shown by WAXD to be a non-crystalline liquid. Solution processing of counterion neutralized fluorosurfactant with similarly neutralized Nafion[®] has shown distinct changes in membrane properties. Fluorosurfactants that readily crystallize into solids generate opaque, brittle membranes. ESEM analysis suggests the surfactant has phase separated from the membrane forming a crystalline layer on the film surface 12 mm in thickness. Neutralized surfactants that behave as viscous liquids in their pure form produce highly plasticized membranes that display highly elastic tensile behavior. Dynamic mechanical analysis of the membranes has shown plasticization of the a and b relaxations in addition to alterations in their relative magnitudes. Plasticization of the matrix by the surfactant remains after solvent extraction indicating either incomplete extraction or permanent alteration of the matrix during the casting procedure due to the presence of surfactant. In all counterion forms, the fluorosurfactant is easily removed from the membrane by swelling either with water or methanol depending on the hydrophilicity of the counterion being used. Initial SAXS results suggest the addition of surfactant alters the electrostatic network within the Nafion[®] matrix causing the average inter-aggregate spacing to decrease by 0.3 nm indicated by a shift of the ionomer peak to larger scattering vector. Solid-state ²³Na NMR was used to probe ionic aggregate and examine the effect of the fluorosurfactant on the extent of aggregation within the membrane. Addition of the sodium salt of the surfactant shifts the center of mass of the aggregate peak upfield 6 ppm. After solvent extraction of the surfactant, a residual shift of the resonance remains suggesting either incomplete extraction or residual effects.

11:45 AM BB8.12

Abstract Withdrawn

SESSION BB9: Polymer Blends: Dynamics, Interfaces and Theory
Chair: Mark D. Dadmun
Thursday Afternoon, December 2, 2004
Room 309 (Hynes)

1:30 PM *BB9.1

Bulk and Interfacial Behavior of Gradient Copolymers. Kenneth R. Shull¹, Rachel L. McSwain¹, Michelle D. Lefebvre¹, Christine M. Dettmer², SonBinh T. Nguyen², Russell J. Composto³ and Chen Xu³; ¹Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois; ²Department of Chemistry, Northwestern University, Evanston, Illinois; ³Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania.

Traditional block copolymers and random copolymers are just two examples of a more general class of materials referred to as gradient copolymers. These materials can be synthesized by a variety of living polymerization techniques that enable the average chemical composition to be continuously varied from one end of a polymer chain to the other. In this work we describe theoretical and experimental results that can be used to sensibly design gradient copolymers with the desired properties. We begin with a self-consistent mean-field treatment that is used to describe the bulk phase behavior, micellization and interfacial activity of gradient copolymers. Results are obtained for different values of a gradient parameter that varies from zero for a traditional diblock copolymer to

infinity for random copolymer. Next, we describe a poly(norbornene)-based model system, where excellent control of this gradient parameter is obtained via ring opening metathesis polymerization. Tracer molecules suitable for measurements of interfacial segregation are synthesized by using a partially deuterated form of one of the component monomers. Segregation of these copolymers to the interface between the corresponding homopolymers is measured by forward recoil spectrometry, and these results are compared to predictions of the mean field theory.

2:00 PM *BB9.2

Grafting Reactions Producing Diblock Copolymers at Polymer/Polymer Interfaces in Polymer Blends. Bumjoon Kim², Edward J. Kramer^{1,2}, Kirill Katsov², Glenn H. Fredrickson^{2,1}, Huiman Kang³ and Kookheon Char³; ¹UCSB, Santa Barbara, California; ²Chemical Engineering, UCSB, Santa Barbara, California; ³Chemical Engineering, Seoul National University, Seoul, South Korea.

Reactions to produce graft copolymers at polymer interfaces during extruder mixing are important for controlling dispersed phase size by retarding droplet coalescence and reducing interfacial tension while providing interface reinforcement. We investigate such reactions at various temperatures in a model bilayer film system consisting of amine end-functional deuterated polystyrene (dPS-NH₂) in PS and anhydride end-functional poly(2-vinylpyridine) (P2VP-anh) in P2VP as a function of molecular weight M , radius of gyration R_g and initial volume fraction ϕ_0 of the end functional chains. After various times of reaction the interfacial excess z^* of block copolymer formed at the interface is determined by detecting ²H⁻ ions using dynamic SIMS depth profiling. At low ϕ_0 (< 0.01) of dPS-NH₂ and P2VP-anh, such that the normalized interface excess $z^*/R_g < 1$ and the blocks are unstretched, the forward reaction rate constant k^+ decreases as $M^{-0.68}$ in reasonable agreement with theoretical predictions ($k^+ M^{-0.55}$) for this regime. The rate constant is thermally activated with an activation enthalpy of 165 kJ/mol that is independent of M as expected. At larger ϕ_0 (> 0.12) the reaction leads to $z^*/R_g > 1$ eventually. As z^*/R_g exceeds a critical value $(z^*/R_g)_c$, AFM measurements show that the interface begins to roughen with the roughness approaching a constant value above a larger $(z^*/R_g)_d$. Self-consistent mean field (SCF) simulations predict a value of $(z^*/R_g)_c$ where the interfacial tension approaches zero that increases slowly with M . Our values of $(z^*/R_g)_c$ show a similar dependence on M as that predicted by SCF but are systematically lower by a factor of ~ 1.5 . For $z^*/R_g > (z^*/R_g)_d$ we observe emission of block copolymer-coated droplets from the rough interface using both SIMS and cross-sectional TEM. These droplets diffuse away from the interface preferentially into the polymer corresponding to the longest block of the dPS-P2VP block copolymer. **Supported by the NSF-MRSEC Program through the MRL at UCSB.

2:30 PM *BB9.3

Ionomer/Polymer Blends: Phase Behavior and Implications for Compatibilization. Robert Weiss, University of Connecticut, Storrs, Connecticut.

Polymers blends are most often immiscible due to the small combinatorial entropy of mixing for high molecular weight compounds. Miscibility can be achieved by promoting intermolecular exothermic interactions such as hydrogen bonding, ion-dipole interactions, acid-base interactions, and transition metal complexation. An increasingly popular strategy for enhancing the miscibility of two polymers is to attach ionic groups to one polymer in order to form specific attractive interactions with a complementary functional group on a second polymer. That strategy has been used to prepare miscible or compatible polymer blends. An alternative approach for achieving miscibility in a polymer blend is to exploit the "copolymer effect"¹⁻³, whereby strong repulsive interactions along one polymer chain promote mixing of that polymer with another polymer even though the binary interactions between all distinct chemical species are unfavorable. By virtue of the incompatibility of the ionic groups and the hydrophobic backbone of an ionomer, these materials are attractive candidates for achieving miscibility of polymers that would not normally be miscible or even compatible. In this talk, we will discuss why ionomers may represent an extremely versatile class of compatibilization agent. That is, ionomers can mix with a wide variety of other polymers as a result of either specific attractive intermolecular interactions or strong intramolecular repulsive interaction within the ionomer. In this talk, we will discuss the strategies for mixing ionomers with other polymers, e.g., polyamides and polycarbonate, as well as the use of ionomers as a third, interfacially active component in a polymer mixtures. In addition, the presence of the ionic groups and specific interactions can result in unique aspects of such systems with regard to their microstructures, rheology and physical properties. In particular, we will discuss the use of remarkable control of the phase behavior of ionomer/polyamide blends by simply changing the ionomer counterion and the melt

nucleation of polycarbonate crystallization due to the presence of metal sulfonate groups in a blend of PC with a sulfonated polystyrene ionomer. 1. Kambour, R. P.; Bendler, J. T.; Bopp, R. C. *Macromolecules* 1983, 16, 753. 2. Ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* 1983, 16, 1827. 3. Paul, D. R.; Barlow, J. W. *Polymer* 1984, 25, 487.

3:30 PM *BB9.4

A Lattice Model for Segmental Dynamics of Miscible Polymer Blends. Ralph H. Colby¹ and Jane E. G. Lipson²;

¹Materials Science and Engineering, Penn State University, University Park, Pennsylvania; ²Chemistry, Dartmouth College, Hanover, New Hampshire.

Polymer blend thermodynamics has been successfully described using a lattice model that properly accounts for the surface area of polymer chains. We employ this lattice description to model the segmental dynamics of miscible polymer blends. Concentration fluctuations and chain connectivity effects are calculated on the lattice at the scale of the Kuhn length, consisting of 24 lattice sites surrounding a central monomer. Using either the WLF equation or dynamic scaling, we map the concentration distributions onto segmental relaxation time distributions. These distributions are compared with literature dielectric spectroscopy data on miscible blends of polyisoprene with poly(vinyl ethylene); poly(ethylene-alt-propylene) with head-to-head polypropylene; poly(vinyl methyl ether) with polystyrene; and poly(vinyl methyl ether) with poly(2-chloro styrene).

4:00 PM *BB9.5

Local Friction in Random and Alternating Polyolefin Copolymers and Polyolefin Blends. Jutta Luettmer-Strathmann and Sergiy Tkachuk; Department of Physics, University of Akron, Akron, Ohio.

Polyolefin copolymers and blends differ in both thermodynamic and transport properties from the corresponding homopolymers. The local friction experienced by chain segments depends on small-scale chain properties, such as local architecture, and on the local environment of the segments. In addition to the density and the composition, which are the important environmental variables for polymer blends, the sequencing of the monomeric units plays an important role in random and alternating copolymers. In earlier work on polyolefin melts and blends, we developed a simple lattice model to investigate local friction with the aid of small-scale simulations. In this work, we extend the approach to random and alternating copolymers. An effective mixed interaction energy for a copolymer is determined self-consistently from an exact enumeration of contacts between chain segments. The resulting equation of state is combined with small-scale simulations on the mobility to yield information about the local friction coefficient. In this way, we are able to make predictions about the viscosity of random and alternating copolymers from properties of the corresponding homopolymers. We apply the approach here to polyethylene/polypropylene and polyethylene/hydrogenated polybutadiene copolymers and compare our predictions for thermodynamic and dynamic properties with experimental data. We also explore differences in the local dynamics of copolymers, melts, and blends. Financial support through the National Science Foundation is gratefully acknowledge

4:30 PM BB9.6

The Reaction of Telechelic Polymers At Multicomponent Interfaces: A Molecular Loop Study. J. Kevin Rice and Mark D. Dadmun; Department of Chemistry, University of Tennessee, Knoxville, Tennessee.

Many properties of a polymer system can often be improved with the addition of organic or inorganic fillers. This modification may result in a new material with dramatic property improvements that may include mechanical strength, viscoelastic response, chemical resistance, and gas and chemical barrier properties. However, many of the fillers do not disperse well in the polymer matrix, leading to aggregation of the filler particles that can seriously hinder the property improvements of the mixture. A great deal of theoretical and experimental work has been carried out on the compatibilization of immiscible blends of homopolymer pairs. Both theoretical and experimental studies carried out in our lab show that blocky copolymers, as opposed to random or alternating morphologies, are the best compatibilizers of a given polymer blend system. This has been attributed to the fact that blocky copolymers spread across the interface, with each block lying in the homopolymer region in which it is miscible, effectively stitching the interface together. The loops formed at the interface by each block of the copolymer entangle with the homopolymer chains of its respective region and can lead to finer dispersion and less coalescence of the minor phase during melt processing. For this work, we have studied model systems consisting of an epoxy functionalized silicon substrate and both dicarboxy terminated polybutadiene and polystyrene to monitor the reaction

conditions leading to the formation of surface bound molecular loops. Techniques including ellipsometry, contact angle measurements, and ATR-IR were used. We have also investigated the improvement in interfacial strength that loop formation at these interfaces facilitates using peel testing and asymmetric double cantilever beam (ADCB) analysis. Along with a fundamental understanding of how molecular loops form at and affect compatibilization at multicomponent polymer interfaces, it is our hope that the information obtained in this study can be used toward the goal of using molecular loops to strengthen the interface and increase dispersion in filled polymer composites. The surface of the filler particles can be functionalized by surfactants, monolayers, etc., so that a telechelic polymer can then be reacted on the surface, ultimately forming molecular loops that are chemically bound to the filler surface. These loops should then be able to entangle with the polymer matrix and compatibilize the composite material, strengthening the interface and leading to finer filler dispersion.

4:45 PM **BB9.7**

Direct Observation of Diffusion-Controlled Reactions at Polymer-Polymer Interfaces. Shane Harton¹, Richard J. Spontak², Fred Stevie³ and Harald Ade⁴; ¹Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina; ²Chemical Engineering, North Carolina State University, Raleigh, North Carolina; ³Analytical Instrumentation Facility, North Carolina State University, Raleigh, North Carolina; ⁴Physics, North Carolina State University, Raleigh, North Carolina.

Reactive coupling at an interface between polystyrene (PS) and poly(methyl methacrylate) has been characterized in the diffusion-controlled (DC) regime using dynamic secondary ion mass spectrometry. The Damkohler Number, as calculated from independently determined diffusion and reaction coefficients, is used to predict the location of this regime as a function of temperature, polymer molecular weight, and functional groups used. Implementing an extremely robust reaction involving hydroxy-terminated deuterated polystyrene and a random copolymer of methyl methacrylate and methacryloyl chloride, the early stages of the DC regime have been characterized at 120 and 140°C over a 100 h range of times. Results indicate significant reduction of reaction rates at interfacial copolymer coverage much lower than the coverage required for a stretched brush. A dynamic square gradient theory model is implemented to probe the changes in diffusivity near an interface. We have found that these complex interfacial reactions in immiscible systems cannot be completely described within the context of simple reaction- and diffusion- controlled regimes.

SESSION BB10: Poster Session: Ion-containing
Polymers, Blends and More
Chair: Kenneth Shull
Thursday Evening, December 2, 2004
8:00 PM
Exhibition Hall D (Hynes)

BB10.1

Adsorption of DNA Onto Oppositely Charged Spheres. Alison J. Hodrien, Alison M. Voice and Thomas A. Waigh; IRC in Polymer Science and Technology, University of Leeds, Leeds, United Kingdom.

The complexation behaviour of linear DNA (negatively charged) with sub-micron latex spheres, surface functionalised with amine groups (positively charged), is studied by dynamic light scattering (DLS), small-angle neutron scattering (SANS), small-angle x-ray scattering (SAXS), and micro rheology. The complexes are measured in solution as a function of component concentration (C_{DNA} , C_{SPH}) and added salt concentration (C_s). In the absence of salt, measured radius increases with C_{DNA} (C_{SPH} held constant) up to a plateau value where charge of the complex is considered to be neutralised. The presence of salt causes a decrease in the measured complex radius (up to the point where components drop out of solution), which may be due either to increased flexibility of the chains allowing them to form a more compact layer on the sphere surface, or dissociation of the two components due to screened electrostatics. More detailed experiments to determine this are underway. Motivation for this work stems from the growing body of theoretical and simulation literature on the subject, which currently lacks an equivalent body of experimental work for the purposes of comparison. Generally these works describe a range of structures (often in the form of complexation phase diagrams), from the chain tightly wrapping the sphere to the formation of large loops (or leaves) to give a rosette like complex. Parameters in the system under study have been limited to: sphere radius, chain length and salt concentration (affecting both electrostatic screening and chain flexibility), with the scope to vary pH (and therefore the charge on the two components) if required. Although much of the literature only examines systems containing one

chain per sphere, we expect that general trends (e.g. layer thickness increasing as chain stiffness increases) will remain as predicted. As a secondary motivation, the phenomena of complexation between oppositely charged structures is already exploited by man and nature (e.g. industrially for colloidal stabilisation, and for DNA packaging within cells), and a better understanding of the physics behind the systems can only serve to provide further applications.

BB10.2

Study of pH-Induced Swelling Transitions in Poly(allylamine hydrochloride)/Poly(sodium 4-styrene sulfonate) Polyelectrolyte Multilayers. Koji Itano^{1,2} and Michael F.

Rubner¹; ¹Dept. of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²JSR Corporation, Yokkaichi, Japan.

Poly(allylamine hydrochloride)/poly(sodium 4-styrene sulfonate) (PAH/SPS) polyelectrolyte multilayers contain two unique features: a weak polyelectrolyte with a pH-tunable charge density, and a strong polyelectrolyte with hydrophobic aromatic units along its backbone. When assembled at certain pH conditions, these films have been shown to undergo a pH-induced swelling transition which is discontinuous and reversible with hysteresis. This work attempts to understand the mechanism of this transition by examining PAH/SPS multilayers assembled at different solution pH. Swelling transitions and the chemical composition of the films were investigated mainly by ellipsometry, atomic force microscopy and Fourier transform infrared spectroscopy (FT-IR) both during and after immersions at various post assembly pH conditions. PAH/SPS multilayers assembled at pH 8.5 or higher exhibit pH-induced reversible swelling transitions with swelling in low pH water and deswelling in high pH water whereas films assembled at pH 8.0 or lower do not show swelling transitions at any immersion pHs in the range of pH 2.0-10.5. FT-IR data illustrate ionization and deionization of the amine groups in the PAH/SPS films corresponding to the pH-induced transition. In addition, swelling behavior after storage in several different conditions was also examined and it was found that the amount of swelling decreases dramatically after storage in moisture-rich conditions. Swelling transitions in PAH/SPS multilayers are discussed in terms of the interplay between the degree of ionization of PAH and the hydrophobicity in the films.

BB10.3

Monovalent vs. Bivalent Cation Transport Through Polystyrene Sulfonate/Polyaniline Composite Membranes. Sophie Tan and Daniel Belanger; Chimie, Université du Québec à Montréal, Montreal, Quebec, Canada.

Cation exchange membranes (CEMs) allow selective transport of cations and are used in several electrochemical technologies such as electrolysis, electrosynthesis, electro dialysis and fuel cells. However, one of the CEMs limitations is the lack of permselectivity for different types of cations. For example, direct methanol fuel cells require CEMs that allow transport of protons without methanol cross-over. Some applications of electro dialysis processes require a CEM permselective to monovalent cations against bi- or multivalent cations. One approach used to improve the CEMs permselectivity for monovalent cations is to create a positively charged layer within or on a commercial CEM.[1-3] We have previously demonstrated that the presence of polyaniline (PANI) chemically polymerized on a Neosepta[®] CMX membrane, a commercial CEM bearing sulfonate groups, decreased the Zn^{2+} transport by a factor of over ten times less than for the unmodified CMX membrane after electro dialysis in acidic media.[1-2] Here, the results obtained from ion conductivity measurements and their relation to the permselectivity behavior of the composite membranes will be presented. The presence of a polyaniline layer does not seem to increase significantly the the membrane resistance although it inhibits the transport of bivalent cations such as Zn^{2+} and Cu^{2+} . 1. Tan, S.; Viau, V.; Cugnod, D.; Belanger, D., *Electrochem. and Solid-State Lett.*, 2002, 5, E55. 2. Tan, S.; Laforgue, A.; Belanger, D., *Langmuir*, 2003, 19, 744. 3. Chamoulaud, G.; Belanger, D., *Langmuir*, 2004, 20, 4989.

BB10.4

Effect of Different Counter-Ions of Amine Neutralized Sulfonated Polystyrene on Melt-Intercalation with Pristine Montmorillonite. Nikhil Narendra Bhiwankar¹ and R. A. Weiss^{1,2}; ¹Institute of Materials Science, University of Connecticut, Storrs, Connecticut; ²Department of Chemical Engineering, University of Connecticut, Storrs, Connecticut.

Typically, polymer clay nanocomposites are made by melt mixing polymers and organically modified silicates. However, the thermal decomposition temperatures of these organically modified clays are usually comparable to the processing temperatures of most of the polymers. Also, these organic modifiers form brushes on the silicate

layers, thus hindering the possible interactions between the polymers and bare silicate surfaces. We will discuss melt intercalation of pristine montmorillonite (i.e. without any organic modification) with alkyl amine salts of neutralized sulfonated polystyrene. Sulfonated polystyrene (sPS) belongs to a class of ionomers, where in, the sulfonate group is attached to the aromatic portion of the PS chain. By varying the mol% of sulfonation and the nature of counter-ions it is possible to manipulate the morphology and electrostatic interactions in sulfonated polystyrene. These sulfonated polystyrene were neutralized with different organoammonium compounds. Whereas PS, by itself does not intercalate the clays, the Ionomers act as compatibilizers in clay nanocomposites of PS. The effects of viscosity, shear rates and mixing times on the morphology of nanocomposites was studied. The effect of weight% of sulfonated polystyrene in the batch mixtures of sPS and PS was examined by adding 10, 25 and 100 weight % of ionomer during melt-mixing in a brabender plasticorder with cloisite Na+. The effect of size of the counter-ions on intercalation was also studied by varying the alkyl chain length (such as butyl, octyl and hexadecyl). We also compared the effect on the extent of intercalation in these silicate clay galleries as a function of basicity of these counter-ions by changing the number of alkyl substituents that are attached on the N of the amine. X-ray diffractions and transmission electron microscopy were used to characterize these nanocomposites.

BB10.5

Mixing effects on the homogeneity of styrene-co-methacrylate random ionomer mixtures. Joon-Seop Kim, Ju-Myung Song and Yu-Ri Park; Polymer Engineering Dept., Chosun University, Gwangju, South Korea.

The present work aimed to see if the average ion content level in a blend can be treated as the same as the equivalent but non-blended ion content level. In experiments, the dynamic mechanical properties of various blends of poly(styrene-sodium methacrylate) (SMANa) ionomer containing 7.3 mol% of ions were compared with those of the same ionomer, non-blended, with the same amount of ions. It was found that the ionic moduli of the pure ionomer and ionomer mixtures were very similar to each other. This indicates that the mixing process does not change the degree of clustering. However, the slope of ionic plateau became steeper as the difference in the ion contents of two ionomers in an ionomer mixture increased, suggesting that the inhomogeneity of the matrix and cluster phases increased. It was also observed that the difference between the matrix and cluster T_g s increased with increasing divergence of the ion contents of two ionomers in an ionomer mixture. In addition, it was found that when the difference of the two ion contents became ca. 6 mol%, the ionomer mixture started to show a trace of a phase-separation. At ca. 9 mol%, the ionomer mixture exhibited a third loss tangent peak, possibly due to the presence of well phase-separated matrix regions. The SAXS study showed that, even though the three-dimensional arrangement of multiplets in an ionomer matrix was not changed upon the mixing of two ionomers, the inhomogeneity of phases increased.

BB10.6

Blends of NIST Linear Polyethylene Fractions with Commercial Branched Polyethylene. Thermal Behavior and Morphology Studies. Cristian Puig, Materials Science, Universidad Simon Bolivar, Caracas, Miranda, Venezuela.

Melting and crystallization behaviors and lamellar morphologies studies are carried out of blends of linear polyethylene (LPE) fractions and commercial branched polyethylene (BPE). The main concern is on blends that are fast cooled from the melt. Blends that are homogeneously mixed in the melt phase segregate upon cooling due to their different molecular architecture. Two NIST LPE 1483 and 1484a were blended with BPE. Acetone at a temperature close to its freezing point was used for quenching experiments. LPE content in binary blends was 10% or lower. Differential scanning calorimetry (DSC) was used to investigate their thermal behavior, whereas morphology studies were carried using transmission electron microscopy (TEM) of ruthenium tetroxide stained thin sections. The use of two NIST samples of different molecular weights provides the opportunity to study their role into cocrystallization and segregation effects taking place during cooling. Heating traces of quenched 3% LPE blends provide double melting behavior, characteristic of a two-phase morphology as shown by TEM. A depression in melting temperature for the LPE rich crystals is observed. By taking fresh quenched blend samples, a thermal treatment that involves heating to an intermediate temperature (118°C) between the two melting transitions was employed. Then, crystallization temperature on cooling was recorded as a function of LPE blend content. An increase in crystallization temperature (T_c) is observed when compared with neat BPE, about 4°C. Both sets of blends showed contrasting behavior, 1483 blends hardly showed T_c dependency with blend composition. Subsequent heating showed corresponding results, i.e. larger variation in melting temperature was obtained for 1484a

blends. In both sets of blends a lower melting temperature is observed when compared with neat BPE, in 1484a blends the melting temperature is slightly lower than in 1483 blends. DSC results also revealed the appearance of an additional melting peak in 1483 blends only, located above 118°C. The melting transition was further studied by varying storage time at 118°C, and the blend was heated to 160°C instead of cooling after isothermal treatment completion. The DSC traces showed the development of a melting transition at 122°C as a function of storage time. The peak is thought to be due to the crystallization at 118°C of LPE segments that had previously been incorporated within BPE rich crystals. Lamellar morphology studies of isothermally stored at 118°C 1483 blend samples confirmed the existence of an isothermally grown lamellar population.

BB10.7

Abstract Withdrawn

BB10.8

The effect of hydrodynamic interactions on reactive ternary mixtures. Olga Kuksenok¹, Kevin Good¹, Gavin Buxton¹, Valery V. Ginzburg² and Anna C. Balazs¹; ¹Chemical Engineering Department, University of Pittsburgh, Pittsburgh, Pennsylvania; ²Dow Chemical Company, Midland, Michigan.

We study the structural evolution of an A/B/C ternary mixture in which the A and B components can undergo a reversible chemical reaction to form C. We formulate a two-order parameter phase field model and adopt a lattice Boltzmann algorithm to simulate the evolution of this mixture. Using this approach, we study two different cases. In the first case, the C component is mostly localized at the interface between the A and B components and acts like a compatibilizer (i.e., C lowers the interfacial tension between the A and B fluids). We analyze the growth of the A(B) domain, as well as the saturation of the A/B interface, for different reaction rates. We compare these results for fluids in the diffusive and viscous regimes. In the second case, we consider symmetric ternary mixtures where the energetic cost of forming A/C (and B/C) interfaces is the same as the cost of creating A/B interfaces. Therefore, all three components are undergoing phase separation, i.e., the C component also forms distinct domains within the mixture. For this system, we consider the case of photosensitive reactions, which can be activated by light of the appropriate wavelength. We show that by switching the reactions on and off at the appropriate stages in the evolution of the mixture, we can precisely control the morphology and sizes of the different domains within the system.

BB10.9

Behavior of Partially Miscible Fluids in the Presence of a Temperature Gradient. Christopher Mark Pooley, Olga Kuksenok and Anna Balazs; University of Pittsburgh, Pittsburgh, Pennsylvania.

Using a novel thermal lattice Boltzmann model, we examine the rich phase behavior that develops when partially miscible fluids are subjected to a temperature gradient. In particular, we consider a binary AB fluid confined between two plates in a gravitational field. The upper plate is fixed below the critical temperature T_c and hence the nearby fluid phase-separates into A rich and B rich domains. The lower plate is fixed above the temperature T_c , and the surrounding fluid is in the homogeneous phase. This temperature gradient convects the fluid between the two plates. A coupling between convection and phase separation gives rise to unique pattern formation. A number of regimes are identified: a purely conducting state with near zero velocity, steady-state columns with convection, the periodic dripping of these columns, traveling columns, and finally, chaotic dripping from the upper surface. We suggest a simple scaling model to explain these observations. These results highlight new dynamical behavior in partially miscible mixtures.

BB10.10

Characterization of Morphology Mechanical Grafting in Immiscible Polymer Blends. Jayant Joshi, Richard L. Lehman and Thomas J. Nosker; Ceramics and Materials Engineering, Rutgers, The State University of NJ, Piscataway, New Jersey.

Blends of immiscible polymer are widely studied as routes to develop structural polymers with improved mechanical properties. Generally the weakness of the interface is limiting with regard to load transfer and compatibilizers must be used to promote structural stability and to achieve good mechanical properties. Uncompatibilized blends are comparatively easier and cheaper to process, but properties and structural stability are often lacking. Recent work in our laboratories has shown that certain blends of polymers can be processed to demonstrate structural synergism, i.e. the realization of rule of mixtures performance or better, without the use of compatibilizers. The synergism arises at specific ratios of the constituent polymers where excellent mechanical interlocking occurs due to the development of co-continuous phases. We have coined the term,

"mechanical grafting" to describe the high load transfer efficiency that occurs in these systems. Clearly this synergism is different from the kind observed owing to the partial miscibility at the interfaces, in which case the blend is synergistic for the entire composition region. In this paper, we present data and discuss the polymer properties, such as viscosity ratios and the presence of crystallinity, that are critical to the development of synergistic mechanical behavior. Viscosity ratios are important in the processing of the blends and the development of co-continuous morphologies. Crystallinity is critical in the development of mechanical forces between the phases that are the essence of mechanical grafting. These effects have been observed both in recycled PS/HDPE and virgin PS/PP blends and data will be presented in both systems. Quenching experiments that lead to reduced crystallinity of the semi-crystalline phase have been used to further analyze the role of the crystalline component in the blend on this synergistic behavior. Varying extrusion speeds produce morphologies with widely differing domain sizes at a fixed composition. A minimum striation thickness concurrent with a maximum flexural modulus at an intermediate speed demonstrates that this synergism can be improved by domain size reduction. Further analyses will explore the effect of viscosity ratios on the synergistic behavior, and a qualitative model developed to explain the microstructural-mechanical interactions in all the studied blends.

BB10.11

Modeling Reaction Induced Phase Separation in Multi-Component Polymer Blends. Ian Charles Henderson and Nigel Clarke; Department of Chemistry, University of Durham, Durham, United Kingdom.

Phase separation in polymer blends is of interest from both fundamental and applied points of view. Numerous studies, both theoretical and experimental, have been reported on the dynamics of phase separation in polymer solutions and blends following a temperature jump or quench from the one-phase region of the polymer phase diagram. Phase separation may also be induced by increasing the molecular weight of one of the components of the polymer blend. This reduces the entropy of the system, making it unstable with respect to the single phase and leads to phase separation. In such a case, the blend is quenched from a stable state in the one-phase region to an unstable state in the two-phase region, where it undergoes spinodal decomposition via reaction induced phase separation. At a fixed temperature the blend becomes more unstable as conversion, p , increases. We model the phase separation process using Cahn-Hilliard theory for polydisperse polymer blends¹. This study explores phase separation in multi-component blends (ternary and quaternary) and extends the model to include the appearance of a crosslinked network. (1) Clarke, N. Eur. Phys. J. E 2001, 4, 327.

BB10.12

Implantation of Poly(Ethyl Acrylate) in Mesoporous Poly(Styrene-Co-Divinylbenzene) Microspheres and a Study on Sound Absorption Behavior of the Particulate Composite Formed. Liang Hong^{1,2} and Yeap Hung Ng¹; ¹Chemical & Biomolecular Engineering, National University of Singapore, Singapore, Singapore; ²IMRE, Singapore, Singapore.

Porous microspheres of poly(styrene-co-divinylbenzene) (SD) have been synthesized by means of suspension polymerization, in which the monomer feed consisted of 40% of 3,4-DVB and 60% of styrenic monomers by mole; beside the crosslinker and monomers, the dispersed phase also contained an equal volume of binary diluent (decane/toluene). The portion of microspheres sorted out from the SD powder synthesized for the use as substrate in the present study had diameters ranging from 5 to 50µm, and presented a narrow porosity gap (64-67%) and a mean pore-radius range (106-117 Å) brought about by the variation of the decane/toluene ratio in the diluent. The resultant mesoporous voids were then utilized to lodge ethyl acrylate (EA), and the subsequent polymerization of EA could be restricted inside the pores and matrix of the beads via dispersing them in a particular heating medium. This feature was assured by field-emission SEM, IR and Hg-porosimetry. Two specific loadings of PEA were attained: 11% and 28% by weight. The particulate composite harvested (PEA-SD) contained basically three phases, the SD network, the semi-interpenetrating network and the tiny domains of PEA deposited in bigger pores, according to DSC analysis. Subsequently, an investigation into the acoustic absorption behaviors of PEA-SD and SD microspheres was performed by placing a round disk (6cm x 2mm, made of a particular batch of microspheres and 2wt% of binder) in the mid position of the Perspex testing tube of which a speaker and a microphone were fastened at two ends respectively, and the extent of sound absorption was evaluated by the attenuation coefficient [$\alpha = I(\text{attenuated})/I(\text{incident})$]. The investigation was carried out using the two arbitrary audio frequency bands, 100-700 Hz and 4000-5000Hz. Compared with porous SD microspheres, PEA-SD microspheres could apparently relax the incident frequency, and the magnitude of which became large in the

higher frequency sound range, and attenuate the higher frequency sound waves more effectively. The maximum attenuation level (α) was about 80% (dB). It was found that increasing PEA loading could improve rather limit the attenuation level in the higher frequency range.

BB10.13

Nanoporous Polymer Films from Immiscible Polymer Blends. Tong Liu, Rahmi Ozisik and Richard W. Siegel; Department of Materials Science and Engineering and Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, New York.

Nanoporous polymer films have been prepared using immiscible blends of polyetherimide (PEI) and poly(caprolactone diol) (PCLD). The films were prepared by spin-coating from a common solvent - dichloromethane (DCM). To create the nanoporous films, PCLD was removed by immersing the films in acetone, which dissolves PCLD only. The pore structure of the films was affected by many factors such as composition of the blend, molecular weights of the polymers, evaporation rate of the solvent during spin-coating, and various processing parameters. Field emission scanning electron microscopy was used to study the pore structure of the nanoporous films. Different porosity, pore size and pore size distribution were observed as the composition of the blend was changed. It was also found that by decreasing the PCLD molecular weight, the mean pore size was decreased and the pore size distribution became much narrower. The formation of nanometer size pores was mainly due to the fast phase separation process during spin-coating. This work was supported by IBM and the Nanoscale Science and Engineering Initiative of the U.S. National Science Foundation.

BB10.14

Characterization of Early Stages of Diffusion-Controlled Reactive Coupling at Polymer-Polymer Interfaces using NEXAFS. Shane Harton¹, Jan Luning², Fred Stevie³ and Harald Ade⁴; ¹Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina; ²Stanford Synchrotron Radiation Laboratory, Stanford, California; ³Analytical Instrumentation Facility, North Carolina State University, Raleigh, North Carolina; ⁴Physics, North Carolina State University, Raleigh, North Carolina.

Due to its surface sensitivity (approx. 1-10 nm) and highly resolved chemical analysis capabilities, near edge x-ray absorption fine structure spectroscopy (NEXAFS) can be used to quantify the early stages (approx. 1-100x disentanglement time) of reactive coupling at a polymer-polymer interface. The reaction between dPS-OH and P(MMA-co-MAC) has been monitored at these early stages, after removing to PS/PS-OH layer, in an attempt to provide detailed information for comparison to existing theories. Using ultra high resolution NEXAFS at the Stanford Synchrotron Radiation Light Source (SSRL), we have been able to distinguish between reacted dPS at the interface and unreacted PS matrix polymer that is "stuck" at the interface due to entanglements. Secondary ion mass spectrometry (SIMS), which provides real-space depth profiles, is used to validate this new method for characterizing reactions at interfaces. It is evident that NEXAFS yields quantitative information regarding reactive coupling at interfaces at timescales that are unresolvable with SIMS.

BB10.15

Probing Reaction Mechanisms at Polymer-Polymer Interfaces using Supercritical CO₂. Shane Harton¹, Richard J. Spontak², Fred Stevie⁴, Jonathan Sokolov³, Miriam H. Rafailovich³, Tadanori Koga³ and Harald Ade⁵; ¹Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina; ²Chemical Engineering, North Carolina State University, Raleigh, North Carolina; ³Materials Science and Engineering, SUNY Stony Brook, Stony Brook, New York; ⁴Analytical Instrumentation Facility, North Carolina State University, Raleigh, North Carolina; ⁵Physics, North Carolina State University, Raleigh, North Carolina.

Recently, scCO₂ has attracted considerable attention as an environmentally safe alternative to conventional organic solvents used throughout the chemical and polymer industries. Here, direct evidence is provided, using secondary ion mass spectrometry (SIMS) and x-ray reflectivity, that reactive coupling at a PS-PMMA interface can be achieved in the presence of scCO₂ at temperatures substantially below the intrinsic glass transition temperatures (T_g 's) of the polymers employed. By using scCO₂ to cover a large range of diffusivities within a rather small range of temperatures (36-50°C) and highly reactive functional groups, the diffusion-controlled regime can be explored over a range of characteristic times with nearly identical reactivities. It is also shown that longer effective residence times, as scaled with known diffusivities, indeed show a simple reaction-controlled type behavior that establishes two proposed mechanisms within early stage diffusion-controlled reactions. One mechanism involves gradient diffusion of reactive polymers to the interface, and the other involves slow penetration of the unstretched

block copolymers near the interface.

BB10.16

Abstract Withdrawn

BB10.17

Morphological, Mechanical and Thermal Properties of Ternary Composites with Poly(ethylene terephthalate)

Matrix. Mert Kilinc and Goknur Bayram; Department of Chemical Engineering, Middle East Technical University, Ankara, Turkey.

Ternary composites were prepared using a recycled poly(ethylene terephthalate), PET as the matrix material, short glass fiber as the reinforcing filler and thermoplastic elastomer as the toughener. Bottle grade recycled PET was mixed in a twin screw extruder with a thermoplastic elastomer which is a terpolymer of ethylene/methyl acrylate/glycidyl methacrylate (E-MA-GMA), and E type short glass fiber is fed to the extruder from a side feeder. In this study, PET was mixed with from 10 to 50 % elastomer, and SGF was added to the system in the range from 10 to 40 % by weight. Processing parameters were kept constant during extrusion. The produced composites were characterized in terms of their morphologies, mechanical and thermal properties. SEM photographs showed that adhesion between the matrix and fiber increased considerably with elastomer addition. Tensile properties of the composites showed maxima with elastomer and SGF contents. In samples with 10% elastomer, highest tensile strength values were observed. Optimum young modulus value was obtained for the composite containing 20% elastomer/20% glass fiber/60% recycled PET. Results of impact tests showed that impact strength increased significantly after 30% elastomer. Thermal analyses were done by using a DSC (differential scanning calorimeter). Degree of crystallinity decreased with increasing elastomer content, but melting points of the composites were not affected significantly. Effect of fiber length distribution has been also studied on selected composites.

BB10.18

Processing and Characterization of Short Glass Fiber / ABS / Polyamide-6 Composites. Guralp Ozkoc¹, Goknur Bayram² and Erdal Bayramli³

¹Department of Polymer Science and Technology, Middle East Technical University, Ankara, Turkey; ²Department of Chemical Engineering, Middle East Technical University, Ankara, Turkey; ³Department of Chemistry, Middle East Technical University, Ankara, Turkey.

The main objective of this study is to determine the effects of short glass fiber (SGF) content and extrusion processing conditions such as screw speed and barrel temperature, on the mechanical properties, and morphologies of structural composites produced by compounding SGFs with poly(acrylonitrile-butadiene-styrene), ABS. It was also aimed to determine the effects of fiber/matrix adhesion at the interface, which was promoted by incorporation of polyamide 6 (PA6) to the ABS/SGF composites. The first part of the study showed that adhesion capacity of γ -aminopropyltrimethoxysilane coupling agent (APS) treated glass fibers were highest among the others studied; therefore APS was selected as the coupling agent of the study to be used in processing experiments. Increasing the SGF concentration in ABS matrix from 10wt% to 30wt% resulted in improved tensile strength, tensile modulus and flexural modulus, but drastically lower strain at break and impact strength. The average fiber length decreased when the concentration of glass fibers increased. The increase in screw speed decreased the average fiber length; therefore tensile strength, tensile modulus, flexural modulus and impact strength were affected negatively and strain at break was affected positively. The increasing extrusion temperature decreased the fiber length degradation; therefore tensile strength, tensile modulus, flexural modulus and impact strength increased. At higher temperatures, ABS matrix degraded and the mechanical strength of composites decreased. The use of PA6 in the composites increased the average fiber length owing to the low melt viscosity of PA6 incorporated composites. Tensile strength, tensile modulus, flexural modulus and impact strength values increased with an increase in the PA6 content of ABS/PA6/SGF systems. These results were also supported by the SEM micrographs of ABS/PA6/SGF composites indicating that there exists improved adhesion between SGFs and ABS/PA6 matrix.

BB10.19

Abstract Withdrawn

BB10.20

Increasing the Compatibility of Polymer Blends through Supercritical Carbon Dioxide Exposure.

Mitchell Stephen Fourman¹, Edmund Palermo², Ronald

Occhiogrosso¹, Miriam Rafailovich¹, Jonathan Sokolov¹, Mayu Si¹, Tadanori Koga¹ and John Jerome¹; ¹Materials Science and Engineering, Stony Brook University, Stony Brook, New York;

²Cornell University, Ithaca, New York.

Most polymer blends are incompatible, which adversely affects their mechanical properties. Recently Koga et al [Europhys. Lett, 60 (4), 559-565, (2002)] have shown that supercritical CO₂ (scCO₂) can penetrate to within a few polymer radii of gyration near polymer surfaces when it is in a regime known as the density fluctuating state. In this region a large dilation of the polymer occurs regardless of the polymer/scCO₂ miscibility. Hence in this narrow interfacial region scCO₂ can act as a universal co-solvent for all polymer blends. Here we show that this principle can also be used to decrease interfacial tension in bulk samples of immiscible polymers mechanically blended together in a Brabender type mixer, resulting in a significant increase in the mechanical properties of the blends. The following immiscible polymer blends, Polymethyl methacrylate and Polybutadiene (PMMA-PB), PMMA and Ethylene Vinyl Acetate (PMMA-EVA), and PMMA and Polystyrene (PMMA-PS), were melt mixed, molded, and exposed to scCO₂ at variable pressures. The mechanical properties were then measured using Dynamic Mechanical Analysis (DMA) combined with Instron tensile tests. The results showed dramatic improvements in both moduli and ductility when the blends were exposed to scCO₂ at pressures and temperatures along the density fluctuation regime. The morphology of the samples was studied with Scanning Electron Microscopy (SEM), which showed that significant foaming had occurred in the supercritical regime. The foaming also increased the surface to volume ratio and hence increased the ability of the scCO₂ to penetrate into the materials in the along the density fluctuating ridge. Transmission Electron Microscopy (TEM) of splines revealed a large degree of compatibilization had occurred between the polymers confined in the fiber-like structures. Further research will be performed regarding UV and humidity resistance, corrosion and deterioration rate of the blends produced by this method.

SESSION BB11: Polymer Blends: Phase Behavior, Structure, and Properties

Chairs: Ralph Colby and Robert Weiss

Friday Morning, December 3, 2004

Room 309 (Hynes)

8:30 AM BB11.1

Reduction of Melt Miscibility in Polymer Blends with Coexisting Phase Transitions. Howard Wang¹ and Boualem

Hammouda²; ¹Materials Science and Engineering, Michigan Technological University, Houghton, Michigan; ²National Institute of Standards and Technology, Gaithersburg, Maryland.

Individual phase transitions in polymers have been studied extensively during the last five decades, and are relatively well understood, whereas systematic studies that focus on the interplay between two or more transitions have just begun. We have investigated the phase behavior of blends of hydrogenated polyethylene and deuterated amorphous polypropylene, which exhibit both liquid phase separation and crystallization transitions. The metastable liquid phase separation boundaries, which are predicted from small angle neutron scattering of blends at temperatures above the equilibrium melting temperature, lie below the equilibrium melting temperature. However, real liquid phase separation temperatures are found far above the extrapolated mean field values while right below the equilibrium melting temperature. The reduction of melt miscibility in this blend is attributed to additional driving forces for segregation in supercooled melts. The existence of this liquid phase separation is meaningful only in the scope of metastability and non-equilibrium thermodynamics.

8:45 AM BB11.2

Liquid Crystal Influenced Self-assembly in Mesogenic Polymer and Liquid Crystal Blends. Lanfang Li, Carmen Otilia

Catanescu and Liang-Chy Chien; Liquid Crystal Institute, Kent State University, Kent, Ohio.

Due to different mechanisms of interaction, a solution system will manifest different attributes. Especially in anisotropic solvents, in possession of anisotropy, a liquid crystalline monomer will form different polymer morphologies due to the templating effect of anisotropic liquid crystal hosts during polymerization induced phase separation. This effect will lead to control of nanoscaled polymer morphology. Various applications of such morphology in micro-prisms and nanoscaled optical devices are possible. In this work, the liquid crystal templating effect - transferring of the ordered structure form host to guest - on diacrylate mesogenic monomer lead to a well ordered self-assembled polymer structure and this system was studied systematically by performing photo-polymerization in liquid crystal hosts under different conditions, such as, UV light intensity, monomer concentration, photoinitiator concentration, temperature and mesophases. Well ordered polymer morphologies were explored by the SEM studies. The electro-optical properties corresponding to the

variation of polymerization conditions was studied as well.

9:00 AM BB11.3

Morphology Development Associated With Polymer Blends. Tomoko Hashida, Ying Hua and Shaw Ling Hsu; Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts.

Morphology development in crystallizable polymer blends has been characterized. Specific emphasis was given to poly(hexamethylene adipate) (PHMA) and poly(hexamethylene sebacate) (PHMS) mixed with non-crystallizable poly(propylene glycol) (PPG). Although these two polyesters have similar chemical structure, PPG/PHMA blends are generally immiscible while PPG/PHMS blends are miscible. These differences in phase behavior dictate the morphological development at many different scales. The crystallization kinetics and morphological features can be most directly investigated using optical microscopy. Vibrational (both infrared and Raman) spectroscopic features associated with the chain conformation ordering process have also been identified. Although such structural information does not represent the overall crystallization process, we are able to obtain spectroscopic data with high temporal and spatial resolution. The conformational order is then used to represent the crystallization process. Detailed composition distribution within various morphological domains can also be analyzed. PPG/PHMS miscible blends exhibit a homogeneous morphology developed from the one-phase liquid. In contrast the immiscible PPG/PHMA blends resulted in a morphology composed of a PHMA-rich phase and PHMA-poor phase. Crystallization in the PHMA-rich phase is found to be faster than that in the PHMA-poor phase. The observation is also made that crystallization initiates at interfaces between the PHMA-rich and PHMA-poor phases and the crystals grow inward in PHMA-rich phases. In heterogeneous nucleation, the interfaces enhance nucleating ability. Interfaces in the liquid-liquid phase separation promote the nucleation process in immiscible blends. The crystallization kinetics of polyesters in blends has been investigated using infrared spectroscopy. When cooled from the melt, the intensity of crystalline bands of polyesters increases. The crystallization rate in PPG/PHMS miscible blends is much slower than that in PPG/PHMA immiscible blends. The degree of crystallinity calculated from the normalized intensity of crystalline bands is lower in PPG/PHMS miscible blends. The effect of local concentration on the crystal growth process is considered. PHMS is homogeneously distributed in PPG/PHMS miscible blends. Different distributions of crystallizable components between immiscible and miscible blends will change the crystallization kinetics and associated morphology development. Detailed composition distribution obtained from micro-Raman reveal the relationship between morphology development and miscibility behavior.

9:15 AM BB11.4

The Effect of Molecular Orientational Order on the Polymerization of 3,4-Ethylenedioxythiophene. Xiaoli Zhou, Carmen Otilia Catanescu and L. C. Chien; Liquid Crystal Institute, Kent State University, Kent, Ohio.

The paper presents the retention of molecular orientation in cross-linked polymer networks obtained by photopolymerization of different diacrylate monomers in a liquid crystal (LC) host (smectic and cholesteric), and the effect of this order on the polymerization of 3,4-ethylenedioxythiophene (EDOT), as the conductive monomer. The conductivity measurements showed anisotropy in conductivity for the poly(3,4-ethylenedioxythiophene) (PEDOT) obtained from polymer network formed in smectic phase, while the PEDOT/polymer network composite films obtained in the cholesteric phase showed a uniform conductivity regardless of the molecular orientation of the polymer networks.

9:30 AM BB11.5

Monodisperse droplet formation in binary mixtures between rough, chemically patterned surfaces. Rolf Verberg¹, Christopher M. Pooley¹, Julia M. Yeomans² and Anna C. Balazs¹; ¹Chemical and Petroleum Engineering Department, University of Pittsburgh, Pittsburgh, Pennsylvania; ²Theoretical Physics, Oxford University, Oxford, United Kingdom.

From optimizing the processing of polymeric materials to controlling blood flow in natural or synthetic channels, it is necessary to understand the dynamic behavior of complex fluids in confined geometries. Developing such an understanding is complicated by the fact that in the systems of interest, the confining walls can display chemical or physical heterogeneities and the fluid usually contains multiple components. Furthermore, this multi-component mixture is driven by an imposed flow (which transports the fluid through the processing chambers or the blood vessels). In such systems, the fluid-wall, fluid-fluid and fluid-flow interactions can all affect the phase behavior and morphology of the confined mixture. While

researchers have recently examined how chemical variations in the confining walls affect the flow patterns of driven complex fluids, there have been few studies on the effect of surface roughness on such systems. Using a computational model, we undertake the first study of a phase-separating blend that is driven to flow past surfaces, which contain well-defined roughness or asperities. We focus on binary, immiscible fluids since this is the simplest multi-component mixture that can display distinct pattern formation in response to the presence of the asperities. As we will show, the relative size and shape of the asperities has a dramatic effect on the flow patterns, dictating whether or not the system reaches a steady-state structure or displays periodic structure formation within the confined system. In the latter case, the AB mixture forms monodisperse droplets of A within the B phase; such emulsions are crucial constituents in the pharmaceutical, food and cosmetic industries. What sets the proposed method apart from other techniques for creating these mixtures is that the droplet size is controlled by the surface morphology and chemistry, which can be readily manipulated by standard micro-contact printing methods. Thus, it becomes possible to form monodisperse droplets of a variety of chemical compositions and range of sizes through a relatively economic process.

9:45 AM BB11.6

The Effect of Chain Sequence Distribution on the Dynamics of Copolymers in a Homopolymer Matrix: A Monte Carlo and Neutron Reflectivity Study. Sudesh Kamath and Mark D. Dadmun; Department of Chemistry, University of Tennessee, Knoxville, Tennessee.

Copolymers can be used as interfacial modifiers in phase separated polymer blends and selective surface segregation. Important parameters in this process include the amount of copolymer that migrates to the surface and the rate of this process, both of which are altered by changing the copolymer microstructure. We have monitored the diffusive behavior of various copolymers of Styrene(S) and Methylmethacrylate (MMA) in a PMMA matrix using neutron reflectivity experiments. These results are compared to results from dynamic Monte Carlo simulations on a model blend containing copolymers of different architectures dispersed in a homopolymer matrix. In conjunction, these studies provide valuable insights into the effects of chain architecture on the structure and dynamics of copolymers in a homopolymer matrix.

10:30 AM BB11.7

Target Morphologies In Polymer Blends. Nigel Clarke and Ian Henderson; University of Durham, Durham, United Kingdom.

Exploiting the ability of nature to turn raw ingredients into remarkable materials has long been a goal of fundamental and applied science. One active area of research involves polymer mixtures that phase separate to form elegant structures with microscopic dimensions. The resultant materials often have properties substantially greater than the sum of the parts. A drawback of phase separation in polymer blends is that a lack of control over the final structure limits our ability to tune the properties. One proposed method for gaining greater control is to undertake a two-step quench process. The blend is quenched to an unstable state in the two-phase region where it undergoes spinodal decomposition. The mixture is allowed to coarsen before a second quench was applied to further within the unstable region. During the initial stages following the second quench smaller secondary domains appeared briefly in the primary domains obtained from the first quench step [1]. We have also proposed a second approach [2] in which polymer particles are dissolved in a liquid bath of a chemically different polymer. If the temperature is altered before complete dissolution, the two types of polymer will phase separate, but with the initial structural development being strongly influenced by the presence of the inhomogeneities present due to incomplete dissolution. To illustrate this concept theoretically, we show how ring-shaped particles can be coaxed into briefly forming from circular particles; the shell being composed of the same polymer as the original particle, but the core is filled with the bath polymer. The method opens a new avenue for fabricating tailored structures, whose range and dimensions are constrained only by the variety of sizes and shapes of the original particles. [1] Ian Henderson and Nigel Clarke, *Macromolecules* 2004; 37: 1952. [2] Nigel Clarke, *Physical Review Letters* 2002; 89: 215506.

10:45 AM BB11.8

Local Control of Periodic Pattern Formation in Sheared Polymer Blends. Olga Kuksenok¹, David Jasnow² and Anna C. Balazs¹; ¹Chemical Engineering Department, University of Pittsburgh, Pittsburgh, Pennsylvania; ²Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, Pennsylvania.

Via a coarse-grained model, we simulate the dynamics of a binary, immiscible polymer blend that is driven through a three dimensional microchannel. At the inlet of the channel, we assume a checkerboard

arrangement of the components. We find that local perturbations in the temperature at the center of this checkerboard pattern can be exploited to create periodic, oscillatory patterns along the length of the channel. We derive scaling arguments that allow us to estimate the period of the oscillatory structures. We also analyze the stability of these patterns and the mechanism for the wavelength selection within the system. We find that relatively small changes in the local perturbations at the inlet of the channel can lead to dramatic changes in the morphology along the channels length and can be used to design well-controlled periodic structures.

11:00 AM **BB11.9**

Linear, Graft and Branched Vinyl and Lactone Copolymers by Ti Catalyzed Living Polymerizations Initiated from Epoxides and Aldehydes. Alexandru D. Asandei^{1,2}, Isaac W. Moran¹, Gobinda Saha¹ and Yanhui Chen²; ¹Institute of Materials Science, University of Connecticut, Storrs, Connecticut; ²Chemistry, University of Connecticut, Storrs, Connecticut.

The Ti(III)Cp₂Cl-catalyzed radical ring opening of epoxides or reduction of aldehydes affords in situ Ti alkoxides and carbon centered radicals. Thus, radical polymerizations can be initiated from the epoxide derived radical. As such, polymers or monomers containing pendant epoxide groups (e.g. glycidyl methacrylate) allow for radical grafting reactions or for the formation of branched structures by self condensing vinyl polymerization. Moreover, paramagnetic Ti(III) complexes act as persistent radicals and mediate living radical polymerization via reversible capping of the growing chains. In addition, Ti alkoxides initiate the living ring opening polymerization of caprolactone. Thus, complex copolymer architectures such as multiarm star/graft copolymers can be conveniently synthesized in a living fashion by this methodology.

11:15 AM **BB11.10**

Quantification of Environmental Stress Cracking in Polymer Blends through Eyring Modeling. Peyton L. Hopson and Robert B. Moore; Department of Polymer Science and Engineering, University of Southern Mississippi, Hattiesburg, Mississippi.

A new test method has been developed and applied to both miscible and immiscible polymer blends to quantify polymer blend environmental stress cracking resistance (ESCR), independent of the inherent mechanical properties of the separate blend components. Standardized ESCR test methods, which rely heavily on the flexural and tensile properties of the material, often fail to effectively quantify the effect of fundamental polymer blend properties such as morphology, crystallinity and miscibility on ESCR. The new test method assumes a mechanism of chain slippage and cleavage, similar to many yield theories including the Eyring model, for crack/craze formation. By performing tensile tests at various strain rates in the presence of a fluid, the temperature normalized yield stress may be plotted versus the natural log of the strain rate as per Eyring's theory. Plots for all blends and fluids tested resulted in a linear correlation, indicative of activating a single relaxation, allowing the calculation of the activation energy (E_a) and activation volume (V_a) for crack/craze formation. In order to deconvolute the contributions of the environment on the cracking/crazing behavior, the Eyring values obtained in air for each blend were used to formulate reduced E_a and V_a values allowing the independent investigation of the previously stated fundamental polymer blend properties with ESCR. In order to validate the test method, the method was applied to two polymer blend systems: a miscible blend, polycarbonate/copolyester (PC/PCTG), and an immiscible blend, polycarbonate/poly(butylene terephthalate) (PC/PBT). For the two systems, the results for both E_a and V_a followed theoretical predictions showing an exponential decrease in ESCR with a decrease in interfacial tension at the polymer/liquid interface. For the PC/PBT blend system, it was found that for interfacial tension values above 15 cal/cm², the blends had lower ESCR compared to the two pure polymers, while for interfacial tension values below 15 cal/cm² the blend ESCR followed nearly an additive rule. The interfacial tension value of 15 cal/cm² corresponds to the point of greatest decay in the ESCR vs interfacial tension plot for both pure polymers. The miscible blend system, PC/PCTG, results in a near additive dependence on ESCR for all the blends except for interfacial tension values below 10 cal/cm², which is in direct contradiction to the results found for the immiscible blend. This result may be attributed to the diffusion of fluids with smaller molar volume, and higher interfacial tension, within the polymer phase interface of the immiscible blend effectively lowering the ESCR.

11:30 AM **BB11.11**

Hard Particle Toughening of Amorphous Polymer Blends: Iso-Tg Blend Series. Roger L. Aronow¹, Robert E. Cohen¹, Ethan M. Parsons² and Mary C. Boyce²; ¹Chemical Engineering, MIT, Cambridge, Massachusetts; ²Mechanical Engineering, MIT, Cambridge, Massachusetts.

While soft-particle toughening of thermoplastics is well-accepted, significant hard-particle toughening has only been demonstrated in semicrystalline polymer matrices. The present work investigates the possibility of and criteria for toughening amorphous polymer systems with rigid spherical particles. The polymer matrix is a blend of poly(methyl methacrylate), poly(vinyl chloride), and dioctyl phthalate, a plasticizer. This blend is shown to be homogeneous over a significant portion of its composition space when processed via melt mixing. Properties such as glass transition temperature and stress-strain behavior are shown to vary smoothly with composition in the miscible region. Thus, when a filler is added to the system, the properties of the interparticle polymer ligaments can be tuned and correlated with the behavior of the composite. Using an empirical model for the T_g of this blend, constant-T_g contours are calculated. Composites are made by incorporating barium sulfate filler (100 nm, quasi-spherical particles). The properties of the unfilled blends along one constant-T_g contour, as well as filled composites thereof, are analyzed via mechanical and rheological techniques. Increases in modulus and Izod impact strength are observed in the filled composites relative to the unfilled blends.

11:45 AM **BB11.12**

Morphological effects on glass transitions in immiscible polymer blends. Vivek Thirtha, Richard Lehman and Thomas Nosker; Ceramics and Materials Engineering, Rutgers University, Piscataway, New Jersey.

Immiscible Polymer Blends (IMPB) are of significant interest due to their potential to provide properties near the constituent rule of mixtures without requiring alloying or compatibilization of the blend. The most successful IMPBs also combine complementary functionalities of the components, such as the well-known PS/HDPE system that exhibits toughness similar to high-density polyethylene and stiffness more characteristic of polystyrene. Present work in our laboratory focuses on optimizing blend properties through closely controlled melt formulation and melt processing techniques. This paper describes the interesting effects of these morphologies and structures on the glass transition of glassy polymers in a semicrystalline matrix. Immiscible blends of PS/PP, PMMA/PP, and PS/HDPE were prepared from commercially available polymers using melt processing and extrusion without additives. The volume fractions of the components were varied from 0 to 1. SEM analysis of the blends showed a range of morphologies over the composition range from small fibrous inclusions at low volume concentrations through intertwined co-continuous structures at specific intermediate compositions, and a reversal of this configuration at high volume fractions. The glass transition of the glassy polymer was measured with differential scanning calorimetry using the sensitive and high resolution modulated DSC method. For the first time a systematic change in glass transition of glassy polymers is observed as a function of composition in various immiscible polymer blends. Results show that the glass transition of the glassy phase increases with a reduction in volume fraction by approximately 4°C for polystyrene and 6°C for polymethylmethacrylate. T_g peak broadening effects, indicative of a distribution of T_g values, and the variation in peak intensity effects, indicative of supercooling, are also discussed. Several models are under consideration to explain this novel behavior. Since the increase in T_g is greatest when the glassy fraction is low and the fiber diameter is small, the effect may be due to constrained relaxation of the glassy phase thus increasing T_g. Alternatively, the crystallization of the semicrystalline polymer with a concomitant volume reduction may provide sufficient pressure on the glassy phase to increase its T_g. Experimental data will be discussed in the context of these models.

SESSION BB12: Multicomponent Polymers: Electronic and Optical Properties

Chairs: Z.Y. Cheng and Jutta Luettmmer-Strathmann
Friday Afternoon, December 3, 2004
Room 309 (Hynes)

1:30 PM **BB12.1**

Color Tuning In Polymer Light Emitting Diodes Utilizing Micrometer and Nanometer Phase Separated Blends. Nisha Ananthakrishnan¹, G. Padmanaban², S. Ramakrishnan² and John R. Reynolds¹; ¹Chemistry, University of Florida, Gainesville, Florida; ²Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India.

We report on the utilization of orange emitting poly(2-methoxy-5-(2-ethylhexyloxy)-phenylenevinylene) (MEH-PPV), blue emitting poly[[9,9-dihexylfluorenyl-2,7-diyl]-co-(9-ethyl-3,6-carbazole)] (PFH-PEtCz) and poly(methyl methacrylate) (PMMA) in designing phase separated blends for polymer LEDs with color tuning in the visible region. Blends containing low compositions of (1 to 20 wt $\frac{0}{00}$)

of both conjugated polymers together in PMMA form disk-like structures ranging in size from 300 - 500 nm giving rise to nano and micrometer light-emitting domains. By increasing the amount of PFH-PeTcZ in the blend relative to MEH-PPV, the maximum wavelength for emission shifts from 580 nm down to 550 nm, along with an emission peak evolving at 420 and 440 nm. The resultant colors observed for the emitted light were red orange, yellow, green and blue (along with a whitish light) as a fraction of total conjugated polymer content and their ratio in the blend. The colors of emitted light from devices were characterized using formalism and definitions established by the Commission Internationale de l'Eclairage (CIE). The in-plane morphology showed domains tending to bloom up on the surface and were characterized by atomic force microscopy and scanning electron microscopy. Electroluminescence studies showed that a range of colors could be obtained as a function of voltage for a given blend composition.

1:45 PM **BB12.2**

Probing Electronic Processes at Polymeric Heterojunctions With Pressure-Dependent Optical Spectroscopy.

Johanna P. Schmidtke, Arne C. Morteau, Carlos Silva and Richard H. Friend; Cavendish Laboratories, University of Cambridge, Cambridge, United Kingdom.

Polyfluorenes are promising materials for optoelectronic applications due to their high photo- and electroluminescence yields. Among the most efficient light-emitting diodes constructed with this class of materials are those fabricated from blends of hole- and electron-accepting derivatives. 'Distributed heterojunction' structures, formed by de-mixing of the two components from common solution, display high luminous efficiencies (19 lm/W for green emission), and operate at low voltages (2.1 V for 100 cd/m²). This is because electron-hole capture across the heterojunction is arranged to be a barrier-free process to form a stable interface state (termed an exciplex) which can be converted to bulk exciton states endothermically (with activation energy of 100 meV). Due to the importance of intermolecular states to processes such as electron-hole capture at heterojunctions as well as transport through the bulk polymer, a better understanding of the nature of these states is desirable. Hydrostatic pressure is a useful tool to probe intermolecular interactions without the need for chemical alterations to the materials. We present time-resolved photoluminescence and Raman spectroscopic studies on thin films of polyfluorene homopolymers and multi-component blends under hydrostatic pressure to show the significance of intermolecular interactions for the excited state energetics and dynamics in polyfluorene blends.

2:00 PM **BB12.3**

Control over the Morphology of Regioregular

Poly(3-Hexylthiophene). Shijun Jia, Rui Zhang, Malika Jeffries-El, Richard McCullough and Tomasz Kowalewski; Carnegie Mellon University, Pittsburgh, Pennsylvania.

Poly(3-alkylthiophene)s have been widely studied during the past two decades due to their potential applications in photonics and electronics. Within this time period synthetic routes have been developed that allow for the synthesis of regioregular head-to-tail poly(3-alkylthiophene)s (HT-P3AT)s, creating materials with improved electronic and photonic properties over regiorandom analogs. While there are numerous papers addressing the synthesis and application of HT-P3HT, there are limited studies on the relationship between the morphology of HT-P3HT films and the factors that affect film formation. The final structure of HT-P3HT thin solid films prepared by solution casting is dependent on both thermodynamic and dynamic factors, such as architecture, molecular weight (MW), solvent, temperature, and external force field. In this study we attempted to elucidate this relationship by using atomic force microscopy (AFM) to monitor the morphology of thin films prepared from P3HT and P3HT based diblock copolymers of various different MW, cast from several different solvents. Our results indicate that both the homopolymer HT-P3HT and its block copolymer with polystyrene (HT-P3HT-b-PS) can self-organize into well-defined narrow, elongated aggregates (nanowires). For HT-P3HT, we systematically investigated the effects of solvent and MW on the morphology of thin films. We found that low MW HT-P3HT easily forms nanowires upon casting from toluene, chloroform, and xylene. In the high MW HT-P3HT, the formation of nanowires was suppressed in chloroform due to the fast rate of solvent evaporation. Similar solvent dependence of morphology was observed in HT-P3HT-b-PS copolymers. Interestingly, nanowires of block copolymers could be aligned by casting their solution onto flat silicon substrate patterned with interdigitated gold electrodes in the presence of an electric field. The ability to control the morphology at this level may be important for achieving better understanding of structure-electrical properties relationship in semiconducting polymers and may allow performance optimization of devices utilizing these materials.

2:15 PM **BB12.4**

Study and tailoring of composite and nanocomposite materials for lithium battery electrode application.

Vincent Gaudefroy, Delphine Guy, Eric Ligneel, Bernard Lestriez, David Albertini and Dominique Guyomard; Institut des Matériaux Jean Rouxel, UMR CNRS 6502, Nantes, France, Nantes, France.

The electrode of a lithium battery is a very complex medium which needs to bring efficiently the ionic reactants and the electrons to the surface of the active material (AM) particles. Such a composite material is generally obtained by mixing together the AM grains with non-electroactive additives such as a very fine powder of carbon black (CB) and a polymeric binder (B). The CB additive is supposed to ensure electronic percolation within the composite electrode. The polymeric binder has a complex and multiple role. It brings its mechanical strength to the electrode and it allows for a good electric contact between the electrode and the current collector. For long-lasting battery operation, the composite electrode complex medium needs to be chemically and electrochemically stable. It also needs to maintain a good mechanical cohesion in the presence of the liquid electrolyte and during the volume changes which occur when inserting and extracting Li⁺ ion within the AM grains. The purpose of the present work is to get some understanding of the role of the morphology and organization of the different components inside the composite electrode on the electrode performance, in order to be able to further optimize it. The study of the effect of some non-electroactive components of the battery on its performance corresponds to a new research area which has barely been studied yet. In this presentation we compare the microstructure of various composite electrode studied by SEM, TEM, AFM, DSC, DRX, and RMN techniques. Model composite electrodes are prepared in which the surrounding of the same AM was changed by playing with the nature of the polymer binder, its plasticization, and using mixed polymers with complementary properties. In each case the electrical and electrochemical response was followed. Well performing composite electrode material with efficient electronic conduction network was achieved from a more homogeneous CB distribution due to good binder-CB interactions and from optimum ratios between plasticized binder and CB [1]. 1 - D. Guy, B. Lestriez and D. Guyomard, Adv. Mater., 16, 553 (2004).

2:30 PM **BB12.5**

Multicomponent Materials as Lithium-Ion Conductors.

Nicole L. Wagner, Susan J. Babinec, Huiqing Zhang, Andrew T. Talik and Wendy J. Klein; Materials Sciences, Dow Chemical, Midland, Michigan.

Portable electronic devices require a safe, flexible, high-energy density and light weight power source. Solid-state lithium-ion batteries composed of polymeric electrolyte materials can help to address this need. The paradox of designing a solid polymer electrolyte is introducing the physical properties of a *solid* while maintaining the *liquid-like* properties necessary for commercially and practically significant ionic conduction. We have approached this challenge in a step-wise fashion, by initially establishing an extensive baseline of conductivity and physical property data on poly(ethylene oxide) homopolymers. Several multicomponent systems were then designed which incrementally increased the chemical complexity of the electrolyte. The system variables included random and block copolymers of poly(ethylene oxide), sources of lithium ions (e.g. lithiated nanoparticles), and incorporation of low molecular weight additives. A detailed study was performed correlating conductivity with thermal properties, viscoelastic properties, and electrolyte composition (molecular weight, molecular architecture, and lithium source). While there are scattered reports of various materials in the literature, comparison is somewhat difficult due to differences in details of methodologies. We offer a comparison across this design space from a single experimental protocol.

2:45 PM **BB12.6**

Interpenetrating Polymer Networks Containing Poly(3,4-Ethylenedioxythiophene): New Interesting Electrically Stimulable Materials.

Claude Chevrot, Dominique Teysse, Frederic Vidal and Cedric Plesse; Laboratoire de Physicochimie des Polymères et des Interfaces, Université de Cergy Pontoise, Cergy Pontoise, France.

Interpenetrating polymer networks (IPN) have been developed since many years and are very interesting in order to prepare materials having improved properties [1]. The incorporation of a conducting polymer in an IPN (or a semi-IPN) leads to a conducting interpenetrating polymer networks (CIPN) which constitute electrically stimulable new materials [2]. We will describe the synthesis, properties and some applications of CIPN obtained from the chemical polymerization of 3,4-ethylenedioxythiophene (EDOT) leading to the corresponding polymer (PEDOT) inside the IPN. IPN are prepared mainly as a two or three components system. We started

from cross-linked polyoxyethylene (PEO) and polycarbonate (PC) or polybutadiene (PB) to elaborate the IPN in which EDOT is then polymerized. These IPNs are flexible or rigid following to the PEO/PC (or PB) ratio in the IPN. After introduction of an electrolyte (for example LiClO₄/solvent) in the CIPN, this one can be used notably because the electrochemical properties of PEDOT inside the CIPN are kept compared with that of a PEDOT film electrodeposited on a platinum electrode. Consequently, the electrochromic effect is kept in the CIPN leading to interesting devices [3]. Furthermore, we will describe that these CIPNs work in air as an actuator for a long time under a low applied potential (2-3 volts) if the electrolyte is a room temperature ionic liquid such as 1-ethyl-3-methylimidazolium salt [4]. We observed that no degradation of the actuator and no drying occurred during period as long as three months. These actuators can achieved more than 7millions bendings from 1 to 18 Hz. 1- L. H. Spierling, D. Klemperer, L. A. Utracki (Eds). "Interpenetrating polymer networks" Washington (1991), American Chemical society. 2- F. Vidal, J-F. Popp, C. Chevrot, D. Teyssie, Proceedings of SPIE, 4695, (2002), 95-103. 3- French patents n° 03/08647. 4- F. Vidal, C. Plesse, D. Teyssie, C. Chevrot, Synt. Met., 142, (2004), 287-291.

3:30 PM **BB12.7**

Density Functional Theory and Molecular Dynamics Studies on Energetics and Kinetics for Electro-Active Polymers: PVDF and P(VDF-TrFE). Haibin Su¹, Alejandro Strachan² and William A. Goddard¹; ¹Caltech, Pasadena, California; ²Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

Poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoroethylene (TrFE) exhibit excellent electro-mechanical properties such as ferroelectricity, piezoelectricity, pyroelectricity, and nonlinear optical properties. Very recently, it has been showed that it is possible to make use of electric field-induced phase transformations between polar and non-polar phases in nano-structured (via electron irradiation) P(VDF-TrFE) to obtain large electrostrictive strains (~ 5 %) at high frequencies (1000 KHz) and with good energy densities (comparable to the best piezoceramics). We use first principles methods to study static and dynamical mechanical properties of the ferroelectric polymer Poly(vinylidene fluoride) (PVDF) and its copolymer with trifluoroethylene (TrFE). We use density functional theory [within the generalized gradient approximation (DFT-GGA)] to calculate structures and energetics for various crystalline phases for PVDF and P(VDF-TrFE). We find that the lowest energy phase for PVDF is a non-polar crystal with a combination of trans (T) and gauche (G) bonds; in the case of the copolymer the role of the extra (bulkier) F atoms is to stabilize T bonds. This leads to the higher crystallinity and piezoelectricity observed experimentally. Using the MSXX first principles-based force field (FF) with molecular dynamics (MD), we find that the energy barrier necessary to nucleate a kink (gauche pairs separated by trans bonds) in an all-T crystal is much lower (14.9 kcal/mol) in P(VDF-TrFE) copolymer than in PVDF (24.8 kcal/mol). This correlates with the observation that the polar phase of the copolymer exhibits a solid-solid a transition to a non-polar phase under heating while PVDF directly melts. We also studied the mobility of an interface between a polar and non-polar phases under uniaxial stress; we find a lower threshold stress and a higher mobility in the copolymer as compared with PVDF. Finally, considering plastic deformation under applied shear, we find that the chains for P(VDF-TrFE) have a very low resistance to sliding, particularly along the chain direction. The atomistic characterization of these "unit mechanisms" provides essential input to mesoscopic or macroscopic models of electro-active polymers. Reference: Haibin Su, Alejandro Strachan, and William A. Goddard, III, "Density functional theory and Molecular Dynamics Studies on Energetics and Kinetics for Electro-Active Polymers: PVDF and P(VDF-TrFE)" (in print, Phys. Rev. B 2004)

3:45 PM **BB12.8**

Cocrystallization and Dynamics of Ferroelectric P(VDF-TrFE) Copolymer Blends. Shihai Zhang¹, Xi Zhang² and Q.M. Zhang^{2,1}; ¹Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania; ²Electrical Engineering Department, The Pennsylvania State University, University Park, Pennsylvania.

Poly(vinylidene fluoride-co-trifluoroethylene) [P(VDF-TrFE)] copolymers exhibit very strong electromechanical properties and they can be used as materials for sensors, actuators, and transducers. Recent studies found that their response to electric field can be significantly improved after introducing defects to the crystals by high energy electron irradiation or copolymerization with a third comonomers. Defects may also be physically created by introducing a second polymer or plasticizer into the copolymer, if proper sample preparation procedure is used. In this study, we report our new results on the blends of 68/32 and 55/45 P(VDF-TrFE) copolymers. These two copolymers are miscible in all compositions at room temperature. DSC results reveal a single melting temperature and a single but

broad curie transition process, both are located between corresponding transitions of the two components following the mixing rule. This suggests that the two different copolymers cocrystallize into a single crystalline phase. The influence of the blending on the dynamics and electromechanical properties will also be discussed and it is demonstrated that the transitions can be tuned and the electromechanical response can be optimized by controlling the blend composition and annealing conditions.

4:00 PM **BB12.9**

Thermal and Electric Properties of P(VDF-TrFE) and P(VDF-CTFE) Copolymer Blends. Zhimin Li^{1,2}, Yuhong Wang² and Z.-Y. Cheng^{1,2}; ¹Materials Engineering, Auburn University, Auburn, Alabama; ²Materials Research and Education Center, Auburn University, Auburn, Alabama.

PVDF-based electroactive polymers exhibit high electromechanical performance that is attractive for developing high performance actuators and sensors. In an effort to develop very inexpensive electroactive polymers, P(VDF-TrFE)/P(VDF-CTFE) copolymer blends are studied. The structure and morphology of the blend system were investigated and reported. The miscibility of the blends and the effect of process temperature on the miscibility of the blends were studied using x-ray diffraction and DSC. The optimized thermal treating condition and composition for the blends were identified to have homogeneous materials. It is found that the addition of P(VDF-CTFE) has a strong influence on the ferro-to-paraelectric phase transition behavior of P(VDF-TrFE). It is also found that the phase transition behavior of the blends can be significantly modified using thermal and mechanical treating conditions. In a stretched polymer blend, a polarization level about 60 mC/m² at external electric field of 150 V/mm was obtained with a small remnant polarization, less than 10 mC/m². The dielectric behavior and electromechanical properties of the blends were characterized. A high electric-induced strain response and a low dielectric constant were obtained. Considering the high Young's modulus, the results indicate that the copolymer blends have a high electromechanical coupling factor, an important parameter for electromechanical application.

4:15 PM **BB12.10**

Interfacial Layer - A New Mechanism for Electromechanical Response. Z.-Y. Cheng and Zhimin Li; Materials Engineering, Auburn University, Auburn, Alabama.

Polymers have many attractive characteristics: lightweight, inexpensive, fracture tolerant, and easy to process. New polymers - electroactive polymers (EAPs) - have emerged that respond to electric stimulation with a significant shape or size change. The progress of developing EAPs has added an important capability to the smart materials. The EAPs are attracting the attention of engineers and scientists from many different disciplines. Since they behavior very similar to biological muscles, EAPs have acquired the moniker "artificial muscles". From materials science point of view, it is very interesting to study the mechanism responding for the high strain response obtained in EAPs. Electric field induced phase transition was used to explain the high strain response in some PVDF-based EAP. However, it is hard to understand some features (such as the relationship between the strain and preload) of elastomer - an important type of EAPs. In this presentation, we first report the recrystallization study of high-energy-electron irradiated P(VDF-TrFE) copolymer. The morphology and structure as well as the structure transformation in the recrystallized copolymers were studied by means of x-ray diffraction, DSC, FTIR, dielectric and polarization properties. The effect of crosslinking induced by the irradiation is discussed based on the results. Based on the results, a new interface layer, which is partially ordered, is induced. The partially ordered interfacial layer is a novel micro-origin of high polarization obtained in EAP. Based on the concept, the effect of preload on the electromechanical performance of the elastomers can be well explained. A new method to develop high performance electroactive polymer is outlined by using the interface state.

4:30 PM **BB12.11**

Processing the Right Actuator: the Relationship Between Nanostructure and Materials Properties of Higher-Order Pyrroles. Brian D. Pate, Rachel Z. Pytel and Edwin L. Thomas; Institute for Soldier Nanotechnologies and Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts.

Extended systems based on α -coupled pyrrole include cyclic porphyrinoids and linear polymers. While the former are of interest primarily for their ability to harvest light, conducting polymer actuators based on polypyrrole are attractive due to their high active strains and power densities. β - and N-substitution allow for electronic and structural modulation of these macromolecules. We discuss the preparation of novel derivatized pyrroles, the controlled chemical polymerization thereof, and the effect of various thin film and fiber

processing techniques on the mechanical, optical, and electronic characteristics of the resulting nanostructured materials.

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