SYMPOSIUM EE
Nanostructures in Polymers
April 24 – 26, 2000

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*Invited paper
SESSION EE1 HYBRID MATERIALS
Claire P. Gress
Mon, Morning, April 24, 2000
Concord (Argent)

8:30 AM EE1.1
BLOCK-COPOYMER TEMPLATING OF ORDERED INORGANIC-ORGANIC COMPOSITES. B.F. Chimelka, N. Melosh.
Univ of California, Santa Barbara, Dept of Chemical Engineering, Santa Barbara, CA; P. Davidson, Univ de Paris-Sud, Paris, FRANCE;
G.D. Stucky, Univ of California, Santa Barbara, Dept of Chemistry, Santa Barbara, CA.

The use of amphiphilic block copolymers, in combination with sol-gel chemistry methods, allows the preparation of composite polymer/inorganic oxide systems with high degrees of nano/mesoscopic organization and macroscopic processability. These materials combine the soft assembly and processing advantages presented by the block copolymer with the high thermal/mechanical stability of the densely cross-linked inorganic oxide networks. In such systems, interactions between different block copolymer moieties and the inorganic component(s), often across a shared interface, are key for selective partitioning and organization of the inorganic species to occur. Using methods of two-dimensional solid-state NMR spectroscopy, X-ray diffraction, and TEM/SEM/optical microscopy, we have examined molecular, mesoscopic, and macroscopic structural ordering in poly(etherketone)-poly(propyleneoxide)-poly(etherketone) (PEK-PPO-PEK) silicate systems. Recent results will be presented on the synthesis and characterization of such composites, including those with high degrees of mesoscopic organization, orientational order, and optical transparency.

9:00 AM EE1.2
FABRICATION AND ELECTRICAL PROPERTIES OF SELF-ASSEMBLED PLANAR ARRAYS OF METALLIC NANOPARTICLES AND NANOWIRES IN DIBLOCK COPOLYMERS. W.A. Lopes, H.M. Jaeger, James Franck Institute, The University of Chicago, Chicago, IL.

We have self-assembled arrays of metallic nanoparticles and nanowires using a two-step, self-assembly process. We start by spin coating an ultrathin film of asymmetric PS-P2MMA diblock copolymer onto a 100 nm thick molybdenum film. Upon annealing the diblock copolymer micro-phase separates into a template that acts as a mask for arrays. Thermally evaporated metal preferentially deposits only the metal block of the template. By adjusting the metal block coverage conditions, we can form arrays of either nanoparticles or nanowires. Using lithographically patterned, in-plane electrodes, we have aligned the diblock template during the annealing process and investigated the electrical properties of the finished arrays. In the case of the nanoparticles, we find highly nonlinear current-voltage characteristics; we also find that the conductance of the arrays is modulated by the voltage of a nearby gate electrode. We will report on both the fabrication of the arrays and their electrical properties as well as the dependence of the electrical properties on gate voltage and temperature.

9:15 AM EE1.3
STRUCTURE AND OXYGEN SENSING PROPERTIES OF The SOL-GEL PREPARED NANOIZED TiO2 THIN FILMS. M.Z. Atashbar, Department of Electrical and Computer Engineering, Western Michigan University, Kalamazoo, MI.

Titanium dioxide (TiO2) thin films due to their high refractive index, good chemical stability, and large dielectric constant are suitable for many applications from optical coatings to microelectronic devices. The change of its conductivity due to the gas environment has made it a good candidate for gas sensing applications. In this study, the effect of structure, microstructure, and composition on the oxygen sensing properties of the (TiO2) film has been investigated. (TiO2) thin films were prepared from starting precursors via sol-gel route in dry nitrogen atmosphere (<100 ppm). The used precursors were titanium butoxide [Ti(OC4H9)4] with an analytic purity, which was dissociated in analytical grade methanol and ultrasonic mixing at room temperature for 12 hours the precursor solution was dropped on the substrate and spun at different speeds. The thickness (30 to 100 nm) was controlled by changing the solution concentration and spinning velocity. After ultrasonic mixing at room temperature between 45 to 75 °C, TiO2 thin films were obtained. The morphology, microstructure, crystalline structure, and composition of the deposited films were analyzed by SEM, XRD, XPS and RBS. The SEM analysis showed that this film is porous and the etching of the film is inhomogeneous. The Raman spectra of the films were obtained from 300 to 1000 cm^-1. The XPS and RBS results indicated that the film is stoichiometric with carbon as the dominant impurity at the surface. XRD analysis showed that the films are purely Anatase up to annealing temperature of 600°C. As annealing temperatures increase, the film is transformed to the Rutile form. Titania films have been noticed along with the Anatase phase. A detailed analysis of these results on the oxygen sensitivity of the film has been discussed. The electrical resistance of the film has been examined for the detection of oxygen at concentrations of 1 ppm to 1%. As a result of doping, sensitivity increased and operational temperature decreased.

9:30 AM EE1.4
SYNTHESIS AND CHARACTERIZATION OF HYBRID ORGANIC-INORGANIC NANOPARTICLES USING CONTROLLED/"LIVING" RADICAL POLYMERIZATIONS. Timothy van Wenne, Ian M. Stelhorn, Steven C. Farner and Timothy E. Patten, Univ of California-Davis, Dept of Chemistry, Davis, CA.

Nanoparticles, depending upon their composition, exhibit novel magnetic, optical, and mechanical properties that can be exploited for their small size and large surface area. The incorporation of nanoparticles into polymeric materials and the ordering of nanoparticles into superlattices or extended periodic arrangements are important steps in exploiting the properties of these hybrid materials. Recently, several approaches to preparing well-defined nanocluster-based structures have been reported. These methods involve the use of DNA conjugates, self-organization, and monolayer formation to define the spatial orientation of the nanoclusters. A polymer-coated approach to organizing nanoclusters would combine the spatial definition afforded by the aforementioned techniques with the versatile film-forming and mechanical properties of polymers. We have developed a method to prepare novel, well-defined organic-inorganic nanoparticles by integrating the techniques of colloid and nanocluster synthesis with those of newly developed controlled/living radical polymerization. A monolayer is transferred to a polymer surface using a name transfer polymerization technique (ATRP). The monolayer is then used as a template to grow a layer of nanoparticles. This process is repeated to yield macroscopic arrays of nanoparticles. Following the growth of the polymer layer, the nanoparticles are removed using a solution of trichloroethylene, followed by washing with water. The macroscopic arrays of nanoparticles are then characterized using microscopy and DLS measurements. These hybrid nanoparticles are cast from solvent solutions to yield composite nanoparticle-polymer films and hexagonal ordering of the inorganic cores was observed when dilute solutions were used for casting.

9:45 AM EE1.5
DEPOSITION OF BIOACTIVE POLYMER FILMS ONTO DRUG PARTICLES FOR CONTROLLED-RELEASE FORMULATIONS. James D. Falconer, Yiwen Cao, Anton Wong, Patricia Siddharta, Gunther Hochman, James Fitz-Gerald, Rajiv Singh.

Deposition of nano-thin coatings of biodegradable polymers, such as poly-L-lactic acid (PLLA), poly(hydroxyalkyl lactone) (PHAL) and poly(ethylene glycol) (PEG), onto micronized drug particles has been used to reduce the release rate and improve localized delivery. Pulled Laser Deposited (PLD) coatings are applied using an excimer laser (248 nm) directed at a polymer target in a vacuum chamber, which is absorbed and expands from the surface in a plume of polymer clusters that is directed over a fluidized bed of drug particles. Optimization of the coating parameters such as laser energy density, background gas pressure, fluidization efficiency and the absorption efficiency of the polymer target material has been performed on several drug powders including budesonide, tramadol hydrochloride, rifampin, bupivacaine, and various proteins for sustained-release applications. Characterization of the polymer degradation and molecular weight distribution, as well as the drug release rate in vitro, aerodynamic flow properties, and in vivo toxicity and localized release in a rat pulmonary model has shown this technique to be an excellent alternative process to spray coatings.

10:15 AM EE1.6
PHOTOCHEMICAL DEVELOPMENT AND MATERIALS CHARACTERIZATION FOR COMPOSITE MEMBRANES OF ELECTROSPUN NANOFIBERS AND MICROPARTICLES. David Ziegler, Changmo Sung, Univ of Massachusetts Lowell, Dept of Chemical and Nuclear Engineering, Lowell, MA; Heidi Gibson, US Army Research, Natick Soldier Center, Supporting Science and Technology Dept, Natick, MA.

The goal of this work is to develop novel production methods for making composite membranes with nanocomposite filters which either contain or entraps nanoparticles to optimize membrane strength and functionality. Electrospinning produces fiber mats with fiber diameters in the micron to submicron range that behave like microfibrous membranes. Exploiting this fiber mat morphology such as superabsorbency or reactivity, particles have been added by two
different methods. Dry aerosol spraying and encapsulating techniques are the two different methods of particle incorporation that are compared in the paper. In encapsulation, the particles are suspended in the disordered polymer solution, then electrosprayed. Mechanical, chemical, and electron microscopy results will be reported and processing conditions and methods will be evaluated with respect to the fiber/particle system performance.

10:30 AM EE1.7
DIRECT MEASUREMENT OF POSITIVE TEMPERATURE COEFFICIENT OF RESISTANCE ANOMALY OF CARBON BLACK FILLED POLYETHYLENE BY ELECTROSTATIC FORCE MICROSCOPY.

Systems of cross-linked composites composed of a polymer matrix and a conducting rod-like filler are found to exhibit a sharp increase in resistance at a certain temperature, which is referred to as the positive temperature coefficient of resistance (PTCR) anomaly. This phenomenon is believed to be a result of the separation of the conducting particles by polymer expansion in the temperature near the polymer melting region. In this work, PTCR anomaly of carbon black filled low density polyethylene was studied with electrostatic force microscopy (EFM), which can distinguish conductive phase from non-conductive phase with a nanoscale resolution. At room temperature, the width of conductive phase was observed, confirming the formation of conductive particle network. At melting temperature or above, a dramatic reduction of conductive phase was directly imaged and the location and the size of conductive phase changed dynamically. We believe this is a result of repeated forming or breaking of conductive channel at this temperature.

10:45 AM EE1.8
ELASTOMERIC BEHAVIOR OF NANOPARTICLE CHAIN AGGREGATES.

Nanoparticle chain aggregates (NCA) have some properties similar to those of molecular elastomers. Like polymer chains, NCA tend to gather up and become more compact when heated. Studies in our laboratory show that under tensile stress, NCA elongate, and when the tension is released, the chains contract. In our studies, titanium, aluminum and iron oxide NCA were generated by laser ablation. A generator was operated to produce NCA with similar mobility diameters and primary particle size (5 to 10 nm). The NCA were deposited on the carbon or formvar films of an electron micrograph grid. Under the electron beam a hole develops in the carbon film around the NCA which bridges the gap. As the hole widens, the NCA stretch up to twice their original length before breaking at one end and contracting. The titanium, aluminum and iron oxide NCA all showed elastic behavior for primary particles smaller than about 8 nm, where the NCA composed of 36 nm primary particles did not. Inspection of the electron micrograph indicated that the elastic behavior is probably associated with local folding of chain segments due to defects in particles. Under tension, folded chains straighten but when the tension is released, the NCA contracts. A videotape (30 frames per second) was too slow to catch the contraction. Rotation and sliding probably occur at the boundaries between particles during stretching. Overall behavior is determined by the size and structure of NCA, which is composed of transition metal oxides with primary particles smaller than 10 to 15 nm. NCA network stretching may explain why nanoparticle additives such as fumed silica and carbon black improve the properties of rubber. NCA stretching may also contribute to the ductile properties of nanoparticle composites.

11:00 AM EE1.9
A NOVEL USE OF SILICA NANOBeadS FOR ENHANCED DNA DELIVERY.
Dan Lu, Ernest Hua, Nadya Beldeven, W. Mark Saltzman, Cornell University, School of Chemical Engineering, Ithaca, NY.

Transfection, i.e., DNA delivery via non-viral vectors, is a rapidly expanding field, and efficient DNA transfection is critical for advancement of biological research and new clinical therapies, including gene therapy and DNA vaccines. Over the years, many non-viral approaches using chemicals, especially polymers, have been established. In this work, we investigated the transfection efficiency of DNA in vitro in a wide range of transfection conditions and found that transfection efficiency is dependent on the size of the silica nanoparticles. The results suggest that the strong interaction of metal ion and metal salt group promotes compatibility of DNA with nanoparticles.

11:15 AM EE1.10
THERMOVISCOSCOLOGICAL BEHAVIOR OF POLYHEDRAL OLIGOSILSESQUIOXANE INORGANIC-ORGANIC HYBRID POLYMERS.

The properties of nanostructured plastics are determined by complex relationships between the type and size of the nano-phase, the interfaces, and the chemical interactions between the reinforcement and the polymeric chain, along with the microstructural processing and microstructural effects. Recently, families of mono- and multi-functionalized polyhedral oligosiloxane-siloxanes (POSS) macromers with different organic groups have been developed. Depending on the organic group and the functionality used, the morphology of the POSS domain is significantly altered in the blends with polymeric polymers, polyethylene, polypropylene, and polycarbonates. This paper presents an investigation of thermal and viscoelastic properties of these blends of inorganic-organic hybrid systems. We are interested in the influence of nano-scale POSS domain on the dynamic of polymeric chains.

11:30 AM EE1.11
NOVEL PHOSPHINE OXIDE CONTAINING POLY(ARYLENE ETHYRE) AND POLY(IMIDE-INORGANIC SALT HYBRID) NANOCOMPOSITES.

Baphenol A based poly(arylene ether phenyl phosphine oxide) and inorganic metal salts, such as cobalt(II) chloride, copper(II) chloride, were co-dissolved into N,N-dimethylacetamide with different molar ratios. Films were then cast onto glass plates and the solvent was slowly evaporated. The nanocomposite films were transparent suggesting a very fine dispersion. Furthermore, the films could be melted pressed, indicating thermally reversible interactions among phosphonylated metal ions. TEM results revealed that the composite films with low amounts of metal salts (molar ratio of metal ion/phosphoryl group ≤ 0.20) had particle sizes less than 10 nm, while higher amounts of inorganic salts generated larger particles. Cobalt salt significantly increased the glass transition temperature (Tg) of the nanocomposites, but the incorporation of copper salts slightly decreased Tg. This might involve different interactions between the salts and the polymer. Copper ion may show a tetrahedral configuration, whereas cobalt ion octahedral configuration, which could physically link several chains, in contrast to the copper. Incorporating cobalt salt significantly increases the TGA char yield. XPS analysis suggests the formation of cobalt phosphate, which may enhance the fire retardation properties of the polymeric chloride composites. Small amount of salts were also incorporated into polymeric composites to afford transparent films. The glass transition temperature was dependent on the amount of phosphonyl groups as the same ratio of metal ion/phosphoryl group. Likewise, cobalt chloride and copper chloride were also incorporated into phosphonyl containing polymides. The results suggest that the strong interaction of metal ion and metal salt group promotes compatibility of the composites.
diameters of 0.5 - 1 nm, are retained in the polymer and crosslink the polymer chains. Some microphase separation is observed. The crosslinked polymers are no longer soluble, but swell in organic solvents. The amount of absorbed solvent shows a linear dependence on the cluster portion. Thermal depolymerization typical of the undoped polymers is distinctly suppressed by cluster-crosslinking, and disappears when the cluster portion exceeds 1-2 mol%.

SESSION EE2: ELECTROLYTIC SYSTEMS/HYBRID MATERIALS II
Chair: Andrew J. Liu
Monday Afternoon, April 24, 2000
Concord (Argent)

1300 PM *EE2.1
Polyelectrolyte multilayers fabricated from weak polyelectrolytes such as polyelectrolyte (PAA) serve as ideal nanoreactors for semiconducting and metallic particles. Simple pH adjustments of the processing solutions make it possible to control the fraction of PAA carboxylate acid groups available to bind various inorganic ions that can be subsequently converted into nanoparticles. Spatial control over the location of the nanoparticles within these multilayer assemblies can be achieved through the use of polyelectrolyte multilayer bilayer combinations that are not able to bind inorganic ions such as polystyrene sulfonic acid/poly(allylamine hydrochloride). The density of nanoparticles within a film can be varied by controlling the number of multilayer bilayer combinations via the use of multilayer loading procedures. The fabrication and characterization of multilayer heterostructures containing nanoparticles of metals (Ag, Pb) and semiconductors (PbS) will be described.

2000 PM EE2.2
PROBING NANO SCALE STRUCTURE AND EXCITED STATE DIFFUSION IN DYE-LABELED POLYELECTROLYTE MULTILAYERS USING NSOM. Geoffrey M. Lowman, Steven K. Burnott, UC Santa Barbara, Dept of Chemistry and Biochemistry, Santa Barbara, CA.
Near-field scanning optical microscopy (NSOM) has been used as a probe of local structure in self-assembled films of oppositely charged polyelectrolytes. Films were constructed using polystyrene sulfonate (PSS) and poly(allylamine hydrochloride) (PAH) labeled both with Fluorescein (FI) and Rhodamine-B (RBB). Growth of PAH/PSS films has been monitored using UV-Vis spectroscopy and x-ray diffraction. Fluorescence-NSOM shows small variations in film fluorescence correlated to surface topography. Film surface roughness increases as a function of layer number until it plateaus and shows only small variations in roughness with successive layers. We have also used spatial hole burning NSOM (SHB-NSOM) to study excited state diffusion in polyelectrolyte films by monitoring localized photoexcitation as a function of exposure time. The results of these measurements indicate long diffusion lengths on the order of 100 nm. We will discuss possible models for this behavior.

2:15 PM EE2.3
Abstract Withdrawn.

3:00 PM EE2.4
NANOSIZED CLUSTERS IN NAFION(TM) SOLUTIONS STUDIED BY DYNAMIC LASER LIGHT SCATTERING. Ming Jiang, Keqin Xin, Hong Kong Chinese Univ, Dept of Physics, HONG KONG; Gu Xu, National Univ of Singapore, Dept of Materials Science, SINGAPORE.
Nafion(TM) type of perfluorosulfonated ionomer (PFSI) solutions were investigated by dynamic laser light scattering (DLS) to reveal the cause of the nanosized ionic cluster size observed in the solution casting process, which affects negatively the applications in electro-membrane assembly (EMA) for proton-exchange-membrane fuel cells (PEMFC). It was found that only aqueous solution can provide an adequate environment for Nafion ionomers to fully develop the nanosized clusters, which is signified by the existence of a twin peak in the hydrodynamic radius distribution function obtained from DLS. This twin peak disappears and is replaced by a single, broad peak in the case of Nafion/DMSO solution, which leads to a large degree of suppression of the nanosized clusters in the cast membranes. Alternatively, the addition of a small amount of glycerol into the aqueous solution, necessary for the fabrication of the EMA, will also destroy such clusters. The suppression is partially understood by the similar action of lithium salt, and also into the aqueous solution to screen the electrostatic attraction. Although the exact origin of this twin peak is unclear, it can at least be concluded that only dual sized polymer aggregates in solution lead to the full ionic cluster development, which is possible due to the competitive adsorption of larger and smaller building blocks. This offers a possible explanation of why the ionic conductivity drops by four orders of magnitude, found during the previous electric conductivity studies.

3:15 PM EE2.5
MODEL HYBRID ORGANIC-INORGANIC NANOCOMPOSITES. Dale L. Huber, Richard P. Niro, Thomas A.P. Seery, University of Connecticut, Polymer Program, Storrs, CT.
A system for producing organic-inorganic nanocomposites of precisely tailored dimensions has been developed. The inorganic core consists of a gold particle which can be systematically varied from about 1 to 300 nm, and is passivated by an alkane-thiol monolayer. A transition metal catalyst is grafted to an appropriate functionality incorporated into the alkane-thiol monolayer, and the polymerization is initiated at a surface bound gold cyst. The polymerization reaction is spectroscopically monitored in real-time, and is terminated when a desired quantity of polymer has been produced. This system allows the manipulation of the sizes of the inorganic core and of the polymerizing through several orders of magnitude, so that a nanocomposite can be rationally designed, then precisely produced. The sizes of the resultant structures have been characterized by transmission electron microscopy, dynamic light scattering, thermogravimetric analysis, and gel permeation chromatography. While the majority of the work presented here consists of gold core and poly(hexyl isocyanate) coating produced by a titanium(IV) catalyst, the general utility of the technique has been demonstrated and a wide range of structures can be prepared with small modifications in procedure.

3:30 PM EE2.6
THE EFFECTS OF POLYBUTYL ACRYLATE INTERCALATED CLAY ON MORPHOLOGICAL ORIENTATION IN TRIBLOCK COPOLYMER. Kecheng Gong, Honghun Cheng, Polymer Structure & Modification Res. Lab, South China University of Technology, Guangzhou, PR CHINA.
Thermoplastic elastomers(TPEs) represent a class of multiphase polymers which have a typical domain structure on the 10nm length scale, a typical grain structure on the 100nm length scale. A triblock copolymer in which the minor A block is polyisoprene (PI) and the major central B block is either polybutadiene(PBD) or polyisoprene(PII) are a remarkable industrial product. The high tensile strength of this type of TPEs is however adversely affected by temperatures exceeding 60° because of the approach of the glass transition temperature of the polyisoprene microdomains. In this paper, the effects of polybutyl acrylate (PBA) intercalated clay (kaolinite and nanosize mixture) on morphological orientation in triblock copolymer poly(styrene-b-butadiene-b-styrene) (SBS) have been investigated. As a rule, tensile strength and elongation at break is improved by increasing the content of PBA intercalated clay from 0.5 to 10wt% DMA shows two thermal transition at -70° and 155° for PBD and PS-PBA/PMMA blocks, respectively. The morphological orientation is observed by AFM nanoprobe.

3:45 PM EE2.7
PREDICTING PHASE BEHAVIOR OF PARTICLE/BLOCK COPOLYMER MIXTURES. Jane Huh, Valerie V. Gimburg and Ann C. Balch, Univ of Pittsburgh, Dept of Chemical and Petroleum Engineering, Pittsburgh, PA.
We study the phase behavior of binary mixtures of diblock copolymers and hard particles which have a strong affinity for one of the blocks. Using Monte Carlo simulations, we determine the phase map for the mixture as a function of the particle size, block copolymer composition, and the particle volume fraction. When the particle radius becomes comparable to the radius of gyration of a polymer chain, we observe broadened two-phase regions with a depression of a novel cylindrical phase, in which the particles form an inner block of a cylindrical micelle. We develop a strong segregation limit (SSL) theoretical model and find good qualitative agreement between theory and simulation.

4:00 PM EE2.8
POLY(VINYL ALCOHOL)/MONTMORILLONITE NANO COMPOSITES. K.E. Strawhecker, C.A. Fonasse, R.R. Harrison and E. Murins, Materials Science & Engineering, Pennsylvania State University, University Park, PA.
Poly(vinyl alcohol)/sodium montmorillonite nanocomposite hybrids have been prepared from water solutions. The structure of hybrids with varying polymer concentration was characterized using XRD, TEM, FTIR, and TGA. In the polymer content range, a hybrid was formed to consist mostly intercalated structures, whereas at higher concentrations the montmorillonite layers were readily.
exfoliated. Polymer crystallinity was affected by the inorganic layers which promoted what appears to be an epitaxially-induced crystalline form, remaining crystals obtained through unsealing of PVA incidentally, unsealing often degrades the material. This change in polymer structure and incorporation of nanometer-thin high aspect-ratio filler layers have a dramatic effect on PVA material properties, such as lower permeability and uptake, thermal stability and mechanical properties.

**4:15 PM EE2.9**

**SIMULATIONS OF INTERCALATION KINETICS OF POLYMER SILICATE NANOCOMPOSITES.** Jee Youn Lee, Roger F. Loring, Cornell Univ, Dept. of Chemistry, Ithaca, NY; Atleete R.C. Balgobin, San Diego State University, Dept of Physics, San Diego, CA.

One of the ways in which polymer layered nanocomposites are formed is that polymers from a bulk melt intercalate into the galleries of a layered clay. The result is a structure of nanometer thin layers of polymers alternating with comparably thin layers of clay. The process has been modeled through molecular dynamics simulations. In the first set of simulations polymer chains enter a slit of fixed dimension from a polymer melt maintained under constant external pressure. In subsequent studies, polymers enter a slit whose walls are kept at fixed pressure, permitting the slit to open as it is filled by polymer. The walls are decorated with grafted short chains. Polymer is observed to enter the slit for sufficiently strong interaction between polymer and surface. In both models the intercalation rate has been obtained for various degrees of interaction between the polymer and modified silicate. We find that the intercalation process is well described by a diffusion model. Increasing the affinity of the polymer for the modified silicate decreases the rate of intercalation. These results have been applied to interpret x-ray diffraction studies of the intercalation of polystyrene into organically modified layered silicates.

**SESSION EE3: MICROSTRUCTURE-MACROSCOPIC PROPERTY RELATIONS AND SYNTHETIC ROUTES**

Chair: Thomas P. Russell
Tuesday, Morning, April 25, 2000
Concordia (Argent)

**8:30 AM *EE3.1**

**COPOLYMER FRAMEWORKS: A SELF-ASSEMBLY ROUTE TO SUPER-TOUGH SEMI-CRYSTALLINE POLYMER MATERIALS.** Ludwik Leibler, Laboratoire CNRS/Eiffel Atomes (UMR 167), Levallois-Perret, 92200 Paris, France.

Many polymers are brittle under high rates deformation in impact loading especially at low temperatures. This brittleness has been alleviated more or less successfully by incorporation of submicrocrystalline rubbery particles or by reactive blending. The toughness can be only achieved when the average interparticle distance is reduced below a critical value. The particle dispersion is invariably produced by mechanical agitation and by quenching non-equilibrium states resulting from a phase transformation process or chemical reactions. A method of producing desired morphologies from equilibrium self-assembly processes is clearly very desirable. We show that one reliable route to self-assembled super tough materials are blends of semi-crystalline polymer X and suitably designed block terpolymer ABC, consisting of three chemically distinct monomer sequences A, B and C, covalently bonded together. The strategy is to have block C miscible with the thermoplastic X. In the case of PVDF, for example, triblock poly(styrene-b-butadiene-b-methylenecrylate) copolymers form core-shell aggregates of about 80 nanometers of diameter dispersed extremely regularly in polymer matrix yielding a new structured crystalline material with qualities of fluorinated polymers (impermeability and solvent resistance) and with spectacular toughness and thermal stability that cannot be attained by conventional methods. By using triblock rather than diblock copolymers we can finely tune the structuring, the mechanical properties and even more importantly, easily incorporate synthesis imperfections in self-assembled structures.

**9:00 AM EE3.2**

**SWITCHABLE ELECTROMECHANICAL POLYMER BRUSH LAYERS.** David W. Van and David B. Heine, Dept of Chemical Engineering and Dept of Chemistry, Colorado School of Mines, Golden, CO.

The technological use of polymer thin films and brush layers are becoming increasingly sophisticated as our control of the macromolecular structure and interactions becomes more refined at the nanometer scale. In this talk, we describe how a polymer brush layer can be manipulated through electrostatic interactions on very short timescales to produce switchable mechanical, chemical, and optical properties. We present scaling and self-consistent field calculations which show how the stability of both polymer melts and polymer solutions change depending on temperature and concentration, and illustrate with an example of a rapidly switchable surface that can alternate between hydrophilic and hydrophobic properties. The critical electrostatic field at the transition point is, within the scaling theory, independent of both polymer molecular weight and dielectric constant. The wet and dry brush, however, can switch in qualitatively different manners. Some possible nanoscale device applications will be discussed.

**9:15 AM EE3.3**

**MACROSCOPIC PROPERTIES OF EPOXY MODIFIED WITH SELF-ASSEMBLED BLOCK COPOLYMER STRUCTURE.** Jennifer M. Dean, Frank S. Bates, University of Minnesota, Department of Chemical Engineering and Materials Science, Minneapolis, MN; Paul M. Lipic, Proctor & Gamble, Cincinnati, OH.

Comparisons between the mechanical properties of epoxies containing different self-assembled block copolymer structures may provide insight on how the shape and distribution of modifier particles affects the macroscopic properties. Block copolymer modifiers are well suited to this type of study because the self-assembled microstructure varies with the block copolymer architecture. Anionic polymerization is a technique to synthesize block copolymers of a narrow polydispersity index with control over the length of each block. Amphiphilic diblock copolymers containing poly(ethylene oxide) self-assemble in epoxy. At high block copolymer concentrations, ordered microstructures form. Decreasing the amount of block copolymer relative to epoxy induces phase transitions, and ultimately leads to desired core-shell structured vehicles. During the epoxy resin flows in the self-assembled microstructure, allowing for the evaluation of composite mechanical properties. In the current study, the phase behavior and mechanical properties of blends containing epoxy and a symmetric block copolymer (volume fraction of PE= 0.5 and 0.25, respectively) poly(ethylene oxide)-poly(ethylene-alt-propylene) (PEO-PoP) block copolymer are compared. The corresponding block copolymer microstructure is lamellar, while the former symmetric block copolymer self-assembles into hexagonally packed cylinders of PEO. In the symmetric system, addition of epoxy induces curvature at the PPO-PoP interface. This curvature leads to phase transitions starting with lamellar and ending with ordered spheres of PEP. Spherical micelles result at high block copolymer concentrations. However, addition of epoxy to the asymmetric system reduces the curvature at the PPO-PoP interface, producing the opposite trend in the order of phase transitions (cylinders to lamellae). Multilayer and single vehicles result in the limit of low asymmetric block copolymer concentration. This study concludes with a comparison between the modulus and fracture toughness of epoxies containing spherical micelles and vesicles at block copolymer concentrations less than 5 weight percent.

**9:30 AM EE3.4**

**EFFECTS OF PE BLOCK LENGTH ON THE THERMAL BEHAVIOR OF PS-P-PEO TRIBLOCK COPOLYMERS.** Travis S. Bailey, Frank S. Bates, Univ of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN.

Many studies involving ABC triblock copolymers have focused on the unique morphologies that particular molecules express. However, thermal transitions in these molecules have received little attention. A series [7] of poly(styrene-isoprene-ethylene oxide) ABC triblock copolymers were synthesized with varying PE block lengths. Consistency among all triblocks in the series was achieved through ethylene oxide addition to the same α-hydroxy-functionalized poly(styrene-isoprene) diblockMW=18000g/mol, fPE=0.5). Final triblock PEO volume fractions ranged from fPEO=0.15 to fPEO=0.207. All triblocks in the series showed order-to-disorder transitions (ODTs) upon heating, with actual ODTs ranging from 84°C to 215°C. Interestingly, these ODTs are observed to occur from below to well above the ODT of the parent poly(styrene-isoprene) diblock[116°C]. Characterization of these triblocks using a combination of techniques, including reology, small angle x-ray scattering, and transmission electron microscopy shows multiple changes in morphology over the range of compositions studied, as well as possible order-to-order transitions (OOTs) associated with triblocks of specific compositions. Kinetic reversibility of the order-to-order and order-to-disorder transitions will also be discussed.

**10:00 AM EE3.5**

**MICROSTRUCTURAL AND PROPERTY CHARACTERISTICS OF TRIBLOCK COPOLYMER/PHOTONALYMER BLENDS.** Rebecca L. Reberich, Richard J. Sponsak, NC State Univ, Dept. of Chemical Engineering, Raleigh, NC; Scott A. White, Becon Dickinson Technologies, Polymer Science & Technology Dept., Research Triangle Park, NC; Steven D. Smith, Procter & Gamble Co., Corporate Research Div., Cincinnati, OH.
Miscible blends of a microphase-ordered block copolymer and a parent homopolymer have been previously examined to ascertain the importance of composition and blend factors such as chain length ratio and composition on the development of block copolymer nanostructure at non-equilibrium conditions. In the present work, we conduct swelling tests by diffusing a parent homopolymer dissolved in a linear solvent into the compatible lamellae of a lamellar block copolymer. In this case, a poly(styrene-b-isoprene-b-styrene) (SIS) triblock copolymer is impregnated by several homopolystyrenes (hPs) differing in molecular weight to produce mesoglobules. The copolymer/homopolymer analog of mesoglobules formed by preferentially swelling an ordered triblock copolymer with a midblock-selective solvent. The mesoglobule phase was stabilized by high swelling, which was maintained by the high activity of the parent homopolymer. Electron microscopy is employed to declare the extent to which swelling occurs in each mesoglobule as a function of hP composition and molecular weight. Dynamic mechanical analysis has been performed as a function of hP uptake time and shows that the dynamic storage modulus of the mesoglobules decreases with increasing hP content. The extent to which this reduction occurs in SIS/hP mesoglobules is, however, different from what is observed in analogous SIS/hP blends produced by concurrent solution casting, due presumably to the high retention of midblock bridging in the mesoglobules. Limited investigation of nanostructural evolution in the non-equilibrium mesoglobules at elevated temperatures is explored and its ramifications discussed.

10:15 AM EE3.6 NETWORKED NONSTRUCTURED POLYMERS WITH NEGATIVE POISSON’S RATIOS J.N. Grant, K.E. Evans, Department of Chemical Engineering, University of Exeter, Exeter, UNITED KINGDOM.

Materials with negative Poisson’s ratios (auxetic) exhibit the very unusual property of becoming wider when stretched and narrower when squashed. This anomaly results in many beneficial effects in the products and materials and makes them superior to conventional materials in many practical applications. Negative Poisson’s ratios are not a common feature in naturally occurring materials and hence research has focused, in recent years, on designing new polymeric materials which exhibit these unusual properties. We have found that the Poisson’s ratio is highly dependent on the materials nanostructure and the deformation mechanism. In view of this we present here designs for a number of novel networked polymers which may achieve negative Poisson’s ratios. Furthermore, we shall show how these polymers can be tailor-made to have a pre-designed set of mechanical properties through modifications in the polymers nanostructure.

10:30 AM EE3.7 CATIONIC MIXING OF THERMOPLASTIC MEATS AS A MEANS TO PRODUCE SPUN FIBERS WITH INTERNAL REINFORCEMENTS B.L. Gomillion, M.S. Ellsion, School of Textiles, Fiber and Polymer Science and D.A. Zumbrenner, J. Wang, Department of Mechanical Engineering, Center for Advanced Engineering Fibers and Films, Clemson University, Clemson, SC.

A novel blending device has been developed in which separate thermoplastic melt streams are received from screw extruders and combined by chaotic mixing. Recursive stretching and folding processes in the chaotic mixing environment lead to the formation of structured melts and morphology refinement. The focus of this work has been on morphology development by utilizing favorable mixing conditions where structure is evolved and not broken down. The device has been used in initial work to specifically produce die extrusion of the structured melt, monofilaments with internal micro-fibril structure. The microstructures of polystyrene and polypropylene blends are referred for differing extents of mixing and are related to flow conditions with the aid of computational simulations.

10:45 AM EE3.8 MOLECULAR RECOGNITION AND POLYMERS: BRICKS AND MORTAR FABRICATION OF NANOSTRUCTURES Vincent M. Rotello, Department of Chemistry, University of Massachusetts, Amherst, MA.

Multi-scale ordering of materials is central for the application of molecular systems to macroscopic devices. Self-assembly based on selective control of non-covalent interactions provides a powerful tool for the creation of structured molecular-level systems; application of this methodology to macromolecular systems supplies a potential means for the transformation of this structural level. In ongoing research, we are applying the control and diversity possible via supramolecular chemistry to the creation of polymeric systems.

11:15 AM EE3.9 CREATION OF 3D BURIED LATERAL NANOSTRUCTURE IN AMORPHOUS POLYMER FILMS CONTAINING AZOBENZENE SIDE GROUPS. Ulrich Pietzsch, Thomas Geue, Institute of Physics, Univ. of Potsdam, Potsdam, GERMANY, Paul Rocken, Dept. of Physics, Royal Military College, Kingston, Ontario, CANADA, Almerin Natansohn, Dept. of Chemistry, Queens University, Kingston, Ontario, CANADA.

Lateral surface patterns in amorphous polymers containing azobenzene side-chains can be produced by holographic exposure with circularly polarized light at 488 nm [1]. The processing takes place at room temperature, i.e. far below the polymer glass transition temperature and without material evaporation. Depending on the recording parameters, the inscribing laser light the surface pattern appears after about 5 minutes and results in an undulation amplitude up to 500 nm. The lateral scale can vary between 300 and 3000 nm. After creation the surface pattern is stable in ambient light for temperatures up to 70°C. In order to study the dynamics of this material transport we performed temperature and time-dependent laser scattering experiments close to Tg. The probe wavelength (633 nm) was chosen to record significant absorbance of the azobenzene moieties. We used thin films of polymides (pDRIM, Tg=125°C) as well as non-polar (pMEA, Tg = 80°C) azobenzene side-chain homopolymers, spin coated on glass substrates. Surface gratings with lateral spacing of about 3000 nm and an undulation depth of about 30 nm were produced to enable the detection of three diffraction orders in transmission geometry. Their diffraction intensities are a measure of the profile of the surface grating. In agreement with our recent X-ray scattering experiments [2] the surface gratings start melting at temperatures of about T = Tg + 5K. For the non-polar material the diffraction intensities vanish completely upon heating the samples above Tg. This is accompanied with smoothing the sample surface as verified by AFM inspection after cooling down to room temperature. We found a different behavior for pDRIM. Upon annealing the samples at T = Tg + 5K the diffraction intensity does not reduce to zero. After reaching a minimum at about 30 seconds it starts to increase again. After several hours the diffraction intensity is of the same order of magnitude as that of the initial surface grating. Because the surface remains flat the diffraction signal must come from a lateral density modulation below the surface. This is also confirmed by transmission electron microscopy. The created density contrast is estimated at 30%. The lateral spacing of the buried density grating agrees with the initial surface pattern. Despite of the fact that the sample absorbance is very small at the probe wavelength, the rate of formation of the pattern is found to depend on the intensity and the polarization state of the probe laser light. Experiments for studying the physical process of density pattern formation are underway. [1] P. Rocken, E. Buttini and A. Natansohn, Appl. Phys. Lett. 66, 136 (1995). [2] Th. Geue, M. Schultz, J. Grenzer, U. Pietzsch, A. Natansohn and P. Rocken, J. Appl. Phys. 1999. [3] U. Pietzsch, P. Rocken, A. Natansohn, to be published.

11:30 AM EE3.10 MICROSTRUCTURED POLYPEPTIDE LAYERS BY SURFACE INITIATED POLYMERISATION. Hans-Georg Braun, Thomas Kratke-Meier, Institute of Polymer Research, Dresden Microstructure Group, GERMANY.

The modification of surfaces with biopolymers is of increasing interest. Protein layers on surfaces and interfaces are known to control mineralisation processes, they can control cell growth in contact with artificial non biological materials etc. The binding of biopolymers to surfaces is often done by a grafting to technique. In this technique the surfaces are modified with end groups which can then be used to appropriate binding groups of biomolecules from solution. We use a grafting from technique to prepare thin polymer polypeptide layers
polyethylene or polyurethane layers on gold, silicon or aluminum surfaces. The polymerization technique is combined with lateral surface patterning by microcontact printing in order to obtain micropatterned thin polyamide layers. The procedure starts with microcontact printing of initiator molecules (e.g., primary amines) to the surface. In contact with activated amino acids these surface bound initiator molecules start the polymerization of the polyamides by the N-carboxy anhydride method. Microstructured polyamide layers of 5 nm to about 40 nm are formed depending on the polymerization conditions. The molecules grow in a helical conformation but can undergo structural transformations on the surface either induced by different solvents or by variation of pH values. The changes are reversible as well as swelling of the polyamide layers. Polyamides with hydrophilic, hydrophobic or amphiphilic behavior can be prepared and offer interesting model systems to study specific protein interactions.

11:45 AM EE4.1

Block and segmented copolymers are well known to permit the establishment of micro- or nanophase structures beyond a certain critical block length. Interestingly, the utilization of poly[arylene ether phosphine oxide]s has been demonstrated to allow for organic/inorganic hybrids based upon coordination complexes of transition metal salts, transition, or even inorganic acids, such as phosphonic acids. In certain cases, the utilization of structurally segmented systems should enable one to develop ordered regions that have dimensions characteristic found in block or segmented copolymers. The synthesis of the resulting multiblock materials has utilized a variation on our earlier published procedure, wherein hydroxyl-terminated poly[arylene ether oxide]s can be quantitatively condensed with dimethylamino functional poly(dimethylsiloxane) oligomers to produce high molecular weight multiphase copolymers. High molecular weight systems, which form transparent tough films with morphologies expected from volume fraction considerations have been prepared. Complexation of the phosphine oxide unit has been demonstrated and results will be indicated and supported by a variety of thermal analysis measurements, as well as scanning and transmission electron microscopy.

SESSION EE4: NANOSTRUCTURES/SYNTHETIC ROUTES, DENDRIMERS, AND HYPERBRANCHED POLYMERS

Chair: Bradley F. Chmelka
Tuesday Afternoon, April 25, 2000
Concordia (Argent)

1:30 PM EE4.2
SYNTHESIS OF NANOSTRUCTURES MEDIATED BY TETHERED ORGANOMETALLIC CATALYSTS. Thomas A.P. Seery, Qinghong Fu, Hanrong Gao, Dale Huber, Sara Jeffers, Fatim Varma, Institute of Materials Science, University of Connecticut, Storrs, CT.

Organic-inorganic hybrids can be synthesized by tethering initiators for chain growth processes to a variety of metal and oxide surfaces. Recent interest in these systems has led to the development of methods for initiating radical or ionic processes from noble metal and silicon oxide surfaces. This approach to interface modification will find its greatest impact in fields where thin, robust layers are critical for enhancing performance, e.g., microelectromechanical systems. Our efforts have been directed towards developing methodologies to tether organometallic catalysts to surfaces via initiator ligands for chain growth polymerization. The surface functionalization methodology leads to dense layers that are currently being investigated for barrier properties, hydrogen and herbicide bonding.

1:45 PM EE4.3
EFFECTS OF NANOSTRUCTURE AND SELF-ASSEMBLY ON POLYMERIZATION KINETICS. Brian J. Elliott and Christopher N. Bowman, Univ. of Colorado, Dept. of Chemical Engineering, Boulder, CO.

Polymeric nanostructures can be formed by the polymerization of monomers in a liquid crystal solvent resulting in structures such as lamellae, hexagonal, and bicontinuous. Polymerizations of ordered solvents result in altered kinetics relative to bulk polymerizations or isotropic solutions. The local concentration of the monomer due to the nano-phase separation generally leads to an increased polymerization rate in ordered systems. Polymerizations of various (meth)acrylates have been performed in liquid crystalline solvents, such as ABA type triblock copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO). These triblock copolymers are hydrophilic, hydrophobic, and amphoteric blocks that form micellar, lamellar, hexagonal and bicontinuous microstructures in aqueous solutions. Our research involves using hydrophilic monomers that should tend to partition into the aqueous regions in these hydrophilic liquid crystals. By polymerizing monomers that are in self assembled systems, the nanostructure can be fixed provided the polymerization does not induce phase separation (larger than the nanoscale ordering). Polymerization kinetics were monitored using GPC-DRI and FTIR spectroscopy. The self assembled, mid-FTIR spectroscopy can not be used to study these systems due to the presence of 10-40% water. The nes-IR technique probes the overtones of fundamental, mid-IR absorptions and is less affected by the presence of water but does not mask the absorbance of the C=O of the [meth]acrylate functional group.

2:00 PM EE4.3
MATERIAL WIRES IN NANOMETER SIZE FROM SELF-ASSEMBLED OPV-PFG DIBLOCK COPOLYMERS. H. Hsiao, Argonne National Laboratory, Chemistry and Materials Science Divisions, Argonne, IL, Poppagandhi Thiyagarajan, Volkker S. Urban, Argonne National Laboratory, Intense Pulsed Neutron Source, Argonne, IL, Luping Yu, Hengbin Wang, University of Chicago, Department of Chemistry, Chicago, IL.

The self assembly process of block copolymers is a current research interest because it provides a viable route to prepare one-, two-, and three-dimensional nanostructured materials. With built-in functionality in the block copolymers, one may utilize the self assembly process as a driving force to reach ordered materials with interesting physical properties. The self-assembly of OPV-PFG [poly(phenylenevinylene) and PEG] is polyethylene glycol, is such a molecule by design. The OPV segment is hydrophobic and rigid while the PEG segment is hydrophilic and flexible. We have discovered that the OPV-PFG macrocomplexes in organic solvent with concentration larger than 0.05wt% self-assemble into giant rod-like micelles. From modified Guinier analysis for rod shapes, we obtained a rod radius of 77.1 ± 0.7 Å for an OPV-PFG containing 13 phenyl rings, 12 C=O bonds, and 4 ethylene glycol monomer units. The model for the micelle consists of OPV inner core and PEG outer shell. The radius includes contributions from both OPV and PEG segments. In order to measure the inner core directly, we carried out contrast matching experiments. The neutron scattering length densities for OPV, d-PFG, and d-Thf (tetrahydrofuran) are 0.79, 0.26, and 0.36 x 10^-5 cm^-2, respectively. Under these conditions, the scattering contributions from d-PFG can be effectively filtered off. With the size of the inner core, we are able to construct better models to understand the self assembly process. The randomly oriented long rods of OPV-PFG in solution can be ordered with addition of water. At 10% water concentration, a dramatic phase transition occurred. The phase transition is interpreted as the formation of closely packed rods. From a correlation peak a = 0.333 Å^-1, a rod-rood distance of 190 A is obtained. The rod-rood distance can be tuned by controlling the polymer concentration. These rod-like micelles can also be dispersed with use of TEM on cast films. The characterization and physical properties of these novel diblock copolymers will be presented. This work was supported by the U.S. Department of Energy, Basic Materials Sciences, under W-31-109-ENG-38, H. Hsiao and L. Yu acknowledge the support from UC/ANL Collaborative Grants and L. Yu acknowledges U.S. AFOSR support.

2:15 PM EE4.4
NOVEL PROPERTIES OF DENDRIMERS AND OTHER HIGHLY BRANCHED MACROMOLECULAR ARCHITECTURES. Craig J. Hawker, Marcello Picotti, Eric Harth, IBM Almaden Research Center, San Jose, CA, Jeon M.J. Frechet, Department of Chemistry, University of California, Berkeley, Berkeley, CA.

The synthesis of dendrimers with a non-polar surface layer surrounding a polar interior containing a predetermined number of active functional groups is one of the major achievements of dendrimer science. A number of discrete, nanometer sized molecules to catalyze standard SN2 and E1 organic transformations was examined and the effect of changing the nature of the internal functional groups on the dendrimer size on catalytic activity studied. The highest catalytic activity was observed for the 4th generation hydroxymethyl functionalized dendrimers, which showed turnover numbers of approximately 17 400. The dendrimer could be recycled without loss of activity.

2:45 PM EE4.5
DENDRIMERS: MACROMOLECULAR CARTOONS FOR CHEMISTRY AND PHYSICS. Brian J. Baker, Polymers Division, NSTI, Guilderland, NY.

Dendrimers represent a new class of polymers having shape and structural uniformity. Unlike typical polymers that we model as strings of flexibly linked beads, the pattern of regular branching in
dendrimers creates molecules with unique properties. To consider the fabrication of devices with dispersed or deposited dendrimers, or the incorporation of metals or guest molecules into a dendrimer, it is necessary to understand their structure and their interactions with the surroundings. With increasing volume fraction, as dendrimers in solution crowd each other, they can interpenetrate or collapse. In our work at high volume fractions we demonstrated self-assembly structure, indicating that the spatial arrangement of the molecules does not change and we have shown that the dendrimer collapses, with little interpenetration, in order to maintain their random close packing. The morphology and size of small angle x-ray scattering (SAXS) techniques used to investigate a variety of dendrimers in solution, in bulk, in mixtures with other polymers, and incorporated into networks. As a result of their special structure, these molecular materials have interior and exterior segments that can be designed with different chemical functionality. Clearly the dendritic copolymer nature reinforces a molecular identity to a far greater extent than is achieved for traditional synthetic polymers. This capability for intricate molecular patterns and potential applications. At the very least, because they can be engineered reliably, dendrimers are powerful research tools.

3:45 P.M. EE4.6
SOLID STATE 13C NMR INVESTIGATION OF RING-FLIPPING DYNAMICS OF BENZYL ETHER DENDRIMERS AND DENDRIMER BLENDS. Joseph S.H. Huang, Christopher A. Klug, Dept. of Chemical Engineering, Stanford University, Stanford, CA; Craig J. Hawker, IBM Research Division, Akamai Research Center, IBM, San Jose, CA.

Due to the highly controlled nature of the hyper-branched dendritic systems, their potential applications at the nano-scale range from drug-delivery vehicles to low-k appa dielectric matrix, their behavior in the solid state is still largely unexplored. In this study, solid-state 13C NMR was used to probe the dynamics of the benzyl ether dendritic systems, focusing on the first generation globular dendrimers, dendrimer-polystyrene copolymers, and blends of the dendrimer-polystyrene copolymer with polystyrene. Investigations of the 13C T2 relaxation behavior of the dendrimers show that multi-exponential relaxation behavior occurs for the carbons associated with the outer rings for all three systems. Dipolar Rotation Spin-Echo (DRSE) was used to measure 13C-1H dipolar coupling for protonated carbons of outer rings. From comparisons to simulations, we have determined that the outer rings are undergoing 18k flips. Since the rings are undergoing motion for all three systems, we conclude that the blending dendrimers with polystyrene does not freeze out the motions of the outer rings.

4:00 P.M. EE4.7
HIERARCHICAL STRUCTURE FORMATION IN LINEAR-DENDRITIC BLOCK COPOLYMERS. Dennis J. Podmor, Materials Science and Engineering, University of Delaware, Newark, DE; Ivan Gitsov, Department of Chemistry, SUNY-ESF, Syracuse, NY.

Traditional mesoscale (10-100 nm) structure formation in block copolymers is defined by the chemical, or primary, structure of the polymer molecules and, to a lesser extent, the processing conditions (solvent selection, temperature treatment, external fields) to which the molecules are exposed during self-assembly. Recent experiments and theory have explored the additional molecular parameters of conformational asymmetry and molecular architecture in forming new structures. Linear/dendritic block copolymers provide a direct means of molecular shape as an additional, flexible, and controllable parameter in molecular design for new mesoscale structure formation. In addition, crystallinity in the linear block, combined with the unique shape disparity between blocks, provides an opportunity for hierarchical structure formation spanning the nanoscale (crystallinity) to the mesoscale (microphase separated lattices) all the way to the macroscopic regime (well developed, spherical superstructure). All three morphological levels may be possible in the same system dependent on processing conditions. Initial characterization experiments exploring the bulk morphological behavior of amphiphilic polyester dendrimerine diblock and triblock copolymers will be discussed.

4:15 P.M. EE4.8
ULTRATHIN MULTILAYER FILMS OF DENDRIMER NANOSECONDARY COMPOSITES. Lajos Balogh, Peter Balogh, Donald A. Tomalia, University of Michigan, Department of Biologic NANOSECONDARY, Ann Arbor, MI; Shun M. Redmond, Steven C. Rand, University of Michigan, Dept. of Physics, Dept. of Electrical Engineering and Computer Science, Ann Arbor, MI.

Dendrimer-based nanocomposites (DNs) are recently discovered hybrid materials composed of nongenic guest domains and a dendritic polymer host containing no covalent bonds between host and guest(s). These aromatic core nanocomposite materials are highly uniform and can be made in controlled sizes. They often display unique physical and chemical properties as a consequence of the atomic/molecular level dispersion of their components. Solubility and processability are determined by the host polymer molecule; however, these nanocomposites also possess many of the desirable chemical and physical properties of the guest molecule(s) or atom(s). Self-assembled monolayers (SAMs) of molecules are capable of molecular recognition and have many potential applications. In this work poly(amine) dendrimers were used to prepare a piezoelectrically controlled multi-layer of dendrimers and dendrimer nanocomposites on different substrates by using hyper-branched polymers. The studies of using dendrimer and dendrimer nanocomposites as well as characterization and optical properties of the metal containing organic multilayers will be compared and discussed.

4:30 P.M. EE4.9
DENDRIMER-Templating AS A NEW ROUTE TO QUANTUM DOT LUMINESCENT PROBES. Bruce J. Lennox, Richard M. Crooks, Texas A&M University, Dept. of Chemistry, College Station, TX.

We present a new approach to the synthesis of luminescent semiconductor quantum dot (QD) probes in which particle growth is templated with poly(amine) (PAMAM) dendrimers. The dendrimer/QD assemblies (D/QAs) are prepared under conditions much gentler and less toxic than the current molten reagent organometallic synthesis, yet still exhibit a high degree of control over particle size. Due to quantum confinement effects, small changes in QD size allow for dramatic changes in optical properties. D/QA assemblies prepared using small to low generational dendrimers produce smaller diameter particles compared to those using larger, higher generation dendrimers. For example, CdS QD growth templated with fourth generation dendrimer results in particles with absorbance and emission maxima at 280 nm and 320 nm, whereas CdS growth templated with sixth generation dendrimer yields particles with red-shifted maxima at 320 and 460 nm. Once prepared, the dendritic shell of the D/Q structures are then modified in a variety of ways to direct the behavior of the assemblies. For example, hydrophilic amine-terminated D/Q assemblies can be made hydrophobic via reaction with end groups with long-chain aliphatic acids. These probes may also be modified via electrostatic interaction of the dendritic shell with other materials. Dendrimers serve to act as effective agents for the transfection of genetic material into living cells. D/QD hybrids represent a new, desirable class of easily synthesized color-tunable luminescent probes.

SESSION EE5: POSTER SESSION
Chair: Thomas Thoma Albrecht
Tuesday Evening, April 26, 2000
8:00 P.M.
Metropolitan Ballroom (Argent)

EE5.1

Surface topography of amorphous polymers poly(methyl methacrylate) and polystyrene has been investigated by scanning probe microscopy technique and analysed with the help of auto-correlation function approach. Spatial correlations in the arrangement of sub-macromolecular fragments on the surface are studied depending on the molecular mass, preparation conditions, and whether the surface was free, i.e. in contact with air, or confined with the silicon substrate. The correlation length of roughness distribution on the surface of amorphous polymers corresponds to internal dimensions of unperturbed polymer chains (radius of gyration). Scaling behaviour of roughness is analysed with the Hurst approach, and found to be different for the free surface and for the confined one. As a result of annealing at a temperature above the glass transition temperature of the bulk polymer, both surfaces converge to similar fractal dimensionalities and correlation lengths.

EE5.2
FLUOROPOLYMER NANOTUBE COMPOSITES FOR COATING AND NANOSCOPIC PROBES. Hiren Shah, Dennis Smith, Clemson University, Department of Chemistry, Clemson, SC; Richard Cserer, David Carroll, Clemson University, Department of Physics, Clemson, SC; Lori Goldner, Jeesanug Han, National Institute of Standards and Technology, Gaithersburg, MD; John Bunko, Clemson University, Department of Ceramic and Materials Engineering, Clemson, SC.

In situ thermal cyclopolymerization of bis(3-triethoxysilyl) with
aromatic other compounds in the presence of multi-walled carbon nanotubes affords high molecular weight thermoplastic or thermo-
settable fluoropolymers, furthering well known and isolated carbon nanotubes (0.05 wt %). Optically clear films and fibers can be prepared by thermal processing. Films were character-
ized by thermal and electrical conductivity and UV/Vis spectroscopy. Random inclusion of nanotube composite fibers can result in exposure of a single isolated carbon nanotube protruding (0.4 microns in length) from the fiber tip as observed by TEM. Synthesis, composite fabrication, and potential use as AFM or NSOM probe tips, and conductive coatings for space vehicles will be presented.

EES.5 LAYER BY LAYER DEPOSITION OF NANOPARTICLES AND POLYELECTROLYTES ONTO COLLOIDAL PARTICLES. Rachel A. Caruso, Frank Caruso and Helmut Möhwald, Max Planck Institute of Colloids and Interfaces, Potsdam, GERMANY.

The use of colloidal templates, such as InxSe, on which layers of nanoparticles are deposited by the alternating adsorption of oppositely charged polyelectrolytes and nanoparticles has resulted in nanoparticle multilayer shells surrounding the colloidal core. This process allows nanometer control of both the final diameter of the material, by choice of the initial colloidal diameter, and the wall thickness of the nanoparticles, depending on the number of layers deposited. The colloidal core can be removed by various methods, including heating of the sample in a manner induced crystallization of the organic material, or exposing the sample to acid solutions, leaving behind a hollow inorganic or organic/inorganic hybrid shell. From electron microscopy studies these shells remain intact, even after sonication. The deposition of various nanoparticles, (e.g., silicon and iron oxide) imparts tailored properties to the materials.

EES.6 NANOSTRUCTURE AND MECHANICAL PROPERTIES OF THERMOPLASTIC ELASTOMERS FILLED WITH SOLID PARTICLES. Arnaud Chiche, LPMC, Collège de France, Paris, FRANCE; Virginie Ponsart, UMR CNRS/Rhinol, Cranbury, NJ; Gervaise Mazer, Institute Curie, Paris, FRANCE.

Block copolymers are macromolecules made of sequences of two or more chemically different monomers in a homopolymer-like fashion. The temperature, the blocks segregate, forming nanometer-size structures. The relative volume fractions of the blocks monitor the obtained morphologies and, together with the preparation method, the degree of order. This microphase separation gives the material unique mechanical properties. We have been interested in triblock copolymers forming thermoplastic elastomers: the main middle part of the chain constitutes a fluid continuous phase, whereas two small and rigid blocks at the ends of the chain segregate in glassy nodules acting as crosslinking knots. When the system is heated above the glass transition temperature of the nodules, it loses its elastic properties and can for example be molded. In the triblock thermoplastic elastomer system studied, we have introduced submicron magnetic particles, bearing a permanent magnetic moment. A process of alignment under magnetic field at high temperature and during cooling, is aimed at producing a magnet and anisotropically organized sample, likely to exhibit magnetically-controlled elasticity. The system was studied by small-angle X-ray scattering, transmission electron microscopy and mechanical tests, varying the type of triblocks and the particle volume fraction. This shows that the microstructure of the particles, even at very small volume fractions, does not modify significantly the nanostructure of the polymer system. The effect of the particles on the viscoelastic properties strongly depend on the type of particles used: when elongated particles bigger than the nanostructure characteristic size were used, the presence of the particles induced a strong increase of the viscosity of the sample, whereas with other particles of spherical shape and nanometric size, no such effect was found. Both the size of the particles and their coverage of the surface have an effect on the mechanical properties of the mixed system.


The characterization and behavior of thin polymeric porphyrin membranes prepared by interfacial polymerization is reported. Membrane thickness and thickness changes by tapping mode atomic force microscopy [TMAFM]. UV-Vis spectroscopy, luminescence and electrochemical studies allowed for investigation of these membranes for application to chemical sensing and molecular sieving. Specifically, the polymeric membranes were formed from pairs of reactive comonomers where either one or both were functionalized tetraphenyl porphyrins. Slight modifications of the polymerization conditions (porphyrin monomer functionality, monomer concentration, solvents and solution pH) greatly affect the photophysical properties and size selectivity of the resulting membranes. TMAFM imaged revealed that the membranes were continuous with uniform thickness (80.2 to 10 μm) and varying roughness (10 to 350 nm). Compositional mapping of membrane morphology and structure using phase contrast tapping mode microscopy revealed face-specific heterogeneous interfacial phase segregation which can be controlled by modification of polymerization conditions. We also demonstrated that the highly efficient photochemical properties of these materials can be used for chemical sensing via changes in luminescence. The polymer porphyrin frameworks demonstrate photophysical behavior similar to the porphyrin precursors with strong luminescence emission centered at 650 nm. Upon exposure to a series of analytes the membrane emission was reduced by varying degrees. Membrane porosity was characterized by optical and electrochemical transport studies involving probe molecules of varying size. Electrochemical studies allowed for quantification of the small-molecule permeation as a function of film thickness and morphology. Preliminary experiments designed to provide enhanced control over the membrane pore size will be presented. The goal is to form polymeric films with cavities of well-defined shape and finite size by utilizing functionalized nanoscale molecular sources as the monomer precursors. More rigid control over the membrane internal structure will be very advantageous for selective sensing and separation applications.

EES.8 MOLECULAR DYNAMICS SIMULATION STUDY OF NORBORNENE-POSS POLYMERS. R.K. Bhakdiw, Systran Federal Corporation, Dayton, OH; R. Berry, H.L. Farmer, Air Force Research Laboratory, Materials and Manufacturing Directorate, WPAFB, OH.

Atactic molecular dynamics simulations have been used to delineate the effect of introducing polydodecylammoniumsilsesquioxane (POSS) moieties substituted by cyclopentyl (C5POSS) and cyclohexyl (C6POSS) rings as pendant groups on norbornene. Simulations were also performed on polyboronene for comparison. Calculated volume-temperature behavior and X-ray scattering profiles matched well with experimental results. Most importantly, the effects of incorporating the POSS moieties into the polymer have been identified via simulations. These were judged on the basis of the increase in the glass transition temperature, retardation of the chain dynamics and improvements in the calculated elastic tensile, bulk and shear moduli of the POSS containing polymers compared to the norbornene homopolymer. The most important conclusion from the study is that segregation of the POSS moieties is not required for the beneficial effects to be realized. Indeed, the simulations show that there is no tendency for aggregation to occur among the POSS moieties if they are well dispersed to begin with. Analysis using various intermolecular site-site radial distribution functions show the packing of the polymer chains around the C5POSS is more efficient compared to that in C6POSS and is attributed to the unusually nature of the C5POSS moiety. In addition, the mean squared displacement of the POSS moieties in the polymer was found to be very small at all temperatures leading to a slowing of the segmental dynamics of the backbone polymer chain, and thereby impacting the macroscopically observed stiffness. It is reasoned that the chief source of reinforcement stems from the POSS moieties at the pendant points in the polymeric matrix. This has more to do with the complex nature of these moieties versus any specific intermolecular interactions.

EES.9 PROBING NANOENVIRONMENTS IN POLYMER FILMS BY SINGLE MOLECULE SPECTROSCOPY. Jana P. Schmidt, Paul J. Carson, and Steven R. Baten, Dept. of Chemistry and Biochemistry, UC Santa Barbara, Santa Barbara, CA 93106.

Recent single molecule detection have opened up new avenues for probing nanoeuvnironments in thin polymer films. In our work, single organic carbonylamine dye [D1C8] molecules have been used to probe the nanoeuvnironments of poly (methyl-methacrylate), polystyrene, and poly(ethylene oxide). Films were studied using a homebuilt Laser Scanning Confocal Microscope (LSCM) coupled to a CCD spectrometer. We have characterized the local environment of these thin polymer films by measuring the distribution of fluorescence spectra and intensity fluctuations of D1C8 within each polymer matrix. The distribution of peak maximum, FWHM, and intensity auto-correlation times show distinct characteristics with decreasing polarity of the host matrix.
EE5.8 SCANNING TUNNELING MICROSCOPY OF GOLD FILMS AND POLYMERICIZATION OF LANGMUIR-BLODGETT FILMS OF DIACETYLENES. Nicholas G. Semkovich, Queen Mary and Westfield College, University of London, Physics Department, London, UNITED KINGDOM.

The surface morphology of thin gold films thermally evaporated on glass, mica, CaF₂, and Si substrates was investigated by scanning tunneling microscopy and compared to each other. The surface roughness of the CaF₂ and Si substrates was very similar, being around 10 Å. The morphology of the films on glass and mica was significantly different, with a higher density of nanoscale features on glass. Electron microscopy showed that the gold film on glass had a more uniform thickness, while the film on mica had more defects and irregularities. This observation suggests that the substrate material can significantly affect the final film structure.

EE5.9 CHEMICAL IMAGING WITH SOL-100 NM RESOLUTION USING APERTURELESS SCANNING NEAR-FIELD INFRARED MICROSCOPY. Bern B. Akeret,延期 and Gilbert C. Walker, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA.

Infrared spectroscopy is often used to determine chemical composition and molecular conformation, but until now, it has not been possible to apply it to the study of nanometer size objects. Conventional infrared microscopy has a 10 μm limitation in spatial resolution. Scanning near-field microscopy is a new technique which allows us to overcome the diffraction limit (λ/2) in spatial resolution. We are combining the high spatial resolution achievable by apertureless near-field microscopy with spectroscopy in mid-infrared range. Here we present data that demonstrate the high spatial resolution and spectroscopic performance of the technique.


The optical properties, such as spectral line-shape and size selectivity of photochromism (PL), quantum yields, cw photoinduced absorption (PDA) and the X-band PL-detected magnetic resonance imaging (MRI) response of polyparaffin (PPV) films and films of isolated PPV chains ordered on the nanometer scale (nano-PPV) are presented and compared. The ordering effect on the photoluminescence intensity of the matrix was measured by self-coalescence. The formation of a regular hexagonal array of hollow cylinders (channels) with an outer diameter of about 40 nm containing the conjugated polymer chains. The optical spectra and the spectral dependence of the PLDM show that the incorporation of the polymer chain into the self-assembled matrix largely eliminates the interchain charge transfer excitons and only allows for intrachain migration of single excitons (SEs). This isolation alters the emission properties of nano-PPV as well as the transition energies of the interchain triplet and polaron states as found from PIA. In particular, from the observed small dependence of the PL intensity on the excitation density in nano-PPV, which is in strong contrast to the perfectly linear dependence in bulk PPV, we find that SEs which are subject to intrachain migration are strongly nonradiatively trapped. The linear growth of the channel length with time is observed in the channel, but moreover the size of the channel is not affected by the photoinduced migration of PPV. From a comparison of the spectral dependence of the PLDM in nano and bulk PPV, we find that the chains are not only isolated in the channel, but moreover are composed of distinct shorter isolated conjugated segments and connected longer conjugated segments.

SESSION EE6/FF6: JOINT SESSION: NANOSTRUCTURES FROM THIN FILMS TO BULK

Chairs: Peter F. Green and Sangee K. Kumar

8:30 AM *EE6.1/FF6.1 STRUCTURE, DYNAMICS, AND PROPERTIES OF POLY-VINYL-CLOSOHEXANE BASED PENTABLOCK COPOLYMERS. Enrico S. Balsamo, Martin Vigil, Robert J. Chadd, Chua, University of Minnesota, Minneapolis, MN; Glenn Frederickson, UC Santa Barbara, Santa Barbara, CA; Stephen Hahn, Dow Chemical Company, Midland, MI.

Polyvinylcyclotetrasiloxane (V), which is produced by catalytically hydrogenating polysiloxane, is characterized by a glass transition temperature of 147°C, a high modulus, and excellent optical properties. However, owing to a large entanglement density, it is not possible to prepare thick transparent polymeric films by conventional solution processing. These films are inhomogeneous and optically cloudy. The melting process, on the other hand, allows the production of films with a smooth surface and optical clarity. This process uses a combination of thermal and mechanical forces to reduce the entanglement density and improve the optical properties of the polymer. The films are then subjected to a post-molding process to further improve their optical properties.

6:00 AM *EE6.2/FF6.2 DOMAIN MORPHOLOGY IN LIQUID CRYSTAL POLYMERS. B. L. Breslau, Amelia M. Loges, and J. J. Lim, UCLA, Department of Chemistry and Biochemistry, Los Angeles, CA; and Sharon C. Glotzer, Stephen A. Langer, NIST, Gaithersburg, MD.

Small molecule liquid crystals and polymers dimerize into two-coexisting phases, one rich in polymer and isotropic, and the other rich in liquid crystal material. The transition between the two phases is characterized by several distinct effects associated with the change in architecture from tricolin to pentablock including heteroepitaxial shrink-induced microstructure alignment and improvements in toughness. These findings will be discussed in the context of current theory and experiment regarding the thermodynamic and dynamic behavior of block copolymers.

9:30 AM *EE6.3/FF6.3 ENTROPICALLY DRIVEN PHASE SEPARATION OF HEAVILY BRANCHED/LINEAR POLYOLEFIN BLENDS. Yingying Chen, Frank S. Bates, Timothy P. Lodge, Univ of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN.

Small Angle Neutron Scattering (SANS) has been used to examine the melt phase behavior of heavily branched random copolymer (polyethylene/fetehylene) blended separately with two linear random copolymers: polymer (polyethylene/fetehylene) and (polypropylene/ 1,4-polyethylene) (PPV). Molecular architecture is the only difference between the two components of the blends. The molecular weights of the two linear random copolymer (polyethylene/fetehylene) are 57,500 and 75,250, respectively. The heavily branched polymer has a molecular weight of 750 kg/mol. Unlike many previous studies that concentrate on the short-branched species, this heavily branched random copolymer consists of 54 long branches on average, where each of them has molecular weight of 13 kg/mol. Three different volume compositions of 25/75, 50/50, and 75/25 have been investigated for both types of blends. SANS results indicate that all blends contain the low molecular weight linear polymer (57 kg/mol) form single phase.
We studied phase separation in thin horizontal layers of binary and ternary colloidal polymeric fluids subjected to a vertical temperature gradient. Under particular conditions surfactomediated, buoyancy-driven convection occurs in the liquid layer that is imposed on phase separation in the system. Convection produces hexagonal and roll patterns with a high degree of order and symmetry on the length scales substantially smaller than in single-component systems. We demonstrate that convection patterns can be trapped in a solid state by using UV-induced polymerization of the reactive oligomers.

Surface segregation in miscible binary polymer blends: M. G. Wignall, J. S. Lin, Oak Ridge National Laboratory, Solid State Division, Oak Ridge TN; R. G. Almey, Florida Agricultural and Mechanical University and Florida State University, Department of Chemical Engineering, Tallahassee, FL; J. D. Londono, DuPont Central Research and Development, Wilmington, DE; L. Mielke, Florida State University, Institute of Science and Technology, Tallahassee, FL; M. H. Kim, Oak Ridge National Laboratory, Chemical and Analytical Sciences Division, Oak Ridge, TN; G. B. Brown, Exxon Chemical Company, Baytown Polymers Center, Baytown, TX.

Differential scanning calorimetry (DSC), transmission electron microscopy (TEM), small-angle neutron and X-ray scattering (SANS and SAXS) have been used to investigate the solid state morphology of blends of linear (high density) and model short-chain branched (low density) polyethylene (HDPE/LDPE). SANS indicates that the mixtures are homogenous in the melt for all compositions when the ethylene branch content in the copolymer is low (i.e., <4 ethylene branches/1000 carbon atoms for a typical molecular weight of 100,000). However, due to the structural and melting point differences between HDPE and LDPE, the components phase segregate in the solid state and form a lamellar morphology with a periodicity, typically 10 nm. The degree of separation is controlled by the crystallization kinetics and DSC, TEM, SAXS and SANS experiments have been used to investigate the solid state morphology as a function of component composition, the thermal history and the rate of cooling. It is shown that the combination of scattering microscopy and calorimetric techniques can provide detailed insight into the morphology on nm-length scales and give the compositions of the various populations of the lamellar crystals and the amorphous regions at the same time.

*Managed by Lockheed Martin Energy Research Corporation under contract DE-AC05-84OR2140 for the U.S. Department of Energy.
domains as small as 10 nm are observed after alloying for 10 hrs. Post-annealing of the blends above the T_g of PMMA (which is dependent on molding time) induces morphological evolution which, varies for blends with PI and PEP. In blends composed of PEP, thermodynamic incompatibility expectedly drives phase separation within the system so that the intimate mixing gained as a result of milling is largely lost. Conversely, PI molding induces higher intermolecular mobility so that the milling-induced nanoscale mixing between PMMA and PI is, for the most part, retained even after annealing for long periods at high temperatures. These results indicate that the intermolecular interaction allows a viable means of producing intimate blends of immiscible polymers that can, depending on interchain reaction, retain their nanoscale morphology.

11:45 AM EE 10/FG 10
STRUCTURE EVOLUTION DURING POLYMER DEWETTING AND DEMIXING. Manfred Stamm,3 Peter Mueller-Bachmann,2 Jochen Gutmann,1 1Institute fuer Polymerschung Dresden e.V., Dresden, GERMANY; 2Technical University, Garching, GERMANY; 3Max-Planck-Institute fuer Polymerschung, Mainz, GERMANY.

Polymer thin films on a solid substrate can be unstable and then show the tendency depending on film thickness and temperature to dewet the substrate. In a polymer blend of incombable components the dewetting is in competition with surface and interface segregation effects, and lateral phase separation will generally occur. These phenomena can be used to generate nanostructures, where regularly spaced droplets or regions of different material form. Structures are investigated by scattering techniques as well as by direct imaging techniques, which are shown to be complementary. By Fourier transform of scanning force microscope images a power density pattern is obtained, where a prominent length scale may be recognized. Scattering techniques on the other hand also provide information from the interior of the sample, where phase separation may have taken place. A wide range of structured surfaces and different roughnesses at the surface of thin films can be formed.

SESSION EE 7: NANOCTRUCTURES PHYSICAL SELF-ASSEMBLY, TEMPLATING AND CHARACTERIZATION
Chair: Steven Dunn
Wednesday Afternoon, April 26, 2000 Concord (Argent)

1:30 PM *EE 7.1
NANOCTRUCTURE SELF-ASSEMBLY WITH ULTRATHIN DIBLOCK COPOLYMER FILMS. H.M. Jaeger, W.A. Lopes, James Franck Institute, The University of Chicago, Chicago, IL.

The microphase separation properties of diblock copolymers provide a convenient path toward the self-assembly of large scale nanopatterns with repeat spacings in the 1-10nm range. I will discuss new possibilities that have emerged for ultrathin copolymer films, with thickness close to the characteristic spacing. In such films, interfacial energies associated with the boundary conditions at the film surfaces can stabilize novel copolymer domain morphologies that do not exist in bulk. An important feature of many of these morphologies is that domains can be controlled on the other block of the copolymer thin film, all the way to the film surface and provide, on nanometer scales, for a lateral modulation of the physical and chemical surface properties. This lateral modulation is key for use of such films as templates in subsequent self-assembly steps in which molecules or nanoparticles selectively aggregate on (or in) one of the domains but not the other. The challenge, however, comes from the fact that the underlying copolymer morphologies correspond to non-equilibrium states. I will present experimental results for the PS-b-PEO diblock copolymer system that show how these non-equilibrium states evolve as a function of time and temperature, and how they can be controlled and exploited for device fabrication.

2:00 PM *EE 7.2
NANOSTRUCTURED TEMPLATES FROM ORIENTED BLOCK COPOLYMER FILMS. Thomas Thurn-Albrecht, Jaegern Schater, Mark Tekumla and Thomas P. Russell, Dept Polymer Science and Engineering & Dept of Physics, Univ of Massachusetts, Amherst, MA.

Block copolymers having microphase structures formed by self-assembly, are promising candidates as starting materials for nanostructure templates. Achieving precise control over the ordering and orientation of block copolymer microdomain structures is an important first step toward this goal. We report about the alignment of Poly(styrene-b-methyldene) (PS-b-MMA) with cylindrical microdomains in a thin film geometry under the influence of an electric field. As a result of the competition between interfacial interactions and the influence of the electric field, we observe two different orientational states which are separated by a well defined threshold field strength. At low strength the electric field is insufficient to overcome van der Waals interactions. Only above the threshold field strength the electric field forces the cylindrical domains to completely orient parallel to the electric field and perpendicular to the substrate. We developed a selective degradation procedure which allows to transform the PMMA cylinders to hollow channels. The channels have a typical width of 10 nm and extend all the way through a micron thick sample. The resulting porous films can be used as templates for nanostructured materials. As an example the deposition of magnetic material into the nanowires will be discussed.

2:30 PM EE 7.3
MASSAGING COMPLEX SELF-ASSEMBLY IN BLOCK COPOLYMERS. Francisca Drent, Glenn H. Fredrickson, Eric Flewelling, University of California, Dept of Chemical Engineering and Materials Research Lab., Santa Barbara, CA.

We discuss an implementation of polymer selfconsistent mean field theory for block copolymers that facilitates combinatorial screening of new types of nanostructures. We illustrate the method by screening for new mesophases in linear ABCA and star ABC block copolymers. The method is very general and can be easily extended to include additional components such as solvents or homopolymers. The case of a mixture involving a monodisperse AB diblock and a polydisperse A homopolymer is specifically discussed.

2:45 PM EE 7.4
CONTROLLING THE SELF-ASSEMBLY OF A RIGID-ROD POLYMER AT SURFACES. Paolo Samori, Humboldt University Berlin, Department of Physics, Berlin, GERMANY; Klaus Muller, MPI for Polymer Reserach, Mainz, GERMANY; Jürgen P. Rabe, Humboldt University Berlin, Department of Physics, Berlin, GERMANY.

The self-assembly of π-conjugated polymers on insulating solid substrates represents a strategy for building well defined and stable nanostructures with chemical functionalities and physical properties, which are of potential use for active components in electronic devices. Since transport phenomena in materials depend on the interplay between electronic structure and order in the molecular assembly, it is important to control the 2D and 3D polycymatic architectures by making use of intramolecular, intermolecular and interfacial forces. We report here on the self-assembly of soluble, alkylicyclic, end-functionized poly-para-phenylenethylenes (PPE) at surfaces and we demonstrate how their growth from solution can be controlled in order to develop well defined micro- and nano-sopic oriented architectures. Dried macromolecular assemblies of PPE prepared by solution coating were studied with Scanning Force Microscopy (SFM) in Tapping Mode. Varying several parameters during the self-assembly, like the substrate, the solvent, the concentration of the solution and the average length of the macromolecule along the conjugated backbone, allowed us to drive the growth of these architectures toward either oriented, micrometer long nanoribbons [1]. These nanostructures are typically two monolayers thick with their alkyl chains oriented perpendicular to the substrate. The distribution of ribbon widths is a good agreement with the molecular weights distribution according to the Schulz-Zimm distribution. This result indicates that SFM offers an alternative valuable route to evaluate molecular weight distributions for a rigid rod polymer [1]. These macromolecular architectures which upon thiol functionalization at their edges are nanostructures ready to bridge Au nanotubes in a molecular nanowire device.


3:15 PM EE 7.5

We report a generalized approach to chemically-induced material porosity in organic-inorganic hybrid systems, based on controlled incorporation of so-called "bulky cage" cyclic and large ring skeletal substituent-groups within the network architecture. Systematic incorporation of such nanostructured templates is demonstrated to result in mesopores (i.e. void inclusions of order 4-40 nm diameter). Template dimers are postulated: (a) increased intramolecular free volume from included void fraction within the skeletal cage structure; (b) increased intermolecular free volume due to decreased chain packing efficiency (i.e. higher density of intrastructure), and (c) increased permeation from bulkiness of the introduced cage structure. Results from various polymer architectures with two independent "bulky-cage" model systems derived from POSS (Polyhedral Oligomeric Silsesquioxane) chemistry with cage length-scale ~ 15 Å, and 3-Cyclooctetitan chemistry with cage length-scale ~ 7 Å, imply the approach is generic and effective as a route to porosity control.
THE FABRICATION OF NANOMETER-SCALE TOOLS USING POLYMER TEMPLATES: Mei-Wei Tsao, Jirong Li, John F. Rabolt, University of Delaware, Department of Materials Science and Engineering, Newark, DE.

In recent years, precision-molded polymer structures have become widely used in electrophotographic applications where the low-cost and light-weight of polymers is highly desirable. Contact printing, on the other hand, is also being investigated as a potential method to create patterned surfaces for sensor and microfluidic applications. In this study, we use high-impact glassy polymers as molds, to fabricate gratings with sub-micron feature sizes. Polydimethylsiloxane (PDMS) has been used to form the grating replica after crosslinking. The nanoscale (~1.50 nm) PDMS gratings have then been used for contact printing. The effects of resin/hardener ratio, curing conditions such as temperature and humidity, will be discussed. In addition, contact printing and micro-capillary channel filling will be demonstrated. Results from AFM and Raman microscopy will be discussed.

A SELF-CONSISTENT FIELD STUDY OF SUBSTRATE CHEMICAL PATTERN RECOGNITION BY COPOLYMERS.
Jan Gengler, Department of Chemical Engineering, North Carolina State University, Raleigh, NC.

We extend the one-dimensional self-consistent field (SCF) scheme of Schützgen-Fleer to three dimensions (3D) and use this 3D SCF model to investigate the adsorption of A-B copolymers from a homopolymer matrix onto planar substrates composed of two chemically distinct sites (C and D), one of which has a preferential affinity for the B segments of the copolymer. To address the role of the substrate chemical heterogeneities on copolymer adsorption, we keep the number of the C and D sites constant (50% of each site) and vary their spatial distribution on the substrate. The interplay between the surface chemical heterogeneity and the chain microstructure is examined for A-B diblock, A-B-B-A, B-A-B-A, and A-alt-B alternating copolymers. Our results indicate that regardless of the type of the surface chemical heterogeneity the A-B diblock and triblock copolymers adopt brush-like structures with the B block being anchored to the substrate while the A-alt-B chains is zipped to the substrate. For a fixed chemical potential of the copolymer in the A-B/A mixture, the amount of the adsorbed copolymer depends on i) the number of the B segments, ii) the copolymer microstructure, iii) the surface adsorption energy of B, and iv) the distribution of the C and D regions on the substrate. 3D maps of the spatial density of copolymer segments provide insight into copolymer deformation at the mixture/substrate interface and also the ability of the copolymer to transfer the substrate pattern into the polymer mixture. In addition, we discuss the circumstances under which the substrate pattern is transferred deep inside the A-B/A mixture and those which lead to strong damping of the substrate motif as one moves away from the substrate/mixture interface.

CONFINEMENT-INDUCED TRANSITIONS IN ULTRA-THIN FILMS: B.M. Overney, C.K. Baervihe, Dept of Chemical Engineering, University of Washington, Seattle, WA; R.J. Winkman, IBM Storage Systems, San Jose, CA; G.W. Tindall, J. Frommer, IBM Almaden Research Center, San Jose, CA.

With the advancement in technology that drives critical length scales into the dimension of molecular distances, ensemble confinement and interfacial interactions become apparent. Bulk theories and properties fail to describe the behavior of mesoscale material, such as molecularly thin films. In the cutting edge technology of lubrication and thin film coating, it is essential to gain information about spreading, thin film equilibrium, flow conditions, and molecular mobility. In this paper, we introduce a technique that has been recently applied in our group to determine surface glass transition temperatures of polymers and shows great potential in measuring entropic transitions in ultrathin liquid-like protective coatings. The technique uses sinusoidal shear responses of a scanning force microscope (SFM). We demonstrate on perfluoropolyether film transitions which are governed solely by confinement imposed on the liquid film by the solid substrate. This information has been obtained with a lateral probing depth on the angstrom scale. The results obtained by this novel technique are compared to kinetic data measuring relative molecular mobility in the same molecularly thin films. The paper also addresses the length scale of interfacial interactions on viscoelastic properties of ultrathin films.

PATTERN GENERATION IN MOLECULARLY THIN POLYMER FILMS: Martin Schmelz, Oswald Prucker, Jürgen Röhrle, University of Freiburg, Institute for Microsystem Technology (IMTEK), Freiburg, GERMANY.