

SYMPOSIUM EE
Nanostructures in Polymers

April 24 – 26, 2000

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* Invited paper

SESSION EE1: HYBRID MATERIALS

Chair: Peter F. Green
Monday Morning, April 24, 2000
Concordia (Argent)

8:30 AM *EE1.1

BLOCK-COPOLYMER TEMPLATING OF ORDERED INORGANIC-ORGANIC COMPOSITES. B.F. Chmelka, 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 self-assembly and processing advantages presented by the block copolymer species with the high thermal and mechanical stabilities 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(ethyleneoxide)-poly(propyleneoxide)-poly(ethyleneoxide) (PEO-PPO-PEO)/silica 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 casting an ultrathin film of asymmetric PS-PMMA diblock copolymer onto a 100 nm thick self-supporting, silicon nitride film. Upon annealing, the diblock copolymer micro-phase separates into a pattern that acts as a template for our arrays. Thermally evaporated metal preferentially decorates one of the blocks of the template. By correctly choosing the metal and 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 NANOSIZED TiO₂ THIN FILMS. M.Z. Atashbar, Department of Electrical and Computer Engineering, Western Michigan University, Kalamazoo, MI.

Titanium dioxide (TiO₂) thin films due to the 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 exposure 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 (<10%RH). The used precursors was titanium butoxide (Ti(OC₄H₉)₄) with an analytic purity, which was dissolved in analytical butanol. After ultrasonic mixing at room temperature for 12 hours the precursor solution was dropped on the substrate and spun at different speeds. The film thickness (30 to 100 nm) was controlled by changing the solution concentration and spinning velocity. After annealing between 400°C to 800°C crack-free TiO₂ thin films were obtained. The morphology, microstructure, crystalline structure and composition of the deposited films were analysed by SEM, XRD, XPS and RBS. The SEM analysis showed that that film is porous and grain size is ranging between 15nm to 60nm. The XPS and RBS results indicated that 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 temperature increased to 800°C a small Rutile component has 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 von Werne, Ion M. Suehiro, Steven C. Farmer and Timothy E. Patten, Univ of California-Davis, Dept of Chemistry, Davis, CA.

Nanoparticles, depending upon their composition, exhibit novel magnetic, optical, and materials properties that can be ascribed to their small size and large surface areas. The incorporation of nanoclusters into polymeric materials and the ordering of nanoclusters into superlattices or extended periodic arrangements are important steps in exploiting the properties of these unusual 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-based 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 polymerizations. A monolayer of atom transfer radical polymerization (ATRP) initiators that possess alkoxy silane functional groups were attached to spherical SiO₂ or core-shell CdS / SiO₂ nanoparticles to yield macroinitiators for ATRP. The attachment of the initiator was confirmed using elemental analysis, solid state CP-MAS NMR, and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. Particle diameters and the unaggregated state of the particles were confirmed in films using TEM and in solution using dynamic light scattering (DLS). These macroinitiators were used in styrene and methyl methacrylate ATRP to yield nanoparticles with an inorganic core and a polymer outer layer. Growth of the polymer from the surface of the nanoparticle was confirmed using kinetics and DLS measurements. These hybrid nanoparticles were cast from organic solvents 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 BIODEGRADABLE POLYMER FILMS ONTO DRUG PARTICLES FOR CONTROLLED-RELEASE FORMULATIONS. James D. Talton, Intira Coowanitwong, Patricia Sidharta, Gunther Hochhaus, James Fitz-Gerald, Rajiv Singh.

Deposition of nano-thin coatings of biodegradable polymers, such as poly(L-lactic acid) (PLLA), poly(lactic-co-glycolic acid) (PLGA), and poly(ethylene glycol) (PEG), onto micronized drug particles has been used to reduce the release rate and improve localized delivery. Pulsed 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 particle. Optimization of the coating parameters such as laser energy density, background gas and pressure, fluidization efficiency and the absorption coefficient of the polymer target material has been performed on several drug powders including budesonide, triamcinolone acetonide, rifampicin, 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 cell toxicity and localized release in a rat pulmonary model has shown this technique to an excellent alternative process to spray coatings.

10:15 AM EE1.6

PROCESS 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 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 nanometer and submicron fibers which either contain or entrap microparticles to optimize membrane strength and functionality. Electrospinning produces fiber mats with fiber diameters in the micron to submicron range that behave like microporous membranes. To give this fiber mat added function, such as superabsorbancy 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 this study. Encapsulation involves incorporating the particles into the dissolved polymer solution, then electrospinning. Mechanical, chemical, and electron microscopy results will be reported and processing methods and conditions will be evaluated with respect to the fiber/particle system performance.

10:30 AM EE1.7

DIRECT VIEW OF POSITIVE TEMPERATURE COEFFICIENT OF RESISTANCE ANOMALY OF CARBON BLACK FILLED POLYETHYLENE BY ELECTROSTATIC FORCE MICROSCOPY. J. Hahn, G.H. Buh*, S.A. Choi, D.Y. Kim, C.M. Ko, J.H. Lee, LG Cable Ltd, Polymer Processing Tech. Group, Anyang-shi, KOREA; *Seoul National Univ, Dept of Physics, Seoul, KOREA.

Systems of crosslinked composites composed of a polymer matrix and a conductive filler exhibit a sharp increase of electrical resistivity at 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 microscope (EFM), which can distinguish conductive phase from non-conductive phase with nanoscale resolution. At room temperature, the richness of conductive phase was observed, confirming the formation of conductive particle network. At melting temperature or above, 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. K. Ogawa, T. Vogt, M. Ullmann, S. Johnson, S.K. Friedlander, Dept of Chemical Engineering, University of California, Los Angeles, Los Angeles, CA.

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 relaxed, the chains contract. In our studies, titania, alumina and iron oxide NCA were generated by laser ablation. The 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 loose at one end and contracting. The titania, alumina and iron oxide NCA all showed elastic behavior for primary particles smaller than about 10 nm, whereas titania 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 van der Waals forces. Under tension, folded chains straighten but when the tension is relaxed, 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. We hypothesize that elastic behavior is a general property of NCA 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 compacts.

11:00 AM EE1.9

A NOVEL USE OF SILICA NANOBEADS FOR ENHANCED DNA DELIVERY. Dan Luo, Ernest Han, Nadya Belcheva, 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 therapies and DNA vaccinations. Over the years many non-viral approaches using chemicals, especially polymers, have been established (e.g., transfection of DNA via cationic lipids and starburst polyamidoamine dendrimers). However, current non-viral transfection methods are still remarkably inefficient with only a small fraction (<10%) of the administered DNA finding its way into the cytoplasm and an even smaller fraction expression in the nucleus (about 0.3%). Here we report a new phenomenon: silica nanoparticles, which by themselves do not deliver DNA, are able to enhance DNA transfection mediated by other commonly used transfection polymers. The method is extremely simple and effective (up to 10-fold over the best

commercially-available transfection), and the enhancement is seen in all transfection reagents tested, including cationic lipid-based and dendrimer-based. The enhancement was dependent on the size of the silica nanoparticles (450 nm, but not 50 nm) and the specific ratio of silica beads in the complexes. The beads have no cytotoxicity. Microscopic observation with fluorochrome labeled DNA and lysosome-trackers demonstrated that the enhanced transfection efficiency is related to enhanced endocytosis. This novel usage of non-cytotoxic silica nanobeads can be employed not only to increase transfection efficiency, but also to explore the general mechanisms of DNA uptake. We expect that our results will assist in designing other biomaterials that facilitate highly efficient DNA delivery.

11:15 AM EE1.10

THERMOVISCOELASTIC BEHAVIOR OF POLYHEDRAL OLIGOSILSESQUOXANE INORGANIC-ORGANIC HYBRID POLYMERS. Andre Lee, Michigan State University, Dept of Materials Science and Mechanics, East Lansing, MI; Shawn H. Phillips, Rusty L. Blanski, Air Force Research Laboratory, Edwards AFB, CA.

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 macroscopic processing and microstructural effects. Recently, families of mono- and multi-functionalized polyhedral oligomeric silsesquioxane (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 organic polymers such as polystyrene, polymethyl methacrylate, or 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 nanoscopic POSS domain on the dynamic of organic polymeric chains.

11:30 AM EE1.11

NOVEL PHOSPHINE OXIDE CONTAINING POLY(ARYLENE ETHER) AND POLYIMIDE-INORGANIC SALT HYBRID NANOCOMPOSITES. Sheng Wang, M. Sankarapandian, H. Zhuang, Q. Ji, A.R. Shultz and J.E. McGrath, Virginia Tech, Dept. of Chemistry, Blacksburg, VA.

Bisphenol 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 melt pressed, indicating thermally reversible interactions among phosphonyl and metal ions. TEM results revealed that the composite films with low amounts of metal salts (molar ratio of metal ion/phosphonyl group ≤ 0.20) had particle sizes less than 10 nm, while higher amounts of inorganic salts generated larger particles. Cobalt salts significantly increased the glass transition temperatures (T_g) of the nanocomposites, but the incorporation of copper salts slightly decreased T_g . This might involve different interactions between the salts and the polymer. Copper ion may show a tetrahedral configuration, whereas cobalt favors octahedral coordination, 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 polymer-cobalt chloride composites. Small amount of salts were also incorporated into copolymers to afford transparent films. The glass transition temperature was dependent on the amount of phosphonyl groups at the same ratio of metal ion/phosphonyl group. Likewise, cobalt chloride and copper chloride were also incorporated into phosphine oxide containing polyimides. The results suggest that the strong interaction of metal ion and phosphonyl group promotes compatibility of the two components.

11:45 AM EE1.12

CROSSLINKING OF POLYOLEFINS BY METHACRYLATE-SUBSTITUTED OXOMETALLATE CLUSTERS. Ulrich Schubert, Gregor Trimmel, Bogdan Moraru, Institut fuer Anorganische Chemie, Technische Universitaet Wien, AUSTRIA.

The so-called POSS-reinforced polymers in which polyhedral silsesquioxanes, mostly the cubic R8Si8O12 are attached to the polymer chains of organic polymers or, less often, crosslink the polymer chains have found considerable interest as novel inorganic-organic hybrid polymers. We have now prepared titanium and zirconium analogues by radical copolymerization of 0.5 - 2 mol% of the structurally well-defined methacrylate-substituted clusters $Ti_6O_4(OEt)_8(OMC)_8$, $Zr_4O_2(OMC)_{12}$ or $Zr_6O_4(OH)_4(OMC)_{12}$ (OMC = methacrylate) with methylmethacrylate, methacrylic acid, or styrene. Structural investigations indicate that the clusters, having

diameters of 0.5 - 1 nm, are retained in the polymer and crosslink the polymer chains. Some microphase separation is observed. The cluster-doped 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: Andrea J. Liu
Monday Afternoon, April 24, 2000
Concordia (Argent)

1:30 PM *EE2.1

POLYELECTROLYTE MULTILAYERS AS NANOREACTORS FOR INORGANIC PARTICLES. M.F. Rubner, T. Wang, S. Joly, R.E. Cohen and E.L. Thomas, MIT, Cambridge, MA.

Polyelectrolyte multilayers fabricated from weak polyacids such as poly(acrylic acid) (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 carboxylic 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 via the use of polyanion/polycation bilayer combinations that are not able to bind inorganic ions such as poly(styrene sulfonic acid)/poly(allylamine hydrochloride). The density of nanoparticles within a film can be varied by controlling the number of available acid binding groups or via the use of multiple loading procedures. The fabrication and characterization of multilayer heterostructures containing nanoparticles of metals (Ag, Pb) and semiconductors (PbS) will be described.

2:00 PM EE2.2

PROBING NANOSCALE STRUCTURE AND EXCITED-STATE DIFFUSION IN DYE-LABELED POLYELECTROLYTE MULTILAYERS USING NSOM. Geoffrey M. Lowman, Steven K. Buratto, 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 poly(styrene sulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) labeled both with Fluorescein (Fl) and Rhodamine-B (RhB). 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 photo-oxidation 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, Keqing Xia, 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 (DLLS) to reveal the cause of the nanosized ionic cluster suppression during the solution casting process, which affects negatively the applications in electrode-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 DLLS. 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, added 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 possibly due to the constructional need of the coexistence of larger and small nanosized 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 F. 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 200 nm, and is passivated by an alkanethiol monolayer. A transition metal catalyst is ligated to an appropriate functionality incorporated into the alkanethiol monolayer, and a polymeric coating is formed through a surface bound catalyst. 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 polymeric coating 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 a gold core and a 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, Honghua 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 and a typical grain structure on the 1000nm length scale. ABA triblock copolymers in which the minor A blocks are polystyrene and the major central B block is either polybutadiene (PBD) or polyisoprene (PI) are a remarkable industrial products. The high tensile strength of this type TPEs is however adversely affected by temperatures exceeding 60° because of the approach of the glass transition temperature of the polystyrene microdomains. In this paper, the effects of polybutyl acrylate (PBA) intercalated clay (kaolinite and muscovite 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 6.0wt%. DMA shows two thermal transition at -70° and 157-178° for PBD and PS-PBA/clay blocks, respectively. The morphological orientation is observed by AFM nanoprobe.

3:45 PM EE2.7

PREDICTING PHASE BEHAVIOR OF PARTICLE/BLOCK COPOLYMER MIXTURES. June Huh, Valeriy V. Ginzburg and Anna C. Balazs, 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 broad two-phase regions and the formation 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 NANOCOMPOSITES. K.E. Strawhecker, C.A. Fonseca, I.R. Harrison and E. Manias, 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, DSC, and TGA. For very low polymer concentrations, the hybrid was found to form 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, reminiscent of crystals obtained through annealing of PVA; incidentally, annealing 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 water permeability and uptake, thermal stability and mechanical properties.

4:15 PM **EE2.9**

SIMULATIONS OF INTERCALATION KINETICS OF POLYMER SILICATE NANOCOMPOSITES. Jae Youn Lee, Roger F. Loring, Cornell Univ, Dept of Chemistry, Ithaca, NY; Arlette R.C. Baljon, 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 attraction between polymer and surface. In both models the intercalation rate has been obtained for various degrees of attraction 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. The results have been applied to interpret x-ray diffraction studies of the intercalation of polystyrene into organically modified layered silicates.

SESSION EE3: NANOSTRUCTURE-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/Elf Atochem (UMR 167), Levallois Perret, FRANCE; François Court, Elf Atochem, CERDATO, Serquigny, 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 submicron rubbery particles or by reactive blending. The toughness can be only achieved when the average inter-particle 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 process 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-methylmethacrylate) 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 dimensional 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 T. Wu and David Heine, Dept of Chemical Engineering and Dept of Chemistry, Colorado School of Mines, Golden, CO.

The technological uses 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 time-scales to produce switchable mechanical, chemical, and optical properties. We present scaling and self-consistent field calculations which show the first-order transition-like switching between states, 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 EPOXIES MODIFIED WITH SELF-ASSEMBLED BLOCK COPOLYMER STRUCTURES. Jennifer M. Dean, Frank S. Bates, University of Minnesota, Department of Chemical Engineering and Materials Science, Minneapolis, MN; Paul M. Lipic, Procter & 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 disordered micelles or vesicles. Curing the epoxy resin locks 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 or asymmetric (volume fraction of PEO = 0.5 and 0.25, respectively) poly(ethylene oxide)-poly(ethylene-alt-propylene) (PEO-PEP) block copolymer are compared. The neat symmetric block copolymer microstructure is lamellar, while the neat asymmetric block copolymer self-assembles into hexagonally packed cylinders of PEO. In the symmetric system, addition of epoxy induces curvature at the PEO-PEP interface. This curvature leads to phase transitions starting with lamellar and ending with ordered spheres of PEP. Spherical micelles result at low block copolymer concentrations. However, addition of epoxy to the asymmetric system reduces the curvature at the PEO-PEP interface, producing the opposite trend in the order of phase transitions (cylinders to lamellar). Multi-layer and single vesicles 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 PEO BLOCK LENGTH ON THE THERMAL BEHAVIOR OF PS-PI-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 PEO block lengths. Consistency among all triblocks in the series was achieved through ethylene oxide addition to the same ω -hydroxy-functionalized poly(styrene-isoprene) diblock (MW~18000g/mol, $f_{PS}=0.5$). Final triblock PEO volume fractions ranged from $f_{PEO}=0.029$ to $f_{PEO}=0.207$. 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/ HOMOPOLYMER MESOBLENDS. Rebecca L. Roberge, Richard J. Spontak, NC State Univ, Dept. of Chemical Engineering, Raleigh, NC; Scott A. White, Becton 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 molecular and blend factors such as chain length ratio and composition on the development of block copolymer nanostructure at near-equilibrium conditions. In the present work, we conduct swelling tests by diffusing a parent homopolymer dissolved within a carrier 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 (hPIs) differing in molecular weight to produce mesoblends, the copolymer/homopolymer analog of mesogels formed by preferentially swelling an ordered triblock copolymer with a midblock-selective solvent. Gravimetric analysis yields uptake curves that reveal a significant increase in hPI solubility with decreasing hPI molecular weight. In addition, the uptake of high-molecular-weight hPI exhibits an induction time, indicating that entry into the ordered SIS matrix is initially difficult for large hPI molecules. Electron microscopy is employed in this study to deduce the maximum extent to which swelling occurs in each mesoblend as a function of hPI composition and molecular weight. Dynamic mechanical analysis has been performed as a function of hPI uptake time and shows that the dynamic storage modulus of the mesoblends decreases with increasing hPI content. The extent to which this reduction occurs in SIS/hPI mesoblends is, however, different from what is observed in analogous SIS/hPI blends produced by concurrent solution casting, due presumably to the high retention of midblock bridging in the mesoblends. Limited investigation of nanostructural evolution in the non-equilibrium mesoblends at elevated temperatures is explored and its ramifications discussed.

10:15 AM EE3.6

NETWORKED NANOSTRUCTURED POLYMERS WITH NEGATIVE POISSON'S RATIOS. J.N. Grima, K.E. Evans, Department of 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 materials properties 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-desired set of mechanical properties through modifications in the polymers nanostructure.

10:30 AM EE3.7

CHAOTIC MIXING OF THERMOPLASTIC MELTS AS A MEANS TO PRODUCE SPUN FIBERS WITH INTERNAL REINFORCEMENTS. B.L. Gomillion, M.S. Ellison, School of Textiles, Fiber and Polymer Science and D.A. Zumbrennen, 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 by die extrusion of the structured melt, monofilaments with internal micro-fibrillar structures.

*The microstructures of polystyrene and polypropylene blends are reported 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 extension of this structure to the macroscopic level. In ongoing research, we are applying the control and diversity possible via supramolecular chemistry to the creation of polymeric systems.

Through the use of specific non-covalent interactions, we have synthesized plug and play polymers-materials where molecular properties such as hydrophobicity and electroactivity are controlled via reversible noncovalent modification. Using the modular nature of the self-assembly, we have created a combinatorial array of complex and diverse nanostructures using simple polymer and monomeric building blocks. These supramolecular complexes are thermo- and solvoreversible, allowing thermal processing of the polymeric systems and facilitating both the fabrication and recycling of materials formed via the plug and play self-assembly process. Polymers can also provide a means for assembly of colloidal nanoparticles. In this bricks and mortar strategy, colloidal particles functionalized with recognition elements serve as the bricks, while polymers bearing complementary functionality serve as mortar, holding together the colloidal particles. With this strategy, the conformational flexibility of the polymer compensates for irregularities in the size and shape of the aggregate structure. We have used this method to efficiently propagate structure during the self-assembly process, providing both discrete structures and materials.

11:15 AM EE3.9

CREATION OF A BURIED LATERAL NANOSTRUCTURE IN AMORPHOUS POLYMER FILMS CONTAINING AZOBENZENE SIDE GROUPS. Ullrich Pietsch, Thomas Geue, Institute of Physics, Univ. of Potsdam, Potsdam, GERMANY; Paul Rochon, Dept. of Physics, Royal Military College, Kingston, Ontario, CANADA; Almeria 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 temperature T_g and without material evaporation. Depending on the power of the inscribing laser light the surface pattern appears after about 5 minutes and results in an undulation amplitude up to 500 nm. The lateral spacing can vary between 300 and 3000 nm. After creation the surface pattern is stable in ambient light for temperatures up to T_g . In order to study the dynamics of this material transport we performed temperature and time-dependent laser scattering experiments close to T_g . The probe wavelength (633 nm) was chosen to avoid significant absorbance of the azobenzene moieties. We used thin films of polar (pDR1M, $T_g=129^\circ\text{C}$) as well as non-polar (pMEA, $T_g=80^\circ\text{C}$) azobenzene side-chain homopolymers, spin coated on glass substrates. Surface gratings with lateral spacing of about 3000 nm and an undulation depth of about 300 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 $T=T_g-15\text{K}$. For the non-polar material the diffraction intensities vanish completely upon heating the sample above T_g . 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 pDR1M. Upon annealing the samples at about $T=T_g+5\text{K}$ the diffraction intensity does not reduce to zero. After reaching a minimum at about 30 minutes 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 [3]. 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. Rochon, E. Batalla and A. Natansohn, Appl. Phys. Lett. 66, 136 (1995).

[2] Th. Geue, M. Schultz, J. Grenzer, U. Pietsch, A. Natansohn and P. Rochon, J. Appl. Phys. 1999.

[3] U. Pietsch, P. Rochon, A. Natansohn, to be published.

11:30 AM EE3.10

MICROSTRUCTURED POLYPEPTIDE LAYERS BY SURFACE INITIATED POLYMERISATION. Hans-Georg Braun, Thomas Kratzmueller, 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 surface is modified with anchor groups which can react with appropriate binding groups of biomolecules from solution. We use a grafting from technique to prepare thin polymer polypeptide layers of

polybenzylglutamate or polylysine layers on gold, silicon or aluminium surfaces. The polymerisation technique is combined with lateral surface patterning by microcontact printing in order to obtain micropatterned thin polypeptide layers. The procedure starts with micro-contact printing of initiator molecules (e.g. primary amines) to the surface. In contact with activated amino acids these surface bound initiator molecules start the polymerisation of the polypeptides by the N-carboxyanhydride method. Microstructured polypeptide layers of 5 nm to about 40 nm are formed depending on the polymerisation conditions. The molecules grow in alpha-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 polypeptide layers. Polypeptides with hydrophobic, cationic or anionic behaviour can be prepared and offer interesting model systems to study specific protein interactions.

11:45 AM **EE3.11**

PERFECTLY ALTERNATING BLOCK/SEGMENTED COPOLYMERS BASED ON POLY(DIMETHYLSILOXANE) AND POLY(ARYLENE ETHER PHOSPHINE OXIDE)S. W.D. Polk, S. Wang, J. Yang, Q. Ji, T.E. Glass, S. McCartney and J.E. McGrath, Virginia Tech, Dept. of Chemistry, Blacksburg, VA.

Block and segmented copolymers are well known to permit the establishment of micro or nanophase structures beyond a certain critical block length. Independently, 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, nanosilica, or even inorganic acids, such as phosphotungstic acid. Thus, the utilization of segmented systems should enable one to develop ordered regions that have dimensions characteristically 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)s can be quantitatively condensed with dimethylamino functional poly(dimethyl siloxane) 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 **EE4.1**

SYNTHESIS OF NANOSTRUCTURES MEDIATED BY TETHERED ORGANOMETALLIC CATALYSTS. Thomas A.P. Seery, Qinghong Fu, Hanrong Gao, Dale Huber, Sara Jeffers, Fatma Vatanever, 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, sulfide or arsenide 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 initiated polymerization methodology leads to dense layers that are currently being investigated for barrier properties, lubricity and interfacial bonding.

1:45 PM **EE4.2**

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, hexagons, and bicontinuous. Polymerizations in 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 lyotropic liquid crystals that form micellar, lamellae, hexagonal and bi-continuous microstructures in aqueous solutions. Our research involves using hydrophilic monomers that should tend to partition into the aqueous regions in these lyotropic 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 near-FTIR spectroscopy. Conventional, mid-FTIR spectroscopy can not be used to study these systems due to the presence of 10-40% water. The near-IR technique probes the overtones of fundamental, mid-IR absorbances and therefore the presence of water does not mask the absorbance of the C=C of the (meth)acrylate functional group.

2:00 PM **EE4.3**

MOLECULAR WIRES IN NANOMETER SIZE FROM SELF-ASSEMBLED OPV-PEG DIBLOCK COPOLYMERS. H. Hau Wang, Argonne National Laboratory, Chemistry and Materials Science Divisions, Argonne, IL; Pappannan Thiagarajan, Volker 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 title compound, OPV-PEG where OPV is oligo(phenylenevinylene) and PEG is polyethyleneglycol, is such a molecule by design. The OPV segment is hydrophobic and rigid while the PEG segment is hydrophilic and flexible. Recently, we discovered that the OPV-PEG macromolecules in organic solvent with concentration larger than 0.05wt% self-assembled into giant rod-like micelles. From modified Guinier analysis for rod shapes, we obtained a rod radius of $77.1 \pm 0.7 \text{ \AA}$ for an OPV-PEG containing 13 phenyl rings, 12 C=C bonds, and 45 ethyleneglycol 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-PEG, and d-THF (tetrahydrofuran) are 0.79, 6.26, and $6.36 \times 10^{10} \text{ cm}^{-2}$, respectively. Under these conditions, the scattering contributions from d-PEG 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-PEG 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 at $q \sim 0.033 \text{ \AA}^{-1}$, a rod-rod distance of 190 Å is obtained. The rod-rod distance can be tuned by controlling the water concentration. These rod-like micelles can also be observed 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, BES-Materials Science, under contract W-31-109-ENG-38. H.H. Wang 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, Marcelo Piotti, Eva Harth, IBM Almaden Research Center, San Jose, CA; Jean 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 presented. The ability of these 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 and 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. Eric J. Amis and Barry J. Bauer, Polymers Division, NIST, Gaithersburg, MD.

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 demonstrate self-similar structure, indicating that the spatial arrangement of the molecules does not change and we have shown that the dendrimers collapse, with little interpenetration, in order to maintain their random close packing. Several microscopy and small angle scattering methods have been 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 molecules 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 has consequences for both molecular properties and potential applications. At the very least, because they can be engineered reliably, dendrimers are powerful research tools.

3:45 PM **EE4.6**

SOLID-STATE ^{13}C 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, Almaden 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- κ dielectric materials, but their behavior in the solid state is still largely unexplored. In this study, solid-state ^{13}C NMR was used to probe the dynamics of the benzyl-ether dendritic systems, focusing on the fifth-generation globular dendrimers, dendrimer-polystyrene copolymers, and blends of the dendrimer-polystyrene copolymer with polystyrene. Investigations of the ^{13}C T_1 relaxation behavior of the dendrimers show that multi-exponential relaxation behavior occur for the carbons associated with the outer rings for all three systems. Dipolar Rotational Spin-Echo (DRSE) was used to measure ^{13}C - ^1H dipolar coupling for protonated carbons of outer rings. From comparisons to simulations, we have determined that the outer rings are undergoing 180-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 PM **EE4.7**

HIERARCHICAL STRUCTURE FORMATION IN LINEAR-DENDRITIC BLOCK COPOLYMERS. Darrin J. Pochan, 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 subjected during phase separation. 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 measure of molecular shape as an additional, feasible, 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, spherulitic superstructure). All three morphological levels may be possible in the same bulk system depending on processing conditions. Initial characterization experiments exploring the bulk morphological behavior of amphiphilic polyether dendrimer-linear diblock and triblock copolymers will be discussed.

4:15 PM **EE4.8**

ULTRATHIN MULTILAYER FILMS OF DENDRIMER NANOCOMPOSITES. Lajos Balogh, Peter Balogh, Donald A. Tomalia, University of Michigan Center for Biologic Nanotechnology, Ann Arbor, MI; Shawn M. Redmond, Steven C. Rand, University of Michigan, Dept. of Physics, Dept. of Electrical Engineering and Computer Science, Ann Arbor, MI.

Dendrimer based nanocomposites (DNCs) are recently discovered hybrid materials composed of nanoscopic guest domains and a dendritic polymer host containing no covalent bonds between host and guest(s). These inorganic-organic 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 compatibility of these materials 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 (SAM-s) of molecules are capable of molecular recognition and have many potential applications. In this work poly(amidoamine) dendrimers were used to prepare z-directionally controlled multilayers of dendrimers and dendrimer nanocomposites on different substrates by using layer-by-layer assembly technique. Advantages 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 PM **EE4.9**

DENDRIMER-TEMPLATING AS A NEW ROUTE TO QUANTUM DOT LUMINESCENT PROBES. Buford I. Lemon, 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(amidoamine) (PAMAM) dendrimers. The dendrimer/QD assemblies (D/QDs) 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/QD assemblies prepared using small, low generation 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 shells of the D/QD structures are then modified in a variety of ways to direct the behavior of the assemblies. For example, hydrophilic amine-terminated D/QD assemblies can be made hydrophobic via reaction of the endgroups with long-chain aliphatic acids. These probes may also be modified via electrostatic interaction of the dendritic shell with other molecules. Dendrimers are also known 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 Thurn-Albrecht
Tuesday Evening, April 25, 2000
8:00 PM

Metropolitan Ballroom (Argent)

EE5.1

CHARACTERISATION OF AMORPHOUS POLYMER SURFACES WITH SPM TECHNIQUE. Valery Bliznyuk, Victor Burlakov, Hazel Assender, Andrew Briggs, University of Oxford, Dept of Materials, Oxford, UNITED KINGDOM; Yusuke Tsukahara, Technical Research Institute, Toppan Printing Co., Tokyo, JAPAN.

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 COATINGS AND NANOSCOPIC PROBES. Hiren Shah, Dennis Smith, Clemson University, Department of Chemistry, Clemson, SC; Richard Czerw, David Carroll, Clemson University, Department of Physics, Clemson, SC; Lori Goldner, Jeeseong Hwang, National Institute of Standards and Technology, Gaithersburg, MD; John Ballato, Clemson University, Department of Ceramic and Materials Engineering, Clemson, SC.

In situ thermal cyclopolymerization of bis- and tris-trifluorovinyl

aromatic ether compounds in the presence of multi-walled carbon nanotubes affords high molecular weight thermoplastic or thermosetting fluoropolymer nanocomposites containing well dispersed and isolated carbon nanotubes (<0.5 % wt). Optically clear films and fibers can be prepared by thermal processing. Films were characterized by thermal and electrical conductivity and UV/Vis spectroscopy. Random cleavage of nanotube composite fibers can result in exposure of a single isolated carbon nanotube protruding (0.4 micron 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.

EE5.3

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 latex, 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 incurring pyrolysis of the organic material, or exposing the sample to acid solutions, leaving behind a hollow inorganic or organic/inorganic hybrid shells. From electron microscopy studies these shells remain intact, even after sonication. The deposition of various nanoparticles, (e.g., silica and iron oxide) imparts tailored properties to the materials.

EE5.4

NANOSTRUCTURE AND MECHANICAL PROPERTIES OF THERMOPLASTIC ELASTOMERS FILLED WITH SOLID PARTICLES. Arnaud Chiche, LPMC, College de France, Paris, FRANCE; Virginie Ponsinet, UMR CNRS/Rhodia, Cranbury, NJ; Gervaise Mosser, Institute Curie, Paris, FRANCE.

Block copolymers are macromolecules made of sequences of two or more chemically distinct monomers. In a bulk sample at room 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 triblocks copolymers forming thermoplastic elastomers: the main middle part of the chain constitutes a fluid continuous phase, whereas two small and identical 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 submicronic 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 magnetized 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 introduction of the particles, even at high 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 the nature of their surface have an effect on the mechanical properties of the mixed system.

EE5.5

CHARACTERIZATION AND BEHAVIOR OF POLYMERIC

PORPHYRIN MEMBRANES. M.H. Keefe, C.Y. Herrera, K.J. Stevenson, M.B. Williams, J.T. Hupp, Northwestern Univ., Dept. of Chemistry, Evanston, IL.

The characterization and behavior of thin polymeric porphyrin membranes prepared by interfacial polymerization is reported. Membrane morphology and thickness were characterized 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) were found to greatly affect the photophysical properties and size selectivity of the resulting membranes. TMAFM images revealed that the membranes were continuous with tunable thickness (0.2 to > 10 μ) and varying roughness (10 to 250 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 demonstrate that the highly efficient photochemical properties of these materials can be used for chemical sensing via changes in luminescence. The polymeric porphyrin assemblies 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 squares as the monomer precursors. More rigid control over the membrane internal structure will be very advantageous for selective sensing and separation applications.

EE5.6

MOLECULAR DYNAMICS SIMULATION STUDY OF

NORBORNENE-POSS POLYMERS. R.K. Bharadwaj, Systran Federal Corporation, Dayton, OH; R. Berry, B.L. Farmer, Air Force Research Laboratory, Materials and Manufacturing Directorate, WPAFB, OH.

Atomistic molecular dynamics simulations have been used to delineate the effect of introducing polyhedral oligomeric silsesquioxane (POSS) moieties substituted by cyclopentyl (C5POSS) and cyclohexyl (C6POSS) rings as pendant groups on polynorbornene. Simulations were also performed on polynorbornene 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 aggregation 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 ungainly nature of the C6POSS moiety. In addition, the mean squared displacement of the POSS moieties in the polymer matrix was found to be very small at all temperatures leading to a slowing of the segmental dynamics of the backbone polymer chain, and thereby imparting the macroscopically observed stiffness. It is reasoned that the chief source of reinforcement arises from the POSS moieties behaving as strong anchor points in the polymeric matrix. This has more to do with the ponderous nature of these moieties versus any specific intermolecular interactions.

EE5.7

PROBING NANOENVIRONMENTS IN POLYMER FILMS BY

SINGLE MOLECULE SPECTROSCOPY. Jason P. Schmidt, Paul J. Carson, and Steven K. Buratto, Dept. of Chemistry and Biochemistry, UC Santa Barbara, Santa Barbara, CA.

Recent advances in single molecule detection have opened up new avenues for probing nanoenvironments in thin polymer films. In our work, single organic carbocyanine dye (DiC₁₂) molecules have been used to probe the nanoenvironments of poly(methyl-methacrylate), poly(styrene), 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 DiC₁₂ within each polymer matrix. Distribution of peak maxima, 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 POLYMERIZATION OF LANGMUIR BLODGETT FILMS OF DIACETYLENES. Nikolaos G. Semaltianos, 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 gold films and average area of the grains observed, were investigated as a function of the temperature and length of time of prebake of the substrates. The dependence of the gold surface roughness on substrate temperature is discussed. For substrates held at room temperature the ionic interaction between gold particles and substrate surface determines the size of the grains. Large flat areas of dimensions of the order of 200×200 nm² are obtained for 80 nm thick films grown on glass heated at 300°C for 6 hrs and areas flat over a macroscopic distance greater than 500 nm are obtained on mica heated at 400°C for the same period of time. For CaF₂ gold epitaxial growth starts to occur above 200°C. Epitaxial growth of fcc metals on alkaline halides is discussed. Monolayer and multilayer assemblies of Langmuir-Blodgett (LB) films of 10-12 pentacosadynoic acid (12-8 diacetylene) were deposited on the flat gold substrates. Micrometer size features were patterned by polymerization of the films by using electron beam lithography. Polymerized areas on a monolayer and bilayer, as well as multilayer films, were examined by scanning electron microscopy, atomic force microscopy and resonant Raman spectroscopy. It was established that polymerized areas on a monolayer and a bilayer LB film adhere onto the gold substrate after development. The exposure curve, sensitivity, contrast and resolution of the polymer have been determined by using atomic force microscopy and correlated with the deposition conditions and molecular parameters. Stresses induced in the organic film during polymerization lead to an in-plane buckling of the micrometer size polymer structure. A simple self consistent theory was developed to predict critical strain and critical length for buckling. The observed effect of buckling of polymers might open an avenue for a wide range of important practical applications in the area of nanomechanical engineering such as in nanomachines, nanosprings and nanoenergy storage systems.

EE5.9

CHEMICAL IMAGING WITH SUB- 100 NM RESOLUTION USING APERTURELESS SCANNING NEAR-FIELD INFRARED MICROSCOPY. Boris B. Akhremitchev 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 ~ 10 μm limitation in spatial resolution. Scanning near-field microscopy is a new technique which allows us to overcome the diffraction limit ($\lambda/2$) 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 of our near-field microscope. The sample is poly(dimethylsiloxane-styrene) diblock polymer cast on a gold surface, a building block of functional nanostructures. Tunable CO₂ laser radiation scattering by the oscillating force microscope probe is recorded during raster-scanning of the sample. Chemical contrast due to differences in infrared absorption can be obtained by detecting the light scattered by a metallic probe near the surface. We achieve spatial resolution better than $\lambda/100$.

EE5.10

PHOTO-MODULATION SPECTROSCOPY ON NANO-STRUCTURED POLY(PARA PHENYLENE VINYLENE)-SYSTEMS. E.J.W. List^{1,2}, J. Partee², J. Shinar², W. Graupner³, C. Gadermaier¹, R. Smith⁴, D. Gin⁴ and G. Leising¹. ¹Institut für Festkörperphysik, Technische Universität Graz, Graz, AUSTRIA, ²Ames Laboratory-USDOE* and Department of Physics and Astronomy, Iowa State University, Ames, IA, ³Department of Physics, Virginia Tech, Blacksburg, VA, ⁴Department of Chemistry, University of California, Berkeley, CA.

The photophysical properties, such as spectral line-shape and site selectivity of photoluminescence (PL), PL quantum yields, cw photoinduced absorption spectra (PIA) and the X-band PL-detected magnetic resonance (PLDMR) responses of bulk poly(para-phenylenevinylene) (PPV) films and films of isolated PPV chains ordered on the nanometer scale (nano-PPV) are presented and compared. The ordering is a result of the lyotropic liquid crystalline character of the matrix material, which by self-assembly leads to the formation of a regular hexagonal array of hollow cylinders (channels) with an outer diameter of about 40~ containing the conjugated polymer chains. The

optical spectra and the spectral dependence of the PLDMR 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 singlet excitons (SE4s). This isolation alters the emission properties of nano-PPV as well as the transition energies of the intergap triplet and polaron states as found from PIA. In particular, from the observed sublinear 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 SE4s which are subject to intrachain migration are strongly nonradiatively quenched at trapped polarons. This quenching process is believed to be responsible for the polaron PLDMR. From a comparison of the spectral dependence of the PLDMR in nano and bulk PPV, we find that in nano-PPV the chains are not only isolated in the channels, but moreover are composed of distinct shorter isolated conjugated segments and connected longer conjugated segments. *Ames Laboratory is operated by Iowa State University for the USDOE under Contract W-7405-Eng-82.

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

Chairs: Peter F. Green and Sanat K. Kumar

Wednesday Morning, April 26, 2000

Metropolitan I (Argent)

8:30 AM *EE6.1/FF6.1

STRUCTURE, DYNAMICS, AND PROPERTIES OF POLY-VINYLCYCLOHEXANE BASED PENTABLOCK COPOLYMERS.

Frank S. Bates, Martin Vigild, Kim Chaffin, Chin Chu, University of Minnesota, Minneapolis, MN; Glenn Fredrickson, UC Santa Barbara, Santa Barbara, CA; Stephen Hahn, Dow Chemical Company, Midland, MI.

Polyvinylcyclohexane (V), which is produced by catalytically hydrogenating polystyrene, is characterized by a glass transition temperature of 147°C, a high modulus, and excellent optical properties. However, owing to a large entanglement molecular weight (Me=40,000 g/mol) this material is extremely brittle thus restricting the range of engineering applications. In order to improve the mechanical properties we have prepared VEV triblock and VEVEV pentablock copolymers where E refers to semicrystalline hydrogenated polybutadiene. The phase behavior (morphology and order-disorder transition), rheological, and room-temperature mechanical properties have been characterized revealing several dramatic effects associated with the change in architecture from triblock to pentablock including heretofore unreported shear-induced microstructure alignment and improvements in toughness. These findings will be discussed in the context of current theory and experiment regarding the thermodynamics and dynamics of block copolymers.

9:00 AM *EE6.2/FF6.2

DOMAIN MORPHOLOGY IN LIQUID-CRYSTAL/POLYMER BLENDS. Amelia M. Lapeña, Andrea J. Liu, UCLA, Department of Chemistry and Biochemistry, Los Angeles, CA; Sharon C. Glotzer, Stephen A. Langer, NIST, Gaithersburg, MD.

Small-molecule liquid crystals and polymers demix into two coexisting phases, one rich in polymer and isotropic, and the other rich in liquid crystal and orientationally-ordered. The domain morphology of liquid-crystal/polymer blends therefore depends on the interplay of two kinetic processes, the kinetics of phase separation and the kinetics of phase ordering. We show that the interplay can lead to morphologies not observed in isotropic binary blends and to slower domain.

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 poly(ethylene/ethylethylene) blended separately with two linear random copolymer poly(ethylene/ethylethylene). Molecular architecture is the only difference between the two components of the blends. The molecular weights of the two linear random copolymer poly(ethylene/ethylethylene) are 57 kg/mol and 200 kg/mol, 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 containing the low molecular weight linear polymer (57 kg/mol) form single phase

mixture while all blends containing the high molecular weight linear polymer (200 kg/mol) phase separate.

9:45 AM EE6.4/FF6.4

PHASE SEPARATION IN POLYMERIC FLUIDS SUBJECTED TO A TEMPERATURE GRADIENT. Minqin Li, Shengqing Xu, Eugenia Kumacheva, University of Toronto, Department of Chemistry, Toronto, ON, CANADA.

We studied phase separation in thin horizontal layers of binary and ternary off-critical polymeric fluids subjected to a vertical temperature gradient. Under particular conditions surface-tension- or 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.

10:15 AM EE6.5/FF6.5

PHASE BEHAVIOR AND TRANSITIONS IN POLYMERS COMPRISING MILDLY AMPHIPHILIC MONOMERS. H. Duan, S.D. Hudson, P. Kewsuwan, V. Percec, M.N. Holerca.

A series of oligomeric and polymeric materials comprising mildly amphiphilic monomers have been investigated by OM, TEM and rheological analysis in order to observe the process by which they order and to determine the structure of their ordered phases. Polyoxazolines with pendant yloxyphenyl groups were used. The phenyl groups were bisubstituted in the 3 and 4 positions, or trisubstituted in the 3, 4, and 5 positions, with alkyl tails of various length. Narrow molecular-weight polydispersity samples were obtained with the average degree of polymerization for different samples ranging from 4 to 1000. Low and high molecular weight materials that form the columnar hexagonal phase were compared, and oscillatory shear rheology indicates only in the high molecular weight material that significant fluctuations of order remain up to 20°C above the columnar clearing temperature. Cubic materials comprising quasi-spherical aggregates were also investigated. Electron diffraction and TEM imaging were used to identify their equilibrium structure, and relationships with the molecular structure are examined. The authors gratefully acknowledge the financial support of NSF grants DMR-9806684 and DMR-9708581.

10:30 AM EE6.6/FF6.6

THE MORPHOLOGY OF BLENDS OF LINEAR AND SHORT-CHAIN BRANCHED POLYETHYLENES IN THE SOLID STATE BY SMALL ANGLE NEUTRON AND X-RAY SCATTERING, DIFFERENTIAL SCANNING CALORIMETRY AND TRANSMISSION ELECTRON MICROSCOPY. G.D. Wignall, J.S. Lin, Oak Ridge National Laboratory, Solid State Division, Oak Ridge TN; R.G. Alamo, 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. Mandelkern, Florida State University, Institute of Molecular Biophysics, Tallahassee, FL; M.H. Kim, Oak Ridge National Laboratory, Chemical and Analytical Sciences Division Oak Ridge, TN; G.M. 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 (linear low density) polyethylenes (HDPE/LLDPE). SANS indicates that the mixtures are homogenous in the melt for all compositions when the ethyl branch content in the copolymer is low (i.e. < 4 branches/100 backbone carbon atoms for a typical molecular weight of 100,000). However, due to the structural and melting point differences between HDPE and LLDPE, 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 that surround them.

*Managed by Lockheed Martin Energy Research Corporation under contract DE-AC05-84OR2140 for the U.S. Department of Energy.

10:45 AM EE6.7/FF6.7

CRYSTALLOGRAPHY, CURVATURE AND COORDINATION OF BICONTINUOUS BLOCK COPOLYMER NANOSTRUCTURES. H.

Jinnai, Kyoto Inst of Technology, Dept of Polymer Science & Engineering, Kyoto, JAPAN; R.J. Spontak, North Carolina State Univ, Depts of Chemical Engineering and Materials Science & Engineering, Raleigh, NC; Y. Nishikawa, T. Hashimoto, Kyoto Univ, Dept of Polymer Science & Engineering, Kyoto, JAPAN; S.D. Smith, Procter & Gamble Co, Corporate Research Division, Cincinnati, OH.

Within relatively narrow composition windows, block copolymers and their blends with a homopolymer, a second copolymer or a solvent have been found to microphase-order into bicontinuous nanostructures such as the gyroid, perforated lamellar and sponge (microemulsion in tricomponent blends) morphologies. In-depth investigation of these morphologies by transmission electron microscopy and small-angle scattering is non-trivial due to the complexity of such nanostructures. In this work, we provide a detailed analysis of the gyroid morphology in terms of its crystallographic signature (compared to that of the double-diamond), its interfacial curvature (compared to a constant-thickness model) and its coordination distribution (including structural variation due to a grain-boundary) as discerned from transmission electron microtomography reconstructions. Results obtained from the gyroid indicate that the nanostructure is nearly cubic and possesses Ia $\bar{3}$ d symmetry. Three-fold coordination is, for the most part, observed and the distance distribution between junctions is determined. These results are quantitatively compared to those derived for the sponge, as well as those for polymer blends undergoing spinodal decomposition. The area-averaged mean curvature for these systems is found to be sensitive to composition, whereas the area-averaged Gaussian curvature is not. Structural characteristics exhibiting evidence of universality are identified, and experimental results are compared to self-consistent field predictions for block copolymers in the intermediate segregation regime when possible.

11:00 AM *EE6.8/FF6.8

SURFACE SEGREGATION IN MISCIBLE BINARY POLYMER BLENDS. Christopher Forrey, Polymer Program, University of Connecticut, Storrs, CT; David Pan, Xerox Corporation, Rochester, NY; Jeffrey T. Koberstein, Department of Chemical Engineering and Applied Chemistry, Columbia University, New York, NY.

The composition at the air-polymer interface of a multi-constituent polymer generally differs from that of the bulk material. In an immiscible polymer blend, this phenomenon is referred to as blooming, and depends on surface energy differences and wetting considerations. In miscible systems, the phenomenon is called surface segregation, and the resultant surface composition is dependent on a balance between the exchange chemical potential required to segregate a particular polymer to the surface and the resultant decrease in interfacial free energy. In this paper, we examine surface segregation for miscible blends of polystyrene and poly(vinyl methyl ether), a system with a lower critical solution temperature (LCST). Surface compositions were determined by analysis of surface tension data on polymer blend melts. Surface composition depth profiles were determined by angle dependent x-ray photoelectron spectroscopy. Data are presented for blends containing either normal or perdeuterated polystyrene. Perdeuteration markedly changes the bulk interaction parameter and allows investigation of its effect on the surface segregation of the blend. We model the data using the Schmidt-Binder approach to square gradient theory. For the required equation of state, we employ both the incompressible Flory-Huggins theory and the Sanchez-LaCombe-Balazs extension of compressible lattice fluid theory. The latter approach provides a more appropriate description of the bulk- phase behavior for LCST blends.

11:30 AM EE6.9/FF6.9

SOLID-STATE BLENDING AND COMPATIBILIZATION OF POLYMER BLENDS BY CRYOGENIC MECHANICAL ALLOYING. Archie P. Smith, Richard Spontak, Carl Koch and Harald Ade*, North Carolina State University, Department of Materials Science and Engineering and *Physics, Raleigh, NC.

Cryogenic mechanical alloying has been employed to blend poly (methyl methacrylate) (PMMA) with up to 25 wt% polyisoprene (PI) and poly(ethylene-alt-propylene) (PEP). High-energy ball milling in the solid state is considered here as a highly non-equilibrium processing alternative to avoid the phase separation that often plagues polymer mixing in the melt or in solution. Mechanical milling of the individual polymers reveals that their molecular and bulk properties depend sensitively on milling time, post-annealing and, for PMMA, temperature. While molecular weight reductions are observed for PMMA and PEP, PI undergoes crosslinking due to the formation of free radicals during milling. In addition, the molecular weight decay for PMMA is more pronounced at higher temperatures, in contrast to the expectation of increased brittleness with decreasing temperature. Characterization of the as-milled blends by scanning transmission x-ray microscopy and transmission electron microscopy has demonstrated intimate (nanoscale) mixing within the blends, with the degree of mixing increasing with increasing milling time. Phase

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 milling 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 crosslinking hinders molecular 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 cryogenic mechanical alloying constitutes a viable means of producing intimate blends of immiscible polymers that can, depending on interchain reaction, retain their nanoscale morphology.

11:45 AM EE6.10/FF6.10

STRUCTURE EVOLUTION DURING POLYMER DEWETTING AND DEMIXING. Manfred Stamm^{1,3}, Peter Mueller-Buschbaum², Jochen Gutmann³. ¹Institute fuer Polymerforschung Dresden e.V., Dresden, GERMANY, ²Technical University, Garching, GERMANY ³Max-Planck-Institute fuer Polymerforschung, 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 incompatible components the dewetting is in competition with surface and interface segregation effects, and lateral phase separation will generally occur. Those phenomena can be used to generate nanostructures, where relatively regularly spaced droplets or regions of different materials form. Structures are investigated by scattering techniques as well as by direct imaging techniques, which are shown to be complementary. By Fourier transform of a scanning force microscope image 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 the thin films can be formed.

SESSION EE7: NANOSTRUCTURES—PHYSICAL SELF-ASSEMBLY, TEMPLATING AND CHARACTERIZATION

Chair: Steven D. Hudson
Wednesday Afternoon, April 26, 2000
Concordia (Argent)

1:30 PM *EE7.1

NANOSTRUCTURE SELF-ASSEMBLY WITH ULTRATHIN DIBLOCK COPOLYMER FILMS. H.M. Jaeger, W.A. Lopes, James Franck Institute, The University of Chicago, Chicago, IL.

The micro-phase separation properties of diblock copolymers provide a convenient path toward the self-assembly of large scale nanopatterns with repeat spacings in the 10-100nm range. I will discuss new possibilities that have emerged for ultrathin copolymer films, with thickness close to the repeat 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 containing one or the other block of the copolymer can reach 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-PMMA 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 *EE7.2

NANOSCOPIC TEMPLATES FROM ORIENTED BLOCK COPOLYMER FILMS. Thomas Thurn-Albrecht, Juergen Schotter, Mark Tuominen 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 towards this goal. We report about the alignment of Poly(styrene-block-methyl methacrylate) (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 the interfacial interaction. 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 10nm 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 nanopores will be discussed.

2:30 PM EE7.3

MANAGING COMPLEX SELF-ASSEMBLY IN BLOCK COPOLYMERS. Franc is Drolet, 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 self-consistent mean field theory for block copolymers that facilitates combinatorial screening of new types of self-assembly. 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 EE7.4

CONTROLLING THE SELF-ASSEMBLY OF A RIGID-ROD POLYMER AT SURFACES. Paolo Samor , Humboldt University Berlin, Department of Physics, Berlin, GERMANY; Klaus M llen, MPI for Polymer Research, Mainz, GERMANY; J rgen 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 molecular materials depend on the interplay between electronic structure and order in the molecular assembly, it is important to control the 2D and 3D polymeric architectures by making use of intramolecular, intermolecular and interfacial forces. We report here on the self-assembly of soluble, alkylated, end-functionalized poly-para-phenyleneethylenes (PPE) at surfaces and we demonstrate how their growth from solution can be controlled in order to develop well defined micro- and nano-scopic oriented architectures. Dried macromolecular adsorbates of PPE prepared by solution casting 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 towards epitaxially 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 in 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 nanoribbons are molecular architectures which upon thiol functionalization at their edges are nanostructures ready to bridge Au nanoelectrodes in a molecular nanowire device. [1] P. Samor , V. Francke, K. M llen, J.P. Rabe Chemistry - A European Journal 1999, 5(8), 2312.

3:15 PM EE7.5

TEMPLATING MESOPOROSITY VIA CYCLIC & LARGE-RING NANOSTRUCTURES. Ralph E. Taylor-Smith, Katherine A. Winnie, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

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). Two mechanisms 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 microstructural network perturbations) from bulkiness of the introduced cage substituent. Results from various polymer architectures with two independent "bulky-cage" model systems derived from POSS (Polyhedral Oligomeric Silsesquioxane) chemistry with cage length-scale $\sim 15 \text{ \AA}$, and β -Cyclodextrin chemistry with cage length-scale $\sim 7 \text{ \AA}$, imply the approach is generic and effective as a route to porosity control.

3:30 PM EE7.6

THE FABRICATION OF NANOMETER-SCALE TOOLS USING POLYMER TEMPLATES. Mei-Wei Tsao, Jianling 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 electro-optical 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 (~150 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.

3:45 PM *EE7.7

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

We extend the one-dimensional self-consistent field (SCF) scheme of Scheutjens-Fleer to three dimensions (3D) and use this 3D SCF model to investigate the adsorption of A-B copolymers from A homopolymer matrices 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 sites) and vary their spatial distribution on the substrate. The interplay between the surface chemical heterogeneity and the chain microstructure is examined for A-b-B diblock, A-b-B-b-A, B-b-A-b-B triblock, 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 conformation 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.

4:15 PM *EE7.8

CONFINEMENT INDUCED TRANSITIONS IN ULTRA-THIN FILMS. R.M. Overney, C.K. Buenviaje, Dept of Chemical Engineering, University of Washington, Seattle, WA; R.J. Waltman, IBM Storage Systems, San Jose, CA; G.W. Tyndall, 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 films 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.

4:45 PM EE7.9

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

An important challenge for many practical applications of patterned polymer films is a strong anchoring of the generated microstructure to the surface of the substrate. Good adhesion behavior can be achieved by attaching the polymer molecules to the surfaces through a covalent, chemical bond. We present several new approaches to lithographic structuring of surface-attached polymer films, which take advantage of the covalent bonding of the molecules to the surfaces of the substrate. Microstructured polymer films with high vertical and lateral resolution and a tailor-made chemical composition can be prepared following such concepts. For the pattern generation various photolithographic (DUV or x-ray irradiation) and soft lithographic (stamping, ink-jet) techniques are employed. Step-and-repeat procedures using polymers with different functional groups allow the preparation of multifunctional arrays with high spatial resolution.