

# SYMPOSIUM DD

## Polymer Interfaces and Thin Films

November 26 – 30, 2001

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\* Invited paper

SESSION DD1: THEORY, SIMULATIONS AND DYNAMICS I

Chairs: Sanat K. Kumar and Kenneth R. Shull  
Monday Morning, November 26, 2001  
Constitution B (Sheraton)

**8:30 AM \*DD1.1**

INTEGRATED OPTICAL AND FORCE MEASUREMENTS OF THIN FILM DYNAMICS. Steve Granick, Dept. of Materials Science and Engineering, University of Illinois, Urbana, IL.

A rich and perplexing dynamics results when chain molecules adjoin solid surfaces. From recent force-based experiments, a picture emerges in which slip is observed when Newtonian fluids move past smooth or polymer-coated surfaces at shear rates that exceed a critical level; this may reflect the shear-induced nucleation of bubbles. To augment the force measurements by direct spectroscopic observation, femtosecond laser spectroscopy is being employed to measure directly the rates of near-surface molecular diffusion (translational and rotational). A picture emerges in which, for the first time, we are able to test the ensemble-averaged force measurements by direct spectroscopic observations of individual molecules.

**9:00 AM DD1.2**

WETTING AND SPREADING OF SOLVENT ON POLYMER FILMS. Gary S. Grest, Sandia National Laboratories, Albuquerque, NM.

The interplay between solvent wetting and spreading on a polymer film and the penetration of solvent into films is studied using large-scale molecular dynamics simulations. Results for the dependence of the rate of swelling on the chain length of the polymeric chains and on the size and type of the solvent will be investigated using a coarse grained bead-spring model for the polymer and solvent. The effect of changing the solvent quality from a good solvent, which will penetrate the polymer, to a poor solvent, which will not wet the surface, will be studied by varying the relative interaction strength between the solvent and polymer. In one set of simulations, the behavior of a solvent drop placed on top of the polymer film is studied. In the wetting case, the drop not only spreads but also penetrates into the film. For non-wetting drops, the contact angle is measured and compared to drops on an atomically smooth surface. In a second set of simulations, the penetration of a solvent film in contact with the polymeric film will be studied. Of particular interest will be the swelling behavior of a full-entangled polymer melt, which is predicted to be significantly slower than for an unentangled melt. These simulations as well as some additional simulations in which we followed the evaporation of the solvent from the film, clearly demonstrate that it is feasible to follow by molecular simulations the diffusion of the solvent as it simultaneously spreads and penetrates into the polymer film.

**9:15 AM DD1.3**

HETEROGENEOUS DYNAMICS AT THE GLASS TRANSITION IN THIN POLYMER FILMS. Didier Long, Universite de Paris XI, Orsay, FRANCE; Francois Lequeux, ESPCI, Paris, FRANCE.

It has been demonstrated over the last few years that the dynamics close to the glass transition is strongly heterogeneous. Recent experiments have also demonstrated that the glass transition temperature of thin polymer films can be shifted as compared to the same polymer in the bulk. We propose here that the 3D glass transition is controlled by the percolation of small domains of slow dynamics resulting from thermal density fluctuations. We show then that these domains percolate at a lower temperature in the quasi-2D case of thin suspended polymer films and we calculate the corresponding glass transition temperature reduction, in agreement with experimental results. In the case of strongly adsorbed films, we show that the adsorption amounts to enhance the slow domain percolation, resulting in an increase of the glass transition temperature. In both situation the shift in  $T_g$  is given by a power law, the exponent being the inverse of that of the correlation length in 3D percolation.

**9:30 AM \*DD1.4**

SYNCHROTRON RADIATION STUDIES OF THE DYNAMICS OF POLYMER FILMS. Hyunjung Kim, Advanced Photon Source, Argonne Natl. Lab, Argonne, IL; A. Rühm, L.B. Lurio, D. Lumma, Massachusetts Institute of Technology, Dept. of Physics and Center for MS&E., Cambridge, MA; J.K. Basu, Univ. of Illinois, Matls. Res. Lab., Champaign-Urbana, IL; J. Lal, Argonne Natl. Lab., Intense Pulsed Neutron Source, Argonne, IL; S.K. Sinha, Univ. of California San Diego, Dept. of Physics, La Jolla, CA; S.G.J. Mochrie, Yale University, Depts. of Physics and Applied Physics, New Haven, CT.

X-ray photon correlation spectroscopy has been used to probe surface fluctuations on thin supported polymer films as a function of in-plane

wavevector, film thickness and temperature. The measurements were performed on thin polystyrene (PS) films of thickness ranging from 84 nm to 333 nm, and above the glass transition temperature. We find excellent agreement between the measured surface dynamics and the theory of overdamped thermal capillary waves on thin viscoelastic films. We shall discuss the comparison between the values of the viscosity obtained from these data with those of bulk PS.

**10:30 AM \*DD1.5**

MOLECULAR DYNAMICS IN (ULTRA)-THIN POLYMER LAYERS. Friedrich Kremer, Lutz Hartmann, Andreas Huwe, University of Leipzig, Faculty of Physics and Geosciences, Leipzig, GERMANY; Thomas Kratzmueller, Hans Georg Braun, Polymer Institute, Dresden, GERMANY; Annett Graeser, Stefan Spange, Technical University of Chemnitz, Chemnitz, GERMANY.

The molecular dynamics of confined (low molar and polymeric) systems is determined by the counterbalance between surface- and confinement-effects: Due to interactions with the (inner) surfaces (e.g. the formation of H-bonds, grafting, physisorption) the molecular dynamics is slowed down, resulting in an increase in the glass transition temperature of the system. In contrast the confinement may induce an increase in "free volume" thus making the molecular dynamics faster than in the bulk system. This causes a decrease in the glass transition temperature. This counterbalance will be exemplified in the talk by employing broadband dielectric spectroscopy ( $10^2$  Hz -  $10^9$  Hz) to study the molecular dynamics of low molecular weight systems (ethyleneglycol, salol, etc.) and polymers (polyethers) being contained in mesoporous systems (MCM-48, pore-diameter 3.2 - 3.5 nm; MCM-41, pore-diameter: 2.5 nm). Furthermore dielectric measurements on grafted hairy rod-molecules (polyglutamates) in layer thickness of  $29 \pm 2$  nm and  $38 \pm$  nm will be presented and discussed with respect to the bulk system. Recent studies on the dynamics in (ultra) thin layers of isotactic PMMA will be presented as well (6).

References:

1. A. Huwe, F. Kremer, P. Behrens, and W. Schwieger Phys Rev Lett 82:2338 (1999).
2. F. Kremer, A. Huwe, M. Arndt, P. Behrens, and W. Schwieger J Phys Condens Matter 11: A175 (1999).
3. F. Rittig, A. Huwe, G. Fleischer, J. Kaerger, and F. Kremer Phys Chem Chem Phys 1: 519 (1999).
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5. L. Hartmann, T. Kratzmueller, H.G. Braun, and F. Kremer Macromol Rapid Commun 21: 814 (2000).
6. L. Hartmann et al., submitted to European Journal of Physics E.

**11:00 AM DD1.6**

STRUCTURAL, THERMODYNAMIC AND DYNAMIC PROPERTIES OF SURFACES AND THIN FILMS OF POLYMER MELTS FROM ATOMISTIC MOLECULAR DYNAMICS SIMULATIONS. Do Y. Yoon, Jaeeon Chang, School of Chemistry, Seoul National Univ, KOREA; Liu Yang and Jie Han, ELORET Corp., Sunnyvale, CA; Richard L. Jaffe, NASA Ames Research Center, Moffett Field, CA.

The structural, thermodynamic and dynamic properties of surfaces and thin films of polymethylene and polytetrafluoroethylene melts are studied by molecular dynamics simulations using explicit and united atom models. N-tridecane C13H28 and n-C44H90 melt films with a thickness of about 3 nm have been investigated by NVT-MD simulation method at the temperatures from 300 K to 450 K. Simulations give a good agreement for the density and surface tension when compared with experimental data, and the lower surface tension of perfluoroalkanes is correctly estimated. It is observed that for n-tridecane the density of methyl chain-end groups is enhanced in the free surface, while it is depleted in the region below the surface. For longer chains of C44H90 the segregation of chain ends to the surface is clearly seen as a peak. A slight preference for chain segments to orient along the direction parallel to the surface is observed, whereas the orientations of endmost bond vectors are nearly random. Moreover, the molecular diffusivity in the surface region is significantly greater than in the bulk region, especially along the film plane direction. These results for polymethylene melts are compared with those for C12F26 chains which exhibit significantly decreased chain flexibility.

**11:15 AM \*DD1.7**

CREATING LOCALIZED MIXING STATIONS IN MICROFLUIDIC DEVICES. Olga Kuksenok, Anna Balazs, University of Pittsburgh, Chemical Engineering Department, Pittsburgh, PA; Julia Yeomans, Oxford University, Theoretical Physics, Oxford, UNITED KINGDOM.

Microfluidics, involving the transport of minute quantities of liquids in networked channels that are 10-100 microns wide, lies at the heart of the "labs on-a-chip" concept, which has the potential to shrink a

room full of analytical instruments onto a compact, hand-held device. An important stumbling block currently limiting the widespread use of lab-on-a-chip systems is the lack of simple methods for mixing the fluids, a crucial step in many chemical reactions. Liquids in microfluidic devices typically move parallel to each other, exhibiting laminar, rather than turbulent flow; thus, these fluids do not undergo extensive mixing. Here we simulate the flow of binary fluids on a chemically patterned substrate, which contains patches of wettable and non-wettable domains, and show that this surface not only acts as a "switching device", routing the fluids to different regions in the microchannel, but also behaves as a "mixing station" where the fluids form a homogeneous mixture within a spatially localized region of the system.

#### 11:45 AM DD1.8

##### ATOMISTIC SIMULATIONS OF POLYMER THIN FILMS: SURFACE TENSION AND PHYSICAL PROPERTIES.

Sylvain Goudeau, Jocelyne Galy, Jean-Francois Gerard, INSA-LYON, LMM/IMP, Lyon, FRANCE; Jean-Louis Barrat, Univ Claude Bernard Lyon1, DPM, Lyon, FRANCE; Juergen PIONTECK, Institut fur Polymerforschung, Dept polymer reactions and blends, Dresden, GERMANY.

Fully-atomistic simulations using a well-calibrated force-field provide a detailed and accurate insight into intra and intermolecular interactions. Then, a wide range of physical and thermodynamical properties, including the surface tension, can be computed rather directly from such methods, as a function of polymer chemical structure. The polymers studied in this work range from common commercial polymers (PS, PMMA) to high-Tg or specialty polymers (polyethersulfone, polyetherimide, polyphenylene-ether and different linear epoxies). In the case of these high-Tg polymers, the determination of surface tension by modelling techniques is of great importance, since direct experiments in the molten state are not tractable in a broad range of temperature due to high viscosity and / or thermal degradation issues. Moreover, whatever the polymer, glassy-state surface energies cannot be known directly experimentally. Molecular simulations have therefore been carried out at various temperatures on fully atomistic models of these amorphous polymers, consisting of thin films with both free surfaces. Their physical properties were investigated as a function of temperature, and compared with those of bulk models. Surface tensions were computed either by analyzing the potential energy difference between bulk and surface models, or by the virial method which is a direct measurement of the force exerted by the thin film in its plane. The comparison between our experimentally measured surface tensions, when available, and simulation results shows on average an overestimation of simulated values whatever the computation method employed. However, both computation methods provide the same ranking of polymers according to their surface tension, as the experimental one. The temperature dependence of the surface tension, as computed by the energy difference method, is rather lower than the experimental one. The virial method gives nearly exactly the experimental slope, provided the simulation temperature is high enough for the film to relax sufficiently during short simulation timescales. All these features are discussed as a function of simulation procedures and timescales and chain stiffnesses.

#### SESSION DD2: BLOCK COPOLYMER FILMS I

Chairs: Peter F. Green and Edward J. Kramer  
Monday Afternoon, November 26, 2001  
Constitution B (Sheraton)

#### 1:30 PM \*DD2.1

BLOCK COPOLYMER THIN FILMS: PATTERN FORMATION AND EVOLUTION ABOVE THE ODT. Peter F. Green, Ratchana Limay and Jean-Loup Masson, The University of Texas at Austin, Dept. of Chemical Engineering and Texas Materials Institute, Austin, TX.

Thin polymeric films are of interest to researchers due, in part, to their applications as active materials in devices (such as light-emitting diodes and photodiodes), adhesives and lithography. Block copolymers have received much attention due to their inherent ability to self-assemble into ordered, nanoscale geometric structures below an order disorder transition (ODT) temperature. Much on the research on block copolymer thin films is devoted toward understanding and controlling the microstructural and topographical features below the order-disorder transition. Our recent experiments reveal that above the ODT, these materials exhibit structural ordering, accompanied by a hierarchy of transient topographical patterns, depending on film thickness. In this presentation, we will address surface induced ordering and pattern formation and dynamics in the block copolymer thin films above the ODT.

#### 2:00 PM DD2.2

MORPHOLOGY OF BLOCK COPOLYMER THIN FILMS FROM DENSITY FUNCTIONAL THEORY. Amalie L. Frischknecht, Jeffrey D. Weinhold, John G. Curro, Laura J. Frink, Sandia National Laboratories, Albuquerque, NM.

We use polymer reference interaction site model (PRISM) -based density functional theory (DFT) to explore the morphologies of confined block copolymer thin films. We consider symmetric diblock copolymers, modeled as freely-jointed chains. The orientation of the observed lamellar morphologies depends on the interactions with the confining walls and on the film thickness. The use of PRISM with DFT allows the inclusion of local packing effects due to the finite size of the monomers, which is neglected in other theoretical approaches. These packing effects can also influence the equilibrium morphology; for example, if both blocks are equally attracted to the wall, an increase in the strength of the attraction can induce a transition from lamellae parallel to the wall to lamellae that are perpendicular to the wall, in order to increase the density next to the wall. We compare our results to previous calculations using self-consistent field theory.

#### 2:15 PM DD2.3

##### GROWTH AND PATTERNING OF ISLANDS AND HOLES IN SPHERICAL DOMAIN DIBLOCK COPOLYMER THIN FILMS.

Rachel A. Segalman and Edward J. Kramer, University of California, Santa Barbara, Depts of Chemical Engineering and Materials, Santa Barbara, CA; Sergei Magonov, Digital Instruments/Veeco Metrology, Santa Barbara, CA.

Using spherical domain block copolymers for nanolithographic patterning requires an understanding of islands or holes in thin films whose thicknesses, including a brush layer at the substrate, do not correspond to a single layer of spheres. In our system of poly(styrene-*b*-2vinylpyridine) (PS-PVP) that microphase separates into PVP spheres in a PS matrix, an initial film thickness of less than 40 nm gives rise to holes through a single sphere layer revealing a PS-PVP brush on a flat silicon oxide substrate. Thicknesses greater than 55 nm result in islands of spheres on top of the single sphere layer. Both islands and holes in a block copolymer film on a smooth substrate coarsen with annealing time at 180 C, driven by the edge line tension of these structures. If a film of uniform thickness is deposited on a grating with mesas 30 nm high (~ 1 sphere layer thickness) from 1 to 10 mm wide, separated by wells of the same width, the island/hole evolution is quite different than on a flat substrate. Islands on the mesa or in the center of the well eventually disappear, with these spheres being added to stripes of roughly uniform width in the well along its edges, effectively extending the width of the sphere layer on the mesa. In contrast, a film initially with holes evolves to produce a uniform single layer of spheres in the well and a stripe of spheres in the center of the mesa surrounded by brush the same height as the single sphere layer in the well. The edges of these single sphere layer thick stripes lead to a graphoeptaxial ordering of the layer of spheres into a single crystal in much the same way as confinement by the edges of the mesas or wells.

#### 2:30 PM \*DD2.4

DEVELOPMENT OF LONG-RANGE ORDER AND ORIENTATION IN BLOCK COPOLYMER THIN FILMS. Matthew L. Trawick, Christopher K. Harrison, Dan E. Angelescu, Douglas H. Adamson, Paul M. Chaikin, Richard A. Register, Princeton Materials Institute, Princeton University, Princeton, NJ.

Thin block copolymer films make excellent contact masks for surface patterning on the nanoscale. While the local structure of the pattern (e.g., spheres vs. cylinders) and the microdomain size are easily controlled through synthesis, block copolymers naturally self-assemble into a polygrain structure, where the microdomain lattice order typically persists for less than a micron. Such limited long-range order would be a serious drawback for any device where the individual elements need to be addressed, motivating our work to both order and orient the grains in these thin films. Sequential tapping-mode atomic force microscopy (AFM) images can be strung together into "movies" which reveal how defects in the microdomain pattern are eliminated, as we have shown previously for cylinder-forming diblocks (C. Harrison et al., Science, 290, 1558 (2000)). In single-microdomain-layer films of sphere-forming diblocks, the spheres prefer to pack hexagonally, with the defects being spheres which are surrounded by five or seven neighbors. Strings of these "5s" and "7s" constitute the grain boundaries in these films, which we find to be much more dynamic than in the cylinder-forming films, fluctuating greatly between successive AFM images. As with cylinders, the average grain size of the pattern grows with a weak power (approximately 1/4) of annealing time. The annealing temperature has a pronounced effect on the grain size; we are currently examining the combined effects of annealing time and temperature for block copolymers where both the order-disorder and glass transitions can be accessed. Surface features comparable in height to the microdomain

size, such as a simple cleavage step on a mica substrate, are very effective in orienting adjacent spherical microdomains. The (10) face of the two-dimensional hexagonal lattice lies parallel to the edge of the feature, with the order extending away from the line for a distance comparable to the average grain size.

### 3:30 PM \*DD2.5

**CRYSTALLOGRAPHIC REGISTRY IN COIL-CRYSTALLINE BLOCK COPOLYMER THIN FILMS.** Sheng Hong, Samuel P. Gido, Thomas P. Russell, University of Massachusetts Amherst, Polymer Science and Engineering Dept., Amherst, MA.

The evolution of the morphology of a crystalline/amorphous diblock copolymer poly(ethylene oxide -b- 1,4 butadiene) (P(EO-b-BD)) upon crystallization in thin films was studied via interference optical microscopy. Two-dimensional crystallization confined within the PEO lamellar layers was observed with retention of the microphase separated lamellar morphology formed in the melt-state. The morphology was further characterized by TEM and electron diffraction which showed it to consist of alternating layers of PEO and PBD with PEO crystalline chains oriented perpendicular to the lamellar layers of the microphase separated structure. Multiple parallel layers of crystalline PEO were found by electron diffraction to be in crystallographic registry even though they were separated by approximately 10 nm thick layers of amorphous PBD. This crystallographic registry results from connections among adjacent PEO layers resulting from defect structures such as screw dislocations.

### 4:00 PM DD2.6

**SURFACE RECONSTRUCTION OF AN ORDERED COMPLEX FLUID.** Nicolaus Rehse, Armin Knoll, Matthias Konrad, Robert Magerle, Georg Krausch, Bayreuth University, Physical Chemistry II, Bayreuth, GERMANY.

The surfaces of simple inorganic crystals have long been known to exhibit structural deviations from their bulk morphology, so-called surface reconstructions. Typical examples are found on the surfaces of covalently bound materials like, e.g. silicon. One may raise the question whether soft materials exhibiting ordered structures on mesoscopic scales (surfactant systems, block copolymers, liquid crystals, etc.) show similar behavior. We present experimental results on the surface morphology of a microphase separated ABC triblock copolymer exhibiting a lamellar morphology in the bulk. As a model system, we study thin films of poly(styrene)-block-poly(butadiene)-block-poly(methyl methacrylate) (SBM) prepared from cyclohexane as a "non-selective" solvent. In this particular system, the B middle block has the lowest surface energy, while a polar substrate will attract the M end block. Therefore, an alignment of the bulk lamellar structure is expected to occur at the substrate, while an enrichment of B at the free surface as expected from surface energy considerations, is not compatible with the bulk lamellar structure. We demonstrate that this frustration leads to a complex rearrangement of the blocks near the surface of the film. The surface and subsurface morphology is revealed by AFM, FEG-REM and selective plasma etching of the surfaces. Interestingly, the surface morphology shows striking similarities with the Si(100)2x1 reconstruction.

### 4:15 PM DD2.7

**POLYMERSOME MEMBRANES AS FREE-STANDING THIN FILMS: MW-DEPENDENCIES OF STABILITY, ELASTICITY, & SURFACE DYNAMICS.** Harry Bermudez, James Lee, Helim Aranda, Maria Santore, Frank S. Bates, Dennis E. Discher, University of Pennsylvania, Philadelphia, PA.

Hyper-thick membranes of vesicles formed from block copolymers - polymersomes - have already been shown to be remarkably tough. Complementary measures of membrane dynamics are now emerging. Fluorescently probed polymer membranes show a dramatic slowing-down in lateral mobility with chain molecular weight. Both Rouse-scaling and reptation-type diffusion are in evidence. Separate experiments show that mechanically-coupled electrical breakdown of a membrane is far more difficult for a thicker membrane. Stability is nonetheless consistent with relatively simple thermodynamic ideas of electromechanical coupling. However, the dynamics of breakdown are protracted with molecular weight, consistent with the diffusion measurements. Scaling of such nano-scale dynamic properties with molecular weight and membrane thickness provides insight into the unique assembled-state properties of polymersome membranes.

### 4:30 PM DD2.8

**SURFACE AND BULK DYNAMICS IN THIN POLYMER FILMS PROBED WITH X-RAY PHOTON CORRELATION SPECTROSCOPY.** Adrian Rühm, Massachusetts Inst. of Technology, Center for Mat. Sci. and Eng., Cambridge, MA; Hyunjung Kim, Argonne Nat. Lab., Advanced Photon Source, Argonne, IL; Laurence B. Lurio, Massachusetts Inst. of Technology, Center for Mat. Sci. and Eng., Cambridge, MA; Jyotsana Lal, Argonne Nat. Lab., Intense

Pulsed Neutron Source, Argonne, IL; Joydeep K. Basu, Univ. of Illinois, Mat. Res. Lab., Urbana-Champaign, IL; Sunil K. Sinha, Univ. California at San Diego, Physics Dept., La Jolla, CA; Simon G. J. Mochrie, Yale Univ., Depts. of Physics and Applied Physics, New Haven, CT.

Key aspects of the dynamics of thin supported polymer films are not yet well understood, in spite of their technological importance. The emerging technique of X-ray photon correlation spectroscopy (XPCS) turns out to be well suited for probing the dynamics of capillary modes on the surfaces of thin polymer films. Due to the effect of total external reflection, the surface sensitivity of grazing angle x-ray scattering can be conveniently tuned via the angle of incidence. This in fact opens ways to depth-profiling of surface and thin films dynamics. Restricting interactions with the x-rays to the surface under total reflection conditions, we detect dramatic differences between the dynamics of polystyrene homopolymer films and of lamellar diblock copolymer films of symmetric poly(styrene)-b-poly(methylmethacrylate) of comparable molecular weight. At slightly higher incidence angles, surface and bulk dynamics can be probed simultaneously. We demonstrate this on thin films of asymmetric poly(styrene)-b-poly(dimethylsiloxane) in which short PDMS sections, labelling each individual chain, provide the required x-ray contrast for studying the dynamics of the bulk material inside the film.

### 4:45 PM DD2.9

**LIQUIDS UNDER SHEAR EXPLORED BY NEUTRON SCATTERING: A PROBLEM OF LUBRICATION.** Max Wolff, Andreas Magerl, Rainer Hock, Univ. Erlangen-Nürnberg, Lehrstuhl für Kristallographie und Strukturphysik, GERMANY; Bernhard Frick, Institut Max von Laue-Paul Langevin, Grenoble, FRANCE; Hartmut Zabel, Ruhr-Univ Bochum, Lehrstuhl für Festkörperphysik, GERMANY.

Lubrication is an old, but nevertheless barely understood phenomenon. One reason is the difficulty to look at any liquid in between narrow spaced components while these are in motion. By virtue of the high penetration power of neutrons for many engineering materials they can access directly information about the lubricant under realistic conditions of applications. For this reasons we have initiated a study of liquids under shear employing several neutron scattering techniques. Also two different shear cells have been built to investigate both the dynamics and the structural properties: a first cell was optimized for quasielastic and inelastic neutron scattering and a second cell has been designed for reflectivity and diffraction work. While the structural properties of water solutions of the triblock copolymer surfactant P85 are well known from SANS we have investigated its wetting behaviour and the flow and diffusion dynamics under shear. In a reflectivity measurement (EVA at ILL) with either hydrophilic or hydrophobic coated polished silicon wafers used in the shear device we find for a 33% (in weight) solution of P85 in deuterated water the polymer concentration right at the surface to vary between 12% and 52% for different coatings, temperatures (between 18° and 73°C) and for shear rates up to 5000 1/s. Also in the bulk we find for 73°C the lamellar layering to become more pronounced for the hydrophilic plate while this layered structure melts completely for the hydrophobic plate. Dynamical aspects have been studied on a high resolution backscattering instrument (IN10 at ILL). We observe that the sample seems to "stick" to the plates implying an unusual macroscopic velocity distribution which differs from that found earlier for lubrication oils where the sample showed only a very weak adhesion with the boundary material. In addition we report on changes in the quasielastic line width in the direction of the shear gradient with temperature and shear rates up to 10000 1/s showing the diffusion to become accelerated under shear.

### SESSION DD3: THEORY, SIMULATIONS AND DYNAMICS II

Chairs: Richard A. Register and Christopher L. Soles  
Monday Evening, November 26, 2001  
Constitution B (Sheraton)

### 8:00 PM DD3.1

**MESOPHASES OF REGULARLY BRANCHED COPOLYMERS.** Galen T. Pickett California State University, Long Beach, Long Beach, CA.

The phase diagram of A/B block copolymers is determined when the A block is a flexible, linear homopolymer, and the B block has a regularly branched tree structure with G generations. The predictions of a classical-path analysis and a lattice self-consistent mean field calculation are in general agreement. The phase diagram is considerably skewed toward keeping the A blocks inside cylindrical or spherical cores with the branched block forming a corona. There is

little, if any, tendency for the branched arms to fold back to facilitate packing.

#### 8:15 PM DD3.2

SWITCHING SHAPES OF HYPERBRANCHED MACROMOLECULES AT INTERFACES. Sergei Sheiko, Univ North Carolina, Dept of Chemistry, Chapel Hill, NC; Svetlana Prokhorova, Univ Freiburg, GERMANY; Bernd Tartsch, Univ Ulm, GERMANY; David Shirvanyants, Univ Ulm, GERMANY; Martin Moeller, Univ Ulm, GERMANY.

Significant progress in polymer chemistry has been made towards preparation of three-dimensional macromolecules with well-defined shapes, interiors, and surface structures. The most prominent examples are dendrimers and cylindrical brushes. In contrast to solid particles, molecular colloids retain flexibility of the chain segments and demonstrate significant density fluctuations. Thus, they can be regarded as soft molecular particles, which can change the overall shape as well as the interior structure in response to changes in the physical environment. The conformational changes are particularly subtle at interfaces as they are governed by interplay between intramolecular and surface forces. Recently, we have succeeded in monitoring in-situ the conformational changes and motions of individual brush molecules using scanning force microscopy. The degree of order and the macroconformation of cylindrical brushes exhibited critical dependence of the branching topology and the interaction with the surface. The most peculiar properties of cylindrical brushes on surfaces, namely axial contraction, conformational transitions, and an amoeboid-type motion of the molecular clusters will be discussed.

#### 8:30 PM DD3.3

EFFECT OF NANOPARTICLES ON DEWETTING DYNAMICS OF POLYMER THIN FILMS. Haobin Luo, Dilip Gersappe, Dept of Materials Science and Engineering, SUNY at Stony Brook, Stony Brook, NY.

We use Molecular dynamics simulations to study the effect of nanoscale particles on the dewetting dynamics of polymer thin films. We show that the dewetting dynamics is affected by both the size of the particle and the interaction between the particle and the polymer. Our findings indicate that the mobility of the particle can result in self-healing of holes that are developed during capillary fluctuations of the polymer thin film. We also compare our results to the case when the surface is patterned at the nanoscale to isolate the role of the mobility of the particle on the dewetting dynamics. Our findings will provide routes by which we can suppress or decrease the dewetting dynamics of polymer films.

#### 8:45 PM DD3.4

MOBILITY MEASUREMENTS OF FREELY-STANDING CYCLIC PS FILMS. Chris A. Murray, John R. Dutcher, University of Guelph, Dept of Physics, Guelph, Ontario, CANADA; Gregory B. McKenna, Texas Tech University, Dept of Chemical Engineering, Lubbock, TX.

Large reductions in the glass transition temperature  $T_g$  have been observed for very thin, freely-standing films of linear polystyrene (PS), which is indicative of increased segmental mobility. In spite of the topological differences between cyclic and linear chains, the rheological properties of bulk samples of cyclic and linear PS are not substantially different, apart from a factor of approximately two difference in the zero shear viscosity, the plateau modulus, and the steady state recoverable compliance. We investigate the mobility of thin, freely-standing films of cyclic PS chains and films of linear PS chains of similar molecular weight  $M_w$ . Using ellipsometry, we have measured the temperature dependence of the film thickness  $h$  and the index of refraction  $n$  of the films. Cyclic and linear chains of  $M_w \sim 300k$  were compared with cyclic and linear chains of  $M_w \sim 120k$ , to study the effect of chain end density. In all films, we observe irreversible changes in  $h$  which occur for temperatures  $T > 90^\circ\text{C}$ . We relate the results of these measurements to the determination of  $T_g$ , chain diffusion and anisotropy within the films. Chain diffusion was further studied using optical microscopy to measure the growth of holes in the films as a function of film thickness and temperature.

#### 9:00 PM DD3.5

DYNAMICS OF THIN SUPPORTED POLYMER FILMS: MOLECULAR WEIGHT DEPENDENCE. Hyunjung Kim, Argonne National Laboratory, Advanced Photon Source, Argonne, IL; A. Rühm, L.B. Lurio, Massachusetts Institute of Technology, Center for MS&E, Cambridge, MA; J.K. Basu, University of Illinois, Materials Research Laboratory, Urbana-Champaign, IL; J. Lal, Argonne National Laboratory, Intense Pulsed Neutron Source, Argonne, IL; S.K. Sinha, Univ. of California at San Diego, Department of Physics, La Jolla, CA; S.G.J. Mochrie, Yale University, Departments of Physics and Applied Physics, New Haven, CT.

We have carried out x-ray photon correlation spectroscopy (XPCS) to study the dynamics of surface fluctuations in thin supported polystyrene films with different molecular weight. Four molecular weights, ranging from  $30 \times 10^3$  to  $650 \times 10^3$ , were used in the study. The experiments were done in the melt. The length scales in this study are at least ten times shorter than those in conventional dynamic light scattering. The results will be explained using the capillary wave model.

#### 9:15 PM DD3.6

VISCOELASTIC PROPERTIES AND COMPLEX DYNAMICS IN GELLING SYSTEMS. Lucilla de Arcangelis, Second Univ of Naples, Dept of Information Engineering, Aversa (CE), ITALY; Emanuela Del Gado, Antonio Coniglio, Naples Univ, Physics Dept, Naples, ITALY.

Critical dynamics in gelling polymeric systems is intensively investigated and debated as the experimental data interpretation and the theoretical description of the gelation phenomena are quite controversial. In order to study the viscoelastic properties and the relaxation mechanisms at the gelation transition we have recently introduced a percolation dynamic model and we here present the results of extended numerical simulations on the cubic lattice performed on massive parallel system CRAY-T3E. Our model results to reproduce many relevant aspects of the transition and is suited to study the critical behaviour of viscosity and elasticity in a gelling system. The critical behaviour of the viscosity well agrees with the prediction based on the Rouse model for polymer dynamics and with some experimental results. The elastic response in the gel phase is purely entropic and the obtained critical behaviour can be understood in terms of an entropic elasticity model for the percolating cluster. The relaxation process shows a long-time stretched exponential decay in the time autocorrelation functions in the sol phase, as it is experimentally observed in the gelation critical regime: as the connectivity increases the relaxation process involves the rearrangement of the system over many different length scales, producing slow dynamics and non exponential relaxation. Moreover, the structure factor exhibits a power law behaviour at the transition and in the gel phase. Some interesting analogies with the glassy dynamics can in fact be seen in the gelation phenomena.

#### 9:30 PM DD3.7

A BROAD PERSPECTIVE ON THE DYNAMICS OF HIGHLY CONFINED POLYMER FILMS. Christopher L. Soles, Jack F. Douglas, Wen-li Wu, NIST Polymers Division, Gaithersburg, MD; Huagen Peng, David W. Gidley, University of Michigan, Dept of Physics, Ann Arbor, MI.

The chain dynamics in highly confined macromolecular films directly impacts the microelectronics industry in several ways, including photolithography and chip production, lubricants for hard disk drives, and barrier coatings. The industrial relevance and scientific interest in this problem has generated a large body research in this area utilizing a wide variety of experimental, theoretical, and computational techniques. In several instances, the results are contradictory and it remains unclear how to resolve the differences. This is further complicated by differences in the sample preparation techniques and materials between different laboratories. To eliminate this variability, the same series of highly confined polycarbonate films are studied using specular X-ray reflectivity (SXR), beam positron annihilation lifetime spectroscopy (beam PALS), and incoherent elastic neutron scattering (IENS). SXR is used to measure changes in the film thickness as a function of temperature. These changes are contrasted with the thermal expansion of the nm-sized electron density defects, or nanopores, that are characterized by beam PALS. Finally, IENS is used to quantify the level of anharmonicity through the average mean-square atomic displacement as a function of temperature. The similarities and discrepancies among the techniques are discussed in detail, especially with regards to photolithography. The performance of chemically amplified photoresists depends heavily upon dynamics and small molecule transport in highly confined films.

#### 9:45 PM DD3.8

CRYSTALLIZATION DYNAMICS OF POLYMER THIN FILM. Y.T. Wang, W.H. Zhang, M. Rafailovich, J.C. Sokolov, State University of New York at Stony Brook, Dept. of MS&E, Stony Brook, NY.

Crystallization of spun-cast polypropylene and poly(ethylene-vinylAcetate) thin film with different amounts of exfoliated cloisite 6A clay platelets were studied as a function of film thickness and annealing conditions. The morphology was studied with scanning probe microscopy and the rheology properties were studied using shear modulation force microscopy(SMFM) and a home built micro DSC unit. The results show that even a small(less than 1%) amount of clay drastically alters the morphology, crystallization kinetics and surface friction. The relationship between the structure and the

rheological measurements will be presented.  
Supported in part by the NSF-MRSEC program.

#### 10:00 PM **DD3.9**

**BUBBLE SHAPE AND INTERFACIAL PROPERTIES OF CO<sub>2</sub> / POLYMER MELT EXTRUSION.** Peng Yucheng, Guo Mincheng, Li Kailin, Department of Industrial Equipment and Control Engineering, South China University of Technology, Guangzhou, PR CHINA.

The change of gas bubble shape in a liquid is a basic problem of science and engineering (1), including the polymer process such as foam, coating, print, lubrication. They are concerned with their interfacial properties. In this paper, an in-line plastics extruder with a visible glass window to research interface of CO<sub>2</sub> gas / polymer melt is developed. It finds that the pressure difference inside and outside the interface, interface tension and viscosity resistant force of polymer melt have influence on the interface shape of bubble. The physical model of forces on interface is proposed by our experiments of state and movement polymer melt. The results are same from experiment and mathematical simulation. The interfacial morphology of CO<sub>2</sub> gas / polymer melt is observed from SEM. It consists of a brush of polymer molecular chains end with a shell, which connects in series.

#### SESSION DD4: THEORY, SIMULATIONS AND DYNAMICS III

Chairs: Anna C. Balazs and Steve Granick  
Tuesday Morning, November 27, 2001  
Constitution B (Sheraton)

#### 8:30 AM **\*DD4.1**

**STRUCTURE AND DYNAMICS OF TWO-DIMENSIONAL SUSPENSIONS.** Gerald Fuller, Ed Stancik, Martin Widenbrant, Stanford University, Dept of Chemical Engineering, Stanford, CA.

Colloidal particles are attracted to mobile interfaces and can form two-dimensional crystalline structures. These highly organized systems are of interest in studies of phase behavior in two dimensions and because of the use of interfacial particulates to stabilize emulsions and foams. This paper describes experiments designed to examine the response of these systems to imposed flows (shear and extensional). Examples of shear induced melting, recrystallization, and microstructure distortion are presented. In addition, the interfacial rheology of two-dimensional colloidal crystals is discussed.

#### 9:00 AM **DD4.2**

**MOLECULAR DYNAMICS STUDIES OF THE EFFECTS OF WATER SPECIATION ON INTERFACIAL STRUCTURE AND DYNAMICS IN SILICA FILLED-PDMS COMPOSITES.**

Richard Gee, Robert S. Maxwell, Long N. Dinh, Bryan Balazs, Lawrence Livermore National Laboratory, Chemistry and Materials Science Directorate, Livermore, CA.

Significant changes in materials properties of siloxane based polymers can be obtained by the addition of inorganic fillers. In silica filled PDMS based composites the mechanism of this reinforcing behavior is presumably hydrogen bonding between surface hydroxyls and backbone siloxane species. We have chosen to investigate in detail the effect of chemisorbed and physisorbed water on the interfacial structure and dynamics in silica filled PDMS based composites. Toward this end, we have combined classical molecular dynamics simulations and experimental studies employing DMA and NMR analysis. Our results suggest that the polymer-silica contact distance and the mobility of interfacial polymer chains significantly decreased as the hydration level at the interface was reduced. The reduced mobility of the PDMS chains in the interfacial domain reduced the overall, bulk, motional properties of the polymer, thus causing an effective "stiffening" of the polymer matrix. This finding is consistent with both NMR and modal analysis experimental data. The role of the long-ranged Coulombic interactions on the structure features and chain dynamics of the polymer were also examined. Both are found to be strongly influenced by the electrostatic interactions as identified by the bond-reorientation time-correlation function and atom-atom distribution functions. We show that both the motional dynamics of the polymer and the structure in the interfacial region are indeed controlled by the concentration of water in the interfacial region. The results have important implications for the design of nanocomposite silica-siloxane materials.

#### 9:15 AM **DD4.3**

**MULTI-SCALE AGGREGATION OF PMMA STEREOCOMPLEX AT A SURFACE.** Yves Grohens, Gilles Castelain, Pascal Carriere, Jiri Spevacek\*, Jacques Schultz, Institut de Chimie des Surfaces et Interfaces-CNRS, Mulhouse Cedex, FRANCE. \*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague, CZECH REPUBLIC.

After briefly discussing the particularity of the adsorption process of PMMA aggregates in term of aggregative adsorption, the nanoscale patterns formed by poly(methyl methacrylate) (PMMA) stereocomplexes at the surface of silicon wafers, glass and mica, were investigated by tapping mode atomic force microscopy (TM-AFM). The effects of the solvent nature, PMMA concentration, *i/s*-ratio (stoichiometry) and surface nature on the morphology of the stereocomplex thin layer at a surface were addressed. The aggregation phenomena are well described by the diffusion limited cluster-cluster aggregation model (DLA) and the fractal exponent *D* calculated. Solvent was shown to play a major role on the shape of the structure of the polymer assembly observed on silicon. The *i/s*-ratio strongly influences the fractal exponent *D* which is equal to 1.35 for the 1:2 ratio is lower than for the other *i/s* ratios which are 1.46, 1.61, 1.82 for 1:1, 2:1 and 4:1 ratios, respectively. The low values of the fractal dimension *D* are indicative of a fast aggregation process where the probability of cluster-cluster sticking on collision is very high. The shape of the aggregates is rather open in that case. Higher values of *D* correspond to a slow aggregation process where the probability of sticking is low and provides more compact structure of the aggregates. Dilute polymer solutions were used and the concentrations were varied from 0.1 to 1 g/l in acetone to reach a 2D network of connecting aggregates. The size of the aggregates increases with the PMMA concentration and is always higher than the size of the aggregates in solution measured by light scattering. This is the result of an enhanced surface aggregation of the polymer assembly indicated by the difference in size of the aggregates observed on different substrates of varying surface energy.

#### 9:30 AM **\*DD4.4**

**X-RAY STANDING WAVE MEASUREMENTS OF GOLD NANOPARTICLE MOTION IN THIN FILMS.** Rodney S. Guico, Andrew G. Richter, Jin Wang, User Program Division, Argonne National Laboratory, Argonne, IL; Kenneth R. Shull, Department of MS&E, Northwestern University, Evanston, IL.

Polymer/metal nanocomposites have emerged in recent years as an important research area due to their practical and fundamental significance. While much of the current work in this field has focused on the diffusive properties of nanoparticles in polymeric matrices, specifically diblock copolymer templates, fundamental questions can be addressed by studying individual particle interactions with homopolymers. To observe the physics of the situation, we probed polymer/metal interactions using a model system. The diffusion of gold nanoparticles was measured in real time as the polymer thin film is annealed above the glass transition temperature (*T<sub>g</sub>*). Total external reflection x-ray standing waves (TER-XSWs) were used to determine the profile of the metal particles perpendicular to the polymer surfaces over short anneal times before the particles have coalesced.

#### 10:30 AM **\*DD4.5**

**LONG RANGE SURFACE EFFECTS IN THE PHASE BEHAVIOR OF THIN POLYMER BLEND FILMS.** Sanat K. Kumar, Ananth Indrakanti, Ronald Jones, Penn State University, Dept of MS&E, University Park, PA ; Robert M. Briber, University of Maryland, Dept. of Nuclear and Materials, College Park, MD.

The correlation length,  $\xi$ , of composition fluctuations in a thin film miscible polymer blend, where one component is strongly adsorbed to both surfaces, is examined as a function of overall film thickness, *D*, and temperature. These novel measurements reveal a suppressed correlation length parallel ( $\xi_{\parallel}$ ) to the surfaces in films as thick as  $40R_G$ , where  $R_G$  is the bulk radius of gyration. These results argue for very long range effects of surfaces on the thermodynamics of polymer blends, in agreement with theory. The consequence of these ideas on the diffusion in thin films, and on phase transitions in thin films will be examined.

#### 11:00 AM **DD4.6**

**COMPARISON OF MOBILITY MODES IN POLYMER SOLUTIONS UNDERGOING THERMAL-INDUCED PHASE SEPARATION.** Philip K. Chan, Ryerson Univ, Dept of Chemistry, Biology and Chemical Engineering, Toronto, Ontario, CANADA.

The thermal-induced phase separation method is used to fabricate polymer membranes and polymer-dispersed liquid crystal films from polymer solutions. The resultant morphology consists of solvent droplets dispersed uniformly in a solid polymer matrix. Up till now, the modeling and computer simulation of the thermal-induced phase separation phenomenon in polymer solutions have considered the mobility to be a constant or expressed as various functions of concentration. The objective of this presentation is to compare the following three mobility modes: (1) mobility as a constant, (2) mobility following fast mode theory, and (3) mobility following slow mode theory. We present computer simulation results from models

composed of the Cahn-Hilliard theory for phase separation, Flory-Huggins free energy density for polymer solutions, and the three aforementioned mobility modes.

#### 11:15 AM DD4.7

EARLY STAGE OF COMPOSITION SEGREGATION IN POLYMER BLEND FILMS. Howard Wang, Jack F. Douglas, Sushil K. Satija, Charles C. Han, National Institute of Standards and Technology, Materials Science and Engineering Laboratory, Gaithersburg, MD; Russell J. Composto, University of Pennsylvania, Department of Materials Science and Engineering, Laboratory for Research on Structure of Matter, Philadelphia, PA.

The early stage compositional evolution prior to the wetting layer growth at the surface of polymer blend films has been investigated primarily using neutron reflectivity. Closeness to glass transitions of the polymers slows down the dynamics and allows the observation of otherwise rapid processes. Two-step relaxation of composition profile has been observed: a rapid rearrangement of chain conformations and a slower center-of-mass diffusion from the bulk, corresponding to two metastable states, segmental and monolayer saturations, of the surface enrichment.

#### 11:30 AM \*DD4.8

ELECTROHYDRODYNAMIC AND THERMOMECHANICAL FILM INSTABILITIES. Ulrich Steiner, Department of Polymer Chemistry, Materials Science Center, University of Groningen, Groningen, THE NETHERLANDS.

Thin liquid films are often unstable. While usually undesired, film instabilities can also be exploited for structure formation and lithography. In most dewetting experiments the onset of the instability is caused by van der Waals forces. Surfaces and thin films can, however, also be destabilized by externally applied forces. I will discuss three examples for such external factors and demonstrate their application in a lithographic technique.

-Electrohydrodynamic (EHD) Instabilities: An electric field normal to a dielectric boundary causes an effective pressure at this interface. In the case of dielectric liquids, this pressure can lead to the break-up of a dielectric double layer.

-Thermomechanical (TM) Instabilities. A temperature gradient across a polymer film is associated with a momentum flux, which can cause an interfacial instability.

-Acoustic Disjoining Pressure. In a thin film the electromagnetic density of states is restricted by the film geometry. This leads to the electromagnetic Casimir effect. The phonon spectrum in a film is similarly confined, leading to an acoustic disjoining pressure. For commonly studied thin film systems, this pressure is of the same order of magnitude as the electromagnetic disjoining pressure.

-Lithography using film instabilities. Both, EHD and TM instabilities are controlled by the thicknesses of the two layers. If the thickness of one of the layers is modulated using a topographic master, the instability replicates this master pattern.

SESSION DD5/S4: JOINT SESSION  
COMBINATORIAL APPROACH TO POLYMERS  
Chairs: Eric J. Amis and Alamgir Karim  
Tuesday Afternoon, November 27, 2001  
Constitution B (Sheraton)

#### 1:30 PM \*DD5.1/S4.1

AN ELECTRONIC NOSE FROM ARRAYS OF POLYMER COMPOSITE VAPOR SENSORS. Nathan S. Lewis, California Institute of Technology, Division of Chemistry and Chemical Engineering, Pasadena, CA.

A method is described for generating a variety of chemically diverse, broadly responsive, low power vapor sensors. A key to our ability to fabricate chemically diverse sensing elements is the preparation of processable, air stable films of electrically conducting organic polymers. An array of such sensing elements produces a chemically reversible, diagnostic pattern of electrical resistance changes upon exposure to different odorants. Such conducting polymer elements are simply prepared and are readily modified chemically to respond to a broad range of analytes. In addition, these sensors yield a fairly rapid, low power, dc electrical signal in response to the vapor of interest, and their signals are readily integrated with software or hardware-based neural networks for purposes of analyte identification. Principle component analysis has demonstrated that such sensors can identify and quantify different airborne organic solvents, and can yield information on the components of gas mixtures.

#### 2:00 PM \*DD5.2/S4.2

COMBINATORIAL STUDIES OF SURFACE PATTERN FORMATION IN BLOCK COPOLYMER THIN FILMS.

Alamgir Karim, Archie P. Smith, Jack F. Douglas, Amit Sehgal, Eric J. Amis, Polymers Division, NIST, Gaithersburg, MD.

Surface pattern formation in PS-PMMA diblock copolymer films is investigated combinatorially as a function of film thickness  $h$ , molecular mass  $M$  and substrate surface energy,  $E$ . Smooth films are observed for certain  $h$  ranges centered about multiples of the lamellar thickness  $L_0$  and we attribute this effect to an increase in the surface chain density with  $h$  in the outer brush-like copolymer layer. We also observe stable bicontinuous surface patterns for other  $h$  ranges and the average size of these patterns is found to inversely scale with  $L_0$  to the  $-2.5$  power. Hole and island patterns occur for  $h$  ranges between those of the bicontinuous patterns and the smooth regions and their size similarly decreases with  $M$ . A smooth surface band is observed about a certain  $E$  value regardless of  $h$  due to non-preferential interaction of both blocks with the substrate surface.

References:

[1] Physical Review Letters, In press.

[2] Journal of Polymer Science Part B: Polymer Physics, In press.

#### 2:30 PM \*DD5.3/S4.3

INVESTIGATING CRYSTALLIZATION IN THIN POLYMER FILMS USING HIGH THROUGHPUT METHODS.

Kathryn L. Beers, Jack F. Douglas, Eric J. Amis and Alamgir Karim, National Institute of Standards and Technology, Polymers Division, Gaithersburg, MD.

The ability to control orientation and morphology in semi-crystalline polymeric thin films has been an elusive goal in both industry and academia for many years. We present methods of accelerating the pace of research in this area by preparing single films in which orthogonal gradients of various parameters influencing crystallization can be established. Isotactic polystyrene was studied as a model system due to the comparatively slow rates and high temperatures at which it crystallizes. Preliminary studies on isotactic polystyrene (ipS) confirm the applicability of the method to investigating the kinetics of crystallization as a function of undercooling temperature,  $T$ , and film thickness,  $h$ . Growth rates,  $G(T, h)$  spanning temperatures from  $130^\circ\text{C}$  to  $200^\circ\text{C}$  and film thickness from 20 nm to 200 nm were obtained from 2 to 3 films within a few days. As the degree of undercooling  $((T_m - T)/T_m)$  increases along a cross section of the film with uniform  $h$ ,  $G$  passes through a maximum between the glass transition temperature ( $T_g$ ) and the melt temperature ( $T_m$ ) as expected based on literature data.  $G$  also decreases with  $h$  along isothermal cross sections. Changes in crystal morphology were also observed as a function of both  $T$  and  $h$ . Hexagonal plates, spherulites and dendrites of crystalline ipS were obtained simultaneously on the same film. In order to expand the library of materials and accelerate the pace of data collection, alternative methods of sample preparation and probe techniques are being developed. We will discuss current progress in this area.

#### 3:30 PM \*DD5.4/S4.4

COMBINATORIAL INVESTIGATION OF THE MECHANICAL PROPERTIES OF NANOSCOPIC POLYMER STRUCTURES.

Paul F. Nealey, Heidi Cao, Mark Stoykovich, Kenji Yoshimoto, Department of Chemical Engineering and Center for NanoTechnology, University of Wisconsin, Madison, WI; Leonidas E. Ocola, Agere Systems, Murray Hill, NJ.

As the dimensions of industrial relevant polymeric systems shrink to the length scale of individual molecules, significant new challenges are encountered as the material properties become dimension dependent. For amorphous polymeric materials, the characteristic dimensions of individual molecules are on the order of tens of nanometers, and dimension dependent thermophysical properties are routinely observed for films less than 50 nm thick, and under certain conditions for films as thick as 200 nm. In the realm of advanced lithography structures are routinely generated with at least one dimension less than 100 nm. An emerging difficulty in fabricating densely packed structures using standard resists and processing protocols is the collapse of the structures during drying due to capillary forces. Determination of the in-plane mechanical properties of patterned polymeric resist is essential to understand, model, and hopefully circumvent this phenomenon. Currently the techniques for applying in-plane forces to deform the nanoscopic polymer structures and measuring the deformation of the structures in response to the applied forces are limited. We report on the design and implementation of test structures with which well-defined in-plane capillary forces were generated during drying of rinse liquids. Deformation of combinatorial arrays of test structures fabricated from poly(methylmethacrylate) allowed the determination of the force necessary to collapse the structures, and the extent of deformation of the structures as a function of the applied forces. In conjunction with appropriate molecular and continuum models, mechanical properties can be extracted using these combinatorial arrays. The principal concepts of

the test structures, measuring deformation of materials in response to well-defined capillary forces, should be broadly applicable for the determination of in-plane material properties at the nanoscale.

#### 4:00 PM \*DD5.5/S4.5

COMBINATORIAL INVESTIGATION OF ADHESION OF POLYMER THIN FILMS. Alfred J. Crosby, Alamgir Karim, Eric J. Amis, NIST, Polymers Division, Gaithersburg, MD.

The adhesion of glassy polymer interfaces is directly dependent upon several parameters including time of contact, temperature, surface energy, and molecular weight. Collectively, these parameters play a dominant role in determining the interfacial strength of a glassy polymer interface due to the enhancement of interfacial strength by molecular diffusion across the interface. This diffusion can lead to molecular entanglements and/or situations where molecular friction greatly augments energy dissipation near the interface, thus enhancing the total work required to separate the interface. In addition to the above parameters, we can investigate the effect of thickness of a polymer film on adhesion at a glassy polymer interface. To facilitate this investigation, we have developed a novel combinatorial technique to characterize polymer adhesion. The technique involves contact and separation of a matrix of spherical caps on a complementary substrate. During the process of contact and separation, we monitor the contact area for each spherical cap and the relative displacement between the spherical caps and the complementary substrate. With these measured quantities, we build upon the theory of Johnson, Kendall, and Roberts (JKR) to quantify the adhesion across the matrix. By varying such parameters as thickness, temperature, and surface energy along the orthogonal axes of the matrix, we use this new technique to efficiently produce quantitative polymer adhesion vs. variable maps. We present results on effects of thickness, temperature, and surface energy on the self-adhesion of polystyrene thin films.

#### 4:30 PM DD5.6/S4.6

COMBINATORIAL LIBRARIES OF BLEND PHASE MORPHOLOGY ON GRADIENT ENERGY SURFACES. Amit Sehgal, Jack F. Douglas, Eric J. Amis, and Alamgir Karim, Polymers Division, NIST, Gaithersburg, MD; Vincent Ferreiro, C.N.R.S., Lab. de Structure et Proprietes de l'Etat Solide (L.S.P.E.S.), Universite des Sciences et Technologies de Lille, Villeneuve d'Ascq, FRANCE.

The presence of an interface in an ultra-thin polymer blend film guides or even significantly alters the phase separation process. Confinement between the air and substrate interfaces and the preferential wetting of specific components at the walls determines the in-plane and the surface directed compositional distribution and the spatial scales. We use a simple method for chemical modification of chlorosilane self-assembled monolayers (SAMS) on Si surfaces by exposure to a gradient in UV-Ozone radiation to create stable substrates with a range of contact angles ( $H_2O$ ;  $5^\circ - 95^\circ$ ) and surface energies on a single substrate. Thickness gradients (40 nm to 140 nm) orthogonal to the surface energy axis generate simple, yet powerful, two-dimensional maps to probe how the polymer-substrate interaction acts in concert with the film thickness to influence the scales of phase separation. The morphological evolution of a model LCST (PS-PVME) blend was investigated by automated optical microscopy and atomic force microscopy. A non-monotonic change in the lateral scale and surface roughness with surface energy is observed along with the expected systematic increase with thickness. The study was extended to a biocompatible blend of poly( $\epsilon$ -caprolactone) and poly(D-L lactic acid) for application of the systematic variation in topographical scales to assay cellular response.

#### 4:45 PM DD5.7/S4.7

COMBINATORIAL MAPPING OF POLYMER FILM WETTABILITY ON GRADIENT ENERGY SURFACES. Karen M. Ashley, D. Raghavan, Polymer Science Division, Department of Chemistry, Howard University, Washington DC; Amit Sehgal, and A. Karim, Polymers Division, Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD.

We demonstrate the use of combinatorial methods for studying dewetting of thin hydrophobic polystyrene (PS) and hydrophilic poly D-lactacid (PDLA) films on chemically modified gradient energy surfaces. Substrate libraries were prepared by immersing Si-H (passivated Si) in Piranha solution (sulfuric acid / hydrogen peroxide / water) at a controlled rate giving a systematic variation of solvent (water and diiodo methane) contact angles across the surface. Additionally, chlorosilane SAMs on Si surfaces were exposed to UV radiation such that a range from hydrophobic to hydrophilic was obtained across the surface ( $\sim 3$  cm). Libraries of thin films of PS or PDLA coatings on gradient energy surfaces orthogonal to gradients in film thickness were screened for dewetting behavior using automated

optical microscopy. Contrasting trends in the wettability of PS and PDLA were visibly apparent as a function of surface energy of the substrate. The number density of polygons of the dewet films was found to obey a power law relationship with both film thickness and substrate surface hydrophilicity as characterized by contact angle studies. The effect on dewetting morphology with molecular weight (above and below entanglement) will be discussed.

SESSION DD6: POSTER SESSION  
POLYMER INTERFACES AND THIN FILMS I  
Chairs: Thomas P. Russell and Curtis W. Frank  
Tuesday Evening, November 27, 2001  
8:00 PM

Exhibition Hall D (Hynes)

#### DD6.1

PHOTO-ORIENTATION OF MESOSTRUCTURED SILICA. Yasuhiro Kawashima, Masaru Nakagawa, Takahiro Seki, Tokyo Institute of Technology, Chemical Resources Laboratory, Kanagawa, JAPAN; Kunihiko Ichimura, Science University of Tokyo, Research Institute for Science and Technology, Chiba, JAPAN.

The orientation of a photoexcitable molecule is effectively changed by illumination with linearly polarized light in soft materials, where the molecule reorients to a non-excitable (orthogonal) direction to the polarization. The process can be applied to interplays between a photochromic molecular surface and a variety of soft matters, most typically liquid crystals. However, such light-mediated process does not directly work for stiff inorganic substances.

We report a successful photoalignment of mesostructured inorganic materials synthesized through supramolecular templating of surfactants via hierarchical cascade transfer among hetero-interfaces. The directional information (polarization) possessed by light is initially captured by a latent photochromic azobenzene monolayer (light  $\rightarrow$  monolayer), and then fixed by a robust silicon-catenated polymer (monolayer  $\rightarrow$  polymer). The photoaligned polymer film is eventually inherited to a directional nucleation of a surfactant/silica hybrid in the sol-gel polymerization (polymer  $\rightarrow$  inorganic mesochannel). In total, light information is greatly transformed and amplified to produce highly anisotropic morphology of the rigid inorganic matter. This method further allows for micropatterned alignment of the mesochannel. The present work shows the joint of the photoaligning technology and fabrication of mesostructured materials.

#### DD6.2

PATTERNING OF ADSORBED MONOLAYERS OF PHOTOPOLYMERS. Masaru Nakagawa, Takahiro Seki, Tokyo Institute of Technology, Chemical Resources Laboratory, Kanagawa, JAPAN; Kunihiko Ichimura, Science University of Tokyo, Research Institute for Science and Technology, Chiba, JAPAN.

Since photopatterning of organosilane self-assembled monolayers based on the photocleavage of a Si-C covalent bond by deep UV light exposure has been demonstrated by Calvert et. al., imagewise photopatterned monolayers exhibiting heterogeneity of physicochemical properties at a solid surface have been interesting to a lot of materials scientists. This is because the patterned monolayers are promising for the fabrication of electric integrated circuits beyond present photoresist technology and for the fabrication of chemical sensors and biochips as medical usage. Though the significance of the photopatterned surfaces for such advanced technologies is recognized well, there have been only several materials and methods to create photopatterned monolayers. More convenient, effectual, and readily available materials and methods from industrial as well as environmental standpoints should be developed. We report a novel method for the preparation of patterned monolayers adsorbed on a  $SiO_2$  surface by using a positive-type Si-based photopolymer bearing quaternized ammonium units. Both the dip-coating for monolayer fabrication and the development after imagewise irradiation are available in an environmentally benign aqueous system. The photopatterning can be performed at an exposure energy of no more than  $200 \text{ mJ cm}^{-2}$  by irradiation with 254 nm light emitting from a widely used Hg lamp. We also demonstrate a selective metallization process where the photopatterned polymer adsorbates act as a metallization monolayer resist.

#### DD6.3

NOVEL BLOCK COPOLYMERS WITH THERMO-REACTIVE BLOCKS: ORDERING IN THIN FILMS OF SYMMETRIC DIBLOCK COPOLYMERS. Ho-Cheol Kim<sup>1</sup>, Lucy Li<sup>1,2</sup>, Eva Harth<sup>1</sup>, Craig J. Hawker<sup>1</sup>, Thomas P. Russell<sup>3</sup>. <sup>1</sup>IBM Research Division, Almaden Research Center. <sup>2</sup>Departments of Materials, University of California, Santa Barbara, CA. <sup>3</sup>Polymer Science and Engineering Department, University of Massachusetts at Amherst, MA.

The morphology of thin films of novel diblock copolymers containing thermo-reactive blocks was studied. Microdomain formation of the copolymers can be controlled by the reaction temperature or relative incorporation of thermo-reactive group. The copolymers showed different orientations of microdomain on the surfaces of native oxide and passivated silicon. In addition, the use of thermo-reactive blocks provides a simple route to controlling both the formation and orientation of microdomains by changing annealing temperature and surface energy of substrates. A unique way to control the lateral order of microdomains of novel copolymers with thermo-reactive blocks will also be presented.

#### **DD6.4**

**ORGANIC-INORGANIC NETWORK ASSEMBLIES OF NANOPARTICLES AS CHEMICALLY SENSITIVE INTERFACIAL MATERIALS.** Li Han, Scott R. Kowaleski, David R. Daniel, Chuan-Jian Zhong, Dept of Chemistry, State University of New York at Binghamton, Binghamton, NY.

Metal and metal oxide nanoparticles encapsulated with organic shells serve as interesting building blocks for designing chemically and biologically sensitive interfacial materials. Such organic shells range from monolayers to polymers. This presentation reports the results of an investigation of the interfacial molecular recognition and vapor molecule sensing at several types of nanostructured nanoparticle thin films. The nanostructured thin films are prepared from gold, silver and alloy nanoparticles of different core sizes (2~10 nm) and molecular linkers of different binding properties (e.g., 1,9-nonanedithiol, 11-mercaptoundecanoic acid, and multi-functionalized polymers). By coupling interdigitated microelectrode resistance measurement and quartz-crystal microbalance, we investigate the responses of the nanostructured electronic conductivity upon vapor sorption at the interface. The molecular interactions and reactivities at these nanostructured films are demonstrated to be dependent on the core size of the nanoparticles and the chemical nature of the linking molecules. The data are correlated with the surface infrared reflection spectroscopic data on the inter-shell interactions, and with the atomic force microscopic data on the morphological changes. The implications of the findings to the delineation of design parameters for constructing core-shell nanoparticle assemblies as chemically-sensitive interfacial materials will also be discussed.

#### **DD6.5**

**NEAR-INTERFACE STRUCTURE OF POLYMERIC CHAINS IN POLYMER-BASED NANOCOMPOSITES.** Catalin Picu, Murat Ozmusul, Rensselaer Polytechnic Institute, Dept Mechanical Engineering, Troy, NY.

It is well known that chain conformations and dynamics are affected by the presence of a rigid wall. This modification leads to changes in the mechanical properties of the polymeric matrix, and is believed to be the leading factor controlling the significantly different properties of nano-filled polymers compared to the similar micro-filled systems. Although many studies have addressed the flat interface/surface configuration, results for curved interfaces (e.g. of the polymer matrix with a rigid spherical filler) are scarce. We performed lattice Monte Carlo simulations of polymer chains in the vicinity of spherical rigid particles and investigated the effect of various system parameters on the size of the affected zone, and on the chain conformations within. We considered first the system in its athermal limit, in which only excluded volume interactions take place. If there is no persistence length along the polymer chains, the affected region sampled at the atomic scale is two monomer wide, and it is independent of the chain length and particle curvature. When sampled at a scale comparable with the particle diameter, a perturbed layer of thickness equal to about 1.5 gyration radii is evidenced. Larger scale sampling reveals a homogeneous matrix. The atomic layer right next to the surface of the particle is enriched in chain ends, although the atom number density is similar to that in the bulk. When an interaction potential between the nanoparticle and the matrix material is added, the atom number density varies over a distance from the surface equal to the range of the potential. The local atomic-level structure of the polymer is obtained by a convolution of the athermal result with the atom number density profile. An attractive potential leads to a decrease in chain end segregation to the interface, while a repulsive one, increases this effect. The larger scale structure is not affected by the added potential interactions. These conclusions hold qualitatively at all temperatures. Considering, in addition, inter-chain interactions leads to surface energy effects. The changes associated with this modification will be also discussed.

#### **DD6.6**

**PREPARATION AND CHARACTERIZATION OF C<sub>60</sub>-PERDEUTERATED STYRENE CO-POLYMER NANOFILMS.** Zhang Lin, Tu Haiyan, Du Kai, Luo Xuan, Zhou Lan, Zhang Houqiong, Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang, Sichuan, CHINA.

Polymer nanofilms are a new kind of functional material and can be found many important technological applications in different fields, e.g., integrated optics, biosensors, and coatings on optical surface, supermirrors, and waveguides. Since C<sub>60</sub> and Perdeuterated polymers have many unusual performances, we studied the preparation of C<sub>60</sub>-Perdeuterated styrene co-polymer nanofilms (especially the Langmuir-Blodgett films, i.e. LB films). This paper describes the preparation procedures of the C<sub>60</sub>-Perdeuterated styrene co-polymer LB films, and the microstructure of the LB films are characterized by scan electronic microscope and atomic force microscope also. C<sub>60</sub> and Perdeuterated styrene are used as the original reactants, by use of radical initiated polymerization reactions, we can get C<sub>60</sub>-Perdeuterated styrene co-polymers. Dissolving C<sub>60</sub>-Perdeuterated styrene co-polymers in a volatile solvent (such as dichloromethane, methenyl chloride, and benzene etc.), dropping the co-polymers solution on the subphase (super-pure water) which is held in the trough of a LB film deposition equipment. Once spread upon the surface of the subphase, we can deposit the C<sub>60</sub>-Perdeuterated styrene co-polymer LB film onto the surface of a previously cleaned substrate by lifting and raising the substrate through the compact monolayer on the subphase surface. The parameters, which would influence the quality of the LB film products, are studied. It is found that the feasible environment temperature, upward speed and compressive speed are 15 to 30 °C, 8 to 15mm/min and 15 to 25mm/min respectively. The thickness of the monolayer LB films can be varied with the molecular weight of C<sub>60</sub>-Perdeuterated styrene co-polymers. With characterization of scan electronic microscope and atomic force microscope, we find that the LB films have some small peaks among them. By LB film preparation technique, now we can prepare the C<sub>60</sub>-Perdeuterated styrene co-polymer nanofilms with thickness of 20-80nm. Keywords: C<sub>60</sub>-Perdeuterated styrene co-polymer, Langmuir-Blodgett film, nanofilm, Preparation; Characterization.

#### **DD6.7**

**PHASE SEPARATION OF A BINARY FLUID IN THE PRESENCE OF IMMOBILE PARTICLES: A LATTICE BOLTZMANN APPROACH.** Domenico Suppa, Olga Kuksenok, Anna Balazs, University of Pittsburgh, Chemical Engineering Department, Pittsburgh, PA; Julia Yeomans, Oxford University, Theoretical Physics, Oxford, UNITED KINGDOM.

Using a Lattice Boltzmann model, the phase separation of a binary fluid in the presence of immobile particles is studied in two dimensions. The particles are preferentially wetted by one of the fluids. In the hydrodynamic over-damped limit, where the flow is entirely driven by capillary effects, the domain growth is found to depend on the strength of the interaction between the particles and the favorable fluid. In particular, we isolate two different regimes: for relatively strong coupling between the particles and fluid, the hydrodynamic flow promotes the coalescence of the domains in the early stage of phase separation while, in the later stage, the domain growth is pinned at a finite domain size, essentially independent of the hydrodynamics. For weaker coupling, however, the coarsening dynamics as well as the ultimate size of the domains are enhanced by hydrodynamic flow. These results indicate that the size of the domains can be tailored by varying the chemical nature of the particles.

#### **DD6.8**

**SIZE VARIATIONS OF LAMELLAR MICRODOMAINS OF THIN DIBLOCK COPOLYMER FILMS BY NANOPARTICLES IN THE NANOREACTOR SCHEME.** B.H. Sohn, B.W. Seo, S.M. Park, S.H. Yun, W.C. Zin, Pohang Univ of Sci & Tech, Dept of MS&E, Pohang, KOREA.

Microdomains of block copolymers can be utilized as so-called nanoreactors to synthesize a variety of nanoparticles. That is, nanoparticles can be selectively synthesized within the microdomains of diblock copolymers. In this nanoreactor scheme, microdomains should be expanded to incorporate nanoparticles and have limited amounts of nanoparticles synthesized in them. In bulk samples, however, it would not be easy to perform a precise measurement of size variations of microdomains by nanoparticles. Thus, we employed a multilayered nanostructure of alternating parallel lamellae of diblock copolymers in thin films. Then, gold nanoparticles were selectively synthesized within one of the blocks, resulting in alternating pure polymer lamellae and gold nanoparticle-containing lamellae parallel to the substrate. Using AFM, increases of the lamellar size by nanoparticles were precisely measured from increases of the quantized total thickness  $(n/2)L_0$  as well as the height  $L_0$  of islands and holes that were formed on the thin film due to an incommensurable thickness effect. ( $L_0$  is the lamellar domain spacing.) The amount of nanoparticles incorporated was also obtained quantitatively by a quartz crystal microbalance. Therefore, the relationship between the lamellar size and the amount of nanoparticles was elucidated. Using the same methodology, we are currently investigating size variations of lamellar microdomains by

staining agents such as osmium tetroxide, ruthenium tetroxide, and iodine used for contrast enhancement in TEM.

#### **DD6.9**

**IMPROVED COMPATIBILITY OF IMMISCIBLE BLEND SYSTEM IN A SUPERCRITICAL CO<sub>2</sub>.** J. Jerome, Y.-S. Seo, T. Koga, J. Sokolov, M. Rafailovich, SUNY at Stony Brook, Dept of Material Science and Engineering, Stony Brook, NY; J. Conlon, E. Palermo, R. Occhiogrosso, Bay Shore High School, Bay Shore, NY; S. Satija, CNCR, NIST.

We have used in situ neutron reflectivity the effect of supercritical CO<sub>2</sub> (SC-CO<sub>2</sub>) on the interfacial structure of immiscible polymers C PS and PMMA. We show that on the density fluctuation ridge the interfacial width between the polymer in thin bilayer samples increasing by more than a factor of 3. This increment is observed both in situ and if CO<sub>2</sub> is removed rapidly. The effects of this interfacial broadening in the dewetting process were also measured by AFM. The dependence of the Young's contact angles as well as the adhesion between the two polymers when exposed to SC-CO<sub>2</sub> will be presented.

#### **DD6.10**

**PHASE SEPARATION IN TERNARY POLYMER BLEND FILM.** Y.T. Wang, W.H. Zhang, M. Rafailovich, J.C. Sokolov, State Univ. of New York at Stony Brook, Dept. of MS&E, Stony Brook, NY; S. Schwarz, V. Zeitsev, Dept. of Physics, CUNY Queens College, Flushing, NY; H. Ade, A. Winesett, North Carolina State Univ., Dept. of Physics, Raleigh, NC.

Phase separation behavior of ternary polymer blend films for amorphous and crystalline polymer were studied. The amorphous system, Polystyrene/Poly(Methy-Methacrylate)/Poly(Ethylene-Propylene) films was spun cast onto HF treated silicon wafer before being annealed at 170°C for different amount of time up to 7 days. Crystalline blends of Poly(Ethylene-VinylAcetate)/Polyethylene/Poly(Ethylene-Propylene) were prepared in the same way. Three dimensional vector functions of the phase segregation patterns were produced from complementary data of time-of-flight secondary ion mass spectrometry(TOF-SIMS), scanning transmission x-ray microscopy(STXM) and atomic force microscopy(AFM). The effect of 10% exfoliated 6A cloisite clay on the phase behavior was also investigated. Two distinct wave vectors were observed to characterize the dynamics. The time dependence as well as the effect of crystallization in confined geometries will be discussed.

#### **DD6.11**

**THE EFFECT OF SOLUTION CONCENTRATION ON DIBLOCK COPOLYMER ADSORPTION AT SOLID-LIQUID INTERFACES.** Angela M. Buffone and Shenda M. Baker, Department of Chemistry, Harvey Mudd College, Claremont, CA.

Past research has shown a significant decrease in surface coverage,  $\Gamma$ , of poly(styrene)-*b*-poly(ethylene oxide) (PS-PEO) adsorbed from selective solvents onto silicon oxide surfaces for concentrations greater than the critical micelle concentration (cmc). Through the use of Fourier Transform Infrared Spectroscopy in the mode of Attenuated Total Reflectance (FTIR-ATR) and multi-angle light scattering, the effect of the copolymer solution concentration on  $\Gamma$  and on the kinetics of adsorption have been studied. Adsorbed polymer, that has saturated the surface and is stable to rinsing, can be affected by subsequent increase of solution concentration. In fact, subjecting a saturated surface to solution concentrations greater than the cmc removes significant mass from the surface. Our results suggest that above the cmc, the diblock copolymer is more thermodynamically stable in the micelle than on the surface.

#### **DD6.12**

**DIFFUSION STUDIES OF PS AND PMMA THIN FILMS WITH CLAY PARTICLES.** Xuesong Hu, Miriam Rafailovich, Jonathan Sokolov, State University of New York at Stony Brook, Dept. of Materials Sci. & Eng., Stony Brook, NY; Vladimir Zaitsev, Steven Schwarz, Queens College of City University of New York, Dept. of Physics, Flushing, NY; Dennis Peiffer, ExxonMobile Research and Engineering Company, Annandale, NJ; Anshul Shah, Ward Melville High School, Setauket, NY.

The mobility of polymer chains in the precedence of filler particles is an important factor affecting all aspects of the rheological response. We report on tracer diffusion measurement of monodisperse Polystyrene(PS) and Polymethyl methacrylate(PMMA) in the precedence of functionalized clay particles (Cloisite 6A). Using AFM and TEM, we show that nearly complete exfoliation and orientation occurs when the clay particles are co-dissolved with the polymer and spun cast on Si substrate to form thin films approximately 2-300nm thickness. Bilayer and trilayer samples of dPS/hPS and dPMMA/PMMA were made where 10% by volume Cloisite 6A clay was dissolved in one or both polymer layers. The tracer diffusion

coefficient  $D_0$  of dPS or dPMMA (20% by weight) in the layer was measured using time of flight secondary ion mass spectrometry. In addition, the diffusion of the clay particle was measured by detecting the Si ion concentration profile as a function of annealing time at  $T=137^\circ\text{C}$ . The results show that  $D_0$  is reduced about a factor of 2 for dPMMA when clay is precedent. On the other hand, the reduction is no larger than 20% when the clay is dissolved in the dPS layer. The mobility of the clay particles appeared to be greatly hindered in both PS and PMMA matrices. These results are consistent with TEM micrograph which show preferential segregation of clay particles in the PMMA phase.

#### **DD6.13**

**SUBSTITUENT EFFECTS ON A PHOTO-INDUCED ALTERNATION OF THE LOWER CRITICAL SOLUTION TEMPERATURES OF POLY(N-ISOPROPYLACRYLAMIDE) WITH AZOBENZENE UNITS.** Haruhisa Akiyama, Nobuyuki Tamaoki, Molecular Function Group, Inst for Materials & Chemical Process, Natl Inst of Advanced Industrial Sci & Tech, Ibaraki, JAPAN.

We synthesized copolymers of N-isopropylacrylamide (NIPAM) and azobenzene-containing acrylates or acrylamides by free radical polymerization, and investigated the water solubility of these polymers on irradiation with ultra-violet and visible light. Poly(NIPAM) is known to have the lower critical solution temperature (LCST). A water solution of poly(NIPAM) with small amount of azobenzene units has been reported to show a photo-induced alternation of LCST. In such polymer, it is thought that a balance of polar and non-polar moieties is important to control an LCST, so that a polar cis form of azobenzene can increase solubility for water as compared with a non-polar trans form. In our study, substituents of azobenzene moieties had much effect on the alternation. Isopropyl groups were introduced to azobenzene moieties with an expectation of the blocking of the aggregation or stacking among azobenzenes in water. The polymer with only isopropyl substituents at an azobenzene unit showed a higher LCST on irradiation with ultra-violet light than on irradiation with visible light. The value of the LCST difference between on ultra-violet and visible light irradiation depended on a ratio of NIPAM and azobenzene units and the nature of the substituents on azobenzene units. The addition of surplus azobenzene moieties into the polymer made it insoluble because of over hydrophobicity. On the other hand, no detectable difference was observed in the azobenzene substituted with both an ester and isopropyl group. The calculation against the model compound of ester-substituted azobenzene moieties indicated less difference of the dipole moment between the cis and trans form than that of isopropyl-azobenzene moieties. The introduction of pyridylazobenzene derivative to poly(NIPAM) resulted in no improvement in the solubility for water in comparison with the isopropylazobenzene polymer. Finally we investigated the photo-induced change in the wettability of the crosslinked films of the polymers.

#### **DD6.14**

**SURFACE-INITIATED POLYMERIZATION OF THICK POLYMER BRUSHES ON PATTERNED SAMS IN WATER.** Darren M. Jones and Wilhelm T.S. Huck, Melville Laboratory for Polymer Synthesis, Department of Chemistry, Cambridge University, Cambridge, UNITED KINGDOM.

This paper describes the formation of up to 150 nm thick polymer brushes from surface-bound initiators. By employing 'living' polymerization conditions we have achieved very rapid, controlled growth of polymer brushes and block co-polymers at room temperature (RT) in water and methanol. We have produced patterned polymer brushes from patterned self-assembled monolayers (SAMs) on Au, prepared via microcontact printing. We have also studied the influence of monolayer composition by forming polymer brushes from mixed monolayers of initiator and dialkyl disulphides. Characterization has been carried out using contact angle goniometry, ellipsometry, AFM, FTIR and XPS. The key advantages of our procedure are the virtual absence of polymerization in solution, the mild reaction conditions, the avoidance of organic solvents, and the rapid formation of thick films.

#### **DD6.15**

**CONDUCTIVITY OF C60 DERIVATIVES PREPARED BY SELF-ASSEMBLY MONOLAYER PROCESS ON Au FILM SUBSTRATES.** Nobuyuki Iwata, Toshie Shimizu, Hiroyuki Imai, Hiroshi Yamamoto, Nihon Univ, College of Sci. & Technol., Chiba, JAPAN; Masayuki Chikamatsu, Koichi Kikuchi, Tokyo Metropolitan Univ, Faculty of Science, Tokyo, JAPAN.

The purposes of this work are to prepare a self-assembly monolayer (SAM) of C60 derivatives with alkanethiol at the end of long alkyl chain and to study the electronic transporting properties of the C60 SAM. The C60 SAM process was studied by using Au films formed on organic resin sheets as substrates. The covering ratio of C60

derivatives was evaluated from the results of the XPS peak intensity for C-C bond energy. It was found that the adsorption reaction almost saturated in the specimens soaked for 10h - 15h in a 0.01mM benzen solution of C60 derivatives at room temperature. By a novel thermal annealing atomically flat surfaces with a half-unit-cell-high step-and-terrace feature were realized on MgO(100) substrates. The C60 SAM was also prepared on ultrathin Au films/the MgO surfaces. The anisotropically aligned structure of fine-wires was observed in AFM images of the SAM on the MgO surfaces. The microstructure was resulted in from the growth of Au films along the edges of terraces of MgO surfaces. The conductivity of the C60 SAM was investigated in relations to its characteristic microstructure.

#### **DD6.16**

**SINGLE-ASPERITY NANOTRIBOLOGY AND NANORHEOLOGY OF THIN POLY(DIMETHYLSILOXANE) FILMS.** Susheng Tan, Wayne L. Gladfelter, Univ of Minnesota, Dept of Chemistry, Minneapolis, MN; Greg Haugstad, Univ of Minnesota, IT Characterization Facility, Minneapolis, MN.

The lubricating and non-stick characteristics of poly(dimethylsiloxane) (PDMS) have been exploited for years. As with many tribological systems, technological application led scientific understanding: experimental methods were not available to precisely control intersurface separation, contact geometry and loading conditions about individual surface asperities. In the last 15 years analytical tools have become available for this purpose. Uniquely, scanning force microscopy (SFM or AFM) employs a single microasperity and feedback-actuated tracking of surface topography. Thus 'nanotribologists' now can investigate the fundamental unit of tribological systems: a single asperity with measurable radius of curvature, deforming into a material under measurable load, and sliding tangentially to the surface. Many nanotribological studies have involved simple systems, e.g. clean single-crystal inorganic surfaces or ordered ultrathin organic films lubricating such surfaces. Relatively little work has been on higher molecular weight, disordered films ranging in thickness from boundary lubrication (extremely thin) to bulk hydrodynamic (very thick). Yet real technological systems span this range. In the present work, SFM was employed to study nanotribology and nanorheology on poly(dimethylsiloxane) films varying from several to hundreds of nanometers thick. A wide range of molecular weights was examined, corresponding to bulk viscosities from 350 to 1,000,000 cS. Friction and pull-off forces were found to increase as a small fractional power of velocity over several decades. Similar, scaled-up behavior was observed using a cantilever-attached microsphere (R=10,000 nm) in place of the usual tip (R~10 nm). A dramatic increase in friction and adhesion was observed above a critical film thickness of approximately three times the radius of gyration. Accompanying this increase was a qualitative signature of liquid-like behavior seen in force-versus-distance measurements.

#### **DD6.17**

**DIELECTRIC PROPERTIES OF MULTI-LAYER HIGH-K POLYMER COMPOSITE FILMS.** Wataru Sakai, C.K. Chiang, Polymers Division, National Institute of Standards & Technology, Gaithersburg, MD.

High dielectric constant film of polymer composite is one of the key materials for new development of wireless communication devices. High-K material is particularly useful for distributing and storing electric energy in the vicinity of devices when the electronic application is operated at high frequencies. To design and process such a composite thin-films, we need to understand the complex dielectric properties resulting from the interactions between the filler particles and the host polymer. The dielectric electrical characterization for thin polymer films is not only critically important to their application, but also is of fundamental interest. We have observed the dielectric constant of the composite film. It followed an empirical semi-log relation with filler concentration. To further investigate the role of the interface polymer in the composite, we have developed several multi-layer thin-film structures. In a basic ABA structure, a middle B layer film performs a controlled interface which mediates the interaction between two high-K outer A layers. Experimental results from various designs of multi-layer structures will be compared with theoretical calculations and discussed.

#### **DD6.18**

**THE GLASS TRANSITION IN THIN POLYMER FILMS: A POSSIBLE ANSWER TO MANY QUESTIONS.** Stephan Herminghaus, Ralf Seemann, Karin Jacobs, University of Ulm, Applied Physics Lab., Ulm, GERMANY.

The fact that the glass transition temperature,  $T_g$ , of thin polymer films, both supported and free standing, is substantially different (mostly lower) as compared to the bulk is one of the major challenges in current polymer theory. We present a simple and predictive model trying to explain this observation on the basis of the viscoelastic

eigenmodes of the film. Quantitative agreement is achieved, with the elastic modulus at  $T_g$  as the only fitting parameter. Quantitative predictions for surface melting of homopolymers directly follow from the theory.

#### **SESSION DD7: ADHESION, MECHANICAL PROPERTIES I**

Chairs: Alfred J. Crosby and John M. Torkelson  
Wednesday Morning, November 28, 2001  
Constitution B (Sheraton)

#### **8:30 AM \*DD7.1**

**GLASS TRANSITION PHENOMENA AND MECHANICAL PROPERTIES OF ULTRATHIN POLYMERIC FILMS AND NANOSCOPIC SYSTEMS.** Kevin van Workum, Thomas Boehme, Tushar Jain, Juan J. de Pablo, University of Wisconsin, Dept of Chemical Engineering, Madison, WI.

From an engineering point of view, the elastic constants of a material provide some of the most important information needed in practical design applications. The mechanical properties of thin polymeric films and nano-scale structures are of particular interest to the nanotechnology industry. For example, the catastrophic collapse of nano-patterned features (in thin polymer films) used for manufacturing of microelectronic devices is related to their mechanical strength. We have developed a simulation formalism where by the elastic constants of glassy polymers in the bulk and nano-scale structures can be calculated with good precision. As expected, our results for bulk materials show that the storage modulus exhibits a pronounced decrease at the glass transition temperature. Our results also indicate that elastic constants of nanoscopic structures deteriorate significantly as their size decreases. A comparison of finite-element continuum calculations and molecular simulations reveal pronounced differences in the stress and strain distributions at the molecular level, particularly in plastically deformed amorphous-polymer structures.

#### **9:00 AM DD7.2**

**INTERDIFFUSION AND CROSSLINKING AT POLYMER INTERFACES.** Achod Aradian, Elie Raphaél, Pierre-Gilles de Gennes, Collège de France, Paris, FRANCE.

In many industrial processes, pieces of the same polymer material are brought into contact at a temperature above the glass transition. Interdiffusion takes place across the interface and leads to a strengthening of the junction. Often, a crosslinker agent is also added in order to improve the global mechanical properties of the material, as in the formation of latex films from dispersed solutions of polymer particles. We studied theoretically the competition between the interdiffusion and the crosslinking reaction, and found that the control parameter tuning the balance between these two processes is  $\alpha = Q\tau_0 A_0^* N^3 b^3 / N_e$ , where  $Q\tau_0$  accounts for the reactivity of the crosslinker,  $A_0^*$  is the initial concentration of sites capable of crosslinking on the polymer chains,  $N$  is the polymerization index,  $N_e$  the number of segments between entanglements and  $b$  a distance comparable to the segment length. The case of practical interest is  $\alpha \ll 1$ : the reaction locks the interfacial chains once a significant mixing has developed, resulting in films with good mechanical properties.

#### **9:15 AM DD7.3**

**NANOSHEAR MODULATION AS A PROBE OF POLYMER SURFACES AND INTERFACES.** Craig Dykstra, Wayne L. Gladfelter, Univ of Minnesota, Dept of Chemistry, Minneapolis, MN; Greg D. Haugstad, Univ of Minnesota, IT Characterization Facility, Minneapolis, MN; Christopher W. Macosko, Philip Cole, Univ of Minnesota, Dept of Chemical Engr & Matls Sci, Minneapolis, MN.

We have developed a low-frequency shear-modulated probe, based on a modified atomic force microscope, that utilizes Fourier analysis of nonlinear polymer response. The technique is uniquely sensitive to the onset of plastic deformation in the nanometer regime. We present a methodology for data analysis that identifies and separates elastic and creep response. In creep response we find a much more sensitive quantitative signature of the onset of wear than possible in subsequent topographic image analysis. Parameters governing the onset of wear were examined in polystyrene films. The importance of molecular weight, i.e. entanglement, was identified in nanowear response. The method was applied to examine an interface between poly(methyl methacrylate) and poly(acrylonitrile). This miscible system exhibits zero contrast under conventional (non-plastic) force microscopies, i.e. force modulation, friction force, and phase imaging. Contrast based on plastic deformation is clear, not only in the modified topography but also in the creep response. The latter exhibits a continuous transition across the polymer-polymer interface

with high signal-to-noise ratio. This suggests the ability to probe interdiffusion and entanglement with resolution below 100 nm.

#### 9:30 AM \*DD7.4

INTERDIFFUSION AND ADHESION AT NETWORK-NETWORK INTERFACES. R.M. Briber, Dept. of Materials and Nuclear Eng., U. Perez-Salas, Chemical Physics Program, University of Maryland, College Park, MD; M. Rafailovich, J. Sokolov, Dept. of MS&E, SUNY, Stony Brook, NY; W.A. Hamilton, Neutron Scattering Group, ORNL, Oak Ridge, TN.

Interfaces between crosslinked polystyrene-polystyrene interfaces have been studied by neutron reflectivity and symmetric double cantilever beam fracture tests. Crosslinking of the polystyrene samples was done by gamma ray irradiation from a Co60 source. Crosslinked thin films for neutron reflectivity were prepared from both deuterated and normal polystyrene and floated on to a Si substrate to form a bilayer. Annealing was performed at 150°C and the interfacial width was followed as a function of time. The interfacial width,  $\delta$ , rapidly increased with annealing to an equilibrium plateau value which scaled with the network mesh,  $N_c$ , as  $N_c \delta^\alpha$  with  $\alpha = 0.47 \pm 0.05$ . The diffusion process was modeled using the Fokker-Planck equation with an parabolic external potential. The effective diffusion constant obtained was essentially independent of  $N_c$ . The interfacial fracture energy,  $G_c$  between bulk crosslinked samples was found to scale as  $G_c N_c^{1.35 \pm 0.27}$  consistent predictions by de Gennes and coworkers with failure occurring by either chain pull-out or scission and not crazing.

#### 10:30 AM DD7.5

MICROPROBING OF INTERFACIAL BEHAVIOR OF SOLID POLYMERS BY MEANS OF NORMAL AND SLIDING MECHANICAL CONTACTS. Yev Garif, William Gerberich, Christopher Macosko, University of Minnesota, Chemical Engineering and Materials Science, Minneapolis, MN; Alphonsus Pocius, 3M, Adhesive Technologies Center, Saint Paul, MN.

Adhesion properties of solid polymers were examined by means of normal (JKR) and sliding (Scratch) mechanical contacts and analyzed in terms of composition, molecular parameters, rate and temperature dependence, and environmental conditions. For the JKR test, cylindrically shaped samples of acrylic pressure sensitive adhesives (PSAs) were synthesized in capillary tubes in presence of a cross-linking agent in order to obtain an elastic PSA-like network (PSA-LN). For the scratch test, a flat cross-section of thin multi-layer polymer films was established using ultra-microtoming. At low rates of interfacial separation ( $< 1 \mu\text{m}/\text{sec}$ ), intrinsic and practical adhesion energies were measured with the JKR test. The scratch test was used to access higher rates. The results from both tests mutually confirm power law increase of adhesion at higher rates of interfacial separation. Further results will be available soon. Bulk viscoelastic dissipation and electrostatic interactions at the interface are thought to govern this behavior. The goal is to establish a relationship between intrinsic work of adhesion, bulk properties and practically observed levels of adhesion.

#### 10:45 AM DD7.6

STICK-SLIP FRACTURE OF POLYMER/METAL INTERFACES. B.P. Somerday, R. Shediak, Sandia National Laboratories, Livermore, CA; M.P. Ivill, Dept of Materials Science, Univ of Florida, Gainesville, FL; Y. Toivola, Dept of Chemical Engineering and Materials Science, Univ of Minnesota, Minneapolis, MN.

The adhesion of thin-film PMMA to substrate surfaces consisting of Ti or Al has been measured using the four-point bend technique. Initial results revealed that cracks propagated along the PMMA/metal surface interfaces at a stable rate. More recent results demonstrate that interface crack propagation is intermittent, with alternating periods of rapid crack bursting and crack arrest. This intermittent ('stick-slip') fracture was observed after changes in two variables. First, fabrication of four-point bend beams from two separate lots of Ti-metallized silicon wafers produced different fracture behaviors along the PMMA/Ti interfaces; i.e., stable crack propagation in one Ti-metallized wafer lot vs. stick-slip fracture in the other. Second, increasing the time between beam preparation and four-point bend testing promoted stick-slip fracture. The objective of this study is to identify the origin of stick-slip fracture along PMMA/metal surface interfaces. The surface compositions and topographies of different lots of Ti-metallized silicon wafers are characterized to determine whether these variables are associated with interface fracture behavior. In addition, as-fabricated four-point bend beams are subjected to vacuum or controlled humidity environments as a function of time then tested after these exposures. These experiments are designed to test the hypothesis that solvents can evaporate from the PMMA or water can be absorbed into the PMMA to promote stick-slip fracture. This work is supported by the U.S. Dept of Energy under contract # DE-AC04-94L85000.

#### 11:00 AM DD7.7

VISCOELASTIC EFFECTS ON THE SCRATCH RESISTANCE OF POLYMERS: RELATIONSHIP BETWEEN MECHANICAL PROPERTIES AND SCRATCH RESISTANCE. Pierre Morel, University of Tennessee, Knoxville, TN; Vincent Jardret, MTS Nano Instruments Innovation Center, Oak Ridge, TN.

Scratch resistance of polymers has been the subject of numerous studies which have lead to more specific definitions for plastic and fractured scratch behavior. Viscoelastic and viscoplastic behavior during a scratch process has been related to dynamic mechanical properties that can be measured via dynamic nano-indentation testing. Yet, the understanding of the origin of the fracture process of a polymer surface during scratch remains approximate. Parameters like tip geometry and size, scratch velocity and loading rate, applied strain and strain rates, have been considered critical parameters for the fracture process, but no correlation has been clearly established. The goal of this work is to analyze the evolution of scratch resistance parameters as a function of temperature, compared to the evolution of dynamic mechanical properties obtained from indentation tests over the range of temperature for PMMA. Additional compression and tensile properties have been compared to the scratch results for more complete understanding of the material's behavior. The analysis of the evolution of the properties of PMMA at various temperatures, along with the evolution of the fracture toughness during scratch with temperature and scratch velocity has helped in identifying a correlation between the tensile stress-strain behavior and scratch fracture toughness for PMMA. This correlation brings a new understanding of the origin of fracture mechanisms during a scratch process.

#### 11:15 AM DD7.8

INTERFACIAL FRACTURE TOUGHNESS MEASUREMENTS ON POLYMER-POLYMER MULTI-LAYER SYSTEMS BY MEANS OF MICRO-SCRATCH PROBING. Yev Garif, William Gerberich, Christopher Macosko, University of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN; Alphonsus Pocius, Adhesive Technologies Center, 3M Company, Saint Paul, MN.

A new technique called Cross-Sectional Scratch (CSS) has been established. The main advantage of the technique is that it allows to measure/quantify interfacial toughness levels in multi-layer polymer films that are only a few microns thick. In addition to advanced scale capabilities, CSS has successfully tested both glassy and soft polymer interfaces. Thus, PS/PE, PET/PE and PS/PMMA co-extruded films were chosen as sample systems and tested at room temperature. The results agree with expectation that compatibility, molecular weight distribution and most of all visco-elastic dissipation near the interface are the key parameters determining interfacial strength in polymer systems.

#### 11:30 AM DD7.9

NANOWEAR PATTERNING AS AN ACTIVATED CRAZING PROCESS. Ronald H. Schmidt, Lund Univ, Dept of Pure and Applied Biochemistry, Lund, SWEDEN; Greg Haugstad, Univ of Minnesota, IT Characterization Facility, Minneapolis, MN; Wayne L. Gladfelter, Univ of Minnesota, Dept of Chemistry, Minneapolis, MN.

The friction and wear characteristics of nanoscale organic coatings are critical to new and emerging technologies (e.g. microelectromechanical devices). Fortunately the need to understand this behavior has coincided with the development of tools to measure shear forces on the nanometer scale, including the scanning force microscope (SFM). At the scientific frontier these methods have enabled careful studies of confinement effects on polymer dynamics, e.g. the glass transition. In contrast to traditional scientific disciplines like condensed matter physics and physical chemistry, the nanotribology community has only begun to examine the role of temperature in material response. The response of 'soft' condensed matter to external forces can be dominated by entropic (temperature dependent) effects; further, nonequilibrium molecular conformations may introduce kinetic (rate dependent) effects. Rigorous studies of thin-film polymer nanotribology therefore must include methodologies to quantify the interrelated roles of temperature and rate. In the present work, wear on polystyrene films was studied via the commonly observed surface-patterning phenomenon, induced by raster scanning. This was examined in detail as a function of load, scan history (repetitions), scan line density, scan velocity, and temperature (40-115°C). Film response was highly linear with respect to load and the number of successive visits of the sliding tip. Results suggest that the scanning process induces damage in the film analogous to crazing in brittle bulk polymers. The temperature and rate dependences were analyzed within the Bingham-Voigt-Arrhenius model of plastic flow. Activation energies, extracted from vertical and lateral quantifications of surface roughening, were intermediate to known values for alpha and beta relaxations in the bulk polymer.

**11:45 AM DD7.10****FREQUENCY SPECIFIC CHARACTERIZATION OF VERY SOFT POLYMERS USING NANO INDENTATION TESTING.**

Nicolas Conte, University of Tennessee, Knoxville, TN; Vincent Jardret, MTS Nano Instruments Innovation Center, Oak Ridge, TN.

Polymer thin films and surfaces are playing a major role in the functionality of many components in the microelectronic, automotive industries. The characterization of their mechanical properties at a nanometer scale remains a technological challenge. Instrumented Nano Indentation testing completed with dynamic analysis provides access to viscoelastic measurement of near surface properties of organic materials. Although dynamic indentation testing has been successful in measuring storage and loss moduli of fairly stiff materials, the need for measuring softer materials at various frequencies requires further understanding of the contact mechanics applied to indentation testing. Development of biological tissues raises the interest for testing organic materials with storage modulus of less than 1 MPa. For very soft materials, both physical and chemical changes taking place at the surface can have a significant influence on the indentation data. Also, the level of forces and stiffness generated by small contacts on very soft materials requires that other contact phenomena be taken into account in the data reduction. The measurement and understanding of these effects in addition to the development of specific testing methodologies for very soft polymeric materials are included in this work. Results on various polymers illustrate the various indentation behavior of different types of polymeric structure.

**SESSION DD8: BLOCK COPOLYMER FILMS II**

Chairs: Robert M. Briber and Samuel P. Gido  
Wednesday Afternoon, November 28, 2001  
Constitution B (Sheraton)

**1:30 PM \*DD8.1****THIN FILM MORPHOLOGY OF ABC TRIBLOCK COPOLYMERS: INFLUENCE OF PREPARATION CONDITIONS.** Georg Krausch, Bayreuth University, Physical Chemistry II, Bayreuth, GERMANY.

We discuss recent experiments exploring the thin film structures of poly(styrene)-block-poly(2 vinylpyridine)-block-poly(tert butyl methacrylate) for different routes of preparation. Different solvents have been used for solvent vapor "annealing". Both the solvent vapor pressure and the rate of solvent extraction have been varied. We observe a variety of complex, yet highly regular micro domain morphologies going significantly beyond the expected equilibrium structure. To provide at least a qualitative explanation of the experimental results, we have determined the concentration dependent Flory Huggins interaction parameters between the respective homopolymers and the solvents. This has been achieved by a systematic study of the swelling behavior of thin homopolymer films by spectroscopic ellipsometry. Additional experiments on the three binary random copolymers of the constituent components yield the concentration dependence of the polymer/polymer interaction parameters as well.

**2:00 PM \*DD8.2****GRAPHOEPITAXY OF BLOCK COPOLYMER THIN FILMS.**

Rachel A. Segalman, Glenn H. Fredrickson, Edward J. Kramer, Depts of Chemical Engineering and Materials, Univ of California-Santa Barbara, Santa Barbara, CA.

Single crystals films of A-B diblock copolymer spheres, one B-sphere domain thick, can be grown from initially disordered films using topological features on the substrate to template the growth. Such single crystals may be useful for nanolithographic applications but before these can be realized, we need a deeper understanding of the parameters that control the order. We produce mesas and wells, 1 to 10  $\mu\text{m}$  wide and 30 nm high, in a  $\text{SiO}_2$  layer grown on silicon by standard photolithography and etching methods. As the block copolymer orders into its spherical structure, the lateral step edge of the mesa serves to orient rows of spheres in the well parallel to the edge. A single long grain thus forms along the edge initially during ordering while further from the edge a small grained polycrystal is formed. As ordering proceeds further the boundary of the long grain along the edge migrates toward the center of the well, thus eliminating the polygrain structure if the well is not too wide. The single crystal layer of spherical domains once formed has a rather high density of dislocations that decreases slowly with further annealing to values approaching  $1 \mu\text{m}^{-2}$  in the best case. The single crystal growth process is very sensitive to both the growth temperature T and the degree of polymerization  $N_B$  of the shorter B block through variations of the product  $\chi(T)N_B$  where  $\chi(T)$  is the Flory interaction parameter between A and B segments. If  $\chi(T)N_B > 10$  the kinetics of order development are very slow and the system seems kinetically trapped. If  $\chi(T)N_B < 8$  the dislocation density that can be ultimately achieved

increases, perhaps reflecting the decrease in shear modulus of the ordered structure as the  $\chi(T)N_B$  is approached where a transition to a micelle fluid phase occurs.

Supported by the NSF-DMR-Polymers Program.

**2:30 PM \*DD8.3****ROLE OF BLOCK COPOLYMERS ON BOTH ADHESION AND CRYSTALLINITY IN SEMI-CRYSTALLINE POLYMER ASSEMBLIES.** L. Léger, C. Laurens, R. Ober, H. Hervet, Laboratoire de Physique de la Matière Condensée, URA CNRS 792, Collège de France, Paris Cedex, FRANCE; C. Creton, Laboratoire PSCM, ESPCI, Paris Cedex, FRANCE.

We present an investigation of the adhesion mechanisms between polypropylene (PP) and polyamide 6 (PA6) in systems where block copolymers are formed in situ at the interface during the annealing of the assemblies. We show that the adhesion energy, as measured through a double beam cantilever test, is driven by the surface density of copolymer molecules present at the interface,  $\sigma$ . Very similarly to what is known for amorphous polymers, the fracture proceeds through the formation of a localized craze zone, ahead the fracture tip. This craze zone finally breaks through fibrils rupture. The adhesion energy follows a  $\sigma^2$  law, and can be quantitatively described through the Brown's model, as for amorphous systems. Under certain annealing conditions however (close to the melting temperature of PA6) the efficiency to enhance adhesion of long enough block copolymers can be increased by a factor four. Systematic experiments aiming to characterize the local crystallinity and orientation in the immediate vicinity of the interface, through X Rays diffraction on thin films assemblies, show that these annealing conditions and the presence of the long copolymer molecules are able to enhance the tendency of epitaxial orientation between PP and PA6. We shall discuss these specific crystalline effects and analyze their consequences on adhesion energy.

**3:30 PM \*DD8.4****DEVELOPMENT OF SMART POLYMER SURFACES.**

S.H. Anastasiadis, H. Retsos, Foundation for Research and Technology-Hellas, Institute of Electronic Structure and Laser and University of Crete, Department of Physics, Heraklion, Crete, GREECE; S. Pispas, N. Hadjichristidis, University of Athens, Department of Chemistry, Zografou, Athens, GREECE; S. Neophytides, Foundation for Research and Technology, Hellas, Institute of Chemical Engineering and High-Temperature Processes, Rio Patras, GREECE.

The aim of this study is to develop the methodology for creating polymer surfaces, which can respond to their environment. The methodology is demonstrated for surfaces that can alter their wetting characteristics when exposed to water vapor. For this, we take advantage of the surface partitioning of block copolymers at the polymer / air interface and utilize a hydrophilic group at the end of the surface-active block. The surface-active block of the copolymer (anchor) drives the surface segregation while the other block forms a dangling tail mixed with the matrix homopolymer. The hydrophilic end group is hidden below the surface when it is in contact with air. However, when the surface is exposed to water vapor, the hydrophilic end-group re-surfaces thus significantly reducing the water contact angle. We investigate the effect of additive concentration, block-length ratio, and end-group type on this behavior. It is shown that this function can be reversed and repeated again by successive exposures of the polymer surface to dry or wet environment, respectively.

**4:00 PM DD8.5****MONTE CARLO SIMULATIONS OF COPOLYMER ADSORPTION FROM COPOLYMER/HOMOPOLYMER MELTS NEAR PLANAR CHEMICALLY PATTERNED SURFACES.** James Semler, Jan Genzer, North Carolina State University, Dept of Chemical Engineering, Raleigh, NC.

Understanding polymer organization near heterogeneous solid surfaces is of both practical and fundamental interest. Such systems are critical to many industries for preparing surfaces that are protective against toxins, resistant to corrosion and wear, and multifunctional for numerous applications. Relevance is also found in the biological world where recognition of receptor sites by living entities becomes essential for transmembrane signaling. In this computational study, we present results focused on understanding the driving forces for A-B copolymers to selectively adsorb onto chemically heterogeneous substrates from A-B copolymer/B homopolymer melts. Our investigation centers upon the roles of the copolymer monomer sequence distribution, the polymer/surface interaction energies, and the spatial distribution of the surface's chemical heterogeneities. To carry out the simulations, a 3-dimensional version of the bond fluctuation model is used in conjunction with configurational biased Monte Carlo. The simulation box has dimensions of  $48 \times 48 \times 48$  and contains 250 polymer chains with 30 monomers each. A monomer

volume fraction of 0.54 is used with approximately twenty-five percent of the polymer chains being A-B copolymers with predefined alternating or diblock sequences, while the remaining chains consist of B homopolymers. The effects of interaction energy is investigated by performing a series of simulations where the pair-wise interaction energy between A and C is set to -0.1, -0.5, and -1.0, while all other pairs remain neutral. Surface effects are studied by incorporating two heterogeneous surfaces patterned with C and D monomers, where C is attractive to A and D is neutral to all species, at the extremes of the z direction. These surfaces are patterned in a checkerboard motif with square sizes of 1x1, 2x2, 3x3, 4x4, 6x6, 8x8 and 12x12. These simulations allow us to construct 3-dimensional adsorption profiles clearly illustrating how well the surface pattern is duplicated and the extent to which it is preserved away from the surface into the bulk film. In addition to the profiles, specific entropic configurations adopted by the polymer chains (i.e., loops, tails, and trains) exemplify the coupling that occurs between the sequence distribution, the interaction energy, and the substrate domain sizes.

#### 4:15 PM **DD8.6**

**SURFACE AND CONFINEMENT INDUCED RECONSTRUCTION OF CYLINDRICAL ABA BLOCK COPOLYMER MICRODOMAINS.** A. Knoll, A. Horvat, G. Krausch, R. Magerle, Phys Chem II, Universität Bayreuth, GERMANY; E.S. Lyakhova, A.V. Zvelindovsky, Soft Condensed Matter Group, University of Leiden, THE NETHERLANDS.

We studied the microdomain structure of ultra thin films of SBS (polystyrene-*b*-polybutadien-*b*-polystyrene) and other ABA block copolymers which form cylindrical microdomains in bulk. Spin cast films were treated with a controlled partial pressure of solvent vapor (CHCl<sub>3</sub>) in order to reach local minima in the free energy of the system. The resulting microdomain structures were frozen in by quickly drying the samples and were studied by Tapping Mode AFM. The films typically form islands and holes with thicknesses smaller and larger than the original thickness, corresponding to energetically favored thicknesses. Layers with thickness larger than one cylinder-layer spacing show typical stripe-like patterns in the AFM images corresponding to polystyrene cylinders lying parallel to the surface. In thinner layers two additional morphologies were found, one corresponding to a perforated lamella and one without any topographical features corresponding to a lamella phase. The results are in excellent agreement with computer simulations with the MesoDyn code which is based on dynamic density functional theory. A detailed comparison between experimental and modelling results reveals that the microdomain reconstructions are caused by the preference of one of the two different blocks to the interfaces.

#### 4:30 PM **DD8.7**

**ORIENTATION KINETICS IN CONCENTRATED BLOCK COPOLYMER SOLUTIONS EXPOSED TO ELECTRIC FIELDS.** Alexander Böker, Volker Abetz, Axel H.E. Müller, Univ of Bayreuth, Makromolekulare Chemie II, Bayreuth, GERMANY; Volker Urban, ESRF, Grenoble, FRANCE; Hubert Elbs, Helmut Hänsel, Armin Knoll, Heiko Zettl, and Georg Krausch, Univ of Bayreuth, Physikalische Chemie II, Bayreuth, GERMANY.

Recently, we investigated the microdomain alignment of block copolymers during preparation from solution by virtue of an external electric DC field. Bulk samples cast in the presence of an electric field exhibited lamellar microdomains highly oriented parallel to the electric field vector, as shown by small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). In order to elucidate the underlying kinetics of the orientation process, we have performed in-situ Synchrotron-SAXS investigations of the orientation behavior of diblock and triblock copolymer solutions as a function of polymer concentration and electric field strength. (Model systems: polystyrene-*b*-polyisoprene in toluene and polystyrene-*b*-poly(2-hydroxyethyl methacrylate)-*b*-poly(methyl methacrylate) in THF). We find reorientation of lamellar and cylindrical microdomains in the external electric field at concentrations between 30 and 50 wt.-% starting slightly above the order-disorder concentration (ODC). For most data sets, the reorientation kinetics can be fitted by a simple exponential law with time constants varying from a few seconds near ODC to some minutes with increasing concentration. From the experimental results we can determine an optimum concentration range around the ODC, in which the interplay of chain mobility and gain in free energy in the electric field allows for improved preparation of highly anisotropic bulk polymer samples.

SESSION DD9: POSTER SESSION  
POLYMER INTERFACES AND THIN FILMS II  
Chairs: Paul F. Nealey and Alamgir Karim  
Wednesday Evening, November 28, 2001  
8:00 PM  
Exhibition Hall D (Hynes)

#### **DD9.1**

**A UNIVERSAL MECHANISM FOR HOLE FORMATION IN SOLVENT CAST POLYMER FILMS.** Daniel Podzimek, Karin Jacobs, Ralf Seemann, Annemarie Saier, Stephan Herminghaus, University of Ulm, Applied Physics Lab., Ulm, GERMANY.

It is demonstrated that the strain universally present in solvent cast polymer films gives rise to the nucleation of holes, thus mediating dewetting of the film. The areal number density of the holes is found to depend exponentially on the film thickness over five orders of magnitude, suggesting a rather fundamental mechanism. We present a simplified theory of the coupling between the strain in the film and the capillary waves. It accounts for both the exponential law and the shape of the individual indentations finally leading to hole formation.

#### **DD9.2**

**EFFECTS OF CHAIN LENGTH ON POLYMER DEWETTING MORPHOLOGIES.** Karin Jacobs, Ralf Seemann, Stephan Herminghaus, University of Ulm, Applied Physics Lab., Ulm, GERMANY.

Upon dewetting of thin liquid polymer films, a large variety of different structures may evolve in a cascade of dynamical instabilities, depending on the physical parameters of the system. With polystyrene as a particularly simple model system, we explore this variety, with emphasis on the impact of the molecular weight. It is demonstrated that several characteristic features change qualitatively as viscoelastic effects are increased.

#### **DD9.3**

**MODELLING OF THE THIN ORGANIC FILM/CARBON STEEL INTERFACE.** Mihai V. Popa, Paula Drob, Ecaterina Vasilescu, Maria Anghel, Romanian Academy, Institute of Physical Chemistry, Bucharest, ROMANIA; Agustin Santana Lopez, Julia Mirza-Rosca, Las Palmas de Gran Canaria University, Dept. of Engineering Processes, SPAIN.

The electrochemical impedance spectroscopy (EIS) has been used for the modelling of the alkyd organic film/carbon steel interface in 3%NaCl solution. Both the dielectric properties of the organic film and the corrosion processes of the metallic substrate were investigated with this method. Analysis of the impedance spectra (Nyquist and Bode plots) and the interpretation with the fitting software developed by Boukamp, established the presence of two time constants in the first 250 immersion hours. One time constant concerning the organic layer describes the electrical and barrier properties of film. The second time constant concerning the substrate surface represents the corrosion reactions at the film/metal interface. For long immersion periods, after the formation of the conductive pathways in the film and the development of the diffusion processes, are necessary another two time constants concerning these phenomenons. The error magnitude between the measured and calculated data with these electric equivalent circuits is satisfactory. The physical properties obtained from the principal elements of the equivalent electric circuits with two and four time constants are in concordance with those obtained from others testing methods.

#### **DD9.4**

**MALDI-TOF MS INVESTIGATIONS OF PHOTOCHEMICALLY MODIFIED POLYMER SURFACES.** Robert Saf, Gertraud Hayn, Marian Goriup, Andreas Ruplitsch, Gregor Langer, Wolfgang Kern, Graz University of Technology, ICTOS, Graz, AUSTRIA.

Within the actual project MALDI-TOF MS is used to investigate the composition of polymers modified at the surface. These materials have attracted increasing attention since excellent bulk properties can be combined with specific surface properties being essential for numerous applications (e.g., coating industry, medical implants). Modified photochemical methods are applied to attach functional groups onto the surface of technically important polymers. The methods have the advantage that lithographic projection techniques allow the illumination - and consequently modification - of selected areas of the polymer surface. This is a distinct contrast to other techniques for surface modification, where patterned modifications are difficult to achieve. Experiments will be discussed where MALDI-TOF MS was used to investigate how experimental parameters during the UV photomodification of polystyrene (PS) with gaseous BrCN or Br<sub>2</sub> influence the composition of the polymer surface. The surface modification starts with the UV initiated formation of Br $\Sigma$  and/or CN $\Sigma$  radicals. It will be shown that modification with BrCN can be used for highly selective attachment of CN-groups to the polymer surface. No chain fragmentation was observed in this case. Attachment of Br to the polymer surface was observed for photo-modification with gaseous Br<sub>2</sub>. In this case, concomitant chain fragmentation was observed. Furthermore, the influence of the reaction atmosphere (e.g. traces of oxygen) will be discussed. The MALDI-TOF MS investigations are essential for both development and application of

the surface modification methods under consideration. The central aim is the controlled and well defined introduction of acidic (e.g., -SO<sub>3</sub>H, -COOH), basic (-NH<sub>2</sub>) or neutral (-CN, -SO<sub>2</sub>-NHR) groups on polymer surfaces. This aim is the key to polymers with tailored surface composition and hence to polymers with tailored surface properties being important for numerous applications. Financial support of this work by the Austrian Science Fund (Project P13962-CHE) is gratefully acknowledged.

#### **DD9.5**

**CRYSTALLIZATION KINETICS OF POLY(ETHYLENE OXIDE) IN THIN FILMS.** Salim Ok, A. Levent Demirel, Koc University, Chemistry Department, Istanbul, TURKEY.

We studied the crystallization kinetics of poly(ethylene oxide)(PEO) in thin films using hot-stage polarized optical microscopy and atomic force microscopy. PEO (MW = 55,000 and 100,000) films were prepared by spin coating from dilute solutions in chloroform on oxidized silicon substrates. Isothermal crystal growth rates were measured for various film thicknesses at various degrees of undercooling. Below a critical film thickness, the crystallization kinetics changed significantly with respect to bulk crystallization. The effect of film thickness on the crystallization kinetics and the dependence of critical film thickness on the molecular weight will be discussed.

#### **DD9.6**

**PHOTOCHEMICAL COPPER NUCLEATION ON POLYIMIDE FILM FOR SURFACE PREPARATION OF ELECTRO LESS PLATING.** Hiroto Tokunaga, M. Murahara, The Faculty of Engineering of Tokai University, Kanagawa, JAPAN.

Copper nuclei grow on all aromatic polyimide surface in the presence of copper sulfate water solution with only 10ns single shot of ArF laser. And thick copper film was fabricated on the nuclei after immersing the polyimide surface into the electro less plating solution. All aromatic group polyimide has advantages, which are higher mechanical strength, flame resistance, chemical resistance and heat resistance than that of general polyimide. The general polyimide has been widely used for the flexible electronic circuit printed board. However the all aromatic polyimides has not been used for having chemical stability. If the all aromatic polyimide can be bonded with metal directly, a hybrid material with high heat resistance property can be produced. Firstly, the sample surface was oxidized with UV light in an oxygen atmosphere. And we have substituted copper atoms with dangling bonds of carbon through the medium of oxygen atoms on the all aromatic polyimide surface. In this study we placed fused silica glass on the sample surface, and poured the sulfate water solution into the gap between the silica glass and the sample, forming a thin liquid layer. Then one shot of circuit patterned ArF laser light having 32mJ/cm<sup>2</sup> was irradiated vertically onto the sample. The dissociated copper atoms form the C-O-Cu bond with active oxygen on the polyimide surface. In this treatment there was no change on the all aromatic polyimide surface with the naked eye. However, we were able to grow a copper thin film of about 24 nm after immersing the sample into the electro less plating solution for 15 minutes at 60°C. By washing the sample with an ultrasonic washing machine the clear image of the circuit pattern appeared only in the exposed area, with the unexposed copper foils peeled off.

#### **DD9.7**

**TOWARD A THEORETICAL DESIGN OF LOW-K ORGANIC POLYMERS.** Takashi Ikegami, Koichi Yamashita, Tokyo Univ, Dept of Chemical System Engineering, Tokyo, JAPAN.

Propagation delay of signals by interlayer dielectrics in LSI interconnects is becoming a dominant issue. Materials of low dielectric constant have been widely studied in order to reduce the delay of signals. In this study we try to design theoretically novel low-k materials of organic polymers by predicting their electronic properties with quantum chemical methods. Based on the Clausius-Mossotti equation, the dielectric constant is related to the polarizability and a low dielectric constant corresponds to small polarizability and small number density of the system. Highly accurate quantum chemical methods are necessary for the prediction of polarizabilities, since they essentially depend on the quality of electronic wavefunctions. We used several quantum chemical methods to check their accuracy: RHF, MP2, and B3LYP as the computational methods, and 6-31G\*\* and 6-311G\*\* as the basis sets. We tested the polymers of hydrocarbon, fluorocarbon, silicon hydride, and silicon fluoride. Polarizabilities were calculated by the coupled perturbed Hartree-Fock (CPHF) or Kohn-Sham (CPKS) method and the sum-over-state (SOS) method. Molecular volumes were calculated by the Monte-Carlo method. Calculations have been carried out using the program GAUSSIAN98.

#### **DD9.8**

**DEPENDENCY OF INTERFACIAL FRACTURE ON THIN EPOXY**

**FILMS PREPARATION.** John A. Emerson, Neville R. Moody\*, Rachel K. Giunta, Michael S. Kent, E. David Reedy, Jr. Sandia National Laboratories, Albuquerque, NM. \*Sandia National Laboratories, Livermore, CA.

In adhesion studies of thin polymer films on metal substrates, does the method of sample preparation have an effect on interfacial fracture results? We examined two techniques for spin-on epoxy amine-cured thin films - solvent cast and neat - where film thickness was varied between 0.1-1000 μm. The neat samples were prepared by spin coating at elevated temperatures without furthering the cure. Solvent dilution which lowers the viscosity of Epon 828 epoxy and the curative polyoxypropylenetriamine were spun at different dilutions in order to obtain the desired film thickness. We found that the fracture energies increased with film thickness. Structure and morphology of the thin films will be discussed in term of the interfacial fracture. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

#### **DD9.9**

**STUDY OF POLYMER-POLYMER INTERFACES AT THE MOLECULAR LEVEL IN SITU USING SUM FREQUENCY GENERATION (SFG) VIBRATIONAL SPECTROSCOPY.** Chunyan Chen, Jie Wang, Mark A. Even, Zhan Chen, Department of Chemistry and Department of Macromolecular Science and Engineering, University of Michigan, MI.

Studying polymer-polymer interfaces is important for both fundamental and commercial interests. Using a thin copolymer layer between two homopolymers, or coupling functionalized chain-ends at the immiscible polymer-polymer interface, can increase the joint adhesion to improve polymer properties. Due to the lack of powerful analytical techniques, molecular level structures of polymer-polymer interfaces have not been determined. Theoretical calculations have been performed to understand these interfaces, but they need to be tested by molecular level experiments. Recently, SFG has been developed into a powerful tool to study interfaces at the molecular level and in situ with submonolayer sensitivity. For the first time, we have successfully applied SFG to study molecular level structures of polymer-polymer interfaces. We have studied interfaces between solid polystyrene (PS) and several liquid polymers including poly(ethylene glycol) with dihydroxyl (PEGH), and dimethoxy (PEGM) end-groups, and poly(dimethyl siloxane) (PDMS) with different molecular weights. PS phenyl groups, which orientate closely along the surface normal at the polymer/air interface, tended to lie down at all PS/liquid polymer interfaces. Interface structures of PS/PEGH and PS/PEGM were quite different. The poly(ethylene glycol) backbone dominated the PS/PEGH interface, similar to the PEGH/air interface, but the PEGM structures at the PS/PEGM interface were quite random, very different from the PEGM/air interface. Unlike PDMS/air interfaces, coverage and orientations of PDMS at PS/PDMS interfaces depended on the PDMS molecular weights. The solid PS/solid poly(n-butyl methacrylate) (PBMA) interface has also been studied by SFG. Results showed that the molecular structures of both PS and PBMA at this interface were quite different from their own polymer/air interfaces. For example, both the PS phenyl group and the PBMA methyl group tended to lie down at the polymer-polymer interface, which tended to orientate closely along the surface normal on the polymer/air interfaces.

#### **DD9.10**

**ANGLE EFFECTS ON POLYATOMIC ION DEPOSITION: PREDICTIONS FROM MOLECULAR DYNAMICS SIMULATIONS.** Inkook Jang, Boris Ni, Susan B. Sinnott, The University of Florida, Dept of Materials Science and Engineering, Gainesville, FL.

Classical molecular dynamics simulations are used to investigate the dependence of incident angle on the deposition of polyatomic ions on polystyrene. Earlier combined experimental and computational studies showed that polyatomic ions can chemically modify polystyrene surfaces and that these chemical modifications depend on the chemistry of the ion, its incident energy, and its isomeric structure. In this study we extend this previous work to examine the effect of angle on the results. The simulations predict that as the incident angle increases, ion scattering increases and the types of fragments that adhere to the surface change dramatically. It is proposed that variations in angle are a way to tailor the modification of polymeric surfaces. Supported by the Petroleum Research Fund and the National Science Foundation.

#### **DD9.11**

**DENSITY FLUCTUATIONS INDUCED SWELLING OF POLYMER THIN FILMS IN CARBON DIOXIDE.** T. Koga, Y. Seo, Y. Zhang, M. Rafailovich, J. Sokolov, B. Chu, Dept of Material Science & Engineering, SUNY at Stony Brook, NY; K. Kusano, K. Nishikawa,

Graduate School of Science and Technology, Chiba University, Chiba, JAPAN; K. Shin, S. Satija, Polymer Division and Center for Neutron Research, NIST, Gaithersburg, MD; D. Peiffer, Exxon Mobil Research and Engineering Company, NJ.

Liquid or supercritical carbon dioxide are being used increasingly as a green solvent in polymer processing, polymer synthesis, reactor cleanup, and preparation of pharmaceutical products. The major disadvantage thus far is that only a limited class of polymers, such as fluorinated or silicone-based polymers, can be dissolved in carbon dioxide. Using neutron reflectivity we have found that carbon dioxide can be sorbed to a large extent in thin polymer films even when the bulk miscibility of the polymer with carbon dioxide is very poor. Polymer thin films can be shown to swell by more than 60%, while the density remains uniform, without the formation of voids as previously reported in the bulk. In this presentation, we will discuss that the swelling is associated with the density fluctuations ridge which forms along the extension of the coexistence curve of gas and liquid in the pressure-temperature phase diagram.

This work was funded by the NSF-MRSEC program.

#### **DD9.12**

**EFFECT OF FILLERS ON ADHESION AT POLYMER INTERFACES.** Anshul Shah, Ward Melville High School, East Setauket, NY; S. Mayu, M. Rafailovich, J. Sokolov, SUNY, Dept. of Materials Science and Engineering, Stony Brook, NY; H.-J. Kim, Seoul National University, Seoul, SOUTH KOREA.

The effects of filler particles on adhesion of polymers was tested using the Asymmetric Double Cantilever Beam method. Slabs of polystyrene (PS) and polymethyl methacrylate (PMMA) were molded at 150°C. Films (approximately 100 nm thick) containing carbon black, colloidal silica, or Cloisite 6A clay, dispersed in monodisperse PS or PMMA, were spun cast onto the corresponding mold. PS/PS, PS/PMMA, and PMMA/PMMA were joined for various times at 150°C. Interfacial strength was then determined as a function of filler concentration and joining time. Addition of increasing contents of carbon black to the interface caused a drastic decline in adhesion of PMMA/PMMA, and had a similar but somewhat smaller effect in PS/PS. As joining time was increased, adhesion at interfaces with carbon black was increasingly lower than at pure interfaces. As joining time was increased beyond 30 minutes for PS, however, fracture toughness increased and became larger than in the uncoated samples. For PMMA, the times required to recover adhesion were in excess of 60 minutes, and polymer degradation hindered further measurement. Clay had a similar effect as carbon black at PMMA/PMMA and PS/PS interfaces. Addition of clay to the weak PS/PMMA interface further diminished the adhesion. Clay acted similarly when blended with the polymer slabs as when applied in an interfacial layer. Furthermore, the effectiveness of PS-b-PMMA diblock in compatibilizing PS and PMMA was eliminated by clay. The effect of carbon black results from interactions between the polymer matrix and uncoated carbon black particles, which hinder diffusion; a non-interactive surfactant coating colloidal silica particles negates this effect. Wide clay particles are physical barriers to diffusion and adsorption sites for the polymer chain. The greater impact of clay on PMMA is in agreement with TEM micrographs that show preferential attachment of PMMA over PS to clay.

\*Supported by the NSF-MRSEC program.

#### **DD9.13**

**DIAMOND-LIKE CARBON FILMS DEPOSITED ON POLYETHYLENE TEREPHTHALATE FILMS FOR PACKAGE.** Hideyuki Kodama, Ayako Kimura and Tetsuya Suzuki, Department of Mechanical Engineering, Keio University, Yokohama, JAPAN.

Diamond-like carbon (DLC) films have been studied for their high hardness and high wear resistance, but their advantages of high gas barrier properties have not been paid attention very much so far. Polyethylene terephthalate (PET) plates, coated with DLC film, generally barrier oxygen gas 20 to 30 times than uncoated plates, and therefore expected to apply for food packing field such as plastic bottles. In this study, we deposited DLC films on polyethylene terephthalate (PET) substrates using the rf-plasma CVD method and microwave plasma CVD method, and investigated the color, gas barrier properties and chemical bonding of DLC films as a function of film thickness and microstructures. DLC films were linearly grown as function of the deposition time and the color became darker with the film thickness. From the X-ray photoelectron spectroscopy (XPS), the peak of C1s spectra shifted to high binding energy with the deposition time, indicating that the sp<sup>3</sup> bonding increased and then became stable. From the gas barrier test, the oxygen transmissivity was different in each film even if the film thickness was same. Thus, it was found that the gas barrier properties depended on not only the film thickness but also microstructures of films.

#### **DD9.14**

**PLASTICIZATION EFFECTS OF CARBON DIOXIDE ON POLYMER THIN FILMS.** T. Koga, Y. Seo, Y. Zhang, M. Rafailovich, J. Sokolov, B. Chu, Dept of Material Science & Engineering, SUNY at Stony Brook, NY; K. Shin, S. Satija, Polymer Division and Center for Neutron Research, NIST, Gaithersburg, MD.

It is well known that carbon dioxide can be quite soluble in glassy polymers, owing to its liquid-like density, high diffusivity and low molecular weight, and significantly lowering glass transition temperatures. Our neutron reflectivity results used deuterated polystyrene (d-PS) thin films suggest that, even at the room temperature, d-PS films undergo the glass to liquid transition near the critical pressure (P<sub>c</sub>) of carbon dioxide. In order to further explore the plasticization effect of carbon dioxide, we measured the interdiffusion of polymers as a function of temperature and pressure by means of neutron reflectivity. As a result, we found that d-PS films underwent the glass to liquid transition near P<sub>c</sub> and then became the glassy state again at higher pressures. In addition, we will discuss the dynamics model of polymer chains in polymer thin films-carbon dioxide systems. This work was funded by the NSF-MRSEC program.

#### **SESSION DD10: ADHESION, MECHANICAL PROPERTIES II**

Chairs: Stephan Herminghaus and Juan J. de Pablo  
Thursday Morning, November 29, 2001  
Constitution B (Sheraton)

#### **8:30 AM \*DD10.1**

**FUNCTIONAL POLYMER BRUSHES FOR BIOLOGICAL APPLICATIONS: DNA CHIPS AND CONTROL OF CELL ADHESION.** Jürgen Rühle, Institute for Microsystem Technology, University of Freiburg, GERMANY.

Surface attached polymer monolayers are promising architectures for many possible applications as biomaterials or for biomedical devices. One way to create such polymer brushes is to grow the chains away from the surface by using monolayers of polymerization initiators (e.g. azo compounds for free radical polymerizations). Following this approach, one can use functional monomers to prepare densely grafted polymer brushes that provide a high number of these functional groups on the surface. The layers can subsequently be used directly or after a transformation step to provide functionalities for a desired interaction with biological material or molecules. In this presentation we will present two projects related to this principal approach. As a first example we show that different oligonucleotide strands can be coupled to the functional groups within the polymer brush in the form of a microarray which can then be used as a DNA chip. A comparison to similar chips prepared from silane based monolayers carrying the same functionalities revealed a significantly enhanced sensitivity of the polymer brush based chips. To give another example, we studied the use of such polymer monolayers to promote and direct the outgrowth of cells (typically neuronal cells) on solid surfaces. Using this strategy it was possible to align the cell on two-dimensional grid that is useful for investigating cell communication.

#### **9:00 AM DD10.2**

**ADHESION OF A POLYACRYLATE PRESSURE SENSITIVE ADHESIVE WITH APPLICATIONS IN TRANSDERMAL DRUG DELIVERY.** Marc B. Taub and Reinhold H. Dauskardt, Stanford University, Department of MS&E, Stanford, CA.

Pressure sensitive adhesives (PSAs) are used as the adhesive layer in transdermal devices for drug delivery because of their good initial and long-term adhesion, clean removability, and skin and drug compatibility. However, understanding of the mechanics and chemical determinants of adhesion to the soft dermal layer, together with quantitative and reproducible test methods for adhesion, are lacking. This study utilizes a mechanics approach in which the strain energy release rate during debonding of a cantilever-beam specimen containing at its midline a thin layer of PSA was utilized to quantify the adhesion of a model polyacrylate PSA. Delamination of the PSAs was accompanied by cavitation in the PSA and the formation of an extensive cohesive zone behind the debond tip which provides additional energy dissipation and increased resistance to delamination. A mechanics model was developed to account for both the chemically determined work of adhesion as well as the viscoelastic constitutive behavior of the soft adhesive layer. The effects of varying the composition and molecular structure of the adhesive through controlled modifications of cross-link density and pharmaceutical loading will be discussed. Additionally, the effects of environmental conditions (temperature, humidity, and aqueous environment) will be presented as they relate to cavitation behavior and adhesive performance.

**9:15 AM DD10.3**

TUNING THE SURFACE PROPERTIES OF ELASTOMERS USING MECHANICALLY ASSEMBLED MONOLAYERS. Kirill Efimenko and Jan Genzer, Dept of Chemical Engineering, NC State University, Raleigh, NC.

Chemically and structurally well-defined surfaces are typically prepared by depositing self-assembled monolayers (SAMs). The interplay between the chemical and structural nature of the SAM molecules and the means of their attachment to the substrate sets the packing density of the SAMs, which in some situations limits the stability of the monolayer and its resistance to surface reconstruction. We have recently presented a novel method of tailoring the grafting density of end-anchored molecules on elastomeric substrates [J. Genzer and K. Efimenko, *Science* **290**, 2130 (2000)]. Our methodology is based on combining: 1) the grafting reaction between chlorosilane moieties and surface hydroxyl functionalities, and 2) mechanical manipulation of the surface grafting points. An elastomeric network film is uniaxially stretched (by  $\Delta x$ ) and treated with UV/ozone to produce the surface hydroxyl groups. Chlorosilanes are deposited from vapor and form a SAM. The strain is released from the substrate, which returns to its original size, causing the grafted molecules to form a densely organized "mechanically assembled monolayer" (MAM). We produced MAMs from semifluorinated ( $(\text{CF}_2)_y(\text{CH}_2)_2\text{SiCl}_3$ ,  $y=6$  or  $8$ ) and hydrocarbon ( $(\text{H}(\text{CH}_2)_x\text{SiCl}_3$ ,  $x=8$  or  $18$ ) molecules, SF-MAMs and Hx-MAMs, respectively. Our experiments reveal that the SF-MAM surfaces are super-hydrophobic; the water contact angle,  $\theta_w$ , increases with increasing  $\Delta x$  and culminates at a value of  $135^\circ$  for  $\Delta x \approx 80\%$ . These SF-MAMs are highly resistant to surface reconstruction; while SF-SAMs on non-stretched surfaces reconstructed only after several hours, the surfaces of SF-MAMs immersed in water for a week (followed by a subsequent storage under ambient laboratory conditions for 6 months) stayed virtually unmodified. While the surface energies of the  $-\text{CH}_3$  groups are slightly higher than those of the  $-\text{CF}_3$  termini, the wetting properties of the Hx-MAMs approach those of the SF-MAMs at sufficiently high grafting densities. Specifically, water contact angle measurements show that that  $\theta_w$  as high as  $\approx 125^\circ$  can be achieved for H16-MAMs prepared by depositing  $(\text{H}(\text{CH}_2)_{16}\text{SiCl}_3$  on pre-stretched PDMS ( $\Delta x \approx 70\%$ ) for 30 mins.

**9:30 AM DD10.4**

THIN & ULTRATHIN FILMS CONTAINING ALPHA, OMEGA-PYRENE-END-LABELED PDMS: UNUSUAL AUTOPHOBIC PHASE SEPARATION MORPHOLOGY, FLUORESCENCE, AND RHEOLOGY DUE TO PHYSICAL CROSSLINKING. Sung Dug Kim, Christopher E. Ellison, John M. Torkelson, Northwestern Univ., Evanston, IL.

Unusual behavior that is a strong function of temperature, confinement, and blend composition is obtained in spin-coated films of alpha,omega-pyrene-end-labeled polydimethylsiloxane (PDMS) blended with alpha,omega-amine-end-labeled PDMS. As confirmed via fluorescence emission and excitation spectra, the pyrene end units forms dimers or higher aggregates in the blends, due to insolubility with PDMS. The aggregate level is a strong function of ultrathin film thickness, as the fluorescence response indicative of aggregation changes dramatically with film thickness less than 200 nm. Some of the aggregates form static or near static ground-state structures leading to physical crosslinking and, at sufficiently low temperature, a macroscopic gel as confirmed by rheological measurements. In contrast, the amine-terminated PDMS does not participate in the crosslinking and instead remains as free chains that have a slight preference, in comparison to the pyrene-terminated PDMS, to wet silicon substrates. For film thicknesses from several tens to less than 1000 nm in film thickness, very unusual morphologies are obtained in blends due to a combination of shear effects from the spin coating process used to make the films and autophobic phase separation between the physically crosslinked pyrene-labeled PDMS and the free chains of amine-terminated PDMS. For certain ranges of film thickness, at short times after spin coating, stripes of pyrene-terminated PDMS form in a matrix of amine-terminated PDMS, with stripe orientation indicative of the strong shearing effects that occurred during spin coating. At long times huge, stripes evolve to flat droplets (tens to hundreds of nm in diameter) of pyrene-terminated PDMS, sitting atop a thin film of amine-terminated PDMS that wets the silicon substrate; these droplets coarsen over periods of months. In ultrathin films of these blends, the droplet structure that forms exhibits little coarsening and instead retains features for months indicative of the shearing direction during spin coating.

**9:45 AM DD10.5**

FRACTURE PROCESSES INVOLVED FOR EPOXY NETWORK - AMORPHOUS THERMOPLASTIC INTERFACES. Jean Francois Gerard, Bernard Lestriez, LMM/IMP UMR CNRS 5627 INSA Lyon, Villeurbanne, FRANCE; Jean Paul Chapel, LEMPB/IMP

UMR CNRS 5627 UCB Lyon I, Villeurbanne, FRANCE; Chris Plummer, EPFL/DMX, Lausanne, SWITZERLAND; Hugh Brown, Wollongong Univ, Wollongong, AUSTRALIA.

Model interfaces based on high-Tg thermoplastics such as polyphenylene ether, PPE, or polyetherimide, PEI, and epoxy-amine networks were considered in order to know how to manage the fracture energy of such interfaces measured by means of the asymmetric cantilever beam method, ACDB. Thermoplastic/epoxy-amine interfaces prepared from epoxy networks at different conversions were tested after a complete curing of the epoxy network layer. The amine hardener of reactive mixtures were chosen in order to display no miscibility (DDS) or to be miscible (MCDEA) with the thermoplastic at the curing temperature of the bi-layer. In fact, the epoxy and the amine comonomers can diffuse into the thermoplastic during joining creating interphases. In these interfacial regions, the epoxy mixture leads to a dispersed phase as the reaction proceeds from a phase separation phenomenon. These interphase patterns can be explained from the phase diagrams of the thermoplastic-epoxy blends. For example, Gc of the DGEBA-DDS/PPE interface ranges from 250 to 10 J.m<sup>-2</sup>. The fracture energy values can be related to the presence or not of the grafted PPE chains at the epoxy / PPE interface. In fact, the phenol groups which terminates the PPE chains can react with the functional groups, i.e. epoxy, of the reactive epoxy system to form ether links between the two layers. For high epoxy conversion at joining, availability of the glycidyl reactive groups for grafting is low as their concentration and mobility at the surface is low whereas for low epoxy conversion at joining, a high interfacial toughness is achieved because of the numerous connecting chains created at the interface. Failure observed by TEM and AFM occurs through crazing in the PPE layer. On the other hand, Gc for DGEBA-MCDEA/PPE interphase created from mutual diffusion for low epoxy conversion remains low (70 J/m<sup>2</sup>) in spite of the expected high density of in-situ grafted chains and of the gradient morphology. This can be attributed to the existence of the sharp interface where crack is able to propagate and where the connectors density is supposed to be low.

**10:30 AM DD10.6**

FILM THICKNESS EFFECTS ON INTERFACIAL FAILURE OF EPOXY BONDS. N.R. Moody, Sandia National Laboratories, Livermore CA; D.F. Bahr, Washington State University, Pullman, WA; M.S. Kent, J.A. Emerson, E.D. Reedy, Jr., Sandia National Laboratories, Albuquerque, NM.

Interface adhesion is a key factor in controlling the reliability of thin polymer films on metal substrates where changes in composition and structure during processing and service can lead to interfacial failure. Nevertheless, our understanding of interfacial fracture in these systems is limited. Consequently, we have begun a program to determine the interfacial fracture susceptibility of spin coated Epon 828/T403 on aluminized glass substrates as a function of film thickness. Nanoindentation test techniques were combined with deposition of highly stressed overlayers to induce delamination and blister formation from which interfacial fracture energies were obtained using mechanics-based models. The resulting fracture energies decreased with film thickness and approached a lower limit for films less than 200 nm thick. However, this limit is significantly higher than the true work of adhesion for this film system. This suggests that inelastic or plastic dissipation processes operate even in the thinnest films we can test. It will be shown in this presentation that practical works of adhesion can be obtained for thin free surface polymer films using a combination of nanoindentation and stressed overlayer techniques. It will also be shown that measured fracture energies always contain a contribution due to inelastic or plastic dissipation processes. This work supported by U.S. DOE Contract DE-AC04-94AL85000.

**10:45 AM DD10.7**

QUASI-STATIC AND DYNAMIC MECHANICAL PROPERTIES MULTI-LAYERED PAINT FILMS. Robb M. Winter, South Dakota School of Mines and Technology, Department of Chemistry and Chemical Engineering, Rapid City, SD; Ken T. Gillen and J.E. Houston, Sandia National Laboratories, Albuquerque, NM.

Multi-layered paint films are a unique category of polymer films which present challenges in obtaining spatially resolved measurements of mechanical properties. Spatially resolved mechanical properties can be used in finite element analysis to predict film behavior under a variety of loading conditions, which provides one of the impetus for this study. Typical multi-layered paint films are on the order of 100 microns with individual layers having thicknesses of 10 to 30 microns. Interdiffusion between layers is expected to alter the chemistry of the "bulk" layers and hence affect the mechanical properties in the interface region. We have applied the interfacial force microscope (IFM) to acquire measurements of elastic moduli and AC moduli and phase shifts (dynamic mechanical properties) across the individual layers. The IFM is a scanning probe microscope which utilizes a unique self-balancing capacitance force sensor. Force-displacement

curves and two step creep data obtained with the IFM are analyzed using Hertzian contact mechanics to extract Young's moduli of the individual layers and the interface regions with nanometer spatial resolution. In addition, through the application of a Angstrom level dithering voltage to the Z piezo and a lock-in amplifier the AC modulus and phase shift can be easily obtained. We will show how the mechanical properties transition from one layer to the next and the utility of the IFM in obtaining such data.

#### 11:00 AM DD10.8

ADHESION AND INTERFACES INVOLVING POLYMERS, STUDIED BY ELECTRICAL RESISTANCE MEASUREMENT. Zhen Mei, D.D.L. Chung, Composite Materials Research Laboratory, University at Buffalo, The State University of New York, Buffalo, NY.

The adhesion and interfaces involving polymers were studied by electrical resistance measurement. Adhesive bonding and bond degradation were monitored by measuring the resistance in real time during temperature or stress variation. The resistance measured was either the contact resistance of the joint interface or the apparent volume resistance of one of the two adjoining components in a direction in the plane of the joint interface. The polymers were in the form continuous carbon fiber thermoplastic-matrix composites, due to the importance of these composites for lightweight structures and due to the conductivity of carbon fibers and the necessity of conductivity for electrical resistance measurement. The technique was used for the case of both of the adjoining components being such composites, and for the case of one component being such a composite and the other component being concrete. The concrete case is relevant to the use of the composite to retrofit concrete structures.

#### 11:15 AM DD10.9

NANOSCALE CHARACTERIZATION OF SURFACE AND INTERFACE OF DIFFERENT EPOXY NETWORKS. X. Gu, D. Raghavan, Chemistry Department, Howard University, Washington, DC; T. Nguyen and M. VanLandingham, Building and Fire Research Laboratory, NIST, Gaithersburg, MD.

The effect of network changes on the surface and interface properties of amine-cured epoxy has been investigated. Samples of different crosslinked epoxies are prepared by mixing stoichiometrically pure diglycidyl ether of bisphenol A ( $n=0.03$ ) with different ratios of 1,3-bis(aminomethyl)cyclohexane (terafunctional amine) and cyclohexylmethylamine (difunctional amine). All samples are cured in CO<sub>2</sub>-free air. Both the film surface in contact with air and that in contact with the silicon substrate (the interface) are analyzed using atomic force microscopy (AFM) and nanoindentation. X-ray photoelectron spectroscopy (XPS), neutron scattering, attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, and contact angle measurements, are used to assist in the interpretation of AFM results. Substantial morphological and mechanical differences are observed between the surface and the interface for different crosslinked epoxies. The findings have strong implications on the wettability, adhesion, and durability of amine-cured epoxies.

#### 11:30 AM DD10.10

STUDIES OF SILANE ADHESION PROMOTERS ON SILICA FILLER PARTICLES FOR USE IN MICROELECTRONIC PACKAGING. Maura Jenkins, Gretchen DeVries, Rienhold H. Dauskardt, John Bravman, Stanford Univ, Materials Science and Engineering Dept, Stanford, CA.

Silane adhesion promoters are seeing increasing use in microelectronic packaging interfaces. For example, they are currently used to adhere the passivating polymer overlayer to oxide, and these materials show promise as surface treatments for silica particles in underfill epoxies. Until recently, the exact mechanism of adhesion promotion was postulated. In this paper, we present past studies characterizing silane adhesion promoters on the silicon oxide surface, and apply this knowledge to a complicated system of silica particles which are dispersed in an epoxy matrix after being coated with silane adhesion promoters. Several adhesion promoters were chosen for their potential reactivity with the epoxy. The strength of the silica-silane-epoxy interface was first tested using a fracture mechanics approach. Then, adhesion of the composite formed by filling the epoxy was investigated. As might have been predicted, those adhesion promoters which form the strongest bond with the epoxy result in weaker macroscopic adhesion when the filled epoxy is tested in a multilayer structure. A toughening mechanism and past characterization work are presented to explain this behavior.

#### 11:45 AM DD10.11

COMPOSITIONAL PROFILING OF THE EPOXY/ADHEREND INTERPHASE. M. Libera, D. Arayasantiparb, Stevens Institute of Technology, Hoboken, NJ; and S. McKnight, Army Research Laboratory, Aberdeen Proving Ground, MD.

At a polymer-solid interface, an inorganic adherend may influence the structure and/or chemistry of the polymer in the near-interface region. This region between the adherend and the homogeneous polymer is referred to as the interphase. While there is general agreement that interphases exist, extensive debate revolves around the characteristic length scale of the interphase and its composition and structure. This work examines the size and composition of the epoxy-aluminum interphase using spatially resolved electron energy-loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM). Aliphatic PACM20 [bis(p-aminocyclohexyl)methane] curing agent and aromatic DGEBA [diglycidyl ether of bisphenol-A] epoxy resin were used as a model system. Spatially resolved pi-pi\*, carbon, and thickness profiles were measured using EELS in the epoxy region immediately adjacent to the interface between the bulk epoxy and the nanoporous oxide on the aluminum adherend surface. These profiles systematically show deviations in the spectral intensities characteristic of carbon and aromaticity over distances extending 90±15 nm from the oxide surface. Simulations of such data indicate that these fluctuations result from changes in epoxy composition near the oxide surface. The results show that this epoxy-aluminum interphase is enriched in curing agent, as indicated by a gradual compositional change from 25±5 vol% PACM20 in the bulk epoxy to 8015 vol% PACM20 at the epoxy/oxide interface. This chemical segregation has significant implications for the properties and performance of epoxy-adherend adhesive joints.

SESSION DD11/AA10: JOINT SESSION  
SELF-ASSEMBLY BY POLYMERIC FILMS  
Chairs: Spiros H. Anastasiadis and Georg Krausch  
Thursday Afternoon, November 29, 2001  
Constitution B (Sheraton)

#### 1:30 PM \*DD11.1/AA10.1

STRUCTURE FORMATION AND MOLECULAR DYNAMICS IN THIN LIQUID FILMS. Ralf Seemann, Karin Jacobs, Stephan Herminghaus, University of Ulm, Applied Physics Lab., Ulm, GERMANY.

The principal mechanisms of dewetting and structure formation in thin liquid films are presented and discussed with polystyrene films as a model system. Quantitative agreement of *in-situ* optical and AFM microscopy with theoretical predictions, both analytical calculations and simulations, is obtained. It is found that additivity of van der Waals interactions is a good approximation for computing the effective interface potential. On the basis of the observed features, we are furthermore able to infer the rheological properties of the polymer melt at the small ( $\mu\text{m}$  to  $\text{nm}$ ) scales investigated. This can be applied to a wide range of (complex) fluids, yielding rheological information not easily accessible by other techniques.

#### 2:00 PM DD11.2/AA10.2

MICRODOMAIN STRUCTURE AND DYNAMICS OF SELF-DEWETTING POLYSTYRENE-BLOCK-POLY (ETHYLENE-PROPYLENE) THIN FILMS. A. Horvat, A. Knöll, G. Krausch, R. Magerle, Phys Chem II, Universität Bayreuth, GERMANY.

The structural development of polystyrene-*block*-poly(ethylene-propylene) (PS-PEP) thin films with 28 wt% PS has been studied as a function of film thickness, temperature and annealing time. Above the polystyrene (PS) glass transition temperature various self assembled structures are formed depending on treatment. Tapping Mode<sup>TM</sup> AFM investigations of spin cast samples reveal a stripe like pattern at the film surface corresponding to the bulk structure of cylindrical microdomains. After annealing at 160°C the film shows a disordered spherical microdomain structure of PS domains in a PEP matrix. Upon annealing at 140°C a transition to irregular structures with dimensions much larger than the microdomain spacing occurs. At longer time scales polymer droplets form and move spontaneously across the surface. This phenomenon was followed *in situ* by hot stage Tapping Mode<sup>TM</sup> AFM. The phenomenon is believed to be caused by a delicate balance between the surface and volume contributions to the effective interface potential of the confined polymer film.

#### 2:15 PM DD11.3/AA10.3

SELECTIVE ELECTROLESS METALLIZATION USING MICROCONTACT PRINTING OF FUNCTIONALIZED COPOLYMERS. Tricia L. Breen, Ali Afzali, Sarah J. Vella, IBM T.J. Watson Research Center, Yorktown Heights, NY.

We present a low-cost, additive method that uses microcontact printing and electroless plating to fabricate patterned metal films with minimum feature sizes of ~1 micron. Our approach is based on stamping new copolymers that incorporate two types of functional groups: The first group bonds the copolymer to the SiO<sub>2</sub> substrate;

the second group ligates catalytic colloids used to initiate electroless metallization. After stamping the copolymer onto a substrate, the patterned film is exposed to a solution of an electroless plating catalyst. The catalytic colloids selectively adhere to the stamped regions of the surface. Subsequent metallization in an electroless plating solution yields a metal film only over the catalyzed copolymer regions. Using this method, we have fabricated patterned nickel and copper films over areas as large as 15 cm<sup>2</sup>.

#### 2:30 PM DD11.4/AA10.4

APPLICATION OF SELF ASSEMBLED MONOLAYER TECHNOLOGY TO INVESTIGATE THE FIBER-MATRIX ADHESION. E. Feresenbet, D. Raghavan, Polymer Division, Department of Chemistry, Howard University, Washington DC; G. Holmes, Polymer Division, National Institute of Standards & Technology, Gaithersburg, MD.

Adhesion at the fiber-matrix interface of composite is often related to a combination of factors such as mechanical interlocking, physico-chemical interactions, and chemical bonding of the fiber-matrix interphase region. We demonstrate the use of SAMs technology for studying the impact of these interactions on the adhesion process. Through some unique chemistry, functionalized and nonfunctionalized C11 and C3 chloro silane SAMs were deposited on to the glass fiber. The deposited SAM layer was analyzed using atomic force microscopy (AFM), ellipsometry, X-ray photoelectron spectroscopy (XPS), and contact angle measurements. The adhesion of diglycidyl ether of bisphenol-A (DGEBA) cured with meta-phenylene diamine (m-PDA) to chlorosilane SAMs deposited glass fibers was measured by performing single fiber fragmentation test (SFFT). The extent of adhesion between the fiber and matrix was found to be dependent on the deposition process, carbon chain length, the functional group at the end of the SAM layer, and the structure of the epoxy/amine resin network. Furthermore, the contributions to adhesion by physico-chemical interaction and covalent bonding will be discussed.

#### 2:45 PM DD11.5/AA10.5

SURFACE AND INTERFACIAL PROPERTIES IN THIN POLY(*p*-PHENYLENE VINYLENE) MULTILAYERS PREPARED BY SELF-ASSEMBLY METHODOLOGY. C.A.M. Borges, A. Marletta, R.M. Faria and F.E.G. Guimarães, Universidade de São Paulo, Instituto de Física de São Carlos, São Carlos, São Carlos, BRAZIL.

In this work we studied the influence of different interfaces (metal/film, ITO/film) and surfaces (air/film) on the optical properties of very thin layers (less than 15 nm thick) of poly(*p*-phenylene vinylene), PPV. The PPV films were prepared joining a novel self-assembly method (SA) and a low temperature conversion process for PPV<sup>1</sup>. The main advantage of this SA procedure is that thermal conversion may be performed at considerably lower temperatures (80-100°C) in few minutes, producing high ordered PPV films with very low defect incorporation. In addition, Atomic Force Microscopy (AFM) has shown that 0.4 nm thick PPV can be homogeneously deposited layer-by-layer on different metal (50% transmission Au, Cu, Pt, Ag, Cr films) and glass/ITO surfaces. Absorption measurements revealed that the conjugated  $\pi$ - $\pi^*$  band suffers different blue-shifts for each interface as the PPV thickness decreases, indicating different extension of the interfacial disorder in the PPV layers. The ITO/PPV interface has the highest disorder extension (~12 nm) and surface roughness (RMS~2.5 nm) while the lowest values (~3.5 nm and RMS~0.6 nm, respectively) were found for the quartz/PPV interface. The thermal conversion of 4 nm thick PPV films at different temperatures (100-230°C) and under vacuum conditions demonstrated that a large amount of structural disorder is incorporated when high conversion temperatures are used. Infrared (IR) measurements showed that carbonyl groups are responsible for conjugation length shortening. When the conversion temperature is lowered (around 100°C), no defect incorporation was detected by absorption and IR measurements. Photoluminescence data will be presented for further discussion.

#### 3:30 PM DD11.6/AA10.6

EFFECT OF SOLVENT QUALITY ON THE FRICTIONAL FORCES BETWEEN POLYMER BRUSHES. Aaron Forster, S.M. Kilbey II, Clemson University, Dept of Chemical Engineering, Clemson, SC.

Polymer brushes have shown promise as surface tethered lubricants, and it has been demonstrated that solvent quality strongly influences the frictional forces between two sliding brush layers. It is known that brush layers immersed in a good solvent must be compressed well below their equilibrium height before a frictional force is measured. Conversely, brushes immersed in a solvent at its theta temperature exhibit a frictional force at much lower levels of compression. We used the surface forces apparatus to measure the structural and frictional

force profiles between opposing, sliding brush layers as a function of temperature. Three different polyvinylpyridine-polystyrene [PVP-PS] diblock copolymers were used to make PS brushes. The molecular weights (in thousands) of these PVP-PS materials were [114/103]k, [30/70]k, and [60/100]k. Structural and frictional force profiles in toluene and cyclohexane were measured, with the cyclohexane experiments being done at temperatures ranging from the theta-point to 50°C. We found that the structural force profiles agree with well-known behaviors<sup>1</sup>. The frictional forces depended strongly on the solvent and the solvent temperature: PS brushes in toluene need to be compressed to  $\sim 1/6^{th}$  their equilibrium height before frictional forces are measured, but this onset of frictional force is detected at a much lower level of compression in near-theta cyclohexane. When the cyclohexane temperature is raised the onset of frictional forces decreases toward the good-solvent behavior. At 50°C, the onset of frictional forces occurs at a comparable distance to that in toluene, which is a very good solvent for PS. We will compare this behavior in cyclohexane at various temperatures to the behavior of the brushes in another theta-solvent.

1. S.M. Kilbey, H. Watanabe, M. Tirrell, *Macromolecules* 2001, in press.

#### 3:45 PM DD11.7/AA10.7

MORPHOLOGY AND ORDERING BEHAVIOR OF BLOCK COPOLYMER IN BLOCK COPOLYMER/CLAY NANO-COMPOSITES. Jae Young Lee, Hoichang Yang, Jin Kon Kim, Department of Chemical Engineering and Polymer Research Institute, Pohang University of Science and Technology, Pohang, Kyungbuk, KOREA.

Morphology and ordering kinetics of polystyrene-block-polyisoprene-block-polystyrene (SIS) with various block length ratios and total molecular weights in SIS/clay nanocomposites have been investigated using by transmission electron microscopy, rheology, and small and wide angles X-ray scattering methods. One of SISs employed in this study exhibits the order to order transition of hexagonally packed cylinder microdomains to body-centered cubic microdomains (BCC) at 185°C, then becomes disordered micelles at 225°C. All composites showed that the domain spacing of the clay was larger than compared with PS/clay nanocomposites due to the presence of PI block, but there is no sign of the exfoliation of the clay, that is, the intercalation of clay was observed. But, the domain spacing of block copolymer does not change with the amount of the clay. The degree of intercalation of the clay in nanocomposites does not depend on either PS block length ratios in SIS or the amount of block copolymer in nanocomposites. However, the kinetics of the BCC formation from disordered micelles varied significant with the amount of the clay. Finally, an exfoliated structure for the clay was observed for a nanocomposite when a maleic anhydride functionalized polystyrene-block-poly(ethylene-co-butylene)-block-polystyrene is used instead of SIS.

#### 4:00 PM DD11.8/AA10.8

CHARACTERIZATION OF THIN POLYMER BLEND FILMS USING ESEM - NO CHARGING, NO STAINING. I.C. Bache, C.M. Ramsdale, D.S. Thomas, A.C. Arias, J.D. MacKenzie, R.H. Friend, N.C. Greenham, A.M. Donald, Univ of Cambridge, Cambridge, UNITED KINGDOM.

We have developed the application of Environmental Scanning Electron Microscopy (ESEM) to the study of conjugated polymer blends. ESEM has the special advantage that polymers do not need to be coated to prevent charging. Thin films of conjugated polymer blends are increasingly finding application in novel optoelectronic devices, including LEDs and photovoltaics. The use of blends in photovoltaics is driven by efficient exciton dissociation at the interfaces between the two phases leading to improved performance. In order to optimise the device efficiency, it is therefore necessary to understand the interplay between processing (typically spin casting on an appropriate substrate), morphology (especially the nature of the interfaces) and performance. Traditionally a variety of microscopies have been used to study thin film structure. TEM has various limitations, including the lack of contrast between polymer phases in the absence of staining, and the need for substrate removal. AFM, more recently used, can only study the surface of the blend unless etching or dissolution techniques are used to remove one component preferentially. ESEM provides a powerful technique to study blend films. We have demonstrated that polymers can show significant contrast according to their electronic properties. Thus for these optoelectronically interesting polymer blends, contrast can be seen readily between the phases. This means that morphological changes due to processing conditions can readily be studied, even without removing the device from the substrate. In addition, by sectioning the sample, variations in phase separation through the film thickness can also be imaged. Such images show not only how the surface topography is affected by the phase separation - which can be confirmed by AFM - but also whether the phase separation visible at

the free surface propagates right the way through the film. Understanding this has important implications for device performance.

#### 4:15 PM DD11.9/AA10.9

EFFECTS OF SELF-ASSEMBLED PHTHALOCYANINE AND POLYMER MULTILAYERS ON PHOTOVOLTAIC PROPERTIES OF CONDUCTIVE AND SEMICONDUCTIVE SURFACES. Lin Song Li, QuanXi Jia, Los Alamos National Laboratory, Materials Science and Technology Division (MST-STC), Los Alamos, NM; Alexander D.Q. Li, Department of Chemistry and Center for Materials Research, Washington State University, Pullman, WA.

The recently developed technique of layer-by-layer (LBL) assembly of oppositely charged polymeric and organic materials has been used to fabricate multilayers on various substrates. Using this technique, we have deposited multilayers of nickel phthalocyanine (NiPc) and poly(diallyldimethylammonium) (PDDA) onto ITO and TiO<sub>2</sub>/ITO substrates, respectively. Kelvin probe and surface photovoltage measurements have been used to probe the electronic and charge transfer properties of these self-assembled multilayers. The results showed an oscillating behavior of the surface potential as the surface layer was alternated between these multilayers on both substrates. The average gap of this surface potential oscillation was around a few hundreds of milli-Volt. These changes of surface potential or work function, induced by self-assembled PDDA or NiPc were due to the modulation of electron affinity rather than band bending at ITO surfaces, which was consistent with the surface photovoltage measurements. In photovoltage experiments, we also found that the spectra of photovoltage were a weak periodic function of the number of layers (PDDA or NiPc).

#### 4:30 PM DD11.10/AA10.10

LIQUID CRYSTALLINE ALIGNMENT OF SIDE-CHAIN SMECTIC HOMOPOLYMER FILMS. Jung-Sheng Wu, Paula T. Hammond, MIT, Dept of Chemical Engineering, Cambridge, MA.

Surface properties have profound influence especially on polymer thin film applications. The understanding of LC alignments in nanoscale thin films becomes critical, when the technology trends towards to diminish the film thickness but keep ordered surfaces. From previous results of morphological studies, lamellar side-chain LC diblock copolymers have been synthesized and examined as thin films. LC terraces with the smectic LC layer spacing are observed on the top surfaces to minimize the surface tension. In order to determine LC alignments, homopolymer films with different thickness are examined to give us an idea about LC alignments and use as model system to describe complicated diblock copolymer systems. LC orientations are determined by both experimental (contact angles, angle-resolved XPS, AFM, X-ray specular reflectivity, ellipsometry, SAXS, TEM, and X-ray single crystal diffractometer) and theoretical (molecular mechanism modeling and group contribution theory) approaches. The LC orientation shows homeotropic in the air interface by the non-polar end group, but planar on the substrate by the mesogen core. We have also investigated morphologies and LC alignments of diblock copolymer thin films with lamellae, cylinders, perforated lamellae, and unusual smectic bilayers. They all show homeotropic LC terraces on the air interface. The fundamental understanding of the self-oriented LC polymer thin film behaviors will be helpful for further nano-patterning, and electrical/optical applications.

#### 4:45 PM DD11.11/AA10.11

STRUCTURAL CHARACTERIZATION OF SEGMENTED POLYURETHANES BY SMALL ANGLE NEUTRON SCATTERING. Loren I. Espada, LANSCE-12, Los Alamos National Laboratory, Los Alamos, NM; Joseph T. Mang, DX-2, Los Alamos National Laboratory, Los Alamos, NM; E. Bruce Orler, MST-7, Los Alamos National Laboratory, Los Alamos, NM; Debra A. Wroblewski, MST-7, Los Alamos National Laboratory, Los Alamos, NM; David A. Langlois, MST-7, Los Alamos National Laboratory, Los Alamos, NM; and Rex P. Hjelm, LANSCE-12, Los Alamos National Laboratory, Los Alamos, NM.

The beneficial mechanical properties of segmented polyurethanes derive from microphase separation of immiscible hard and soft segment-rich domains at room temperature. We are interested in the structure of the domains, how these are affected by hydrolytic aging, and how the structure is modified by low molecular weight plasticizers. Segmented poly(ester urethane) with various weight fraction hard segment content, both deuterated and non-deuterated were synthesized and the morphology assessed using small-angle neutron scattering. We also assessed the distribution of the plasticizer in polyurethane. We have analyzed the results in terms of a simple model in which the contrast,  $\Delta\rho = \rho_H - \rho_s$ , between the hard and soft segment-rich domains is varied by the amount of deuterated hard segments or presence of deuterated or hydrogenated nitroplasticizer, using the fact that  $I(Q) \sim \Delta\rho^2$ . Modeling results give us key

information on the domain structure of polyurethane, the segregation of the hard and soft segments in each domain and determined that plasticizer partitions into the soft segment-rich domains.

#### SESSION DD12: POSTER SESSION SELF-ASSEMBLY, ELECTRONIC PROPERTIES

Chairs: Dvora Perahia and Amit Sehgal  
Thursday Evening, November 29, 2001  
8:00 PM

Exhibition Hall D (Hynes)

#### DD12.1

DEPENDENCE OF NANODOMAIN SEGREGATION ON HEAT TREATMENT AND COOLING HISTORY IN POLYURETHANES SURFACES BY PHASE SENSITIVE PROBE IMAGING.

M.E. Hawley, E.B. Orler, D.A. Wroblewski, and R.P. Hjelm, Los Alamos National Laboratory, Los Alamos, NM.

Segmented polyurethanes are an important class of structural polymers that derive their desirable mechanical properties from the nanophase separation of immiscible crystalline (hard) and rubbery (soft) segments that make up the polymer. It is well known that the thermoplastic character of polyurethanes is a result of changes in structure that occur on heating and cooling. Our objective is to study the morphology and nanodomain segregation of the material as a function of heating and subsequent cooling rate as a function of hard segment content. Phase sensitive atomic force microscopy imaging is sensitive to the differences in mechanical stiffness of the hard and soft segments rich domains formed by the segregation of the polyurethane components. Scan rates are small on time scales relevant to the rate of structural changes; thus, the method provides near surface information on the time dependent component segregation after samples are heated to temperatures around 100°C and cooled to room temperature at different rates. In these experiments, hard segment content was varied from 19 to 100% and changes in structure followed over several weeks. Slowly cooled low hard segments samples initially show very little nanophase segregation. However, over an extended period, strand-like nanodomains developed, coalescing into dense mats, the structure of which were dependent on cooling rate. Coincident with this was the formation of a second type of structure with a length scale similar to that observed in small-angle scattering experiments. For the high hard segment content material there was little change in structure, even over extended periods after cooling.

#### DD12.2

X-RAY PHOTON CORRELATION SPECTROSCOPY STUDY OF BLOCK COPOLYMER MICELLES. Péter Falus, Matthew A. Borthwick, Adrian Rühm, Laurence B. Lurio, Massachusetts Institute of Technology, Center for Material Science and Engineering and Department of Physics, Cambridge, MA; Simon G.J. Mochrie, Yale University, Department of Physics, New Haven, CT.

Polymer micelles and vesicles play an important role in many scientific problems while Polystyrene-poly ethylene-butylene poly-styrene (PSEBS) block copolymers have many industrial uses. Directly examining the dynamics of block copolymer micelles is difficult since they are too slow for neutron studies and their opacity hinders light scattering measurements. The emerging technique of X-ray Photon Correlation Spectroscopy (XPCS) provides direct measurements of the micelles' dynamic structure factor on length scales comparable to the individual molecules' size. XPCS can be used to probe both diffusion and shape changes of polymer micelles. XPCS results on wormlike micelles and vesicles are presented together with Small Angle X-ray Scattering.

#### DD12.3

Abstract Withdrawn.

#### DD12.4

SELF-ASSEMBLING PI-CONJUGATED OLIGOTHIOPHENES FOR NANOELECTRONICS: FROM ORGANIZED MOLECULAR WIRES TO MACROCYCLIC CIRCUITS. Elena Mena-Osteritz, Gerda Fuhrmann, Achim Kaiser, Peter Baeuerle, Univ of Ulm, Dept Organic Chemistry II, Ulm, GERMANY.

Alpha-Conjugated oligo- and polythiophenes have successfully developed to promising active components in plastic electronic devices, such as organic field effect transistors (FET) or light emitting diodes (LED). Besides the prominent ability of these semiconducting materials to transport charge carriers and transfer electrons, the control of structural order on the molecular level has important consequences on their electronic properties. Therefore, knowledge on the ordering behaviour in the solid state is an important issue in order to design new materials. Since conjugated oligomers and polymers can be considered as molecular wires and building blocks for

molecular or nano-electronics, we will describe their self-assembling behaviour which was investigated by means of scanning tunneling microscopy (STM). The direct observation of self-assembled two-dimensional crystals of special oligo- and poly(3-alkylthiophene)s on graphite allowed the direct determination of lattice constants and various molecular parameters which then in some cases were directly compared to 3D structure analyses. Very recently, we succeeded in the synthesis and characterization of the first fully alpha-conjugated macrocyclic oligothiophenes, alpha-cyclo[n]thiophenes. These novel ring systems combine the excellent properties of the corresponding linearly conjugated oligomers with the properties of macrocycles. Completely novel perspectives arise due to the cyclic structure: recognition and selective complexation of large guest molecules or other objects which may depend on the redox state of the cyclic host come additionally into play which should result in new fundamental properties and applications. Furthermore, the self-assembling properties of the novel macrocycles are reported. 2D- and 3D-structural characterizations provide intriguing self-organization properties.

#### **DD12.5**

**IN SITU MEASUREMENTS OF THE FORMATION OF IONICALLY SELF-ASSEMBLED MONOLAYERS BY SECOND HARMONIC GENERATION.** C. Brands, P.J. Neyman, J.R. Heflin, Virginia Tech, Department of Physics, Blacksburg, VA; M.T. Guzy, S.M. Shah, R.M. Davis, K.E. Van Cott, Virginia Tech, Department of Chemical Engineering, Blacksburg, VA; H. Wang, H.W. Gibson, Virginia Tech, Department of Chemistry, Blacksburg, VA.

Ionic self-assembled monolayers (ISAMs) have recently been shown to spontaneously exhibit a polar ordering that gives rise to a substantial second order nonlinear optical response. The deposition of ISAMs has been studied in situ via second harmonic generation. This is a particularly sensitive probe of the growth of nanometer-thick films since the centrosymmetry of the immersion solutions, the substrate, and the container yields no SHG contribution from these bulk components. We show that the rate of adsorption and ordering of a noncentrosymmetric nonlinear optical polymer is constant over a wide range of concentrations. Upon immersion in the NLO-active polyelectrolyte solution, the SHG rises sharply over the first minute. Furthermore, when the film is removed from the NLO-active solution and allowed to dry, the ordering increases rapidly as the water evaporates. The results are interpreted in terms of the polar ordering of the NLO chromophores with respect to the preceding and following adsorbed layers. These studies provide greater understanding of the processes by which noncentrosymmetric order is formed in ISAM films and allow design of improved self-assembled nonlinear optical materials. In addition, we report studies of the use of SHG in ISAM films as a sensor for specific adsorption of biomolecular species. In particular, we have examined changes of the SHG signal due to the association of avidin with a biotinylated NLO polymer in ISAM films.

#### **DD12.6**

**A SIMPLE NON-LITHOGRAPHIC FABRICATION OF POROUS FREE-STANDING NANO-CHANNEL SILICATE MEMBRANES.** Theotis Clark, Jr., Julia D. Ruiz, Atul N. Parikh, Hong-You Fan, C.J. Brinker and Basil Swanson, Los Alamos National Laboratory, Los Alamos, NM.

A novel non-lithographic method for the preparation of macroscopic (10-51 mm dia.) free-standing silicate membranes sheets containing uniformly patterned void channels (4-10 nm) in controlled thicknesses (0.1-50  $\mu\text{m}$ ) and morphologies (cubic or hexagonal) is described. The membrane preparation simply involves the directed assembly of mesostructured, surfactant-templated silica sol-gel films onto well-defined hydrophobized substrates. The mesostructured film is subsequently lifted-off the substrate surface simply by peeling the ad-layer or by immersing in pure water in which case the film is transferred from the substrate surface to the air-water interface. These films appear well suited to serve as masks in substrate patterning applications such as photolithography, materials deposition, and electroplating as well as nanofilters for applications in colloidal, nanoparticles, and biomolecular separation technologies.

#### **DD12.7**

**SPIN-ASSEMBLY OF POLYELECTROLYTE MULTILAYERED THIN FILMS: AN ALTERNATIVE FOR SELF-ASSEMBLY.** Hsing-Lin Wang, Bioscience Division, Los Alamos National Laboratory, Los Alamos, NM; Jeanne M. Robinson, Joanna L. Casson, Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM; Peter Chiarelli, Department of Chemistry, Pomona College; Malkiat S. Johal, Division of Natural Sciences, New College of the University of South Florida, FL.

We present an alternative to assemble polyelectrolyte multilayered thin film i.e., spin-assembly. Rather than dipping the glass substrate into oppositely charged polyelectrolyte solutions, the oppositely

charged solution was dropping alternatively on top of a glass substrate with various spin rates. Our spin-assembly technology allows fabrication of multilayered thin films with much greater control over the amount and thickness of each deposited layer. Although the contact time between the dropping solution and the substrate is only a fraction of a second, the amount of the polyelectrolyte deposited via spin-assembly is comparable to that of the dipping process where the substrate was immersed in polyelectrolyte solution for 5 minutes. We will also present UV-Vis and ellipsometric data to illustrate how experimental parameters such as concentration and spin rate effect the thickness and amount of deposited polyelectrolyte layers.

#### **DD12.8**

**POLYELECTROLYTE MULTILAYER FILMS AS PLATFORMS FOR SELECTIVE ELECTROLESS NICKEL DEPOSITION.**

Tom C. Wang, Robert E. Cohen, MIT, Dept of Chemical Engineering and Center for Materials Science and Engineering, Cambridge, MA; Michael F. Rubner, MIT, Dept of Materials Science and Engineering and Center for Materials Science and Engineering, Cambridge, MA.

Polyelectrolyte multilayers fabricated from poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH) have chemical functionalities that can be systematically manipulated through polyelectrolyte solution pH. Previously, we have demonstrated the in-situ formation of metal and semiconductor nanoparticles within PAH/PAA films by exploiting the carboxylic acid functionalities within the films to bind metal cations. Using this approach, we investigate the incorporation of Pd within PAH/PAA films and on their surface as catalysts for selective electroless nickel deposition. By fabricating the PAH/PAA film under pH conditions that produce a surface dominated by the last polyelectrolyte adsorbed and with a high concentration of free acids if PAA is last adsorbed, Pd-complex cations are selectively bound only to PAA-topped multilayers. PAH-topped multilayers resist catalyst binding. Hence, subsequent electroless nickel plating is directed only onto PAA-topped multilayers. Alternatively, Pd nanoparticles can be synthesized within the interior of PAH/PAA multilayers to act as seeds for further growth by electroless deposition of nickel. By controlling the carboxylic acid content within the film through polyelectrolyte pH, the kinetics of the electroless chemistry, and the duration of deposition, Ni nanoparticles of desired sizes and concentrations can be obtained.

#### **DD12.9**

**SOLVENTLESS POLYMERIZATION AT THE GAS/SOLID INTERFACE FOR PATTERNING POLYMER THIN FILMS.** Degang Fu, Bing Xu, Hong Kong University of Science & Technology, Department of Chemistry, Hong Kong (SAR), CHINA; Bingwei Du, Ophelia K.C. Tsui, Hong Kong University of Science & Technology, Department of Physics, Hong Kong (SAR), CHINA.

This paper reports a simple process, combining soft lithography and solventless polymerization, for the formation of patterned polymeric thin films on a solid substrate. Our process involves patterning catalysts on the substrate using soft lithography and polymerizing volatile monomers at the gas-solid interface in the areas that have the catalysts. Comparing to spin-coating process, this process minimizes the use of solvents and polymers, allows polymers forming inside high aspect ratio micro- or nanochannels, offers an opportunity to generate multilayered and multifunctional thin films, and is controlled at the molecular level. We will discuss patterning of variety of polymers including insulating, semiconducting, and conducting polymers via several polymerization processes including ring-opening metathesis, cationic, and radical polymerizations. We expect that this solventless process, as an alternative for spin-coating and plasma polymerization, will be useful in microfabrication and other applications that require patterned polymeric thin films.

#### **DD12.10**

**THE USE OF AQUEOUS ENZYMIC POLYMERIZATION OF AMPHIPHILIC ALKYL TYROSINE BASED DERIVATIVES AS UNIFORM ENVIRONMENTALLY BENIGN COATINGS IN THE MICROELECTRONICS INDUSTRY.** Anastasios P. Angelopoulos, Samuel Oh, Univ of Massachusetts-Lowell, Dept of Chemistry, Lowell, MA; Kenneth A. Marx, Tian Zhou, Univ of Massachusetts-Lowell, Dept of Chemistry and Center for Intelligent Biomaterials, Lowell, MA.

The surface coating properties of enzymatically polymerized decyl esters of d-tyrosine from aqueous solutions onto gold surfaces have been investigated utilizing the complementary techniques of Potentiometric Titration, UV-VIS spectroscopy, and X-ray Photoelectron Spectroscopy (XPS). The aqueous-based coatings are of interest as environmentally friendly and cost-effective replacements for epoxy-based coatings currently employed in the microelectronics industry for both chemical protection and electrical insulation of gold-covered metallic conductors. Experimental results with respect to polymerization pH, immersion pH, and immersion time are presented

and compared to the ionization behavior of the monomers in solution. Optimum processing conditions have been established which yield uniform aqueous-based polymeric coatings on gold conductor surfaces.

#### **DD12.11**

**ELECTRICAL PROPERTIES OF POLYMERIC ORGANIC-INORGANIC COMPOSITE FILMS VIA SOL-GEL PROCESS FOR A-Si:H TFT APPLICATIONS.** G.G. Kim, Y.I. Hwang and K.J. Kim, LG Chemical, Advanced Materials Research Institute, Taejeon, KOREA.

Thin films composed of organic-inorganic hybrid materials have been developed incorporating tetraethoxysilane (TEOS) and titanium tetraisopropoxide as the inorganic components with preformed acrylate polymers prepared from 3-(trimethoxysilyl) propyl methacrylate, benzyl methacrylate (BzMA) and 2-hydroxyethyl methacrylate (HEMA) through the radical copolymerization. The obtained organic-inorganic hybrid films were homogeneous and transparent glassy composite materials in a wide range of the contents of organic polymers without phase separation between the organic and the inorganic network former.

In this work, the electrical properties including the dielectric behaviors of the composite films have been investigated utilizing a capacitance measurement under various experimental conditions. Especially, the effects of inorganic contents and annealing temperature on the phase behavior and dielectric properties were examined. The metal oxide phase was incorporated homogeneously in the matrix polymers as is confirmed by SEM measurements, however, with a higher molecular weight inorganic sol (above  $M_w = 5,000$ ), the composite films were phase separated resulting in the opaque films. For electrical characterization, the metal insulator silicon (MIS) capacitor was fabricated with the composite films. From the C-V measurements, it was found out that the C-V curves shift to the negative direction due to the positive fixed charge which is associated with defects near the interface. With increasing the curing temperature of the composite films, however, the flat band voltage shift (Vfb) to the negative direction is decreased indicating the change of structure in the insulating films as is observed by FT-IR analysis. The C-V curve for MIS structure exhibited a hysteresis which is thought to be related with the interface trap density of the insulating films. The behavior is also declined with increasing the curing temperature and finally disappeared above 300°C. These results suggest that these organic-inorganic composite films could be the potential materials for a variety of microelectronic and a-Si:H TFT insulating films including passivating and dielectric layers.

#### **DD12.12**

**THE EFFECT OF SEMICONDUCTOR AND DYE INTERFACIAL PROPERTIES IN DYE-SENSITIZED SOLAR CELLS.** Jin-An He, Ravi Mosurkal, Jayant Kumar, Center for Advanced Materials, University of Massachusetts Lowell, Lowell, MA; Lian Li, K.G. Chittibabu, Molecular Technologies Inc., Westford, MA; Lynne A. Samuelson, Natick Soldier Center, U.S. Army Soldier & Biological Chemical Command, Natick, MA.

The back recombination processes of electrons from the semiconductor to the oxidized dye and oxidized redox species can dramatically reduce the efficiency of conventional dye-sensitized solar cells (DSSCs). In this work, we have used the electrostatic layer-by-layer (ELBL) assembly technique to specifically manipulate and control the interface between the semiconductor and adsorbed dye layers in DSSCs to potentially minimize this recombination behavior. The influences of interfacial modification by applying different combinations and thicknesses of polyelectrolytes using ELBL method on the I-V characteristics and efficiency of the solar cells are presented. The results indicate that an ultrathin polyelectrolyte film, on the order of Angstroms, between the semiconductor and the dye layer plays a crucial role on the efficiency of the solar cell. More specifically, the efficiencies of the DSSCs do not show any improvement after the interfacial treatment when compared to the control experiment. Surprisingly, the efficiency of the cells decreases to some degree, depending on the thickness of the polyelectrolyte films. This suggests that incorporation of a thin (several Angstroms) passive layer between the semiconductor and dye layer in these devices is more of a resistance controlled effect rather than a means of constraining back electron recombination as was originally anticipated. These results offer interesting mechanistic information regarding the interfacial interactions of semiconductor / dye interfaces in DSSCs.

#### **DD12.13**

**COMPLEX CHARGE TRANSFERS BETWEEN INORGANIC AND ORGANIC INTERFACES.** Alex D.Q. Li, Department of Chemistry and Materials Research Center, Washington State University, Pullman, WA; Lin Song Li and Quanyi Jia, Los Alamos National Laboratory (MST-STC), Los Alamos, NM.

We developed a new chemical solution technology that enabled us to

process ceramic thin films with convenience and flexibility required in materials fabrication. In this paper, we prepared thin films of ruthenium oxides and titanium oxides using this chemical solution deposition technique. Conjugated polymers such as poly(thiophene) were then deposited on such substrates and interfacial charge transfers were studied. The current-voltage relationship (I-V) as functions of electronic structures of the thin film materials was discussed. In addition, Kelvin probe was used to reveal complex charge transfer mechanisms at the inorganic and organic interfaces.

#### **DD12.14**

**INTERMITTENT-CONTACT ATOMIC FORCE MICROSCOPY REVEALS FRICTION ANISOTROPY IN POLY(DIACETYLENE) MONOLAYERS.** Matthew S. Marcus, Robert W. Carpick, University of Wisconsin-Madison, Madison, WI; Darryl Y. Sasaki, Sandia National Laboratories, Albuquerque, NM; M.A. Eriksson, University of Wisconsin-Madison, Madison, WI.

Materials with anisotropic properties are widely exploited in mechanical, optical, and electronic applications. Poly(diacetylene) (PDA) monolayer films exhibit highly anisotropic friction that is associated with the in-plane alignment of its polymer backbone. We show here that phase contrast in intermittent contact (IC) AFM reveals the friction anisotropy of PDA monolayers. IC AFM is extensively used as an effective probe of surface topography, composition, and elasticity, particularly for polymer surfaces. However, the ability to use IC AFM to discern variations of in-plane properties, such as friction and molecular structure, has not been previously reported. Our observations are surprising, because most previous interpretations of IC AFM images neglect any contribution due to friction. In our experiments we acquire phase images in constant amplitude IC AFM. We observe a constant phase within individual crystalline PDA domains. We observe a phase difference between neighboring domains that is proportional to the corresponding difference in friction. We propose that this phase contrast results from sliding between the tip and the polymer sample along the cantilever's axis. This sliding is a consequence of the cantilever's tilt angle and can be explained by analyzing the mechanics of the cantilever's oscillation and its interaction with the surface. Our modeling suggests that sliding between the tip and the sample is a very common phenomenon for many materials including polymers. Such sliding should generally be considered in interpreting IC AFM images, and it also offers opportunities to study in-plane properties such as friction and polymeric structure, previously thought to be inaccessible to IC AFM.

This work supported by NSF and Research Corporation.

#### **DD12.15**

**SYNTHESIS AND PROPERTIES OF POLY-P-PHENYLENE FILMS DEPOSITED ON Au AND ITO ELECTRODES.** Debora Goncalves, Univ Sao Paulo, Inst Fisica de Sao Carlos, Sao Carlos, SP, BRAZIL; Eugene A. Irene, Univ North Carolina at Chapel Hill, Dept of Chemistry, Chapel Hill, NC.

The use of poly-p-phenylene (PPP) as active layer on light-emitting devices has been limited by the low solubility of its pure form when chemically synthesized. Electrochemical means of synthesis of PPP deposited directly on the electrode surface provides an alternative method although severe experimental conditions are necessary to oxidize starting materials such as benzene. Biphenyl oxidizes at a lower potential as compared with benzene, but acidic media are still used for its oxidation. In this work, the electrochemical polymerization of biphenyl was investigated in acetonitrile and tetrabutylammonium tetrafluoroborate on Au and ITO (indium-tin oxide glass-coated) electrodes. Although tetrabutylammonium tetrafluoroborate has been extensively used for preparing PPP films, it was verified that this electrolyte salt is not suitable for use with Au, because an effect of substrate dissolution occurs during the electropolymerization of biphenyl. A higher acidity of the medium modifies even more the Au electrode surface as noticed after adding small amounts of sulfuric acid to the electrolyte solution. The polymerization of biphenyl works well using tetrabutylammonium tetrafluoroborate / without acid on ITO, but for Au, the exposure of Cr used as an adhesion layer occurs as verified by X-ray photoelectron spectroscopy (XPS). Although an organic film grows on the Au surface, dissolution and polymerization steps are competitive. The optical properties of these films were investigated by spectroscopic ellipsometry and compared with those of Au and Cr films.

#### **DD12.16**

**SYNTHESIS OF TPD-CONTAINING POLYMER THIN FILMS BY PHYSICAL VAPOR DEPOSITION.** Hiroaki Usui, Terufumi Yoshioka, Takahiro Katayama, Kuniaki Tanaka, Hisaya Sato, Dept of Material Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo, JAPAN.

Polymeric thin films play important roles in the recent development of

organic electronic devices such as the light emitting diode (LED). Physical vapor deposition, which is frequently used for small molecules, has the advantage of preparing uniform thin films without the problems coming from the solvents. We have shown that thin films of vinyl polymers can be prepared by depositing the acrylate monomers by the ionization-assisted method. This method was applied for the preparation of semiconducting polymer thin films containing tetraphenyl diaminobiphenyl (TPD). TPD derivative acrylate monomer (TPD-ac) was evaporated in high vacuum and deposited on ITO-coated glass substrates. The deposition source is equipped with a hot-cathode filament, which emits electrons for activating the evaporated molecules. IR absorption spectra and GPC analysis showed that the electron bombardment to the evaporated material works efficiently to initiate the polymer formation on the substrate surface, while the simple evaporation produced films consisting of only the monomers. The polymer yield increased from 20 to 50% by increasing the electron emission current from 0.1 to 15 mA. The number-averaged molecular weight was around 5000, and was not largely influenced by the emission current. The polymerization reaction proceeded even on room temperature substrate, but was enhanced by increasing the substrate temperature. At the substrate temperature of 110°C, the polymer yield was 76% and the molecular weight was 12000. LEDs were prepared by depositing Alq<sub>3</sub> emissive layer on the TPD-ac hole-transport layer. The device performance was improved with increasing substrate temperature for the TPD-ac deposition. The luminance was 2860 cd/m<sup>2</sup> at 14.5 V for room temperature substrate, and was 4310 cd/m<sup>2</sup> at 12.5 V for the substrate temperature of 110°. These results show that the ionization-assisted method can be a promising technique for preparing polymeric thin films.

#### **DD12.17**

**EMISSION LIGHT FROM PRISM/SILVER/MOLECULAR ULTRATHIN FILMS AND EXCITATIONS OF MULTIPLE SURFACE PLASMONS IN ATR KRETSCHMANN CONFIGURATION.** Futao Kaneko, Takayuki Nakano, Kazunari Shinbo, Keizo Kato, Takahiro Kawakami, Niigata University, Dept of Electrical and Electronic Eng, Niigata, JAPAN; Takashi Wakamatsu, Ibaraki National College of Tech, Dept of Electrical Eng, Hitachinaka, JAPAN.

Emission light from the Kretschmann configuration of prism/ Ag thin film/ molecular ultrathin films has been investigated using the attenuated total reflection (ATR) method and direct irradiation of a laser beam from air to the film. Rhodamine-B (RB) Langmuir-Blodgett (LB) films of ten monolayers were deposited on cover glasses with evaporated Ag films of about 50 nm thick. RB is a well-known laser dye and was mixed with arachidic acid (C20) for better deposition, of which the molar ratio was [RB]: [C20] = 1:5. The sample was located on the bottom of a half-cylindrical prism. ATR properties have been measured at various wavelengths of laser beams for the Kretschmann configuration, and the dispersion property was obtained from the wavelengths of the lasers and the resonant angles of surface plasmons (SPs). Emission light through the prism was observed when a p-polarized Ar ion laser beam at 488 nm was directly irradiated to the sample surface. Spectra of the emission light were measured as a function of the emission angle where the light was observed, and the spectra strongly depended upon the emission angle. Furthermore, emission light through the prism was also observed when the SP was resonantly excited in the ordinary ATR method using a p-polarized Ar ion laser beam at 488 nm. The spectra also depended upon the emission angle. The relations between the peak wavelength of the spectra and the emission angles corresponded to one of the resonant excitations of SPs in the ATR configuration. It was concluded that the emission light was caused by multiple excitations of SPs. It is thought that the phenomenon will be used as a new sensing device.

#### **DD12.18**

**WAFER BONDING USING DIELECTRIC POLYMER THIN FILM IN 3D INTEGRATION.** Yongchai Kwon, Jian-Qiang Lu, Russell P. Kraft, John F. McDonald, Ronald J. Gutmann and Timothy S. Cale, Focus Center - New York, Rensselaer: Interconnections for Gigascale Integration, Rensselaer Polytechnic Institute, Troy, NY.

Wafer bonding of fully processed 200 mm wafers is a key challenge of the monolithic 3D IC integration. Intimate contact over the entire wafer is required in addition to compatibility with both conventional BEOL processes and subsequent thinning and inter-chip interconnection. Our wafer bonding process using dielectric polymer glue does not involve high temperature, high pressure or electrical bias. Therefore, the required processes are compatible with conventional IC fabrication. The major desirable properties of the bonding glue include: (1) seamless cohesion of the polymer glue interface and good adhesion of the interface between the glue film to the substrate to prevent delamination or crack formation; (2) stability over a range of BEOL processing conditions, requiring a high glass

transition temperature and a rigid structure after bonding; (3) no outgassing during the bonding process; and (4) ability to deposit the glue in thin film to minimize the aspect ratio inter-chip interconnect. The candidates under evaluation are spin-on polymers (e.g., Flare, MSSQ, BCB and HSQ), and vapor deposited polymers (e.g., Parylene-N). Various methods are used in evaluating alternate polymer glues and process conditions. The bond strength is evaluated using razor blade method, contact angle method and pulling test or by CMP or mechanical grinding. Our experiments show that the fraction of bonded area and the bond strength depend on the process temperature, the applied pressure and the ramp rates of both temperature and pressure. With Flare as the glue film, the bond between two wafers was sufficiently strong to withstand large mechanical stress. A large void-free bonded area was obtained. Primary results with thermal cycling and backside grinding indicate that the wafers are well bonded mechanically. Experimental conditions, analyses of bonding results and bonding mechanisms using dielectric polymer thin films will be presented.

#### **SESSION DD13: LITHOGRAPHIC, ELECTRONIC PROPERTIES**

Chairs: John A. Rogers and George G. Malliaras  
Friday Morning, November 30, 2001  
Constitution B (Sheraton)

#### **8:30 AM \*DD13.1**

**CHARGE INJECTION AT THE METAL/ORGANIC INTERFACE.** Yulong Shen, Ken Diest, Man Hoi Wong, George Malliaras, Cornell University, Materials Science and Engineering Dept, Ithaca, NY.

Organic semiconductor films are being considered as active layers in a variety of optoelectronic devices that include light emitting diodes, thin film transistors, photovoltaic cells and photorefractives. The performance of these devices is critically dependent on injection of charge from metal electrodes into the organic semiconductor. Despite the enormous technological interest, the fundamentals of the injection process are not understood in any real detail. We discuss recent electrical measurements that illustrate some unique features of charge injection at the metal/organic interface. Using the contact between Indium Tin Oxide (ITO) and triphenyl diamine doped polycarbonate (PC:TPD) as an example, it will be shown that the injection-limited current in organic semiconductors is proportional to their charge carrier mobility. Data from electrical measurements will be disseminated according to a recent model based on hopping transport. A way to improve injection at metal/organic contacts will be presented and its implications in the performance of organic light emitting diodes will be discussed.

#### **9:00 AM DD13.2**

**STRUCTURE OF MACROMOLECULES IN LITHOGRAPHIC COATINGS.** Ronald L. Jones, Christopher L. Soles, Eric K. Lin, Joseph L. Lenhart, Wen-li Wu, National Institute of Standards and Technology, Gaithersburg, MD; Dario L. Goldfarb, Marie Angelopoulos, IBM T.J. Watson Research Center, Yorktown Heights, NY.

The push to write increasingly smaller lithographic features will soon reach macromolecular size, yet the effects of feature size on 3-dimensional chain conformation have yet to be reported experimentally. Understanding the thickness dependence of chain conformation in a confined neutral polymer is the first step to reduce line edge roughness (LER) thereby enabling even smaller patterns as required by the semiconductor industry. We report novel measurements of the 3-dimensional chain conformation in neutral polymer films where the thickness is on the order of the molecular dimensions using a combination of small angle neutron scattering (SANS), neutron reflectivity (NR), and x-ray reflectivity (XRR). This extension of prior work on 2-dimensional chain conformation in thin films represents the first direct measurements of 3-dimensional chain conformation in thin films. The chain dimensions parallel to the substrate are independent of the overall film thickness, D, while the dimensions perpendicular to the substrate decrease as the film thickness reaches the molecular diameter ( $\approx 2R_G$ , where  $R_G$  is the bulk molecular radius of gyration). For  $D \approx 2R_G$ , the perpendicular structure undergoes a small reduction in size, however the overall average shape is consistent with Gaussian statistics. Further reductions to sub- $R_G$  dimensions induce a non-Gaussian shape. The origins of these shape transitions are further explored using off-specular neutron reflectivity and x-ray reflectivity, and data are compared to theoretical predictions using finite size theory. Finally, the changes in chain conformation are discussed in terms of preliminary measurements of feature dissolution and mechanical properties.

**9:15 AM DD13.3**

FUNCTIONALIZED PERFLUOROPHENYL AZIDES FOR THE COVALENT IMMOBILIZATION OF POLYMER THIN FILMS AND ARRAYS. Mingdi Yan, Michele Bartlett, Portland State University, Portland, OR.

Silane-functionalized perfluorophenyl azides (PFPA) were synthesized for the covalent immobilization of polymer thin films on silicon wafers. Silanization of the wafer surface with PFPA introduced a monolayer of azido groups which in turn covalently bound to polymer films by way of photochemically-initiated reactions. Characterization of the immobilized films with XPS, ellipsometry, contact angle measurements will be presented. Using this method, patterned polymer films and arrays were generated by way of photolithography. These arrays displayed not only spatial features, but also unique surface topographies.

**9:30 AM DD13.4**

THE STRUCTURE OF STRETCHED NaFion. S.F. Trevino, US Army Res. Lab., APG, MD; CNR, NIST, Gaithersburg, MD; Sandra K. Young, Nora Beck-Tan#, US Army Res. Lab., APG, MD. #Present Address: W.L. Grace & Associates, Elkton, MD.

The structure of Nafion, a perfluorosulfonated ionomer, has been the subject of many studies. The methods of Small (SAXS) and Wide (WAXS) Angle X-Ray and Small Angle Neutron (SANS) scattering have been used there. Three principle features in the small angle scattering pattern have been observed. A peak at  $ca\ Q \approx 0.2\ \text{\AA}^{-1}$  is attributed to the clustering of the acid groups (ionomer peak), that at  $Q \approx 0.03\ \text{\AA}^{-1}$  to crystalline regions, and an upturn in intensity at the smallest  $Q$  to large-scale heterogeneities. Some of these works have included samples that have experienced moderate strains by mechanical elongation. In those works, the effect on the ionomer peak has been studied. The WAXS studies lead to a model of the packing of the polymer molecules and the SAX and SANS studies to models of the packing of the ionic clusters. In the present work, neutron diffraction pole figures and SANS measurements on elongated samples of Nafion have been used to obtain data sufficient for the proposal of a model of the structure of the material. The samples studied were elongated at two temperatures, 25 and 150°C. Although many of the scattering features of these two samples are similar, that stretched at 150°C contains new information concerning the nature of the crystalline region. The combination of the pole figure and SANS data lead to a coherent model for the structure of Nafion

**9:45 AM DD13.5**

CONDUCTING POLYMER - ELECTROLYTE BILAYERS INCLUDED IN NOVEL ELECTROCHEMICAL DEVICES. David Nilsson, Miaoxiang Chen, Linköping Univ, Dept of Sci and Tech, Norrköping, SWEDEN; Magnus Berggren, Thomas Kugler, Linköping Univ, Dept of Sci and Tech and ACREO, Norrköping, SWEDEN; Tommi Remonen ACREO, Norrköping, SWEDEN.

Based on solidified electrolytes in combination with the conducting polymer PEDOT:PSS we have realised novel electrochemical devices. We will report on current amplification and rectifying devices together with charge storage devices. Based on these basic devices we have realised simple electronic systems. From these we have realised simple oscillators, smart pixel circuitry for displays and sensors. Especially, we will present the nature of the coupling between ions and electrons here representing the key function utilised in the various electrochemical devices. In PEDOT:PSS both the reduced and oxidised state have conductivity enough to offer fast switching and response in different lateral electrochemical device architectures. We will stress aging, device stability and reproducibility in the devices. Also, due to that electrochemistry is used for device function no very small or narrow dimensions are needed in the devices. This offers a possibility to manufacture the devices using printing techniques. We will also present the different printing routes possible to use for realising the electrochemical devices.

**10:30 AM \*DD13.6**

PRINTED ORGANIC ELECTRONICS AND MOLDED POLYMERS FOR INTEGRATED OPTICS. John A. Rogers, Kirk Baldwin, Zhenan Bao, Julia Hsu and Lynn Loo, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

We describe the successful application of high resolution printing and molding techniques to two classes of systems that incorporate thin films of organic materials: plastic electronics and integrated optical components. The simplicity of these methods and the good performance of devices formed with them suggest their potential utility for emerging applications of organic materials in optics and electronics. We also demonstrate how they can be used to form new types of devices - rubber photonic crystals and electronic paper displays - that cannot be constructed easily using other means or materials.

**11:00 AM DD13.7**

PROCESSING OF POLYMERS TO THIN FILMS AND MULTILAYERS USING AN ION BEAM TECHNIQUE. Robert Saf, Marian Goriup, Gertraude Hayn, Franz Stelzer, Graz University of Technology, Institute for Chemistry and Technology of Organic Materials, Graz, AUSTRIA; Klaus Reichmann, Jürgen Besenhard, Graz University of Technology, Institute for Chemical Technology of Inorganic Materials, Graz, AUSTRIA; Ulli Scherf, University Potsdam, Institute for Physical Chemistry, Potsdam, GERMANY; Egbert Zojer, Graz University of Technology, Institute for Solid State Physics, Graz, AUSTRIA.

The processing is a very important aspects in material science. Its well known that optimal utilization of the intrinsic potential of functional materials can only be achieved after appropriate processing. Techniques used to produce thin films or multilayers of polymers are for example spin-coating, electrostatic layer by layer self-assembly, or special types of coextrusion. Each method has individual drawbacks, e.g. spin-coating has limitations concerning the area. The production of thin films and multilayers using an ion-beam technique will be presented. The technique is based on the electrostatic process. Initially solutions of polymers are dispersed into charged micro-droplets. In contrast to various types of electrostatic painting or processing by ink-jet these droplets are not deposited, they are appropriately dried to produce single or multiple charged ions. The resulting ion-beam can be directed towards conductive as well as isolating targets using electrostatic lenses. The technique offers the possibility to process organic and inorganic materials, even simultaneously. Additionally, the method circumvents problems of other techniques due to the drying step, works under atmospheric pressure, and is a soft method where no significant chemical modification occurs. The examples will focus on multilayers (thickness of individual layers: 20 to 100 nm) of standard polymers (PMMA, PS) as well as on multilayers of electroactive polymers (ladder-type poly(para-phenylene), polyfluorene). Additional experiments will be presented, where the technique was used for the deposition of the active layer of an organic light emitting device (LED: ITO / m-LPPP / Al). The device exhibited properties comparable to those where the organic layer was deposited by spin-coating. This result implies, that the technique might generally allow the production of thin films with a quality satisfactory for applications in electro/photoactive devices. The technique also allows structured deposition. The financial support by the Austrian Science Fund (SFB Electroactive Materials) is gratefully acknowledged.

**11:15 AM DD13.8**

SECONDARY ION MASS SPECTROSCOPY STUDY OF FAILURE MECHANISM IN ORGANIC LIGHT EMITTING DEVICES. Lin Ke, Ramadas Senthil Kumar, Keran Zhang, Soo Jin Chua, Nikolai Yakovlev Institute of Materials Research& Engineering, SINGAPORE.

Secondary ion mass spectroscopy is used to examine the dark, non-emissive defects on the organic light-emitting device. 20 different elements have been traced during SIMS experiment. We found that boundary movements are originated from electrode imperfection. Due to flexibility and movability of polymer layer, distribution variations and a more severe Indium and Calcium overlapping are detected in dark spot defect area. Boundary movements are not in good agreement between different layers. Interfaces became undulate. The closeness and proximity between the In sharp peaks and cathode metal protrusion leads to the initial point of dark spot. We demonstrate that the presence of cathode imperfection and interface roughness of different layers correlated to the device dark spot formation. SIMS results prove that ITO and organic interface plays an important role in the whole device failure. Optimization of the ITO:Organic layer interface is also carried out to get a better organic layer adhesion to ITO layer. The optimized device showed enhanced hole injection into the electroluminescent polymer from anode ITO. Modified device has reduced turn on voltage, increased efficiency and inhibited electrical shorts. The dark spot number reduces significantly and the growth rate is much slower. In, C, Ca profiles have been stabilized. AFM experiments were performed on polymer surface showed that PPV became smoother in modified device than in normal device. Our SIMS, microscopy, AFM and I-L-V experiments results confirm that stabilizing the ITO:organic interface is the crucial part in controlling the whole device degradation process.

**11:30 AM DD13.9**

STRUCTURE OF A COMPLEX POLYMER: PERFLUORO-IONOMER AT THE INTERFACE WITH SOLVENTS. Teresa A. Hill, Clemson University, Department of Chemistry, Clemson, SC; Gian Felcher, Argonne National Laboratories, Material Research Division, Argonne, IL; Dvora Perahia, Clemson University, Department of Chemistry and Material Science and Engineering Program, Clemson, SC.

The interfacial zone between thin films of complex perfluoro ion containing (ionomers) polymers and liquids has been studied. These ionomers are of significant technological importance from thin coatings, to fuel cell membranes, to protective clothing. In most of these applications, selective transfer, mostly of water, is desired while the transport of other substances is not. While the membrane or the coating should be able to contain solvent it should remain intact and not dissolve. However once the membrane has terminated its function, it has to be recycled in an environmentally friendly manner. Perfluoroionomers consist of three non-compatible components, a hydrophobic fluorocarbon chain, a relatively polar side chain and an ionic component. This complexity results in structured polymeric films where the control over the structure can determine the properties of the film. The molecular structure and the relative arrangement of the molecules affect the structure of the polymer film. Neutron reflectivity has been used to study the penetration and distribution of octanol and butanol into thin films of  $[(CF_2CF_2)_n(CF_2CFR)]_m$  where  $R = [OCF_2CF_2SO_3(X)]$  and  $X = H$ , (800 equivalent weight). The dry film consists of three distinct regions: a high density at the interface with the silicon oxide, an intermediate layer with constant density and an air-interface layer where the density decreases. When a 100nm film is exposed to linear octanol and butanol, swelling takes place within the first couple of hours, reaching a steady state which changes only slightly as a function of time. All three ranges swell where the air-interfaces layer swells a bit more than the other two regimes. Surprisingly though, while no chemical crosslinks are present in the system, swelling rate decreases drastically after the first 2 hours and the film does not dissolve. As the solvent penetrates, a clear rearrangement of the polymer film takes place.

#### 11:45 AM DD13.10

STRUCTURAL CHARACTERIZATION OF NOPOROUS PMSSQ THIN FILMS. G.Y. Yang, R.M. Briber, Dept of Materials and Nuclear Engineering, Univ of Maryland, College Park, MD; E. Huang, P.M. Rice, H.C. Kim, W. Volksen, R.D. Miller IBM Almaden Research Center, San Jose, CA.

The semiconductor industry roadmap requires the next generation of interlayer dielectric materials to have a dielectric constant  $k$  below 2.0 and thermal stability to 500°C. Porous poly(methylsilsesquioxane) (PMSSQ) with a  $k$  less than 2.0 is an attractive potential material. Such materials can be obtained by incorporating air into the PMSSQ matrix in the form of nanometer sized pores. A film was prepared by dissolving the matrix precursor materials (MSSQ monomer and oligomer mixture) and porogen (coPMMA) as a template for creating the pores in a common solvent (propylene glycol methyl ether) and spin cast onto a silicon single crystal substrate. The film is subjected to an initial heat treatment in nitrogen at 225°C to cure the matrix (i.e. polymerize and cross-link) and then a second heat treatment to 375 ~ 450°C to degrade the porogen to form the pores. The pore evolution and characterization are performed using small angle neutron scattering (SANS), transmission electron microscopy (TEM) and neutron reflectivity (NR). In-situ SANS experiments revealed that the pores evolution follows a process of phase separation and burnout of the porogen copolymer. TEM observation shows that pore size, morphology and spatial distribution depend on the concentration of porogen in the original hybrid material. Average pore size increases as a function of porogen concentration. Porous morphology changes from isolated pores at low porogen concentration (<10 wt. %) to fully interconnected pores at higher porogen concentration (>40 wt. %). Percolation threshold is located at ~ 30 wt. % porogen content. Neutron reflectivity is used to study the pore structure and distribution normal to the film thickness.

#### SESSION DD14: NANOPARTICULATE-FILLED FILMS

Chairs: Rigoberto C. Advincula and Michael E. Mackay  
Friday Afternoon, November 30, 2001  
Constitution B (Sheraton)

#### 1:30 PM DD14.1

THE EFFECT OF NANOPARTICLES FILLERS ON DEWETTING DYNAMICS. Sarika Sharma<sup>1</sup>, M.H. Rafailovich<sup>1</sup>, H. White<sup>1</sup>, J. Sokolov<sup>1</sup>, A. Ulman<sup>2</sup>, D. Gersappe<sup>1</sup>, H. Liu<sup>1</sup>. <sup>1</sup>Department of MS&E, SUNY at Stony Brook, Stony Brook NY. <sup>2</sup>Dept. of Chemical Engineering Chemistry and Materials Science, Polytechnic University, Brooklyn, NY.

Producing a stable polymer film is a challenge, since dewetting tends to rupture the film. To overcome this drawback, it is essential to control the factors responsible for stabilizing polymer films during processing. Here, we report on a unique strategy to control the rate of dewetting of thin polymer films by dispersion of various nanoparticle fillers. Optical microscopy, Atomic force microscopy and Transmission Electron microscopy have been used to study the surface and

interfacial structure in the vicinity of growing holes. We have carried out systematic and quantitative dewetting studies of polystyrene (PS) on poly(methyl methacrylate) (PMMA) by adding functionalized fillers like Au, Pd, Clay, POSS, Silica and Carbon black. The rate of dewetting is controlled by the size of the particle and the polymer-particle interaction. The rate of dewetting also depends upon nanoparticle concentration in the film. These results are compared with Molecular Dynamics simulations currently being conducted. As for now, these effects are not theoretically proven, but it is clear that by addition of nanoparticles a combination of equilibrium and kinetic effects can be controlled. Two separate models have been developed to prove the mechanism behind the suppression and expression of the dewetting. The effects presented here promise to be an important means of controlling thin film stability.

The work is supported by in part by a grant from NASA microgravity and NSF-MRSEC program.

#### 1:45 PM DD14.2

DENDRIMERS INHIBIT DEWETTING OF THIN POLYMER FILMS. M.E. Mackay, Y. Hong, M. Jeong, Dept. of Chemical, Biochemical and Materials Engineering, Stevens Institute of Technology, Hoboken, NJ; S. Hong, T.P. Russell Polymer Engineering and Science Department, University of Massachusetts, Amherst, MA; C.J. Hawker, R. Vestberg, IBM Almaden Research Laboratory, San Jose, CA; J.F. Douglas Polymers Division, NIST Gaithersburg, MD.

We show dendrimers inhibit dewetting of thin (50 nm) polymer films spin coated onto silicon wafers. The individual components, poly(benzyl ether) dendrimer and 13 kDa linear polystyrene, exhibit gross dewetting upon heating to 140°C. However, 1 wt% of third generation (G3) dendrimer blended with the linear polymer severely retards dewetting. Interestingly, higher generation (molecular mass) dendrimers do not inhibit dewetting, instead rich patterns are seen remarkably similar to those nucleated by a spinodal mechanism. Greater G3 concentrations produce aged films which are predominantly flat although there is possible evidence of ~ 5 nm high volcano-like features distributed throughout the film surface.

#### 2:00 PM DD14.3

THE EFFECTS OF NANOPARTICLE FILLERS IN POLYSTYRENE FREE STANDING FILMS. Jean H. Xavier, M.H. Rafailovich, J. Sokolov, S. Ge, SUNY Stony Brook, Dept of MS&E, Stony Brook, NY; A. Ulman, C. Yee, Polytechnic Univ, Dept of Chemical Engineering Chemistry and Materials Science, Brooklyn, NY.

Fillers such as colloidal gold, palladium, and 6A exfoliated clay particles were, by weight percent, mixed with monodisperse polystyrene (PS) to control the mechanical properties of free standing polystyrene films. These films are interesting since we can focus only on the rheological properties and can neglect the effects of particle segregation to substrates. The size of fillers was measured using TEM. The surface of the films and the effect of fillers in the glass transition temperature ( $T_g$ ) of polystyrene were investigated with Shear Modulation Force Microscopy (SMFM). In order to measure the visco-elastic response of the film, we nucleated a 100 micron size hole and observed its rate of growth as a function of temperature while annealing in a vacuum of  $10^{-7}$  Torr. For films less than 100 nm the hole opened with constant velocity. For constant temperature and film thickness, the magnitude of the velocity was a function of filler size, aspect ratio, and concentration. When the dimension of the filler was less than the polymer radius of gyration ( $R_g$ ), the particle stabilized the film. However, the hole opening velocity increased with concentration when the particle diameter was larger than the radius of gyration. The interplay between the filler dimension, film thickness, and  $R_g$  will be reported.

Reference:

Physical Review Letter, Vol. 85, 2340-2343, 9/19/2000. S.Ge, M.H. Rafailovich, J. Sokolov.

#### 2:15 PM DD14.4

STRUCTURAL AND MECHANICAL PROPERTIES OF SPUTTERED METAL FILMS ON PAMAM DENDRIMER MONOLAYERS. F.T. Xu<sup>a</sup>, M. Curry<sup>b</sup>, F. Huang<sup>a</sup>, P. Ye<sup>b</sup>, A. Rar, S. Street<sup>b</sup>, J.A. Barnard<sup>a</sup>, Center for Materials for Information Technology, <sup>a</sup>Department of Metallurgical and Materials Engineering, <sup>b</sup>Department of Chemistry, The University of Alabama, Tuscaloosa, AL.

Nanotechnology applications demand the development of thin, flat surface films with well-regulated mechanical and tribological properties. A promising approach for this is metal layer deposition on PAMAM dendrimer underlayers. An improvement in mechanical and tribological properties has been reported for Au, Co and Cr films deposited by evaporation onto self-assembled dendrimer monolayers. In this paper we will discuss the formation of metallic layers on dendrimer monolayers by plasma sputter deposition. We investigate

the "survival" of the dendrimer monolayer after plasma deposition of metal atoms, which have higher kinetic energy than evaporated atoms. The film structure and composition were analyzed by XRR and XPS. The surface morphology of deposited films was observed by AFM. The nanoindentation experiments were done on a Hysitron Nanoscope. Nanoscratch experiments were carried out on a Nanoindenter II. We found a large difference in nanoscratch behavior between the samples with dendrimer monolayer and those without. The detailed morphology of the wear tracks was investigated by SEM and AFM. The composition of the wear trench was explored by scanning Auger analysis.

#### 2:30 PM DD14.5

THE SURFACE GLASS TRANSITION OF POLYMERIC GLASSES PROBED BY THE EMBEDDING OF NOBLE METAL NANOCCLUSERS. J. Erichsen, J. Zekonyte, K. Dolgner, V. Zaporojtchenko, T. Strunskus and F. Faupel, Technische Fakultät der Christian-Albrechts-Universität zu Kiel, Lehrstuhl für Materialverbunde, Kiel, GERMANY.

The temperature dependent embedding process of noble metal nanoclusters into polymers was used to probe the surface glass transition. X-ray photoelectron spectroscopy (XPS) was applied to study the embedding of Au and Cu nanoclusters into polystyrene with different molecular weights and film thickness. In addition the probe size and heating rate was also varied. Our results suggest that the temperature dependence of the embedding depth can be used to determine the glass-transition temperature at the polymer surface. We found a depression of the surface glass transition temperature compared with the glass transition of the bulk sample measured with DSC. The influence of molecular weight, film thickness, heating and cooling rate on the surface glass transition temperature was determined. Irradiation of the polymer surface with argon ions increases the surface glass transition temperature even at small applied doses and at low energies.

#### 2:45 PM DD14.6

POLYPROPYLENE-FUNCTIONALIZED PROBES FOR SCANNING FORCE MICROSCOPY. L. Gonzalez-Ronda, Ford Research Laboratory, Dept of Materials Science, Dearborn, MI; S. Kaberline, Ford Research Laboratory, Dept of Chemistry and Environmental Science, Dearborn, MI; E.L. Durieux, Flint Ink Research Center, Dept of Physical Chemistry, Ann Arbor, MI.

Silicon and silicon nitride SFM probe tips have been functionalized with polypropylene (PP) layers by immersion into dilute solution. The immersion process was carefully controlled and monitored using a programmable dynamic contact angle analyzer (DCA) equipped with a microbalance and a motor capable of speeds ranging from 2-24 um/s. Probes were submitted to treatment with ozone prior to coating to eliminate surface contamination, particularly silicone oils, resulting from commercial packaging methods. The chemical composition of the tip surface before and after the cleaning and coating processes was analyzed by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS); cleaned and coated probes were stored in ozone-treated glass containers. The three-dimensional tip shape and dimensions before and after coating were evaluated by scanning the sharp features of a Ti sample and analyzing the resulting images with Digital Instruments' tip evaluation software package. The resulting estimates for tip shape and fitted diameter correlated well with those obtained by scanning colloidal gold spheres 5-35 nm in diameter (Venseka et al., Biophys. J 65, 992 (1993)). Calculated coating thicknesses ranged from 5-20 nm, with the thicker coatings showing a larger degree of non-uniformity. Repeated scanning of the Ti samples showed no evidence of damage to the PP coating, although some elastic deformation may occur in thickly coated probes. The suitability of dip-coated probes for evaluating interactions between polymer surfaces will be discussed.

#### 3:30 PM DD14.7

GOLD NANOPARTICLES IN POLYMERIC MATRIX: EVOLUTION, DIFFUSION, AND INTERACTIONS. Kwanwoo Shin, Howard Wang, Sushil K. Satiya and Charles C. Han, National Institute of Standards and Technology, Gaithersburg, MD.

The systems composed of polymeric materials and metallic nanoparticles are currently attracting much interest in electronics and nanotechnology. To control the morphology of these composite materials, the interactions between to polymer-gold nanocomposites must be understood. In this study, an ultra thin gold layer (<7nm) has been deposited on a polystyrene thin films (dPS) and then covered by another PS thin layer (hPS). We performed a series of X-ray and neutron reflectivity to characterize the gold and polymer layers as a function of annealing time. At the initial stage, the gold layer starts to break and evolves gradually to be spherical nanoparticles over time. At the later stage, the movements of the polymer chains and the gold nanoparticle are monitored independently. We will present the

studies of the mutual diffusion of the deuterated/hydrogenated PS bilayer, which initially separated by a thin gold layer and the motion of the gold by X-ray and neutron reflectivity.

#### 3:45 PM DD14.8

CONTROL OF POLYMER BLEND MORPHOLOGY USING NANOPARTICLES. Wenhua Zhang, Yantian Wang, H. White, M. Rafailovich, J. Sokolov, State University of New York at Stony Brook, NY; R. Tenne, Weizmann Institute Rehovith, ISRAEL; A. Ulman, M. Shafi Brooklyn Polytechnic University, NY; Steven Schwarz, Queens College, NY; A. Winesett, H. Ade, North Carolina State University, NC.

The effect of filler aspect ratio on polymer blend compatibilization was investigated using a variety of complementary imaging methods. Both the equilibrium conformation and dynamics were studied. The particles used were functionalized WS2 nanotubes and Cloisite 6A clay. TEM was performed to determine the location of the tubes and the degree of exfoliation of the clay. The STXM results show that phase segregated domain are immediately formed after spin casting. Upon annealing the domain shrinks with annealing time reaching an equilibrium configuration which is mostly a function of the filler concentration. SANS results show that after annealing the PS-PMMA/Clay samples have domain size smaller than 700A. Micro DSC result shows a new TG implying the formation of a compatibilized PS-PMMA phase.

#### 4:00 PM DD14.9

EFFECT OF INTERFACIAL REACTION BETWEEN GRAPHITE AND POLYMER TO THE PROPERTIES OF THE POLYSTYRENE/GRAPHITE HYBRID PREPARED BY IN SITU ANIONIC POLYMERIZATION. Min Xiao, Jingjing Liu, Kecheng Gong, Polymer Structure & Modification Res. Lab, South China University of Technology, Guangzhou, PR CHINA; Luyi Sun, Department of Chemistry, University of Alabama, Tuscaloosa, AL.

Polymer and layered clay hybrids have received special attentions because of their various advantages in comparison to the traditional polymer composites. The interfacial effect between the silicate layers and matrix polymers is a key factor leading to high performances of the composites. Graphite is a layered material with good electrical and thermal conductive properties. Although more than 100 kinds of graphite intercalation compounds (GICs) have been synthesized, few polymer/graphite nanocomposites have been reported. In our previous work, we synthesized polymer/graphite oxide intercalation compounds, and then obtained polymer/graphite nanocomposites by the reduction of graphite oxide[1-3]. Recently, Shioyama[4] reported delaminated graphite/polymer composite made by alkali metal-GICs initiated unsaturated hydrocarbon vapor polymerization. Their interest focused on the reaction site and reaction activity, while less attention was paid to the graphite/polymer interfacial interaction. In this paper, graphite/polystyrene composite is made by in situ polymerization of styrene in a tetrahydrofuran (THF) solution of potassium(K)-THF-GIC. K-THF-GIC is proved to initiate polymerization of styrene by the anionic mechanism. Various analytical methods such as XRD, TEM, DMA and TGA et al are used to characterize the structure of the composite and to analyze the interfacial interaction between graphite and polymer. Due to the interfacial effect, the composite exhibits higher glass transition temperature, increased thermal stability compared with the polymer matrix. The low percolation threshold in electrical conductivity and the variation of the contact angle of water at the surface of the composite also demonstrate a strong interfacial reaction between graphite layers and the polymer matrix.

#### 4:15 PM DD14.10

GRAFTING OF POLYMERS TO SOLID SURFACES USING SELF-ASSEMBLED MONOLAYERS WITH POLYMERIZABLE GROUPS. Daniel Mäde, Oswald Prucker and Jürgen Rühle, IMTEK - Institute for Microsystem Technology, University of Freiburg, GERMANY.

This paper aims at a more fundamental understanding of the relevant processes involved during the formation of a monolayer of covalently attached polymers formed by copolymerization of immobilized monomers with other monomers in solution. This type of grafting reaction is known for a long time but usually only the increase of the grafted amount of polymer was determined as a function of polymerization time. Consequently, not much is known about the overall mechanism and kinetics of the system. We studied a system that uses immobilized methacrylate groups as anchoring sites for growing polystyrene chains. We will present data from experiments where important reaction parameters such as monomer and initiator concentrations and conversions were systematically varied and the influence on the graft density of the resulting layers was determined. The results are discussed and mechanistic model for the overall process is presented.

**4:30 PM DD14.11****ANIONIC SURFACE INITIATED POLYMERIZATION (SIP) ON SURFACES: SYSTEMS AND STRATEGIES TOWARDS POLYMER BRUSH ARCHITECTURES AND NANOPARTICLE SURFACES.**

Qingye Zhou, Jimmy Mays, and Rigoberto Advincula, Department of Chemistry, University of Alabama at Birmingham Birmingham, AL.

We report the development of surface initiated polymerization (SIP) on SiO<sub>x</sub> surfaces primarily by living anionic polymerization of styrene. Activated 1,1-diphenylethylene (DPE)-chlorosilane initiation sites were formed by self-assembled monolayers (SAM) on silicate surfaces. We have investigated the different parameters affecting the polymerization mechanism. We have characterized these films by contact angle measurements, atomic force microscopy (AFM), FTIR, X-ray photoelectron spectroscopy (XPS), and ellipsometry. Different initiators, reaction condition, and substrate systems highlight the unique aspects of this procedure compared to free-radical, TEMPO, and ATRP polymerization systems. The initiator activation, surface energy, monomer aggregation, and diffusion all play an important role in this unique system. We are currently pursuing block copolymer grafting strategies on surfaces. As model studies, we need to distinguish the concept of surface initiation from our eventual goal, which is initiation and polymerization on particle surfaces.

**4:45 PM DD14.12****POLYMERIZATION OF POLY(ITAICONIC ACID) ON SURFACES BY ATOM TRANSFER RADICAL POLYMERIZATION IN AQUEOUS SOLUTION.**

Amit Sankhe, Scott Husson, S. Michael Kilbey, II, Dept of Chemical Engineering, Clemson, SC.

Self-assembled monolayers allow interfacial properties to be varied in interesting and useful ways. We have been using self-assembled monolayers as the foundation for growing tethered layers of poly(itaconic acid) (PIA) via surface-confined, living radical polymerization. PIA is interesting because it scavenges cationic dyes and metal ions from solution. In this presentation we will describe the structural evolution of surface-tethered PIA layers grown from hydroxyl-terminated SAMs capped with 4-(chloromethyl)-benzoyl-chloride. This polymerization initiator molecule and a copper-based organometallic complex allow tethered PIA chains to be grown at room temperature in aqueous solution. Ellipsometric studies and FTIR spectroscopy confirm the presence and growth of the surface-tethered PIA layer. We will describe how changing the molar ratio of catalyst-to-initiator and the surface density of polymerization initiation molecules alters the layer growth, and demonstrate, via FTIR spectroscopy, that these surface-tethered layers do bind cationic dyes through ion-exchange mechanisms.