Segmental Interpenetration at Polymer-Polymer Interfaces**Final Report**

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Summary of Research

The support of the Department of Energy, Office of Basic Energy Sciences, initiated funding of the research of this PI under a project that dealt strictly with the investigation of diblock copolymers at the interface between two homopolymers. This initial effort was completed and met with tremendous success including the development of neutron reflectivity and dynamic secondary ion mass spectroscopy methods to examine copolymer composition profiles at interfaces. These studies were augmented by theoretical, simulation and experimental methods. The combination of these different methodologies yielded a quantitative picture of copolymer interfacial segregation.

The projects then took several different courses owing to results from this initial funding period. In particular, research on the interfacial behavior of copolymers led directly into the behavior of copolymers on solid surfaces, the effects of surface confinement on block copolymers, the mobility of polymers at a free surface and in thin films and, ultimately, to the modification of surfaces to manipulate copolymer morphology, the most recent thrust of the research project. Each of these accomplishments has been outlined in the yearly summaries of the research submitted to the Department of Energy.

Provided below are the accomplishments of the research during the 1996 period. In addition, a list of publications resulting from this work is given.

Local Control of Microdomain Orientation in Diblock Copolymer Thin Films With Electric Fields

Local control over the domain orientation in diblock copolymer thin films can be obtained by the application of electric fields on micrometer length scales. Thin films of an asymmetric diblock copolymer of polystyrene and polymethylmethacrylate, denoted P(S-b-MMA), having a cylindrical methylmethacrylate microdomains were prepared by spin coating toluene solutions of the copolymer onto substrates previously patterned with planar electrodes. The substrates, 100 nm thick silicon nitride membranes, allowed direct observation of the electrodes and the copolymer domain structure by transmission electron microscopy. The cylinders aligned parallel to the electric field lines for fields exceeding 20 kilovolts per centimeter, after annealing at 250C in an inert atmosphere for 24 hours. The technique has potential applications in nanostructure fabrication.

NEXAFS Studies on the Surface Orientation of Buffed Polyimides

Near edge x-ray absorption fine structure (NEXAFS) spectroscopy has been used to determine the average orientation of chains in a buffed polyimide film.

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Auger and total electron yield measurements provide powerful and direct means of determining the orientation of chains as a function of depth. In the case of a strongly buffed sample, the polyimide chains at the film surface are found to be highly aligned along the buffing direction. A significant alignment of the phenyl rings parallel to the surface was, also, found. The chain orientation was found to decay as a function of distance from the surface, becoming random in the bulk. The $1/e$ alignment depth was found to be 10nm. Studies as a function of load applied during buffing and the distance of buffing show that the near surface orientation saturates at relatively small loads and short distances. The $1/e$ buffing load and buffing distance for the near surface alignment were found to be 1.2g/cm² and 67 cm, respectively.

Polymer Mobility in Thin Films

The lateral diffusion of polymer chains in thin films was investigated by fluorescence recovery after pattern photon bleaching as a function of film thickness. Thin films of polystyrene labeled with a fluorescent dye were spin coated from toluene solutions onto patterned surfaces. Photolithographic methods were used to prepare surfaces with 2 mm chrome lines separated by 2 mm. Spin-on glass was then used to planarize the surface. The thickness of the polystyrene film was changed by changing the concentration of the spinning solution. For film thicknesses greater than 150 nm, the measured diffusion coefficient was identical to that found in bulk samples. However, as the film thickness was decreased from 150 nm, a nearly linear reduction in the lateral diffusion coefficient was found. This result was quite surprising in that this thickness corresponds to the contour length of the polymer chain. These results also demonstrate the long range ability for a surface to perturb the motion of a polymer chain.

A Monte Carlo Simulation of Asymmetric Random Copolymers at the Interface of Immiscible Homopolymers

The distribution of a random copolymer P(A-r-B) at the interface between immiscible A and B phases as a function of the copolymer composition and the segmental interactions was studied by lattice Monte Carlo simulations. A symmetric distribution of the copolymer was found for compositionally symmetric chains when the segmental interaction parameter was independent of concentration. An asymmetric distribution of the copolymer was found for a compositionally asymmetric copolymer with composition independent segmental interactions. It was found that a symmetric distribution of the compositionally asymmetric copolymer can result only when the segmental interaction parameter is allowed to depend upon concentration. Such a symmetric distribution of a compositionally asymmetric copolymer is in qualitative agreement with miscibility, neutron reflectivity and adhesion studies in the polystyrene/poly(methyl methacrylate) system.

Interfacial Segregation in Disordered Block Copolymers: Effect of Tunable Surface Potentials

The response of disordered block copolymers of polystyrene PS and poly(methyl methacrylate) PMMA diblock copolymers, denoted P(S-b-MMA) to variable strength surface fields has been studied by neutron reflectivity. Surface interactions were controlled by end grafting P(S-r-MMA) random copolymers with various styrene content onto Si substrates. The degree of interfacial segregation of the block

copolymer was proportional to the surface potential. A first order transition in the degree of segregation was observed as the brush composition was varied. Conditions were found which yielded neutral boundary conditions simultaneously at the vacuum and substrate interfaces.

Free Surface Confinement of Block Copolymer Multilayers

Thin films of symmetric diblock copolymers self-assemble into multilayered structures due to the strong interactions of one of the blocks with the substrate and/or free surface. If the film thickness, t , is not an integral or half integral multiple of the bulk period, L_0 , depending upon the boundary conditions, then islands or holes with a step height of L_0 will form to relieve the frustration imposed by the film thickness. It was shown that a well ordered multilayer can form prior to the formation of a surface topography with a period that deviates significantly from L_0 . This structure can be stable for weeks. Topographic features eventually appear on the surface, however, allowing the period to attain its equilibrium value. This indicates that free surface confinement is a kinetic, rather than equilibrium, effect. Confinement of compressed periods is much more effective than for expanded periods, indicating that the activation barrier for the nucleation of holes is larger than that for islands.

Publications Resulting From DOE Support

- Entanglements at Polymer Surfaces*, H.R.Brown & T.P.Russell, *Macromolecules*, 29, 798 (1996).
- Well Defined Random Copolymers by a "Living" Free Radical Polymerization Process*, C.J.Hawker, E.Elce, J.Dao, W.Volksen, G.C.Barclay & T.P.Russell, *Macromolecules*, 29, 2686 (1996).
- Observed Surface Effects in Confined Block Copolymers*, G.J.Kellogg, D.G.Walton, A.M.Mayes, P.Lambooy, T.P.Russell, P.D.Gallagher & S.K.Satija, *Phys. Rev. Lett.*, 76, 2503 (1996).
- Neutron Reflectivity Measurements of Homopolymer Interfaces*, R.Kulesekere, H.Kaiser, J.F.Ankner, H.R.Brown, C.J.Hawker, T.P.Russell & A.M.Mayes, *Physica B*, 221, 306 (1996).
- On the Reflectivity of Polymers: X-Rays and Neutrons*, *Physica B*, 221 267 (1996).
- Homopolymers Interfaces Reinforced With Random Copolymers*, R.Kulesekere, J.F.Ankner, H.R.Brown, C.J.Hawker, T.P.Russell and A.M.Mayes, *Macromolecules*, 29, 5493 (1996).
- NEXAFS Studies on the Surface orientation of Buffed Polyimides*, M.Samant, J.Stohr, H.R.Brown, T.P.Russell, J.M.Sands and S.K.Kumar, *Macromolecules*, 29, 8334 (1996).
- Electric Field Induced Alignment of Diblock Copolymer Ultrathin Films*, T.L.Morkved, M.Lu, A.M.Urbas, E.E.Ehrichs, H.M.Jaeger, P.Mansky and T.P.Russell, *Science*, 273, 931 (1996).
- Polymer Mobility in Thin Films*, B.Frank, A.Gast, H.R.Brown, C.J.Hawker, and T.P.Russell, *Macromolecules*, 29, 6531 (1996).
- A Monte Carlo Simulation of Asymmetric Random Copolymers at an Immiscible Interface*, G.D.Smith, R.Kulesekere, J.F.Ankner, H.Kaiser and T.P.Russell, *Macromolecules*, 29, 4120 (1996).
- Characterizing Polymer Surface and Interfaces*, T.P.Russell, *Mat. Res. Soc. Bull.*, 21, 49 (1996).