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Polymers at Engineered Interfaces

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DOE Patent Clearance Granted
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Final report for grant **: DE-FG02-93ER45481**

Dear Dr. Kelley:

Please find below a final report summarizing research projects completed under the above grant. During the period since the previous progress report (1995), we have made studies of polymer interfaces, self-assembly of micelles at surfaces, phase separation in blends, diffusion and dewetting at and near interfaces and nanomechanical properties of thin films. We also put considerable effort into the planned move of our neutron reflection beamline to another location at the Brookhaven reactor where we would have obtained a ten-fold increase in beam intensity. Due to the permanent shutdown of the reactor, this project must now continue (less conveniently) at other sources our work on polymers under shear and in composites. Three graduate students completed their Ph.D.'s on this work: Z.Li, L.Guo and S.Qu. We also supervised a local high school student, M. Schaeffer, whose research was supported under the grant and who became a westinghouse finalist. Below, please find a brief summary of the main projects:

Dislocations in lamellar diblock structures [1], effects of surface tension. The relationship of islands or holes produced in diblock polymer films of thickness not commensurate with the lamellar spacing and underlying defects was revealed using transmission electron microscopy (TEM) and atomic force microscopy (AFM). The somewhat unexpected result was the finding that the defects were not located at the outermost layer, with an essentially defect-free integral number of layers underneath, but rather were located in inside layers and the distortion was propagated to the surface. The defects are prismatic loop dislocations with a screw component. A classical elasticity model for the surface contours above the defects was compared with AFM observations and good agreement with theory was obtained. However, distortion in deeper layers observed by TEM did not fit the theory well and we argued that the large distortions and resulting

chain stretching near the defects rendered the continuum elastic model inapplicable. Flattening of the surface by surface tension leads to a significant compression of the lamellae near a defect which was shown to lead to a transition from lamellar structure to one with perpendicular cylinders at the edges of the islands or holes produced by the defects.

Compliance measurements and profiles of end-grafted polystyrene in solution observed by atomic force microscopy and neutron reflectivity[2]. We studied P_4VP/PS diblocks strongly adsorbed in toluene solutions to silicon substrates with the short P_4VP block used as the anchor. Force curves from AFM were compared with self-consistent field calculations and related measurements of other groups using the surface force apparatus. The precise structure of the polymer profile in solution was determined by independent neutron reflection measurements (at the now-defunct Brookhaven reactor) allowing us to calibrate the actual polymer compression induced by the AFM tips. We also obtained quantitatively the elastic storage modulus as a function of tip penetration into the polymer layer.

Self-assembly of diblock polymer micelles from solution[3]. A simple and convenient way to form large-area arrays ordered micelles at surfaces was developed. Clean silicon substrates were immersed in a solution of toluene and polystyrene-poly-2-vinylpyridine (PS/P_2VP) diblock and withdraw from the solution after immersion times varying from a few seconds up to 24 hours. Following solvent evaporation, hexagonally ordered micelle structures are observed, having inter-micelle distance varying with the length of the PS/P_2VP copolymer (from 400to 750A for symmetric diblock of molecular weight's 400K up to 1.6M). Using *in-situ* atomic force measurements in the liquid, we established that the ordering is a reversible equilibrium process in highly concerted solutions (present near the end of the evaporation step) and that the ordered structures are not formed in the low-concentration solutions or the original substrate-plus-bath combination.

Dewetting dynamics[5]. Bi-layer samples of immiscible polymers polystyrene (PS) and polymethylmethacryate (PMMA) were annealed in vacuum at T=162C to produce dewetting of the PS layers from the PMMA substrate. Dewetting dynamics were followed by measuring the time development of holes in the PS layer as a function of the molecular weights of both components. For high molecular weight PMMA (330K), dewetting velocities were found to be constant and to scale with PS molecular weight in the same manner as the bulk viscosity, in line with a theoretical prediction of F. Brochard-wyart. Low molecular weight PMMA (27K) behaved as a liquid-like substrate, leading to the dewetting velocities becoming nearly independent of molecular weight, also in accord with theoretical predictions. An interesting, unexplained feature of the data was the appearance of deep trenches in the PMMA layer beneath the growing holes. Further work is in progress to understand this behavior.

Polymers on patterned surfaces[6,9]. Using silicon gratings as model patterned surfaces, the propagation of roughness, surface diffusion, and ordering in polymer layers was studied. For homopolymer, the time-evolution of surface topography was measured by AFM and x-ray scattering. This allowed us to accurately determine surface diffusion coefficient.

Block copolymers which order in layered structures were found to have surface corrugation either in-phase or out-of –phase with respect to the grating. And a theory was developed explaining this behavior as due to a balancing of deformation and interfacial energies.

Flory-Huggins interaction parameter for polystyrene/poly-2-vinylpyridine (PS/P_4VP) blends[8]. We used three independent techniques to measure the interaction parameter in this very highly immiscible polymer blend system: 1) determination of micelle spacings in micro-phase separated films by secondary ion mass spectrometry (SIMS), 2) contact angle of PS droplets formed on P_4VP substrates and 3) interfacial width of PS/P_4VP bilayers determined by neutron reflectivity (NR). Connecting these measurements with the interaction parameter using standard mean-field theory results for strongly segregating systems, we were able to establish that the Flory parameter in this system is an order of magnitude larger than that of any non-ionic blend system.

Phase separation-induced patterns in dPS/PVME and dPEP/PEP blends[10]. We used atomic force microscopy (AFM), neutron reflectivity (NR) and secondary ion mass spectrometry (SIMS) depth profiles of partially miscible blends deposited as thin films (800-2000A thick). In these two systems, the same components segregate to both the substrate interface and free surface and surface-directed spinodal decomposition waves are suppressed. Late stage morphologies were patterns of asymmetric droplets, the aspect ratio of which could be estimated using an argument based on minimization of interfacial free energy.

High-resolution lateral imaging studies of phase separation and dewetting by scanning transmission X-ray microscopy (STXM) and photoemission electron microscopy (PEEM)[11,12,13] (in collaboration with H.Ade, North Carolina State University). We applied the recently developed STXM and PEEM techniques, which employ a finely focused x-ray beam from a synchrotron source, to study the phase behavior of the blend Polystyrene (PS) /brominated Polystyrene (PBrS). Due to the presence or absence of the heavy atom Br, this pair of polymers has excellent contrast for STXM and PEEM allowing us to take full advantage of the techniques' inherent high resolution (better than 1000A). By measuring the near edge absorption fine structure (NEXAFS) for various energies, images could be obtained which were primarily sensitive to a). PS content, b). PBrS content or total polymer content (i.e. thickness) and full three-dimensional profiles could be inferred. Upon annealing thin films of PS/PBrS blends, we observed that PBrS became encapsulated by Ps, making the PS phase continuous for all compositions studied. By showing that PS segregated to both Si substrate and vacuum interfaces, we were able to place an upper limit on the dispersive part of the PBrS-Si interfacial tension of 20.6dyn/cm.

Sincerely yours,

Jonathan Sokolov
Miriam Rafailovich

List of publications supported by Department of Energy.

1. Effects of surface tension on the dislocation structures in diblock copolymers, Y. Liu, M.H. Rafailovich, J. Sokolov, S.A. Schwarz and S. Bahal, *Macromolecules*, **29**, 899 (1996).

2. Compliance measurements of confined polystyrene solutions by atomic force microscopy, R. M. Overney, D.P. Leta. C.F. Pictroski, M.H. Rafailovich Y. Liu, J. Quinn, J. Sokolov, A. Eisenberg and G. Overney, *Phys. Rev. Lett.* **76**, 1272 (1996).

3. Self-assembly of diblock copolymers in solution, Z. Li, W. Zhao, Y. Liu, M.H. Rafailovich, J. Sokolov, K. Khougaz, A. Eisenberg, R. B. Lennox and G. Krausch, *J. Am. Chem. Soc,* **118**, 10892 (1996).

4. Enhancement of interfacial adhesion by means of surface segregation in the interface between PC and SAN blends, M. Schaffer, V. Janarthanan, Y. Deng. J. LaScala, L. Guo, M. Rafailovich, J. Sokolov, R. S. Stein, Y. Strzhemechny and S. A. Schwarz, *Macromolecules*, **30**, 1225-1227 (1997).

5. Dewetting dynamics at a polymer-polymer interface, S. Qu, C.J. Clarke, Y. Liu, M.H. Rafailovich, J. Sokolov, K.C. Phelan, and G. Krausch, *Macromolecules*, **30**, 3640-3645 (1997).

6. Confinement of block copolymers on patterned surfaces, Z. Li, S. Qu, M.H. Rafailovich, J. Sokolov, M. Tolan, M.S. Turner, J. Wang, S. K. Sinha, H. Lorenz, J.P. Kotthaus, *Macromolecules,*30, 8410-8419 (1997).

7. Long-range effects on polymer diffusion induced by a bounding interface, X. Zheng, M. H. Rafailovich, J. Sokolov, Y. Strzhemechny, S. A. Schwarz, B. B. Sauer and M. Rubinstein, *Phys. Rev. Letters*, **79**, 241 (1997).

8. Measurements of the Flory-Huggins interaction parameter for polystyrene-poly(4-vinyl pyridine) blends, Clarke, C. J.; Eisenberg, A.; La Scala, J.; Rafailovich, M. H.; Sokolov, J.; Li, Z.; Qu, S.; Nguyen, D.; Schwarz, S. A.; Strzhemechny, Y.; Sauer, B. B., *Macromolecules*, **30**, 4184-4188 (1997).

9. Polymer thin films on patterned Si surfaces, Z. Li, M. Tolan, T. Hohr, D. Kharas, J. Sokolov, M.H. Rafailovich, H. Lorenz, J. P. Kotthaus, J. Wang, S.K. Sinha and A. Gibaud, *Macromolecules,* **31**, 1915 (1998).

10. Phase-separation-induced surface patterns in thin polymer blend films, Karim, A.; Slawecki, T. M.; Kumar, S. K.; Douglas, J. F.; Satija, S. K.; Han, C. C.; Russell, T. P.; Liu, Y.; Overney, R.; Sokolov, J.; Rafailovich, M. H., *Macromolecules*, **31**, 857-862 (1998).

11. Phase separation of polystyrene and bromo-polystyrene mixtures in equilibrium structures in thin films, D. Slep, J. Asselta, M. H. Rafailovich, J. Sokolov, D. A. Winesett, A. P. Smith, H. Ade, Y. Strzhemechny, S. A. Schwarz and B. B. Sauer *Langmuir*, **14**, 4860-4864 (1998).

12. Characterization of composition and interfacial topography in phase separating thin polymer films, H. Ade, D. A. Winesett, A. P. Smith, S. Qu, S. Ge, J. Sokolov and M. Rafailovich, *Euro. Phys. Lett.*, 45, 526-532, 1999.

13. Bulk and surface characterization of a dewetting thin film polymer bilayer, H. Ade, D.A. Weinsett, A.P. Smith, S. Anders, T. Stammler, C. Heske, D. Slep, M. H. Rafailovich, J. Sokolov, J. Stohr, PEEM studies of thin film bilayers and blends of polystyrene and brominated polystyrene, S. Anders, T. Stammler, *Appl. Phys. Lett.*, 73, 3775-3777, 1998

14. Surface-induced ordering in graft copolymer thin films," S. Ge, L. Guo, M. H. Rafailovich, J. Sokolov, D. G. Peiffer, S. A. Schwarz, R. H. Colby and W. D. Dozier, *Langmuir*. 15, 2911-2915, 1999.