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Surface and Interfacial Properties of Polymer Blends

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Department of Physics

This is a summary of the research we have conducted since receiving our DOE grant and research plans for the coming year. As you will notice most of the research objectives of our original proposal were met, especially in regard to measuring surface segregation and interface formation in polymer blends. Our program has therefore expanded into other directions such as the study of the surface visco-elastic properties of polymer liquids and solutions, the conformations of polymer chains grafted onto silica surfaces, and the dynamics of cross linked polymer networks.

A. We have continued our high resolution ion scattering measurements of polymer blend surfaces. The systems we studied were:

i. Polystyrene - Deuterated Polystyrene (PS/DPS). In this system we extended our previous work to measure the time dependence of the surface profile and found that the surface excess, as well as the surface concentration increased on a time scale determined by the bulk mutual diffusion coefficient. The shape of the concentration profile within the first 100Å of the surface was determined to be flatter than theoretical predictions indicating that the interactions at the surface were of longer range than expected. The results of these experiments are described in a paper accepted for publication in *Macromolecules*.

ii. Polystyrene-Polybromostyrene (PS/PBrS) This system is highly immiscible and we are studying the spinodal decomposition of the blend at the surface of thin films. Figure 1 shows an oscillatory concentration gradient, with a different period for segregation and depletion of the PBrS component at the Si and air interfaces respectively. This sample was a 1% blend of 96K PBrS and 575K PS. Figure 2 shows the surface composition profile of a 5% PBrS (20K) and 20K PS sample. The step like profile is a clear demonstration of layering which may either be induced by surface wetting or planar spinodal decomposition. Further experiments on different film thicknesses which will differentiate between these two cases are planned using the SIMS technique.

iii. Using SIMS, we have measured the adsorption of PBrS of various molecular weights to etched and unetched Si substrates out of low molecular

weight (mw = 3K) PS solution. The "goodness" of the PS solvent is a function of the PBrS molecular weight. The results for the etched surface are shown in figure 4a and are in agreement with theory. The differences in profile structure induced by etching the native Si oxide are striking (fig 4b) and as yet unexplained. Further work is in progress to determine the rates of adsorption and also study the effects of the oxide in more detail.

B. In collaboration with Dr. Tom Russell we measured the concentration profile of PS chains terminated with COOH tethered to a silicon oxide surface and dissolved in a blend of 500K D-PS. As shown in figure 3a, using SIMS, we were able to obtain one of the first direct measurements of the profile to determine the conformation of single polymer chains in a blend. The solid line is a fit assuming simple Gaussian statistics of isolated chains terminally attached to a wall. By measuring the increase in grafting density of the chains as a function of temperature, we deduced an enthalpy of -8K cal/mole for the grafting reaction, postulated to be, $\text{COOH} + \text{SiOH} \rightarrow \text{COOSi} + \text{H}_2\text{O}$. This demonstrated conclusively that it was possible to graft chains irreversibly to silica substrates by reacting them at high temperatures. This could not be done previously using solvent matrices since they could not withstand the reaction temperatures. This work was published in a recent Europhysics Lett. paper. Further work is now in progress to study the dependence of the grafted chain profiles on matrix molecular weight, chemical composition, annealing time, and substrate surface preparation. In addition, using neutron reflection we have determined the conformation of the chains within 10\AA of the silica wall. These results are important in testing various theoretical models on the effects of surface interactions on polymer adsorption. Further work is in progress to study the conformation of the chains when the surfaces are modified via metal ion deposition, etching, etc. The proposed experiments will be in collaboration with Dr. Law Fetters of Exxon, who will be synthesizing the polymers.

C. In collaboration with Dr. Robert Briber of NIST, we have begun a series of studies to determine the diffusion of linear polymers into crosslinked networks. Our experiments thus far, on d-PS (mw = 104K) diffusing into γ -ray crosslinked polystyrene films show that the diffusion proceeds by slowly swelling the network followed by rapid diffusion of the linear chains through the swollen matrix.

Further work on this system is planned to determine the dependence of the diffusion rate on the molecular weight of the linear chains and the interaction parameter χ between the monomers of the diffusing chains and the host matrix. In addition the mobility of the crosslinked network will be determined by measuring the interfacial width between two cross linked networks using neutron reflection.

D. The program we are conducting at the BNL Synchrotron Light Source is as follows:

1. We have measured the interfacial width between the highly immiscible polymer system, PS/PBrS and found the interface to become significantly narrower in the liquid state (approx. 30\AA , see fig. 5), than when the measurements were conducted after annealing and quenching below T_g (approx. 40\AA).

ii. In order to determine the relative contributions to the interfacial width of roughness due to thermally excited fluctuations and actual chain interpenetration, we have measured the diffuse scattering from the polymer junction. In addition we have also measured the diffuse scattering from the surface of PS and PEP monolayers and compared the results to scattering from small molecule liquids (i.e. toluene and ethanol). The most striking result was a decrease in the diffuse scattering intensity with increasing temperature above T_g (fig. 6). A model for the interpretation of these results is currently being developed in terms of changes in chain entanglement length as a function of temperature. Further experiments are planned to study these effects on other polymers, and on polymer monolayer films.

In addition, since the diffuse scattering changes drastically between the solid and liquid polymer phases, this technique will be used to measure the precise melting point of monolayer polymer films. (These experiments are in collaboration with Dr. L.J. Fetters of Exxon Corp. who has been providing the PEP polymers.)

iii. Finally, using the newly completed BNL liquid spectrometer, the diffuse scattering from PBrS/toluene solutions as a function of PBrS concentration was measured. Diffuse scattering from small-molecule liquids such as water and ethanol is well understood in terms of thermally excited capillary waves. However, polymer solutions exhibit strong viscoelastic effects and have a rich variety of hydrodynamic modes not present on simple liquids. In order to determine these modes, the scattering from various PBrS/toluene solutions was measured. The results showed that the basic lineshape of diffuse scans for each q_z was similar to that of toluene but the variation of overall intensity with q_z increased with increasing polymer concentration (see fig. 5b). A theoretical model that we developed to calculate the surface wave height correlation function indicated that these effects were due to the relatively large shear modulus in polymer liquids. The solid lines in figure 5b are a fit to this theory using independently measured values for the surface tension (in collaboration with B. Sauer of DuPont) and the shear modulus (in collaboration with Exxon). Further work is planned on polymers with varying viscosities and surface profile distributions.

Research Plans for 1992

Over the next year we basically plan to continue our research in the areas outlined above. In addition;

we have completed the construction of a time of flight spectrometer on a dedicated beam line at the Bellcore Van de Graaff accelerator. The time of flight NREX spectrometer has a cold stage and enables us to freeze polymer solutions and thereby determine directly the concentration profiles of polymers adsorbed at solution surfaces and the swelling of polymer films by small molecule solvents.

B. We plan to expand our scattering program on the NSLS liquid spectrometer and the HFBR liquid reflection spectrometer to study, in collaboration with Professor Bruce Lennox of McGill University, diffuse scattering from polymer membranes and Langmuir Blodgett films.

C. The effects of chain end segregation to surfaces and interfaces have been widely assumed in theoretical models ranging from surface tension to diffusion, but have never been measured. We performed some initial experiments using neutron reflection at the IPNS on deuterium end-labeled hydrogenated polystyrene chains and concluded that no segregation occurs within a factor of 3. Since very little deuteration is present on these chains, the data acquisition time exceeded our allotted beam time. We plan to refine our measurement by acquiring better statistics in a run dedicated only to this experiment in the coming year. We would like to be sensitive to a factor of 50% enhancement both at the air surface and at an interface between immiscible polymers.

D. We plan to greatly expand our neutron reflection profiling program and base it on the BNL-HFBR reflectometer. The horizontal geometry will enable us to study concentration profiles of polymers adsorbed on liquid surfaces, surfactant layers and polymer membranes. These results will be correlated with the direct profiling obtained with FRES.

A list of contributions to conferences and publications since we received our DOE Grant is enclosed. Also included are copies of manuscripts either submitted or in preparation for submission to various journals.

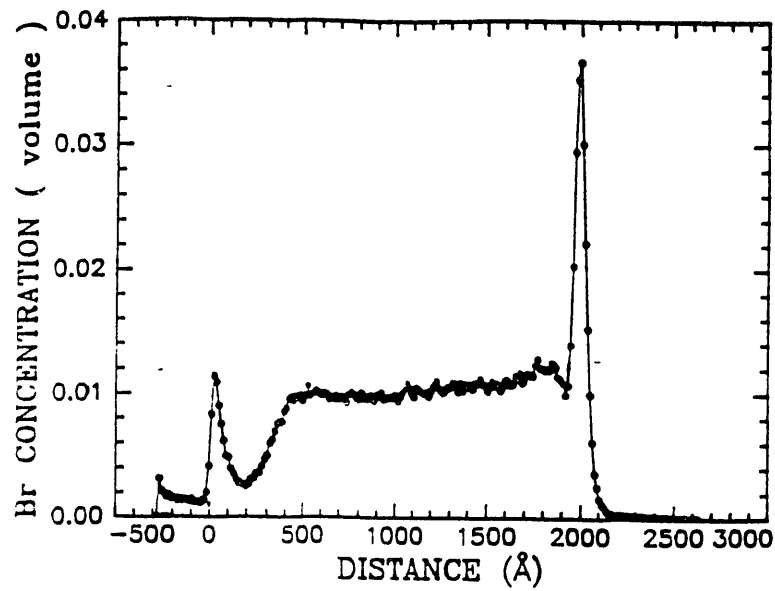


Figure 1 Oscillating concentration profile for a PBrS/PS blend. Note the segregation at both air and Si interface.

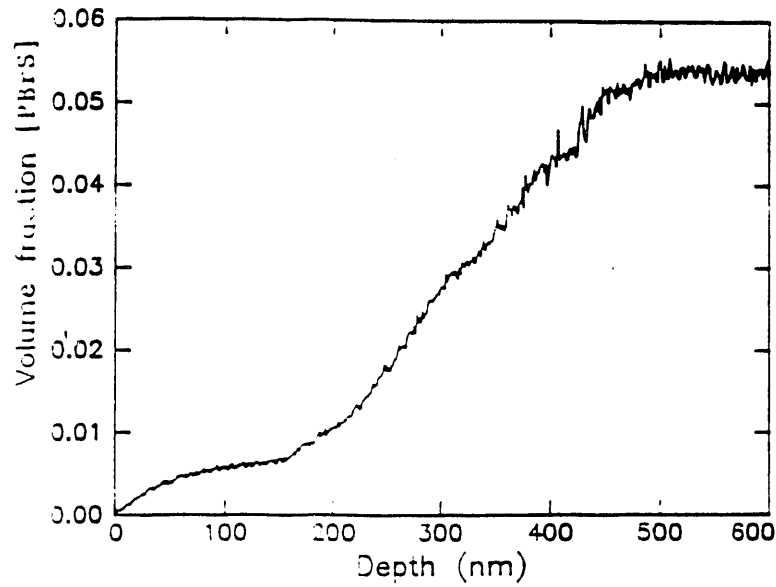


Figure 2 Covering type of segregation in PBrS/PS blend.

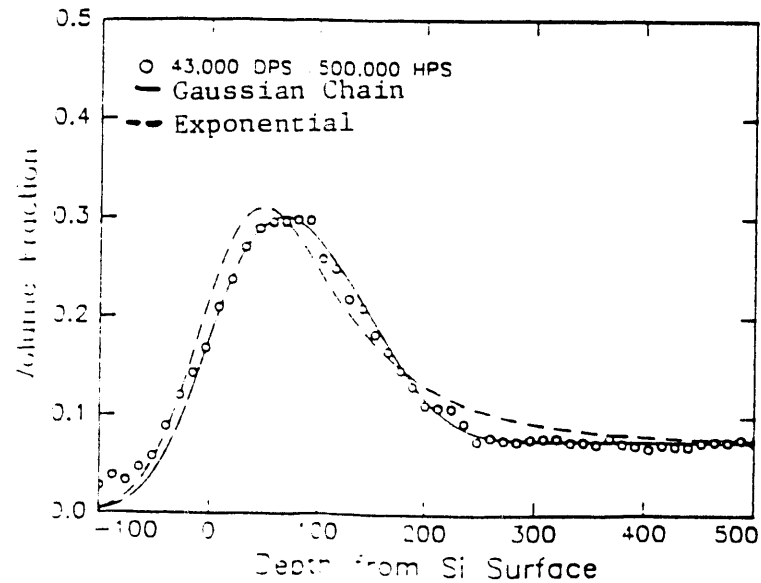


Figure 3 Comparison of experimental data with theoretical models for PBrS/PS blend. The data points represent 43,000 DPS and 500,000 HPS. The solid line is the Gaussian Chain model and the dashed line is the Exponential model.

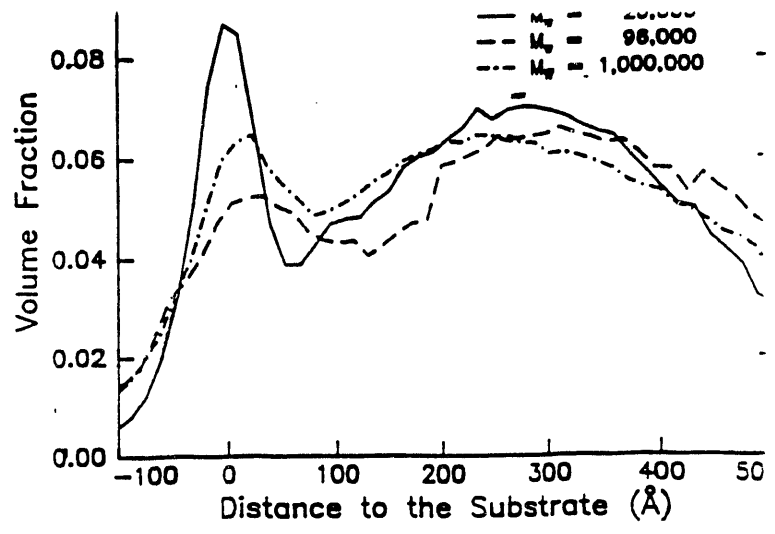
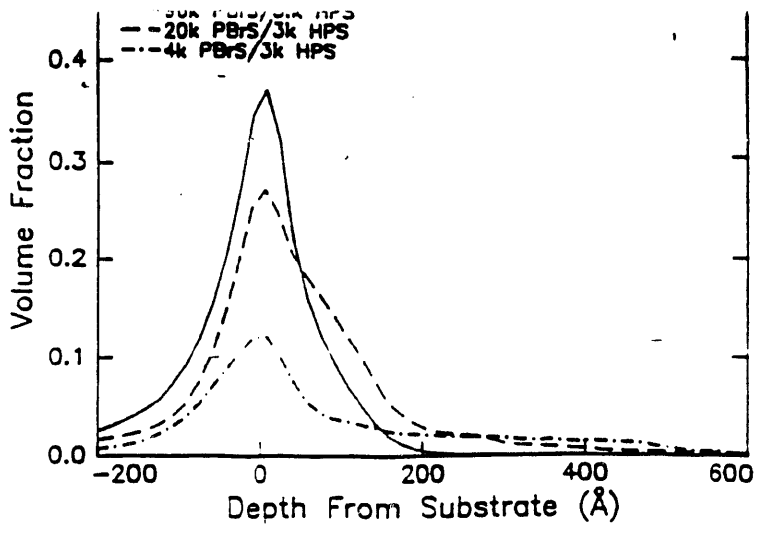


Figure 4a: PBrS adsorbed to an etched Si surface out of a 3K PS solution.

Figure 4b: PBrS adsorbed to a Si surface with native oxide layer.

BILAYER PS770K/PBrSP670K AT T=140°C

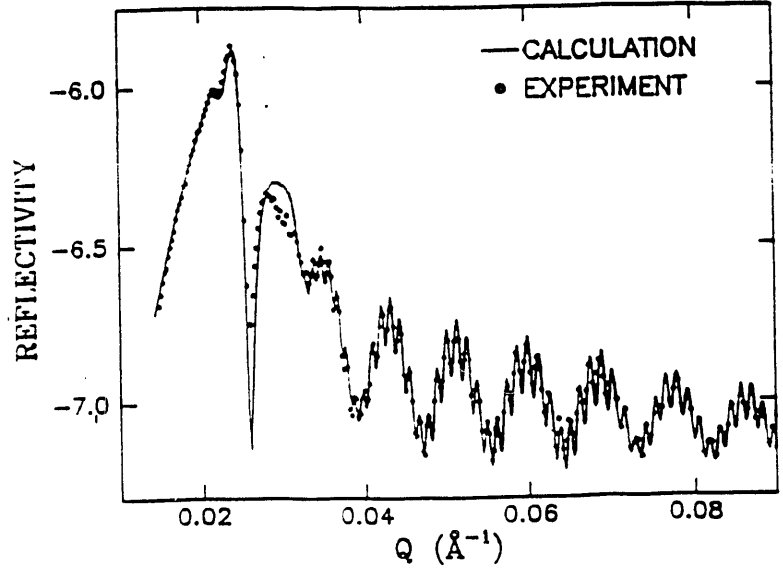


Figure 5 (a) Specular reflectivity (R_{xQ^4} vs. Q) from a liquid interface of PS/PBrS bilayer. (b) Diffuse x-ray reflectivity from PS/PBrS solution.

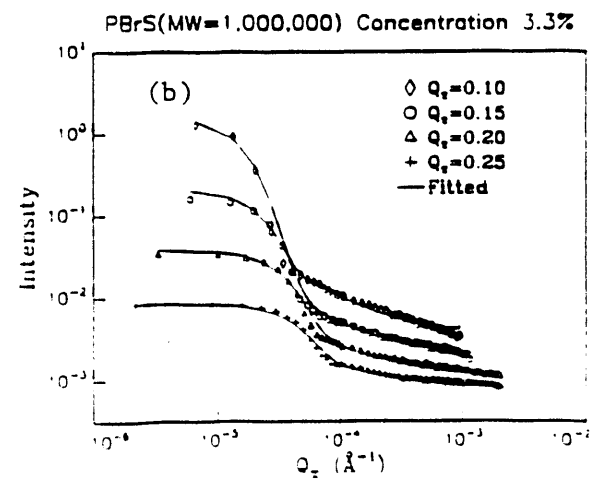
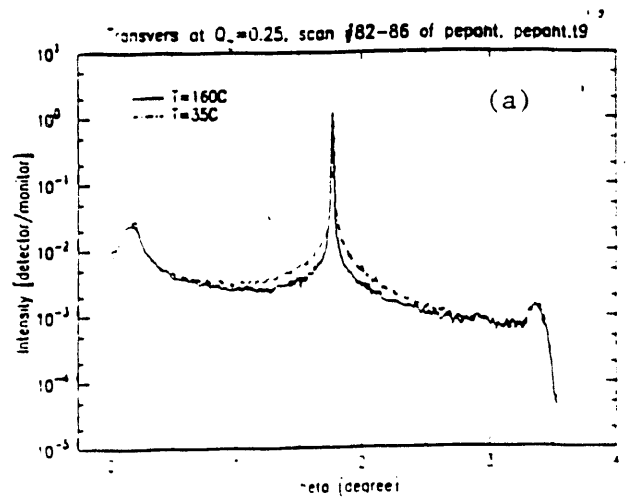


Figure 6 Diffuse x-ray scattering from PEP at two different temperatures

PUBLICATIONS ACKNOWLEDGING OUR DOE CONTRACT NO DE-FG02-90ER45437

1. "Determination of the Concentration Profile at the Surface of a DPS/HPS Blend." X. Zhao, W. Zhao, J. Sokolov, M.H. Rafailovich, S.A. Schwarz, B.J. Wilkens, R.A.L. Jones, and E.J. Kramer, *Macromolecules*, in press.
2. "Conformation of Polystyrene Chains in a Melt," X. Zhao, W. Zhao, M.H. Rafailovich, J. Sokolov, T.P. Russell, S.K. Kumar, S.A. Schwarz and B.J. Wilkens, *Europhys. Lett.* 15, (1991) 725.
3. "Anomalous Reflectivity: A New Method For Determining Density Profiles of Thin Films." International Conference on Neutron and X-Ray Scattering From Surfaces, S.K. Sinha, M.K. Sanyal, K.G. Huang, A. Gibaud, M. Rafailovich, J. Sokolov, X. Zhao and W. Zhao. Springer Verlag, in Press.
4. "Fourier Holographic Reconstruction of Density Profiles of Thin Films Using Anomalous X-Ray Reflectivity," M.K. Sanyal, S.K. Sinha, A. Gibaud, K.G. Huang, B.L. Carvalho, M. Rafailovich, J. Sokolov, X. Zhao, and W. Zhao, submitted to *Phys. Rev. Lett.*

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