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# DETERMINATION OF CONCENTRATION PROFILES AT INTERFACES AND SURFACES OF PARTIALLY MISCIBLE POLYMER BLENDS

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The following is a summary of the research we have performed on the DOE grant DE-FG02-90ER45437. the Research is divided among several topics;

A. Wetting Properties of thin Liquid Polyethylene Propylene Films (W. Zhao, M.H. Rafailovich, J. Sokolov, L.J. Fetters, R. Plano, M.K. Sanyal and S.K. Sinha, Physical Review Lett. 70 (1993) 1453)

Polyethylene-propylene films of various molecular weights, which would normally wet native oxide covered Si surfaces, were observed to dewet the surface when the film thickness became less than the polymer radius of gyration [Fig.1] These films could be made to wet either by increasing the annealing temperature i.e. stripping the oxide or covering with a self assembled monolayer or by chemically modifying the surface. The results are shown to be consistent with an expression for the spreading parameter that incorporates a stretching free energy term for the polymer chains. Measurements of the diffusion constant of the polymer on the silica surface indicated that an activation energy was required to desorb the polymer before diffusion could occur. [Fig.2]

B. Fourier Reconstruction of Density Profiles of Thin Films Using Anomalous X-ray Reflectivity. [M.K. Sanyal, S.K. Sinha, K.G. Huang, B.L. Carvalho, M. Rafailovich, J. Sokolov, X. Zhao, and W. Zhao Europhys. Lett. 21 (1993) 691].

Iterative methods for calculating the reflectivity as accurately as desired from a given density profile have been known for many years. In the inversion process, usually a model form for the density profile is used to calculate the reflectivity and fitted to the observed data. It is not obvious that the solution to the problem is unique, since it is an intensity which is being

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fitted and phase information is absent. This is analogous to the well known "phase problem" in crystallography. We developed a method of obtaining a model-independent electron density profile for a thin film deposited on a substrate using "anomalous" X-ray reflectivity measurements carried out at energies close to, and away from, a convenient absorption edge of the substrate. We illustrate the method using both simulated data from various model profiles and with a synchrotron X-ray experiment carried out on a Langmuir-Blodgett film.

The method we use, uses the fact that the reflectivity of a thin film on a substrate involves an interference between the reflectivity of the film and that of the substrate and hence contains phase information. By changing the amplitude and phase of the reflection from the substrate in a known manner (achieved by tuning the X-ray energy across an absorption edge of the substrate), one can obtain the real and imaginary parts of the Fourier transform of the density profile in the direction normal to the film, and Fourier inversion then yields the unique density profile.[Fig.3]

(i) We reported measurements and calculations of X-ray diffuse scattering from the liquid-vapor interface of toluene and polybromostyrene(PBrS)/toluene solutions for polymer molecular weights 9-0K and 1M at concentrations up to 11.7 volume %, well into the entangled semi-dilute regime. We have calculated the static structure factor S(k) and equal time height-height correlation function C(R) for surface hydrodynamic modes based on a Maxwell viscoelastic model [Harden et al., J. Chem. Phys. 94, 5208 (1991)]. We obtain the leading correction term to the capillary-wave result for C(R) dependent on the solution shear modulus $E_0$ as well as an analytic aproximation valid for large $E_0$, including the case of pure polymer melt.

C. Temperature and Concentration Effects on Grafted Polymers in the Melt [Phys. Rev. Lett. 69 (1992) 776]

The concentration profiles of carboxy terminated polystyrene chains in the melt grafted onto oxide covered silicon substrates were measured using SIMS. [Fig.4] The grafting density increased with temperature and an enthalpy of + 7.4 kcal/mole was deduced for the grafting reaction, SiOH+R(COOH) R(COOSi) + $H_2O$. Relatively high grafting densities ($\sigma$ ˜ 6/6 $mg/m^2$) were achieved with minimal chain distortion or displacement of long chains by shorter ones. Significant stretching of the grafted chains occured for $\sigma$ > 10 $mg/m^2$. An equilibrium constant for the grafting reaction incorporating entropy was developed which was shown to have universal applicability to polymer brushes in all media.

Hoping the above information will be satisfactory to your needs, I remain,

Sincerely yours,

Miriam Rafailovich
Professor

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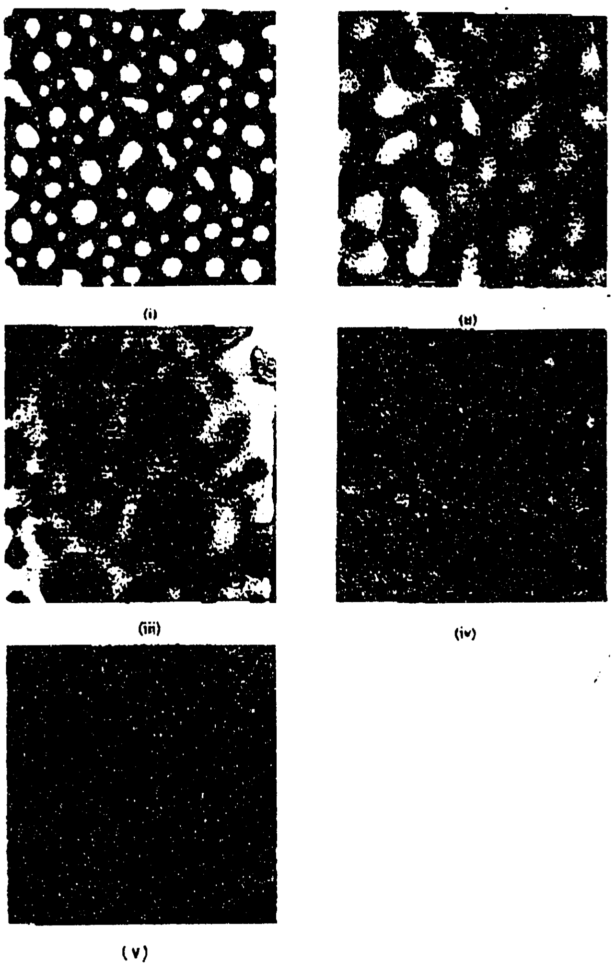


FIG. 1. (a) AFM images of PEP films on oxide-covered Si. Initial thickness: (i) 73 Å, (ii) 98 Å, (iii) 113 Å, (iv) 147 Å, (v) 183 Å.

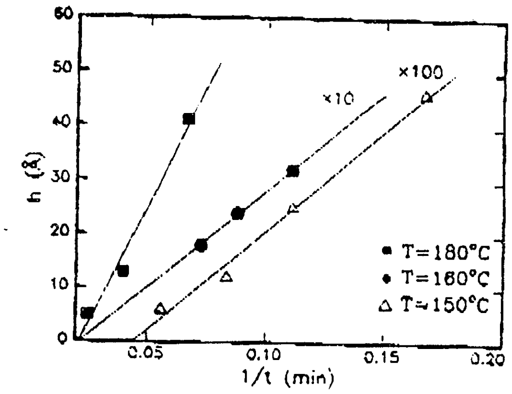


FIG. 2. Average height $h$ as a function of inverse annealing time $(1/t)$ for a 70 Å PEP film of $M_w = 290000$ annealed $T = 180\,°C$ (■), 160 °C (●), and 150 °C (△).

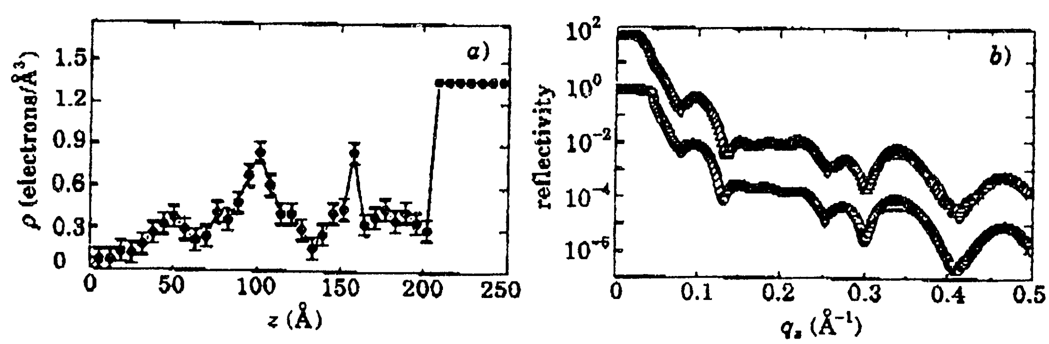


Fig. 3. – *a*) The electron density profile of the Cd arachidate LB film as obtained by the present experiments. The solid line is a guide to the eye. For $z > 202$ Å the profile corresponds to the measured electron density for the Ge substrate. *b*) Reflectivity curves for the LB film on Ge at and away from the *K*-edge of the Ge substrate as measured and calculated using the slicing method from the histogram in *a*). ○ away from edge; △ at the edge (× 100); —— calculated.

**PUBLICATIONS**
**Acknowledging our DOE Grant**

**(1992-1993)**

1. Fourier reconstruction of density profiles of thin films using anamolous 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, Europhys. Lett., 21 691 (1993).

2. Wetting properties of thin liquid polethylene propylene films, W. Zhao, M.H. Rafailovich, J. Sokolov, L.J. Fetters, R. Plano, M.K. Sanyal, S.K. Sinha and B.B. Sauer, Phys. Rev. Lett. 70 1453 (1993).

3. Temperature and concentration effects on grafted polystyrene chains in the melt, X. Zhao, W. Zhao, J. Sokolov, M.H. Rafailovich, J. Sokolov, S.A. Schwarz, M.A.A. Pudensi, T.P. Russell, S.K. Kumar and L.J. Fetters, Phys. Rev. Lett. 69, 776 (1992).

4. Diffuse x-ray scattering study of polybromostyrene (PBrS), toluene solutions, X. Zhao, W. Zhao, J. Sokolov, M.H. Rafailovich, M.K. Sanyal, S.K. Sinha, B.H. Cao, M.W. Kim and B.B. Sauer, J. Chemical Physics, 97, 8536 (1992).

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