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REFLECTIVITY STUDIES ON ADSORBED BLOCK COPOLYMERS UNDER SHEAR

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ABSTRACT

We report neutron reflectivity data on (poly)styrene-(poly)ethylene oxide (PS-PEO) diblock copolymers adsorbed onto quartz from the selective solvent cyclohexane (a non-solvent for PEO and a poor solvent for PS). The PEO "anchor block" adsorbs strongly to form a thin layer on the quartz substrate, while the deuterated PS chains dangle into the solvent. We find that under static conditions the density profile of the PS block in a poor solvent can be well described by a Schultz function which is indicative of a polymer "mushroom." Furthermore, we have studied the same system under shear at shear rates from 0-400s⁻¹. We find that there is a dramatic increase in the thickness of the PS layer under shear in cyclohexane and that the relaxation time from the shear-on profile back to the static profile is on the order of several days.

INTRODUCTION

The ability of polymer chains to uncoil and stretch into solution make them useful in a number of industrial applications. For example, in making latex paint and various types of ink, colored particles are coated with polymers to sterically suspend these particles in solution¹. Another place where polymer extension is used is in enhanced separation processes. By attaching binding ligands to polymer chains instead of directly attaching them to a substrate, the effective binding area is increased. Once such modified chains have captured the particle of choice (whether to purify a liquid or to remove precious materials), the polymers may be removed to concentrate the captured moiety. In both of these examples, one may intuitively expect that the effectiveness of these coatings may depend on the conformation of the polymer chains.

The behavior of grafted polymer chains in solution has been the subject of several theoretical studies^{2,3,4,5,6,7,8}. These studies range from scaling arguments^{2,3,4} to mean field theories^{5,6,7}. The common goal of these theories is to understand the conformation of grafted polymers in a good solvent and to extract predictions of the segment density profile as well as scaling laws. Within this body of work, it was found that there exist two regimes for the polymer segment density profiles. If the grafting points are further apart than twice the Flory

Radius, R_F , then the polymer chains don't interact with one another and the predicted shape of the polymers may be thought of as resembling a mushroom⁴. This gives a profile with a density approaching zero near the interface and peaking some distance away from the surface. On the other hand, if the grafting density is high enough that polymer chains from different binding sites begin to overlap, we get a polymer brush. For the brush, the density profile is predicted to be parabolic⁵ with the maximum in the density occurring at the grafted end and falling to zero in the solvent. In addition to these theoretical studies of the static properties of grafted polymers in solution, other theories have been developed for the more complicated, yet more realistic, case of polymer monolayers subjected to shear flow^{8,9,10}.

In this paper, we describe our recent results of neutron reflectivity experiments aimed at understanding the segment density profiles of grafted polymers in solution subject to shear flow. We studied an adsorbed diblock copolymer, polystyrene-polyethylene oxide (PS-PEO), as a model grafted polymer system. Diblocks in selective solvents were chosen for their ease of sample preparation and because their static properties are well known^{11,12}. Using a newly developed type of shear cell¹³, we were able to measure these density profiles using standard neutron reflection techniques developed for static conditions^{11,12}.

EXPERIMENTAL

Ellipsometric studies of grafted polymers under shear¹⁴ have shown that the shear effects are more pronounced for larger molecular weights. Therefore, we selected the largest molecular weight polymer available from the previous work¹¹ which was a 184,000 MW PS block attached to a 7400 MW PEO block. The sample was prepared by dissolving the polymer in deuterated cyclohexane at a concentration of 0.05mg/ml. Cyclohexane is a non-solvent for the PEO and a poor solvent for the PS (i.e. below the Θ temperature). The concentration was chosen to be well below the CMC. All experiments were performed at room temperature.

The polymers were adsorbed from solution onto highly polished quartz single crystals (polished to better than $\lambda/8$ in flatness and 80/60 scratch and dig). The liquid/solid cell was assembled by clamping the crystals against a Teflon block which was machined with a channel for the liquid. An inlet and an outlet were also machined into the block such that Teflon tubing could be attached in a closed loop between a pump and the cell¹³. The solution was pumped continuously during the experiment to produce a shear force applied to the adsorbed polymer by the flowing liquid. Extreme care was taken in each case to clean the quartz and the Teflon prior to assembly to avoid any surface contamination. The quartz was soaked for several hours in 1:3 HNO₃:H₂SO₄; then it was rinsed with Millipore water, and then it was soaked in 1:3 HNO₃:HCl for several more hours followed by another water rinse. Finally the quartz was exposed to a six hour treatment in a UV-Ozone cleaner. The Teflon was sonicated in protonated solvent for several hours and then air dried.

The cell was loaded by slowly pumping the solution (at shear rates of 90s⁻¹ or less) into the region between the quartz and the Teflon and then back out of the cell. Care was taken to remove all of the bubbles in the cell by tilting the cell as it was filled. After the cell was filled with solution, the pump was turned off, and the polymer was permitted to adsorb to the quartz for at least 6 hours prior to further shear. After adsorption, the solution was vigorously sheared ($\sim 400\text{s}^{-1}$) and then allowed to relax for ~ 10 days.

The measurements were made on the SPEAR reflectometer at the Manuel Lujan Jr. Neutron Scattering Center (LANSCE) at the Los Alamos National Laboratory. The beam at LANSCE is produced by spallation of neutrons from a tungsten target using a pulsed beam (20Hz) of 800MeV protons. The energy spectrum of the neutrons is softened using a liquid hydrogen (20K) moderator. The reflectivity ($R \equiv [\text{\#reflected neutrons}] / [\text{\#incident neutrons}]$) curves were collected as a function of the time-of flight from the moderator to the detector for a fixed angle of incidence of neutrons on the sample. This determined the velocity and hence the wavelength of the incident neutrons. Given that the moderator to detector distance is 12.38m, the maximum neutron wavelength measured without the occurrence of frame overlap was 16Å. The T₀ chopper (used to remove the high energy neutrons) is set to open at a time commensurate with the arrival of 1Å neutron; therefore, the wavelength range used was 1-16Å. Typically, for these runs, the angle of incidence was chosen to be ~0.5 degrees in order to include both the critical edge and reflectivities with reasonable statistics at values of $R \sim 10^{-5}$. Typical counting times for these measurements were 120 minutes. The reflected neutrons were counted using an Ordela model 1202N linear position sensitive ³He detector. The data was reduced and plotted as reflectivity $X Q_Z^4$ versus the perpendicular scattering vector, Q_Z , where $Q_Z = 4\pi \sin\theta/\lambda$ (Fig. 1). The error bars in Fig. 1 represent the statistical errors in the measurements where the resolution error, $\Delta Q_Z/Q_Z$, was nearly constant over this range with a value of ~3%.

RESULTS AND DISCUSSION

In previous neutron reflectivity studies, it was found that for the 184,000 PS-4%PEO in d-toluene, the data can be fit with a parabolic density profile¹¹. A parabolic density profile is predicted by mean field theory⁵ for polymer "brushes." On the other hand¹², it was found for similar diblocks that if the ratio of the size of the anchor block to the swelled block increases, the density profiles obtained from the best fits to the reflectivity data are described by Schultz functions which are consistent with polymer mushrooms⁴. For mushrooms, the maximum in the PS density profile as a function of PS MW occurs at a finite distance from the grafting surface.

In the present work, after the solution had relaxed for approximately 10 days, we performed the neutron reflectometry measurements (Fig. 1). We found that the reflectivity data could be fit using a Schultz-like function with the addition of a thin, dense layer at the quartz surface representing the anchor block. The resulting volume fraction profile is shown in Fig. 3a. Although the previous measurements¹¹ showed that the 184,000 MW PS-4% PEO was a brush in good solvent, this new data suggests that it is a mushroom in a poor solvent. This is consistent, however, since we expect the Flory radius, R_F , of the PS to be smaller when the polymer is in a poor solvent. The smaller R_F allows a cross over from the PS chain interactions dominating the surface structure to a density profile determined by dominant inter-anchor interactions which yields a mushroom-like profile^{2,3}.

In contrast, Fig. 2 shows the measured reflectivity curve for a shear rate of 400s⁻¹. The volume fraction profile for this fit is shown in Fig. 3b. As in the static case, a reasonable fit to the data requires that a thin layer be present at the quartz which represents the PEO

Fig. 1 Neutron reflectivity measurement on the adsorbed diblock under static conditions. The solid line is the fit to the data.

Fig. 2 Neutron reflectivity measurement on the adsorbed diblock at a shear rate of 400s^{-1} . The solid line is the fit to the data.

anchor block adsorbed to the surface. Since the data could not be fitted with a Schultz function, a parabola, or any other simple functional form, the profile was composed of piecewise connected functions.

Since the only constituents in the solvent are PS and d-cyclohexane, we can calculate a volume fraction profile for both of the observed cases. This is shown in Fig. 3. We find that the area under each curve is the same for the two profiles. Therefore, one may conclude that there is no addition or removal of material from the surface during shear. Also, it is clear from Fig. 3 that the polymer is stretched under shear conditions (i.e. shear thickening occurs). The observed shear thickening is consistent with previous theoretical work on sheared polymer brushes^{8,9}. Finally, after the shear was stopped, we repeated the measurements over the next 24 hours. Although a slight shifting of the fringes occurred, we did not see the reflectivity measurements relax back to the unsheared case of Fig. 1. This indicates that there is a very long relaxation time involved in this shear deformation (between 1 and 10 days). This suggests that the stretched PS chains are interacting with each other or with polymer in solution in such a way that they become entangled thus retarding their relaxation.

Fig. 3 Volume fraction profiles from the neutron reflection measurements on 184,000 PS / 4%PEO adsorbed onto quartz from cyclohexane. When the shear is off (a), the data may be fit with a Schultz-like function [13] which is consistent with the mushroom regime. When the shear is applied (b) at 400 s^{-1} , the PS stretches into the solvent (i.e. further to the left side of the figure) to nearly twice its original length. The thin step near 560 Å is the PEO anchor block attached to the quartz surface.

CONCLUSIONS

We have presented new data on the effects of shear on the density profile of an adsorbed diblock in a solvent below T_{Θ} . This is the first time that the density profile has been measured with sub-molecular resolution for an adsorbed polymer monolayer under shear flow. We find that while the PS in this particular diblock is in the mushroom regime under static conditions, the PS block is stretched to nearly twice its static length under applied shear. Once the shear force is removed, the observed relaxation time is found to be of the order of several days.

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