Notes

Diblock Copolymer Adsorption onto a Solid Surface As Revealed by Evanescent Wave Ellipsometry

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The interfacial behavior of diblock copolymers play an important role in many practical applications, for example, polymer compatibilization, adhesion, and colloid stabilization. There has been considerable theoretical[1-4] and experimental[5-8] effort to understand the adsorption behavior of diblock copolymers from a solution onto a solid surface. Recent neutron reflectivity measurements on solutions of symmetric diblock copolymers of polystyrene and poly(methyl methacrylate), denoted P(S-*b*-MMA), near a quartz wall have shown that the PMMA segments adsorb preferentially onto the quartz forming a dense layer. However, the segmental concentration of polystyrene (PS) was too low to be observable.

Evanescent wave ellipsometry, EWE, on the other hand, allows one to determine the density of molecules adsorbed onto a surface without labeling the segments with deuterium.[9,10] Here, EWE results on P(S-*b*-MMA) adsorbed onto a solid substrate are presented as a function of molecular weight. It is shown that the adsorbed amount of copolymer is maximized for a particular molecular weight. This result contradicts theoretical predictions, and a possible origin of this discrepancy is provided.

The experimental setup of EWE has been described elsewhere.[9] The polymer evolution is brought into contact with a glass prism which was first cleaned in Nochromix and then rinsed thoroughly with distilled water, then ethanol, and, finally, carbon tetrachloride, CCl_4 (the solvent used in the study). The characteristics of the copolymers used in this study are given in Table 1. All the copolymers used were purchased from Polymer Laboratories with the exception of the highest molecular weight material, which was kindly provided by Prof. M. Tirrell of the University of Minnesota. PS homopolymer contaminants generated during the synthesis were removed from the copolymer via Soxhlet extraction. All EWE measurements were performed at 21 ± 0.5 °C, where CCl_4 is a good solvent for PS and a poor solvent for PMMA.

Using pure CCl_4, the phase retardation due to the inherent strain in the prism was measured. This background, which is less than 0.5 mrad, was subtracted from the phase retardation measurements of the polymer solution. Most of the measurements were carried out immediately after the sample was introduced. No change in the phase retardation after 30 min was found, indicating that the time required to achieve the adsorption equilibrium was short. However, the very long time stability of the adsorbed layer could not be measured due to the long-term temperature variation.

Table 1. Characteristics and Results of Copolymer Studies

$M_w \times 10^{-3}$	$M_{PS} \times 10^{-3}$	$M_{PMMA} \times 10^{-3}$	$\Delta\Phi_m$ (mrad)	ϕ_{PMMA}	d_{PMMA} (Å)
8.6	4.1	4.5	3.0	0.85	8.5
16	7.1	8.9	3.25	0.6	11.6
35.8	17.8	18.0	3.25	0.45	16
113.6	58.6	55.0	4.1	0.32	30
282.5	152.6	129.9	7.1	0.3	52
535	275	260	4.5	0.16	67
700	400	300	3.0	0.1	79

The total polymer excess (Γ) adsorbed onto the surface of the quartz is[9,10]

$$\Gamma = \int [C(z) - C_b]\, dz = \Delta\Phi(\Theta_t) C_b \epsilon_{solv} / (2k_0 \Delta\epsilon_{ss} \Delta\epsilon_{ps}^{1/2}) \quad (1)$$

where $k_0 = 2\pi/\lambda$, with λ denoting the laser wavelength in vacuum; $C(z)$ is the polymer concentration as a function of distance z from the surface; C_b is the polymer concentration in the bulk solution; ϵ_{solv} is the dielectric constant of the solvent; $\Delta\epsilon_{ss}$ is the difference between the dielectric constants of solution and solvent; $\Delta\epsilon_{ps}$ is the difference between the dielectric constants of prism and solution; and $\Delta\Phi(\Theta_t)$ is the measured phase difference of the ordinary and extraordinary beams at the critical angle (Θ_t).

Measurements on P(S-*b*-MMA) having a molecular weight of 7×10^5 as a function of composition showed that the amount of adsorbed copolymer was independent of concentration up to 0.05 g/cm^3. Consequently, subsequent measurements for all the different copolymers were performed at a concentration of 10^{-4} g/cm^3. The phase shift $\Delta\Phi$ is shown in Figure 1 (solid circles) as a function of the copolymer molecular weight and is seen to reach a maximum at a molecular weight of 3×10^5. $\Delta\Phi$ is directly proportional to the total amount of copolymer adsorbed on the surface and, consequently, the amount of copolymer increases with increasing molecular weight as expected theoretically.[1,2] However, the decrease in the amount of copolymer adsorbed at the higher molecular weights is unexpected.

The consistency of the EWE measurements with other measurements can be determined by calculating $\Delta\Phi$. From neutron reflectivity measurements on the same copolymer, a 30 Å thick layer of PMMA, having a volume fraction of 0.42, was found at the surface. Assuming that the PS block is fully solubilized and approximating this layer with a 4.5×10^4 molecular weight PS, surface force measurements[5,11] yield an

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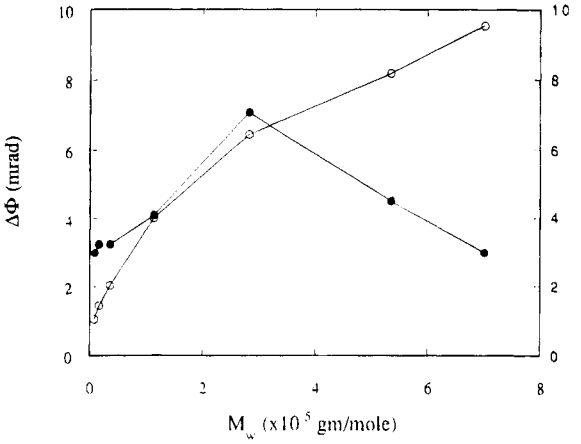

Figure 1. Phase shift due to the polymer adsorption as a function of molecular weight of diblock copolymer, P(S-*b*-MMA). The solid circles are the experimental data and the open circles were calculated from the arguments of Marques et al.[1,2] and neutron reflectivity data.

effective thickness of 830 Å. Based on these values, along with the effective dielectric constant of the adsorbed layer,[9] a phase retardation of 2.2 mrad is calculated which is half the experimental result of 4.1 ± 0.5 mrad. The major source of the discrepancy between the calculated and experimental results is the coarse estimate of the effective PS layer thickness estimated from the surface force measurements.

Since ellipsometry yields the total excess amount of adsorbed copolymer, then this can also be used to calculate the phase retardation. The surface concentration can be calculated from the volume fraction and the thickness of the PMMA adsorbed layer determined from neutron reflectivity. From this, a cross-sectional area per adsorbed copolymer is estimated to be 6.6×10^3 Å^2. Since the numbers of PMMA and PS chains are equal, the contribution to the phase retardation by PS is fixed. From the polymer concentration, an estimated phase retardation of 5.2 mrad is calculated, which is very close to the experimental value. Better agreement is obtained if the volume fraction of PMMA in the adsorbed layer is 0.32. Though this is low in comparison to the reflectivity measurements, this value will be assumed for the remainder of the article. While this assumption may affect the calculated amount of copolymer, it will not alter any trends.

From this analysis, and assuming that the thickness of the adsorbed PMMA block scales with $M^{1/2}$, where M is the molecular weight, then the molecular weight dependence of the experimental phase retardation can be compared with theoretical predictions. Based on the work of Marques et al.[1,2] for diblock copolymer adsorption in a selective solvent,[1] the phase retardation, shown as the open circles in Figure 1, was calculated as a function of copolymer molecular weight. For molecular weights larger than 3×10^5, the calculated and measured $\Delta\Phi$ differ significantly. It should be noted, however, that the arguments of Marques et al.[1,2] do not account for solvent in the adsorbed PMMA layer. In fact, the experiment cannot be explained as long as the amount of solvent in an adsorbed layer is assumed constant. Therefore, the EWE results strongly suggest that the concentration of CCl_4 in the PMMA layer adsorbed on the surface increases with increasing molecular weight. In the case of symmetric diblock copolymers, with increasing molecular weight the cross-sectional area per chain increases. Since CCl_4 is a good solvent for the PS block, there will be a larger force exerted per chain, tending to drag the PMMA into solution by the very favorable interactions between the solvent and styrene segments. This, in turn, can promote solvent penetration into the PMMA layer. Similar results have been observed in the case of asymmetric diblock copolymers of polystyrene and poly(2-vinylpyridine) by Tirrell and co-workers.[12] Shown in Table 1 are the volume fractions of PMMA that best fit the EWE data. As can be seen for the lowest molecular weight studied, 8.6×10^3, a PMMA volume fraction of 0.85 is found. With increasing molecular weight, this volume fraction decreases to 0.1 for the 7×10^5 molecular weight copolymer.

In summary, the total amount of an adsorbed copolymer, P(S-*b*-MMA), on a hydrophilic glass surface as a function of molecular weight was measured by an evanescent wave ellipsometry technique. An optimum molecular weight was found that maximized adsorption, which can be understood by an increasing penetration of the solvent into the layer adjacent to the substrate with increasing molecular weight. This variable solvation of the adsorbed layer must be taken into account theoretically to describe the segment density profiles of diblock copolymers adsorbed onto a surface.

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