Neutron Reflectivity Study of Block Copolymers Adsorbed from Solution

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ABSTRACT: We report neutron reflectivity experiments from solution of symmetric diblock copolymers of polystyrene and poly(methyl methacrylate), P(S-*b*-MMA), near a quartz wall in carbon tetrachloride. This solvent is a good solvent for the PS block but a poor solvent for the PMMA block. When all four combinations of hydrogen and deuterium labeling of the blocks are utilized, it is shown that the PMMA block strongly adsorbs onto the quartz substrate forming a PMMA-rich layer of 30 Å, comparable to its radius of gyration, with a volume fraction of 0.42. However, the concentration of polystyrene segments beyond this initial layer of PMMA is too low to be determined by these experiments.

Introduction

There has been a considerable effort to understand the behavior of homopolymers and block copolymers adsorbed from solution onto a solid surface by numerous techniques, including ellipsometry,[1] surface force measurements,[2,3] X-ray fluorescence,[4] hydrodynamic measurements,[5,6] neutron scattering,[8,9] evanescent wave-induced fluorescence,[10,11] and second harmonic generation.[12,13] These and other techniques have been used to determine the extension of the copolymers from the surface and the total number of molecules adsorbed onto the surface. Optical techniques like evanescent wave-induced fluorescence,[9,10] reflectivity,[12] and second harmonic generation[12,13] can yield important information about the total amount of polymer adsorbed onto the surface, but since the wavelength of light is several hundreds of nanometers, they lack the resolution necessary to describe the concentration profile of polymer segments near the surface. Such information is necessary to compare to existing theoretical treatments.[14-20] For example, it has not been possible, up to this point, to differentiate between power law and exponential dependences of the volume fraction of segments as a function of distance from the solid surface, as predicted by de Gennes[14] and Scheutjens et al.,[16,17] respectively, using currently available techniques.

Recently, neutron reflectivity has been shown to yield unprecedented spatial resolution for the determination of segment density profiles in solid films[21,22] and at the liquid–air interface.[23,24] In this report, neutron reflectivity is shown to be of use in evaluating the segment density profile of diblock copolymers adsorbed from solution onto a solid substrate. This work utilizes two unique aspects of the interactions of neutrons with materials. First, since the reflectivity profile yields a measure of the scattering length density normal to the surface, selective deuteration of the blocks comprising the copolymer can be used to place severe constraints on the model used to describe the results. Second, for studying the behavior of polymers at the liquid–solid interface, the incident neutron beam can be passed through a solid substrate directly onto the interface, provided the solid has a low scattering or absorption cross section for neutrons, which is the case for single-crystal quartz.

In this paper we present results of neutron reflectivity measurements on the behavior of solutions of symmetric diblock copolymers of polystyrene and poly(methyl methacrylate), P(S-*b*-MMA), near a quartz wall. When all four combinations of labeling of the blocks are utilized, the density profile of the PMMA block adsorbed onto the quartz wall can be determined. However, the PS concentration of polystyrene segments beyond this initial layer of PMMA block is too low to be determined quantitatively by our current neutron reflectivity experiments.

Experimental Section

The cell used for the experiment is shown in Figure 1 and is similar in design to that used by Kitchens et al.[25] It consists of a large single crystal of quartz (200 × 75 × 25 mm^3), which was optically polished to $\lambda/20$ on one face. The polishing of the surface was such that the long-wavelength figure error was smaller than the experimental resolution of the spectrometer. Single-crystal quartz was used specifically to reduce the amount of small-angle scattering of the incident beam. The transmission of the neutron beam through the 200-mm length of the crystal was 0.6 using 4.05-Å neutrons. The quartz crystal was clamped with brass bolts between a pair of rigid stainless steel plates. A 0.5-mm Teflon gasket was used as a seal between the quartz crystal and top steel plate. The gap provided by the Teflon gasket (D) was used to define the cell volume (~6 cm^3) for the polymer solutions. The cell was filled through two small openings in the top steel plate. The neutron beam was passed through the quartz and reflected internally at the quartz–liquid interface, with the reflected beam coming out through the quartz on the other side. Using the alternate approach of passing the neutron beam through the solution and reflecting off the solution–quartz interface was

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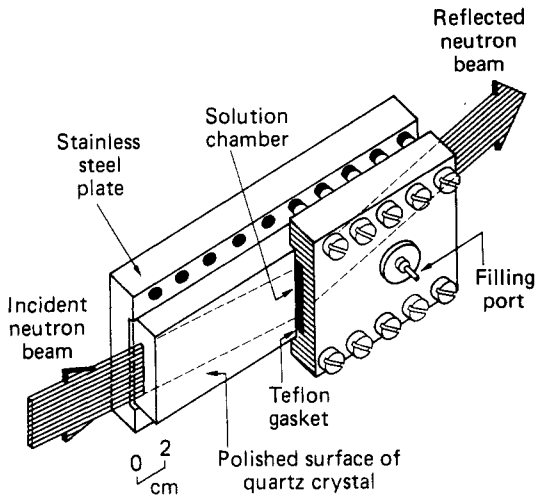

Figure 1. Schematic diagram of the solution scattering cell used in these experiments. Details of the cell are discussed in the text (after Figure 1 of ref 25).

Table I
Characteristics of Copolymers Studied

specimen[a]	M_{PS}	M_{PMMA}	$(M_w/M_n)_{COP}$	f_{PS}[b]
P(S-*d*-*b*-MMA)	52 900	48 000	1.10	0.50
P(S-*d*-*b*-MMA-*d*)	55 600	59 200	1.10	0.51
P(S-*b*-MMA-*d*)	56 300	65 000	1.12	0.47
P(S-*b*-MMA)	58 600	55 000	1.10	0.53

[a] The *d* following the block indicates perdeuteration of that block. [b] *f* is the fraction of PS in the copolymer.

unsuitable for at least two reasons. First, the small-angle scattering from the solution would significantly perturb the measured reflectivity profile. Second, the transmission of the neutron beam through 200 mm of CCl_4 by using 4.05-Å neutrons is much less than 0.1% (due to the large absorption cross section of chlorine), which is clearly unsuitable for these studies.

The measurements were performed on the H-9 triple-axis spectrometer at the Brookhaven National Laboratory reactor. A beryllium filter and graphite monochromator were used to define an incident beam of 4.05 Å. After monochromatization the beam was collimated to a horizontal divergence of 0.03° with a pair of cadmium masks. The beam size was 0.5 mm (in the horizontal) by 25 mm (in the vertical). The horizontal acceptance angle of the slit after the sample was 0.4°. It should be noticed that the use of glancing angles and the large dimension of the beam in the vertical direction required the use of the large quartz single crystal. Projection of the 0.5-mm beam onto the 200-mm surface translates into a minimum glancing angle of 2.5 mrad. The large dimensions of the incident beam are required to intercept as much of the incident beam as possible, which, under the conditions used for these experiments, was 8×10^3 neutrons/s. The reflectivity scans were done under the specular condition, with the grazing angle of incidence at the sample (θ_1) equal to the angle of the reflection. Background was measured by offsetting the detector angle by 0.3° from the specular condition.

Samples of P(S-*b*-MMA) were purchased from Polymer Laboratories and were used as received. The characteristics of the copolymers used in this study are given in Table I. As seen, all four combinations of labeling of the block copolymers were employed in this work. The solvent used was carbon tetrachloride, CCl_4, which at room temperature, 21 °C, the temperature at which these studies were performed, is a good solvent for PS but a poor solvent for PMMA. The Θ-temperature for PMMA in CCl_4 is given as being 27 °C.[26] The total concentration of copolymer in the solvent was 0.4 g/100 cm³.

Before filling the cell with the polymer solution, the quartz crystal and the Teflon gasket were soaked in a concentrated H_2SO_4/Nochromix solution for 1 h. Both of these were thoroughly rinsed with distilled water and blown dry with nitrogen. The top steel plate of the cell was cleaned with a laboratory detergent, rinsed thoroughly in distilled water, dried under blowing nitrogen, and then soaked in pure CCl_4 solvent and dried prior to assembly. Solutions of the copolymer in CCl_4 were injected into the cell and allowed to incubate for 1 h prior to the reflectivity measurement. Each profile required 12 h to complete, and no time-dependent effects were seen. This was confirmed by rerunning entire reflectivity profiles consecutively in two different cases and rerunning selected portions of the profile in the other cases. For three of the copolymer solutions repeat measurements were made beginning with a cleaned cell and fresh polymer solutions. Excellent reproducibility was found.

Table II
Characteristics of Components in the Experiment

component	ρ, g/cm³	$\delta \times 10^6$	b/V, $\times 10^6$ Å^{-2}
quartz	2.3	10.70	4.10
CCl_4	1.59	7.21	2.76
PSH	1.00	3.73	1.43
PSD	1.08	15.90	6.09
PMMAH	1.15	2.66	1.43
PMMAD	1.24	17.75	6.80

Results and Discussion

Prior to the investigation of the block copolymers, it is necessary to characterize the quality of the polished, single-crystal quartz that was used as the substrate. For this purpose, neutron reflectivity measurements were performed by reflecting the neutron beam from air onto the surface of the quartz crystal. The reflectivity, $R(Q)$, obtained from the polished face of the crystal as a function of the neutron momentum transfer, Q, normal to its surface with a magnitude of $(4\pi/\lambda)\sin\theta$ where λ is the wavelength of the neutrons and θ is the grazing angle of incidence, could be well described by[27]

$$R(Q) = R_F(Q)e^{-Q_T Q_T \sigma^2} \quad (1)$$

Here, $R_F(Q)$ is the Fresnel reflectivity, which is the reflectivity that would be observed for a perfectly smooth quartz surface where the scattering length density change at the air–quartz interface is infinitely sharp. The exponential term multiplying $R_F(Q)$ takes into account the reduction in reflectivity due to the roughness of the surface.[27-29] Q_T is the momentum transfer normal to the surface inside the medium (quartz), which is purely imaginary below the critical angle. Due to refraction at the air–quartz interface, $Q \neq Q_T$ and $Q_T = (4\pi n/\lambda)\sin\theta_T$ where n is the refractive index of the neutrons in the quartz and θ_T is the grazing angle of refraction in the quartz. σ is the root-mean-square Gaussian roughness, which was measured to be 5 Å for the bare quartz and assumed to be constant throughout these studies.

When absorption is neglected, the refractive index of neutrons, n, in a medium with a scattering length density, b/V, is given by

$$n = \left[1 - \left(\frac{b}{V}\right)\frac{\lambda^2}{2\pi}\right]^{1/2} = 1 - \delta \quad (2)$$

Shown in Table II are typical values of the mass density, ρ, scattering length density, and δ for the materials used in this study. In most cases δ is positive and $\sim 10^{-6}$ in magnitude, and, consequently, n is only slightly less than 1. Therefore, at the interface between air and any one of these components there exists a critical angle below which incident neutrons are totally reflected. This, for example, was the case for the studies characterizing the surface of the quartz crystal.

The neutron reflectivity profiles for the four different copolymers investigated in this study are shown in Figures 2 and 3. Referring to Figure 1, the neutron beam impinges on the side of the quartz at near normal incidence and

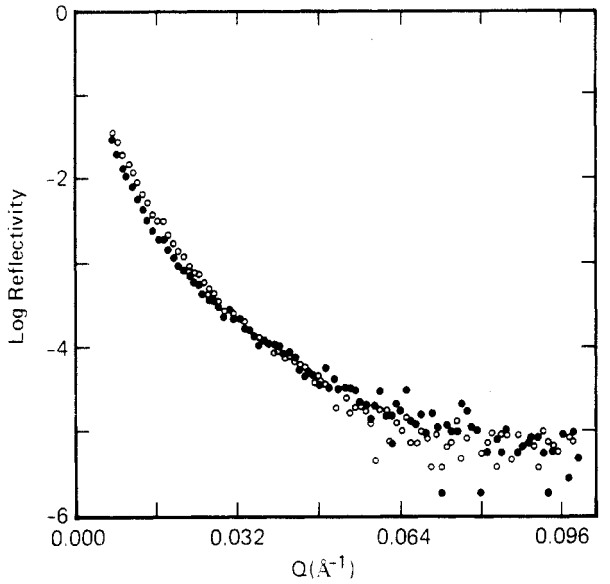

Figure 2. Neutron reflectivity profiles for P(S-*b*-MMA) [○] and P(S-*d*-*b*-MMA) [●] copolymers dissolved in CCl_4 at a concentration of 0.4 g/100 cm³.

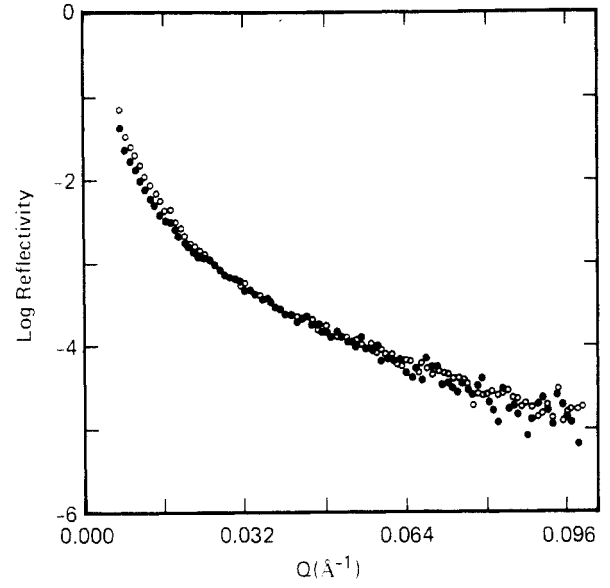

Figure 3. Neutron reflectivity profiles for P(S-*b*-MMA-*d*) [○] and P(S-*d*-*b*-MMA-*d*) [●] copolymers dissolved in CCl_4 at a concentration of 0.4 g/100 cm³.

refraction effects at this interface are negligible. Therefore, the z component of the momentum transfer in the quartz is equal to that in vacuo. Consequently, the reflectivity data are shown as a function of Q where, as before, Q is the momentum transfer in vacuo in the z direction. It should, also, be notted that the reflectivity profiles have been normalized to the incident beam flux transmitted through the length of the quartz crystal. This is important since total external reflection is not observed in any of the solution experiments. The reason for the absence of total external reflection is that the refractive index of neutrons for quartz is lower than that for CCl_4, as can be seen from Table II.

The reflectivity profiles have been grouped by plotting those data for the copolymers with the normal PMMA blocks, i.e., P(S-*b*-MMA) and P(S-*d*-*b*-MMA), in Figure 2 and the data for the copolymers with deuterated PMMA blocks, i.e., P(S-*b*-MMA-*d*) and P(S-*d*-*b*-MMA-*d*), in Figure 3. This was done to emphasize the observation that the reflectivity profiles for the copolymers with identical

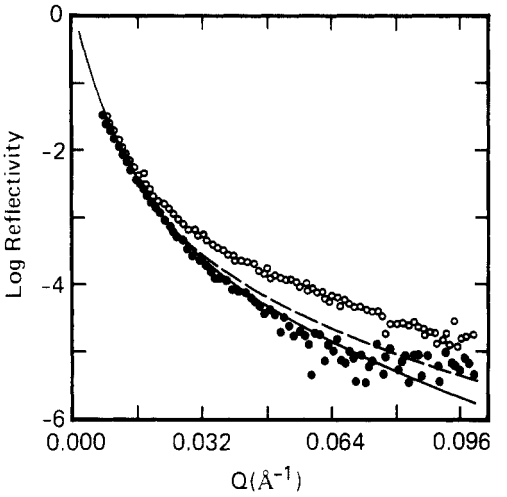

Figure 4. Comparison of the measured and calculated neutron reflectivity profiles for P(S-*b*-MMA) [●] and P(S-*b*-MMA-*d*) [○] using an exponential decay to describe the segment density profile from the quartz surface. The best fit to the P(S-*b*-MMA) was obtained first (—), and that for the P(S-*b*-MMA-*d*) was obtained by changing the scattering length density of the MMA block (- - -). It should be noted that while the solid line agrees with the P(S-*b*-MMA) data, the dashed line does not compare well with the P(S-*b*-MMA-*d*) data.

PMMA labeling are quite similar. Only slightly higher reflectivities are seen at lower Q for the copolymers with normal PS blocks. Deuteration of the PMMA block, however, changes the reflectivity profile significantly at wavevectors higher than 0.02 Å^{-1} as shown by the comparison in Figure 4 of P(S-*b*-MMA) and P(S-*b*-MMA-*d*).

The slight changes in the reflectivity profiles due to the labeling of the PS suggest that the concentration of the PS is too low to assess critically by these experiments. Since CCl_4 is a good solvent for PS and a poor solvent for PMMA, then the picture that emerges from these data, *without any detailed analysis*, is that PMMA adsorbs strongly onto the quartz crystal and the PS blocks are extending into the solution. This would give rise to large differences in the relative concentrations of the PMMA and PS blocks and, consequently, the sensitivity of the experiments to PMMA, the strongly adsorbed block. The preferential adsorption of PMMA onto the quartz crystal for these diblock copolymers, aside from the poor solvent quality of CCl_4, is also observed in the absence of solvent. Recent experiments on thin films of these diblock copolymers in the absence of solvent on silica and silicon substrates in the ordered and disordered states clearly show a strong, preferential adsorption of the PMMA block onto the substrate.[22,30,31] This is, more than likely, associated with the PMMA being the more polar of the two blocks, interacting more strongly with polar moieties on the surface of the substrate. Consequently, both the solvent quality and the specific interactions of the PMMA block with the surface, two distinctly different reasons, favor the adsorption of the PMMA onto the substrate. Separating these two would require the investigation of the adsorption of the block copolymers from solutions of the case where the solvent is a good solvent for both blocks and the case where the solvent is a good solvent for the PMMA block and a poor solvent for the PS block. Experiments are planned to address this issue.

The fact that changing the labeling of the PS block altered the reflectivity profile only slightly suggests, as stated before, that the concentration of the PS segments, beyond the intial layer of PMMA, is too low to be assessed

by our experiment. Consequently, in the analysis of these data, only the concentration of PMMA segments near the quartz surface will be considered, assuming the concentration of PS to be zero. Over the momentum transfer range studied, which was limited by the beam size at low Q and by signal-to-noise ratio at high Q, this assumption does not cause significant discrepancies in the calculated reflectivity profiles. Specific details of the PS segment density profile will be restricted to the low Q region of the reflectivity profile. Analysis of the reflectivity data was performed by approximating the segment density profile perpendicular to the quartz surface by a histogram with layers of different scattering length densities and calculating the reflectivity profile by the usual matrix method.[32]

Different models for the segment density or the scattering length density profile of the polymer solution as a function of the distance from a solid surface have been proposed and were used to fit the measured reflectivity profiles. de Gennes[14] has predicted a power law decay of the form

$$\phi_A(z) = C\left(\frac{A}{Z+B}\right)^{4/3} \tag{3}$$

where $\phi_A(z)$ is the volume fraction of component A a distance z from the surface where $A-C$ are variable parameters. Scheutjens et al.[16,17] suggest that the volume fraction of the polymer segments would vary in an exponential manner as

$$\phi_A(z) = Ce^{-z/\xi} \tag{4}$$

where ξ is a characteristic decay length and C is a variable parameter.

Either of these models and others could be used to describe the reflectivity profile obtained from any one experiment on the copolymers. For example, shown in Figure 4 by the solid line is the comparison between the calculated and measured reflectivity profiles (open circles) for the P(S-*b*-MMA) using the exponential decay (eq 4) with $\xi = 50$ Å and $C = 0.6$. As can be seen this model well describes the measured reflectivity profiles. A similar fit to the profile could be obtained with the power law relation in eq 3. However, if only the labeling of the PMMA block is switched, i.e., going from P(S-*b*-MMA) to P(S-*b*-MMA-*d*), then the exact same parameters should describe the observed profiles when only changing the scattering length density of the PMMA block. Shown in Figure 4 by the dashed line is the reflectivity profile for the P(S-*b*-MMA-*d*) calculated only by changing the scattering length density of the PMMA block. In comparison to the experimentally observed profile, shown by the solid circles, it is clear that at low Q the profiles are in reasonable agreement whereas at high Q large deviations are evident. A similar result was found by using the power law relationship. In the experiments performed here where the labeling of the PMMA block, the portion of the molecule of interest here, was changed, it is mandatory that only one set of parameters describe the PMMA reflectivity profiles irrespective of the labeling of the block. That is to say, provided deuteration does not alter the behavior of the PMMA at the surface, then whatever parameters were used to describe the profile of the deuterated PMMA containing copolymer must also describe the reflectivity profile of the copolymer containing the normal PMMA. For the profiles discussed above this was clearly not the case. The reversal of labeling, in fact, places severe restrictions on the final model that can suitably describe all the data.

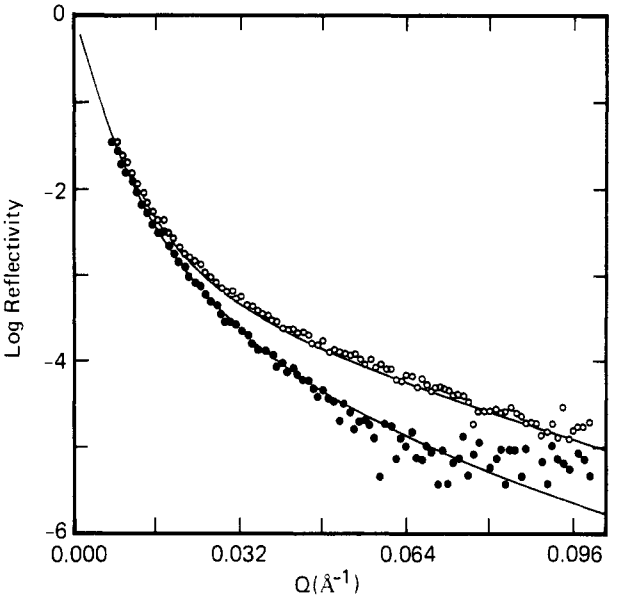

Figure 5. Comparison of the measured and calculated neutron reflectivity profiles for P(S-*b*-MMA-*d*) [○] and P(S-*b*-MMA) [●] using the parabolic concentration profile. Here only the labeling of the MMA block was varied, and the concentration of both copolymers in solution is 0.4 g/100 cm^4.

One density profile that was found to describe the observed reflectivity results was a parabolic profile where the density of solution adjacent to the quartz substrate, $\rho(0)$, is given by

$$\rho(0) = \sum \phi_i(0)\rho_i \tag{5}$$

where ρ_i is the bulk density of component i with volume fraction $\phi_i(0)$ at the substrate ($z = 0$). For the study here it was found that $\phi_{PMMA}(0) = 0.42$ best described the data. As the distance z from the quartz surface increased, the volume fraction of PMMA could be described by

$$\phi_{PMMA}(Z) = \phi_{PMMA}(0)(D^2 - z^2)/D^2 \quad \text{for } z \le D$$
$$\phi_{PMMA}(z) = 0 \quad \text{for } z > D \tag{6}$$

where $D = 45 \pm 8$ Å and $\phi_{PMMA}(0) = 0.42$. This parabolic profile is equivalent to having a layer of a PMMA solution in CCl_4 with a volume fraction of 0.42 and an effective thickness of 30 Å, which is defined from the surface of the quartz to the point at which the concentration of PMMA is 0.21, the 50% level. As inferred from the parabolic profile, this layer is quite diffuse.

Fits of the parabolic density profile to the P(S-*b*-MMA) and P(S-*b*-MMA-*d*) are shown in Figure 5 by using a fixed set of parameters and only changing the contrast for the two cases. As can be seen, this model well describes the reflectivity profiles in both cases. These results indicate that the PMMA molecules are collapsed at the quartz substrate since the total effective layer thickness is approximately equal to the radius of gyration of PMMA in a Θ solvent.[26] Given that PMMA is adsorbed onto an impenetrable wall, this result is not surprising. It is important to note that the parabolic functional form of the concentration profile is just one profile that suitably describes the results. Other profiles comprised of box functions with gradients in the concentrations can equally well describe the data. However, this does not change the basic description of the concentration profile. It is apparent that the copolymers adsorb very strongly onto the quartz substrate, and, in fact, only the PMMA portions of the copolymers appear to adsorb onto the surface. This would leave the PS portions of the molecule to extend from

this adsorbed layer. Since the PS portions of the molecule were not discernible during these experiments, this implies that the concentration of the PS segments is much lower than that of the PMMA. This can only mean that the PS portions of the copolymer must stretch out from the adsorbed PMMA blocks and thereby reduce the scattering length density sufficiently so as not to be observable.

This picture is similar to that obtained by Hadziioannou et al.[3] from surface force experiments on diblock copolymers of polystyrene and poly(2-vinylpyridine), P(S-*b*-V2P), adsorbed onto mica. In these experiments the PS blocks were found to be stretched to about 10 $R_{g,PS}$. They argued that this is equivalent to the case of terminally grafted PS chains in a good-solvent toluene with the surface density of PS chains influenced by the PV2P block. It was assumed that PV2P blocks fully covered the surface with a thickness equal to $R_{g,PVP}$, the radius of gyration of the PV2P block in toluene and beyond this initial layer of PV2P; the PS blocks are stretched to form a layer of closely packed terminally anchored chains. The reflectivity experiments for P(S-*b*-MMA) do indeed show that there is an initial dense layer of PMMA near the quartz surface. The volume fraction of PMMA blocks near the surface is, however, only 0.42 in contrast to the assumed, fully covered PV2P surface.

If it is assumed that the PS chains are fully extended, then, when the concentration of PMMA in the observed 30-Å layer is known, the concentration of PS can be estimated from

$$\phi_{PS} \simeq \phi_{PMMA}\frac{a^2}{\pi R_{g,PMMA}{}^2} \tag{7}$$

where $\phi_{PMMA} = 0.42$, $R_{g,PMMA} = 30$ Å, and a^2, the cross-sectional area per styrene repeat unit, is approximately 30 Å^2.[33] Substitution into eq 7 yields $\phi_{PS} \simeq 4.5 \times 10^{-3}$. While this number represents a lower limit to the concentration of PS near the surface, it is clear, from the insensitivity of the reflectivity experiments to the labeling on the PS block, that the polystyrene concentration must be low. This necessarily implies that the PS chains must be extended; otherwise, the concentration of PS segments would be higher and would affect the reflectivity profiles more than observed.

Recent theoretical studies of Marques et al.[19,20] on the adsorption of block copolymers onto a surface in different types of solvents show that, within a certain range of concentration, an adsorbing A block forms a molten layer. The thickness of this molten layer is dependent upon concentration as well as the asymmetry between the molecular weight of A and B blocks and the molecular weight of the A block. For symmetric block copolymers it can easily be of the order of the radius of gyration of the A block in agreement with the results found here.

In summary, the neutron reflectivity results have shown that, for symmetric, diblock copolymers of PS and PMMA, the PMMA block strongly adsorbs onto the quartz substrate forming a PMMA-rich layer of 30 Å, comparable to its radius of gyration, with a volume fraction of 0.42. The chains in the PS blocks, however, must be sufficiently stretched and extended into the solution to reduce the PS segment density to a level undetectable by neutron reflectivity. It is evident that neutron reflectivity provides key information for evaluating segment density profiles of polymers adsorbed onto a solid surface.

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