Determination of End-Adsorbed Polymer Density Profiles by Neutron Reflectometry

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ABSTRACT: Specular neutron reflection was used to investigate the density profile of polystyrene–poly(ethylene oxide) (PS–PEO) block copolymers adsorbed from d-toluene onto quartz. The neutron beam passed through the quartz substrate and was reflected from the quartz/d-toluene interface. The PEO block, which comprises a small fraction of the total polymer molecular weight, strongly adsorbs onto the quartz substrate, while the PS block remains in solution. Thus, the chains form a terminally attached polymer "brush". The reflectivity profiles are well described by a parabolic or error function polymer density profile normal to the interface, but the data cannot be fitted to exponential or power law decay profiles. The layer thickness values are in good agreement with the results of interlayer force measurements for the same polymer–solvent system adsorbing onto mica. The molecular weight dependence of the layer thickness and adsorbance obtained from the data obey scaling laws in accord with the theory of semidilute polymer brushes.

Introduction

The adsorption of polymers at the solid/liquid interface modifies the forces between two solid surfaces across a liquid medium and is widely used to stabilize colloidal dispersions.[1] Nonadsorbing polymer chains terminally anchored to the solid substrate either via a single functional group or a small polymer block are particularly useful in this connection, as they are free of bridging-attraction effects which can dominate homopolymer adsorption at low surface coverage.[2,3] Furthermore, terminally attached chains at high grafting density can produce considerably more extended macromolecular layers in comparison with adsorbing chains of the same molecular weight.[4–6]

In recent years, the conformation of end-adsorbed polymer chains, as well as the forces acting between surfaces bearing such macromolecular layers, has been the subject of much theoretical and experimental work. Direct force measurements[5–7] confirm that under suitable solvent conditions block copolymers adsorb with one block compact and tightly bound and one extended, swollen block stretching away from the surface. These results also agree quantitatively with the predictions of Alexander's scaling model.[8] For terminally anchored block copolymers in a good solvent, two regimes are anticipated depending on the grafting density. If the grafting density is low, such that the chains do not interact with each other, then they will exist as separate "mushrooms". If on the other hand the grafting density is high, with the distance between anchor points less than the Flory radius of the chains, the polymers take up a more extended configuration forming a semidilute "brush". For high grafting density of the polymer on the surface the most recent mean field theory of Milner, Witten, and Cates[9] predicts a parabolic polymer density (or volume fraction) profile rather than the step function assumed by Alexander and de Gennes.[8,10] Force measurements, however, are not sensitive to differences between the two models.[6] It is of interest therefore to investigate the shape of this profile by some other experimental method.

Neutron reflection experiments provide information on the neutron refractive index profile normal to the reflecting interface and can thus probe the composition of surfaces and interfaces. Recently, the technique of neutron reflectometry has been shown to provide good resolution for the determination of polymer segment density profiles.[11–14]

In the present paper we report results of neutron reflectivity on diblock copolymers of protonated polystyrene and poly(ethylene oxide) (PS–PEO), terminally adsorbed on quartz from deuterated toluene, via the PEO block whose size is small compared to that of the PS. The same block copolymers which were previously investigated with the surface force technique[6] were also used in the present study.

Experimental Section

In order to reduce the complexity associated with an additional air/liquid interface, the geometry was such that the neutron beam passed through the solid substrate and was reflected off the lower surface which was immersed in a reservoir of polymer solution contained in a Teflon cell (see Figure 1). A single-crystal, optically flat quartz slab was used as a substrate in order to achieve acceptable transmission. For a quartz path length of 12 cm the transmission was found to be between ca. 0.6–0.7 for the wavelengths used. The data were measured at different glancing angles of incidence and corrected for transmission in the range of wavelengths used. Adsorbing surfaces of the quartz slab are polished optically flat. The roughness of the quartz surface was determined by X-ray reflectivity measurements and found to be ca. 10 Å. This value was used throughout the analysis of the neutron reflectivity data. Solutions of 0.1 mg mL^{-1} of polymer in d-toluene were introduced into the 2-mm gap between the quartz block and the Teflon base via glass tubes. Adsorption was allowed to take place at 22 ± 2 °C. To check any time dependence of the reflectivity profiles, overnight incubation of the quartz surface in the polymer solution was used for some of the measurements. The results revealed no change in the reflectivity, to within the experimental error, from that observed after

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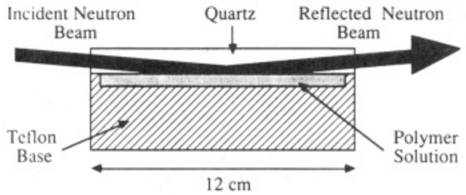

Figure 1. Schematic diagram of the sample cell used in the experiments.

Table I
Characteristics of the PS–PEO Block Copolymers

M_W	M_W/M_N	wt % PEO content	x[a]	y[a]
80×10^3	1.07	5.0	730	90
150×10^3	1.16	1.5	1420	51
184×10^3	1.10	4.0	1700	167
502×10^3	1.10	0.8	4788	91

[a] x and y refer to the polymerization index of the block copolymer $(PS)_x(PEO)_y$.

a few hours of incubation. It is important to ensure that the substrate onto which the polymer is adsorbed is clean. Before each measurement the quartz is first cleaned in 3:1 (v/v) HCl–HNO_3 followed by 3:1 (v/v) H_2SO_4–HNO_3, both for approximately 3 h. It is then washed thoroughly with distilled water followed by absolute alcohol and finally left in toluene. All the glass components coming into contact with the polymer solution are cleaned in chromic acid and thoroughly washed with distilled water.

The reported results were obtained on CRISP at the RAL and SPEAR at Los Alamos. Both facilities use a fixed angle of incidence with a pulsed neutron beam and time of flight (TOF) to measure the wavelength.[13–15] On CRISP a wavelength range of 2.0–6.5 Å and glancing angles of incidence of 0.2 and 0.5° were used. On SPEAR a wavelength range of 1.0–16.0 Å and a glancing angle of incidence of 0.45° were used. The deuterated solvents were purchased from MSD Isotopes, and the polymers were synthesized and characterized by Polymer Laboratories Ltd. (see Table I). Samples with molecular weight (M_W) 150×10^3 and 502×10^3 were measured on CRISP, and those with M_W 80×10^3 and 184×10^3 were measured on SPEAR. All materials were used as supplied.

Results and Discussion

Thermal neutrons exhibit classical optical properties such as reflection, refraction, and interference. The refraction and total reflection of neutrons involve the interference between the incident neutron wave and waves scattered in the forward direction. It can be shown that neutrons are reflected at a "sharp" interface in a completely analogous way to electromagnetic radiation where the electric vector is perpendicular to the plane of incidence. The appropriate reflection coefficient for neutrons is therefore given by the Fresnel reflectance for s-waves. The actual quantity measured is the reflectivity R, defined as the ratio of the reflected to incident neutron intensities. The reflectivity is measured as a function of the scattering wavevector, $Q = (4\pi/\lambda) \sin \theta$, which is defined by the incident angle θ and wavelength λ. The critical wavevector Q_c at which the reflectivity departs from unity is called the critical edge and depends only on the difference between the refractive indices of the two bulk media far from the interface. For scattering wavevectors less than this critical value, the reflectivity is unity and there is no refracted wave.

The standard way to analyze reflectivity data is to employ multilayer optical methods[13,14] in which the refractive index profile between two bulk media may be approximated by a series of layers of constant refractive index. In the fitting routine used to analyze the data, each successive layer in the polymer density profile is treated as a homogeneous film. The reflectance r of the homogeneous film is given by the equation

$$r = \frac{r_{01} + r_{12}\exp(2i\beta)}{1 + r_{01}r_{12}\exp(2i\beta)} \tag{1}$$

where r_{ij} is the Fresnel coefficient at the i/j interface and $\beta = (2\pi/\lambda)n_1 d \cos \theta_1$, where λ is the neutron wavelength, n_1 is the neutron refractive index of the film, d is its thickness, and θ_1 is the angle of refraction in the film. The reflectivity of any profile can then be calculated iteratively by successively adding layers to the last adsorbed layer starting at the substrate. If the surface or interface is not entirely smooth, then its roughness modifies the specular reflectivity. This modification is described by a Debye–Waller type factor which has the same effect as putting a Gaussian roughness at the interface.[13,14] A roughness value of 10 Å was obtained for the quartz surface from X-ray reflectivity measurements and was included in the calculation of the neutron reflectivity throughout the analysis of the data.

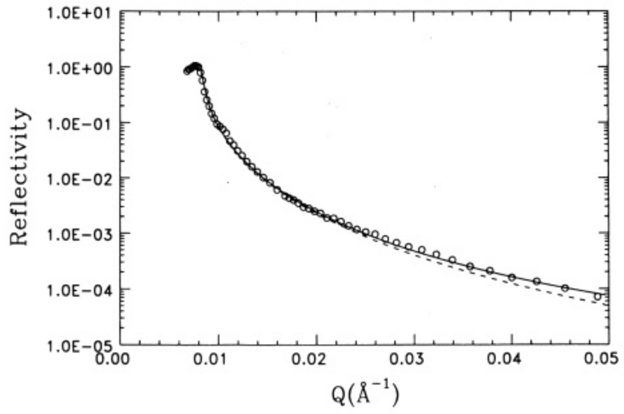

Figure 2. Neutron reflectivity profile of quartz/d-toluene interface (○) fitted to Fresnel's law (- - -) and also with a thin film (ca. 3 Å) of water on the quartz surface (—).

As the quartz has a lower scattering length density (4.22×10^{-6} Å^{-2}) than d-toluene (5.66×10^{-6} Å^{-2}), this allows a critical edge to be measured at low Q, which serves as a useful frame of reference for the entire reflectivity profile. The scattering length density of protonated polystyrene is 1.35×10^{-6} Å^{-2}. Thus, on formation of an adsorbed layer, the value of the scattering length density close to the quartz/d-toluene interface is reduced relative to that of the pure solvent in proportion to the local volume fraction of polymer, providing a good contrast.

The reflectivity of the quartz/d-toluene interface is shown in Figure 2. The data are in close agreement with Fresnel's law at low Q, but at higher Q the observed reflectivity deviates to higher values than predicted by theory. Good fits can be obtained, however, with the introduction of a surface layer ca. 3 Å thick with a scattering length density considerably lower than that of quartz and close to that of water (see Figure 2). Since undried toluene has been used throughout this study, this is thought to be due to a thin layer of water adsorbed at the quartz surface. A similar water layer is thought to adsorb onto mica from undried organic solvents.[16] It is also possible, however, that the observed deviation may be due to the presence of a thin amorphous layer at the quartz/toluene interface.

We have investigated block copolymers of protonated polystyrene (PS) and protonated poly(ethylene oxide) (PEO) of different molecular weights (see Table I) adsorbed onto quartz from deuterated toluene, which is a good solvent for both blocks of the copolymer. This system, and the closely related one of end-functionalized polystyrene, have been studied in detail using the mica force-balance technique.[6] It has been shown that the head group (PEO) which comprises a small fraction of the total molecular weight is strongly adsorbed onto the solid substrate, whereas PS does not adsorb and remains in solution. Due to its small size, the PEO block does not extend significantly away from the surface, so that the overall layer thickness is determined by the extension of the PS chain.

Current theories for end-attached, nonadsorbing polymer chains fall into two categories: scaling and mean field. In the scaling approach of Alexander[8] the chains are grafted to the surface from a good solvent with a mean interanchor spacing s and extend into solution away from the surface to form a layer of thickness L. In the limit $s \ll R_F$, where R_F is the Flory radius of the chain, the layer is in the semidilute regime and its polymer segment density is assumed constant throughout. Each chain can be treated as a series of connected "blobs" which experience osmotic repulsion. This tends to stretch the chains and is counterbalanced by the increase in the elastic free energy as the chains become overstretched. At equilibrium, the blob size is s, while the layer thickness L_0 is

$$L_0 = s\left(\frac{R_F}{s}\right)^{5/3} = s^{-2/3}a^{5/3}N \qquad (2)$$

where N is the degree of polymerization, a is the length of a monomer unit, and the expressions hold to within a prefactor of order unity which is implicit in all scaling arguments.

Various mean field calculations of the configuration of adsorbed chains have been reported.[9,17-20] The main approaches to calculating polymer density profiles of end-attached chains use essentially a self-consistent mean field (SCF) theory. The SCF equations can be solved either numerically[19,20] or analytically as in the recent theory of Milner, Witten, and Cates,[9] which relates closely to the experimental configuration of our system. Milner et al. made use of the fact that the chains in the brush are strongly stretched (i.e., in the semidilute regime) and may be assumed to behave classically. Thus, relating the mean field, which is the effective chemical potential, to the free energy gives, in the classical limit, a parabolic density profile rather than the step function assumed by Alexander and de Gennes in their scaling calculations.[8,10] The layer thickness or brush height calculated by this approach, however, has a form essentially identical to that of the scaling treatment (eq 2 above) from which it differs only by a numerical prefactor

$$L_0 = (12/\pi)^{1/3}(w\sigma)^{1/3}N \qquad (3)$$

where $\sigma \sim s^{-2}$ is the surface coverage and w is an excluded volume parameter.

In view of the parabolic density profile predicted by theory,[9] we have used density or volume fraction profiles of the form $\varphi(x) = A - Bx^n$, where x is the distance normal to the interface and A, B, and n are fitting parameters. A and B are determined by the volume fraction of polymer at the interface and the layer thickness of the adsorbed polymer. The value of n determines the shape of the profile. It is 1 for a linear profile and 2 for a parabolic profile and tends to infinity in the case of a step function. For $0 < n < 1$, the profile becomes concave upward. We have also used a single step with roughness giving a complementary error function density profile of the form $\varphi(x) = (\varphi_0/2)(1 - \mathrm{erf}((x - t)/\sqrt{2}\delta))$, where φ_0 is the polymer volume fraction at the interface, t is the layer thickness, and δ is the roughness of the layer. The angular resolution is also put in as a fitting parameter. Q_c is fixed by our system, since its value depends only on the difference between the scattering length densities of quartz and toluene-d and should therfore be the same for all measurements. Its apparent value may vary somewhat, however, because there is some experimental uncertainty in measuring the angle of the incident beam (particularly on CRISP) which produces a shift in the apparent position of Q_c between measurements. We have thus subjected some of the data to small shifts in Q to correct for the error in measuring the angle. The fitting routine minimizes the sum of the weighted squared differences between the experimental and the fitted reflectivity with respect to the fitting parameters using the Simplex method.[21] Each experimental point is weighted by its statistical error. It was found that it is sufficient to divide the density profile into 10 discrete layers with no interlayer roughness. Further subdivision of the density profile produces no significant difference in the reflectivity within the Q range that we measured. As before, a surface layer of water (ca. 3 Å) was included in the calculation of the reflectivity.

At low to moderate values of the Q range covered by our measurements, the data are well described by a parabolic profile ($n = 2$), in good agreement with the profile predicted by the Milner, Witten, and Cates mean field theory for polymer brushes.[9] If the exponent n is treated as a parameter and allowed to vary, somewhat better fits are obtained but the values of the layer thickness and polymer volume fraction at the quartz/toluene interface are not substantially changed. For example, for $M_W = 80 \times 10^3$, the optimized exponent is 2.6. This gives a χ^2 improvement of about 10% relative to that obtained with $n = 2$. However, the change in L_0 and $\varphi(0) = \varphi_0$ is less than 5% and is thus within the experimental error. Figure 3 shows fits to such a profile using the optimized parameters for the different molecular weights studied (see Table II). In Figure 3e the reflectivity multiplied by Q^4 is plotted as a function of Q for the 184×10^3 molecular weight as this gives a better indication of the goodness of fit and the asymptotic limit of the refectivity at high Q. The exponent n converges to values which are not far from 2 for the three lower molecular weights, but the polymer with $M_W = 502 \times 10^3$ exhibits a much higher exponent (see Table II). This is probably due to the very low segment density associated with this larger polymer, whose scattering length density profile rapidly becomes indistinguishable from that of the solvent at distances away from the surface, which renders the fit less sensitive to the value of n. The very low volume fraction of polymer in the adsorbed layers of high molecular weight terminally anchored PS was also observed in surface force measurements.[6] It is not possible to distinguish between the parabolic and error function type profiles at low values of Q. At high values of Q, however, differences emerge between the two profiles (see Figure 4). In particular, interference fringes are seen for the parabolic function which has a sharp cutoff in the polymer density profile at the height of the brush (see Figure 5). These fringes are absent in the error function profile, and they are also not observed in the experimental data, although at high values of Q the noise in the data does not allow a detailed picture of the exact shape of the brush density profile in the tail region to be made. It must be borne in mind, however, that the classical Milner–Witten–Cates description of the brush regime requires a correction to the end density of a finite brush (i.e., for a system consisting of chains of finite length, there is a region at the outer extremity of the brush where the chains are

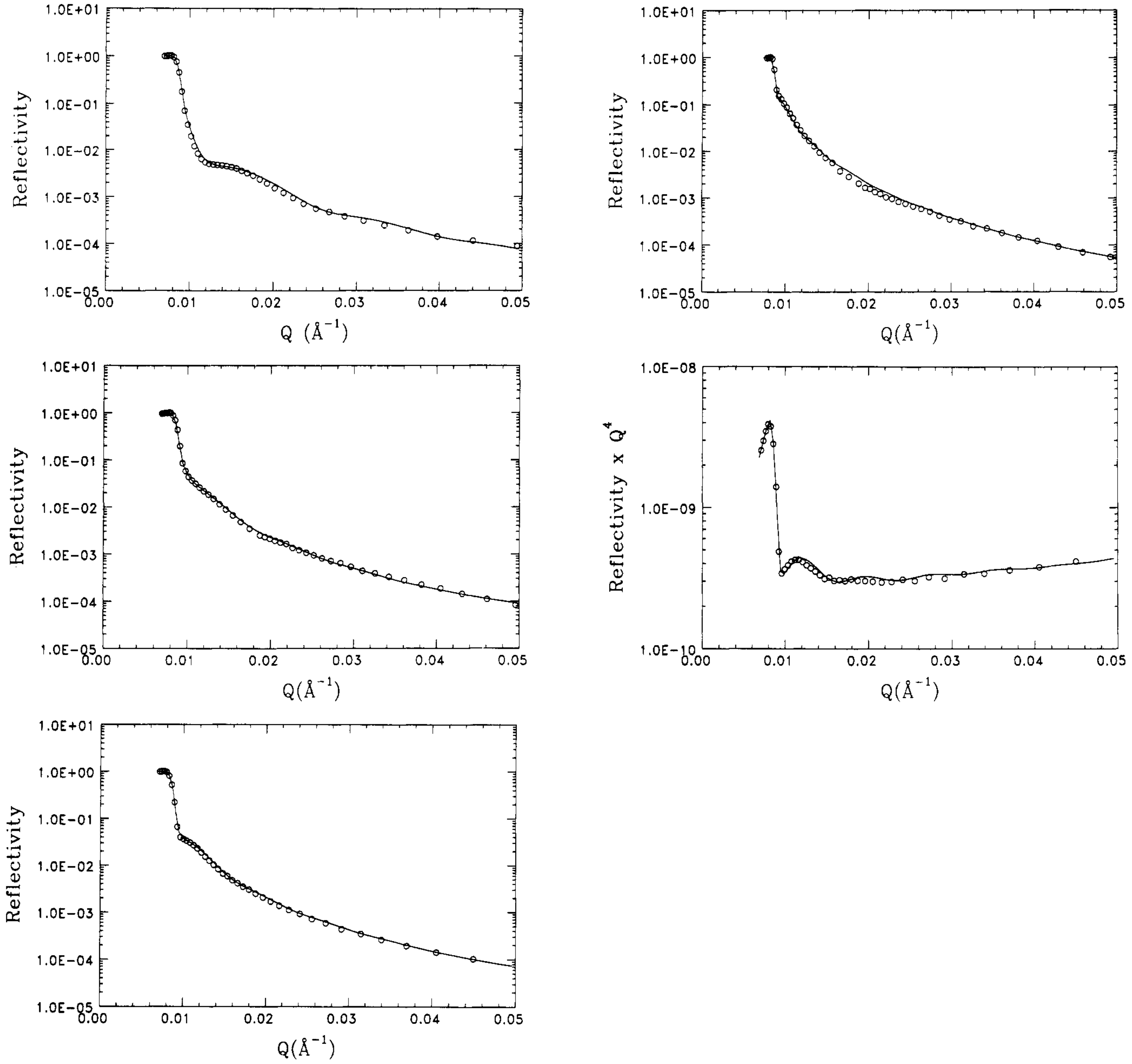

Figure 3. Neutron reflectivity profiles of PS–PEO of different molecular weights end-adsorbed from d-toluene onto quartz (○) fitted with the parameters given in Table II (—). M_w: (a, top left) 80 × 10^3, (b, center left) 150 × 10^3, (c, bottom left) 184 × 10^3, (d, top right) 502 × 10^3, and (e, center right) 184 × 10^3 plotted as RQ^4 vs Q.

Table II
Parameters Obtained from Fits to $\varphi(x) = A - Bx^n$ Polymer Density Profiles[a]

M_W	L_0 (Å)	n	Γ (mg m^{-2})	s (Å)	φ_0 (%)
80 × 10^3	450 ± 30	2.6 ± 0.5	2.9 ± 0.5	70 ± 5	9.0 ± 0.2
150 × 10^3	660 ± 50	2.5 ± 0.5	1.6 ± 0.3	120 ± 5	3.5 ± 0.2
184 × 10^3	800 ± 50	1.9 ± 0.5	2.6 ± 0.4	110 ± 5	5.1 ± 0.2
502 × 10^3	1240 ± 90	4.6 ± 1.5,	1.7 ± 0.3	230 ± 10	1.6 ± 0.2

[a] L_0 is the layer thickness of the grafted PS layer, n is the exponent, Γ is the adsorbance, s is the interanchor spacing and φ_0 is the volume fraction of end-adsorbed PS at the interface, i.e., $\varphi_0 = \varphi(0)$.

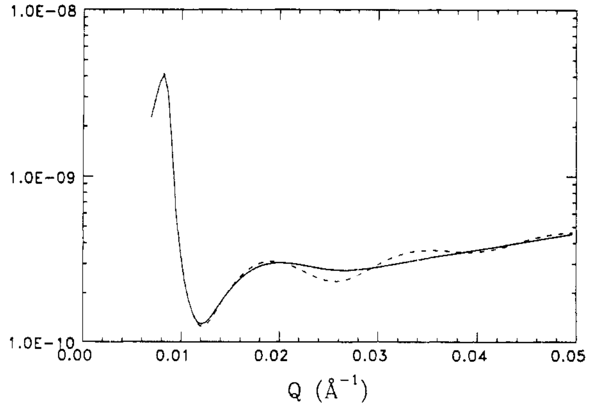

Figure 4. Comparison of neutron reflectivity profiles of error function (—) and parabolic (- - -) density profiles for M_W = 80 × 10^3.

not strongly stretched). This correction to the polymer density is, to leading order, of the form $\exp[-(^2/_3)z^{3/2}]$, where z refers to distances beyond the purely parabolic brush height[22] and thus introduces an asymptotic form qualitatively similar to the error function. The pronounced fringes predicted by a purely parabolic form should therefore be regarded as unphysical. It should also be pointed out that even low levels of polydispersity can significantly influence the region at the height of the brush.[23] Thus, polydispersity effects may also play a role in obscuring the interference peaks that would be expected

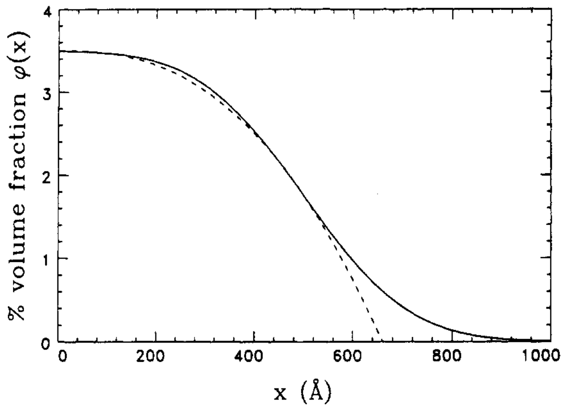

Figure 5. Error function (—) and parabolic (- - -) density profiles for $M_W = 150 \times 10^3$ with the fitting parameters given in Table II for the parabolic fit. The parameters for the error function profile were $\varphi_0 = 0.035$, $t = 500$ Å, and $\delta = 170$ Å.

from a parabola. Close to the surface the two profiles are almost identical in shape (see Figure 5). The profiles are therefore consistent with a parabolic shape with an approximately Gaussian tail. It should be stressed that the data could not be fitted to an exponential profile or one described by a power law of the form $\varphi(x) = Ax^{-n}$ for any of the polymers investigated in this study.

In a recent study Cosgrove et al.[11] used neutron reflectivity measurements to investigate the polymer density profile of a PS–PVP block copolymer terminally adsorbed onto mica from toluene via the PVP block. Although the copolymer employed by these authors had a PS molecular weight much lower (15×10^3) than those used in this study (see Table I), they report good fits to the data using a parabolic polymer density profile, in agreement with our findings. They point out however that certain other qualitatively similar functional forms, such as a Gaussian or a profile based on the Scheutjens–Fleer model,[19,20] also gave good fits to the data. In a similar investigation, Satija et al.[12] studied a symmetric PS–PMMA block copolymer with a total molecular weight of approximately 100×10^3 adsorbed on quartz from carbon tetrachloride. They report that the segment density of the PS block was too low for detailed determination of its density profile but concluded that the PS chains are extended. Auroy et al.[24] have recently used small-angle neutron scattering techniques to study chemically end-grafted chains in both good and poor solvents. They report that in good solvent their results are consistent with the Alexander–de Gennes scaling model. Although they could not determine the polymer density profile exactly, their results indicate that it is smoother than a step function.

The layer thickness values L_0 obtained from our reflectivity data are in very good agreement with the values obtained from force measurements.[6] For example, the same PS–PEO block copolymer of $M_W = 184 \times 10^3$ which was also used in the mica force balance experiments[6] gave a layer thickness of 750 ± 50 Å, in good agreement with the value of 800 ± 50 Å reported here (see Table II). The variation of L_0 with M_W is shown in Figure 6, and the exponent of 0.57 ± 0.06 obtained from this plot is identical within the experimental error to that reported by Taunton et al.[6] Both the scaling[8] and mean-field calculations[9] predict a grafted layer thickness varying linearly with M_W for high grafting density corresponding to a fixed mean distance s between anchor points. As pointed out by Taunton et al.,[6] however, this discrepency may be resolved by bearing in mind that s is not kept fixed in our experiments since the PS chains are not chemically grafted to the mica substrate, but is determined by a balance between the attraction of the PEO block to the quartz surface and the repulsive osmotic interactions between the PS chains. Thus, if the size of the PEO block is kept approximately constant, s becomes essentially a function of the PS chain length and increases with increasing molecular weight of the PS block. Under these conditions, L_0 is expected to vary with $M_W^{3/5}$.[25] We may in fact calculate s by consideration of the adsorbance Γ which is given by the area under the volume fraction profile for each M_W

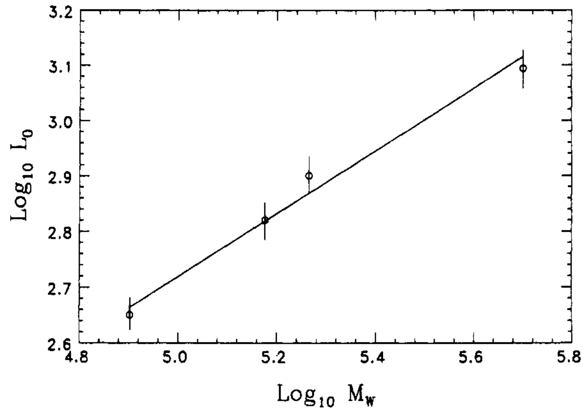

Figure 6. Scaling of the layer thickness L_0 with molecular weight M_W. A gradient of 0.57 ± 0.06 is obtained from the plot.

$$\Gamma = \int_0^\infty \varphi(x)\,\mathrm{d}x \qquad (4)$$

where $\varphi(x)$ is the density profile of the polymer layer. If Γ is expressed in mass per unit area, then

$$s = \left(\frac{N_A \Gamma}{M_W}\right)^{-1/2} \qquad (5)$$

where N_A is Avogadro's number. We thus find that the spacing s increases from ca. 70 Å at $M_W = 80 \times 10^3$ to ca. 230 Å at $M_W = 502 \times 10^3$ while the corresponding polymer volume fraction at the quartz/toluene interface, which varies from ca. 9.0% to 1.6% (see Table II), is clearly in the semidilute regime. Furthermore, the extension ratio $L_0/s \approx 6$ is, as expected, in the brush regime.

The L_0 values determined from our data are also in reasonable quantitative agreement with those calculated from theory using eq 2 or 3. Since the value of R_F is known for a given M_W and s has been obtained from our data, we may use eq 2 to calculate the scaling prediction for L_0 assuming a prefactor of unity. Using the data for $M_W = 150 \times 10^3$, for example, we obtain a value of 690 ± 50 Å (where the error is due to the uncertainty in s and R_F), which compares favorably with the experimental value of 660 ± 50 Å. Similarly, the values obtained from the mean-field approach (eq 3) are also in reasonable accord with the experimental ones.

We note that the adsorbance values derived from our data for the quartz/toluene interface (see Table II) are lower than those deduced from refractive index measurements (using the surface force technique) for end-functionalized PS anchored to the mica/toluene interface.[6] It is not clear whether this reflects differences between the two surfaces or between the two techniques, although it has recently been reported[26] that adsorbance values measured using the surface force apparatus may be over 50% larger than those obtained from other methods. It is important to note, however, that as $L_0 \sim \Gamma^{1/3}$ for a given M_W, moderate changes in adsorbance have only a minor effect on the layer thickness so our values for L_0 remain comparable to those obtained from force measurements.

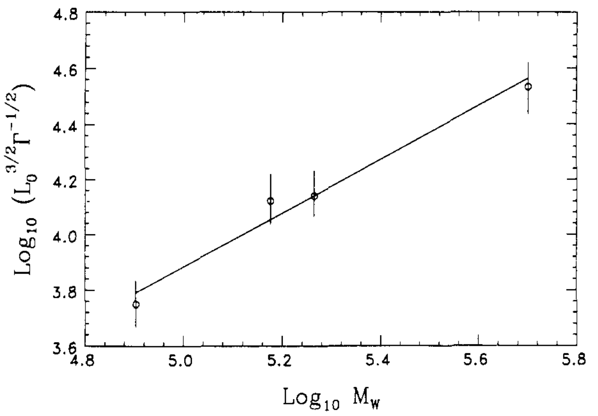

Figure 7. Scaling of $L_0^{3/2}\Gamma^{-1/2}$ with molecular weight M_W. (See eq 6 in the text.) A gradient of 0.97 ± 0.10 is obtained from the plot.

The adsorbance is expected to decrease with increasing PS molecular weight reflecting the increasing interanchor spacing of the chains as they become longer. There is some variability in the trend of the data, however, which may be partly attributed to the variation in PEO content between the block copolymer samples.

For a variable surface density both the scaling[8] and mean-field[9] calculations predict that the product $L_0 s^{2/3}$ varies linearly with M_W. Using this result together with eqs 4 and 5, it is easy to check that the power law

$$L_0^{3/2}\Gamma^{-1/2} \sim M_W \qquad (6)$$

should describe the data, where Γ has the units of mass per unit area. This is shown in Figure 7, where the measured exponent of 0.97 ± 0.10 is close to the theoretical value of 1. This result, together with the scaling of L_0 with M_W shown in Figure 6, suggests that the behavior of the PS–PEO brushes investigated in this study is consistent with an "equilibrium" picture, where the saturation surface coverage is such that the overall osmotic repulsion per chain, due to being attached to the surface, is just balanced by the adsorption energy of the anchoring block on the substrate. Finally, we note that, according to Milner's recent calculations,[22] the size of the tail or "foot" of the brush (measured relative to the brush height of the pure parabolic form) scales with $N^{1/3}\sigma^{-1/9}$. We have used the difference between our fitted parabolic and error function profiles (see Figure 5) to obtain a rough estimate of the foot size as a function of M_W. Although there is considerable scatter, the data suggest a $M_W^{0.3}$ dependence which seems consistent with theory.

Conclusions

In summary, our results show that PS–PEO block copolymers adsorb onto quartz from toluene to form an extended polymer brush. The polymer density profile normal to the substrate is well described by a parabolic or error function, but the data cannot be fitted to a power law or exponential decay profile. The molecular weight dependence of the thickness (brush height) and adsorbance obey scaling laws consistent with the theory of polymer brushes. The results show that neutron reflectivity provides valuable information for the evaluation of the density profiles of polymers adsorbed at the solid/liquid interface. For a more precise and unambiguous determination of such profiles, however, it is desirable to obtain reliable data extending to higher values of Q, as differences between profiles of similar shape emerge predominantly at lower values of the reflectivity.

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Registry No. PS-PEO (block copolymer), 107311-90-0; quartz, 14808-60-7.