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Notes

Neutron Reflectivity Study of End-Attached Telechelic Polymers in a Good Solvent

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In recent years, the conformation and volume fraction profile of end-tethered polymer chains in good solvents, as well as the interaction between surfaces bearing such macromolecular layers, have been the subject of intense investigation.[1−9] It is now well-established that under suitable solvent conditions "monochelic" AB-type block copolymers as well as end-functionalized polymers are capable of terminal attachment to a substrate. At sufficiently high grafting density, this leads to the formation of a semidilute polymer brush. The layer thickness and volume fraction profiles of such brushes have been investigated by a variety of methods, including surface force measurements[1−3] and neutron reflectometry.[4,5] The polymer density profile normal to the interface has been found to be well-described by a parabolic form, as predicted by theory.[6,7,9] More recently, ABA type "telechelic" polymers have received increasing theoretical and experimental attention.[10−18] Since telechelic chains are capable of attachment at *both* ends, one might expect ABA triblock copolymers to adsorb predominantly in a loop conformation. In the case of strongly stretched asymmetric copolymers where the "anchoring" A blocks are much smaller than the "dangling" B block, theory suggests that a telechelic (ABA) layer should possess the thickness of a monochelic AB layer made from the disconnected halves of the ABA chains.

It is of interest, therefore, to investigate the volume fraction profile and equilibrium layer thickness (or brush height) of a self-assembled telechelic brush in a good solvent in order to address this issue. We report here a neutron reflectivity study of brushes formed at the toluene/quartz interface by end-functionalized polystyrene X−PS−X, where X is a zwitterionic end group described previously,[2] as well as poly(ethylene oxide)−polystyrene−poly(ethylene oxide) triblock copolymer, PEO−PS−PEO. It is well-established that both types of polymer exhibit a terminal mode of attachment in toluene (which is a good solvent for PS), while the PS block remains nonadsorbing and dangles in solution.[1,4]

Table 1. Molecular Characteristics of the Polymer Samples[a]

polymer	M_W	x_1	y	x_2	M_W/M_N
$(PEO)_{x_1}(PS)_y(PEO)_{x_2}$	2300/16700/2300	52	161	52	1.10
$X(PS)_yX$	52000		500		1.05

[a] x_1, y, and x_2 refer to the polymerization index of the triblock copolymer $(PEO)_{x_1}(PS)_y(PEO)_{x_2}$. X is the functional group $-(CH_2)_3N^{\oplus}$-$(CH_3)_2(CH_2)_3SO_3^{\ominus}$.

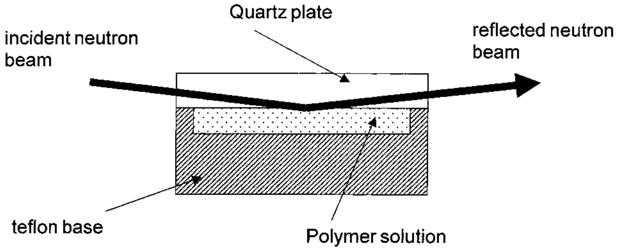

Figure 1. Schematic diagram of the experimental configuration.

The molecular weight characteristics of the polymers are shown in Table 1. The polymers were allowed to adsorb onto quartz substrates from their solution in toluene at a concentration of ca. 50 mg/L. Adsorption times in excess of 12 h were employed at room temperature (23 ± 2 °C).

Neutron reflectivity measurements were carried out at SPEAR, Los Alamos National Laboratory, using the experimental configuration shown schematically in Figure 1. The details of the SPEAR reflectometer have been described elsewhere.[19]

A neutron spallation source is used to obtain neutrons in the wavelength range of ca. 0.5−15 Å, and time-of-flight methods are employed to analyze the specularly reflected intensity to obtain the reflectivity as a function of the scattering vector $\underline{Q}$, whose magnitude is given by $Q = (4\pi/\lambda) \sin \theta$, where θ is the glancing angle of the incident beam and λ is the wavelength.

Figure 2 shows the reflectivity profile R(Q) of the X−PS−X brush together with the optimized least-squares fit to the data points, based on a parabolic volume fraction profile with a Gaussian-like "tail".[20] The inset shows the same profile in the form of Q^4R vs Q to highlight the difference between the pure parabolic form and that which includes the tail correction. The brush characteristics for the polymers studied are presented in Table 2, and the volume fraction profile resulting from the best fit to the data is shown in Figure 3.

To check the commensurability of the brush heights obtained from the present telechelic chains with the scaling of the monochelic brushes reported earlier,[2−4] we have plotted the brush layer thickness L_0 as a function of molecular weight M_W in the form of a master plot for a wide range of end-functionalized PS polymers

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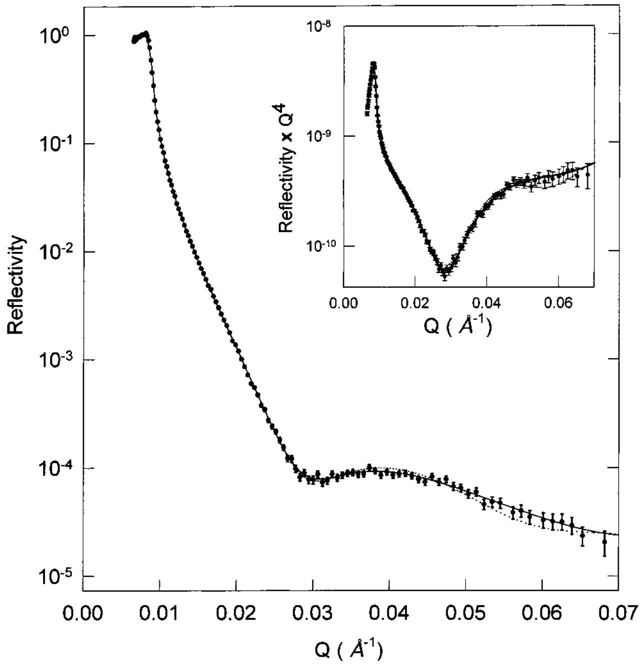

Figure 2. Neutron reflectivity profile of the X−PS−X polymer end-adsorbed onto quartz from toluene-*d* (●) fitted with the parameters given in Table 2, for a purely polynomial form $\varphi(x) = a - bx^n$ (—) and the same form featuring a Gaussian-like tail (···) (see Figure 3 and ref 20) $\varphi(z) = \exp(-{}^2\!/_3 z^{3/2})$. Inset: The same data points and fitted curves are shown in the form RQ^4 vs Q to highlight the large Q region of the reflectivity profile where the effect of the tail is most evident.

Table 2. Parameters Obtained from Least Squares Fits to Polymer Volume Fraction Profiles of the Form $\varphi(x) = a - bx^n$ [a]

polymer	MW_{PS}	L_0 (Å)	n	Γ (mg/m^2)
X−PS−X	52 000	208 ± 10	1.9 ± 0.3	3.8 ± 0.4
PEO−PS−PEO	16 700	106 ± 8	2.1 ± 0.3	2.8 ± 0.4

[a] L_0 is the layer thickness (brush height) of the end-attached PS layer, n is the exponent, and Γ is the adsorbance.

as well as diblock copolymers measured by neutron reflectivity and/or surface forces (Figure 4).

When the "effective" molecular weight of the telechelic polymers is taken as one-half of its actual value, their brush height is found to obey the universal scaling law of monochelic brushes,[2,4] i.e., $L_0 \sim (M_W)^{3/5}$, remarkably well. In particular, it is of interest to compare the neutron reflectivity result for the L_0 value of the X−PS−X polymer ($M_W = 52 \times 10^3$) used in the present study (see Table 2) with the corresponding determination of L_0 by surface force methods for the PS−X polymer ($M_W = 26 \times 10^3$) reported earlier.[2] The L_0 values of 208 ± 10 and 220 ± 50 Å for the X−PS−X and PS−X polymers, respectively, are in very good agreement. We recall that the $^3\!/_5$ exponent is characteristic of self-assembled, "equilibrium" brushes (as opposed to chemically grafted ones) in which the layer thickness results from a balance between the osmotic stretching of the dangling chains and the sticking energy of the anchoring blocks.[4] The power law displayed in Figure 3 spans nearly two decades in molecular weight, and the gradient of the straight line yields an exponent of 0.62 ± 0.02, very close to the scaling prediction of 0.6 as mentioned above. The apparent validity of this scaling law down to very low values of molecular weight is also remarkable.

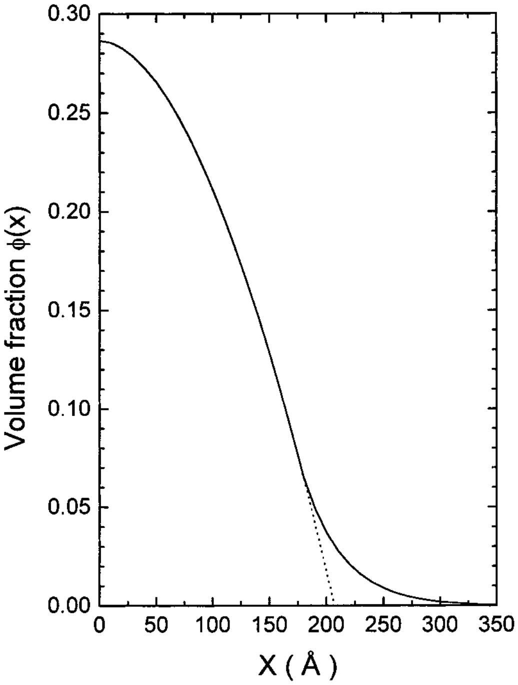

Figure 3. Volume fraction profile of the X−PS−X polymer with the fitting parameters presented in Table 2 for a pure polynomial form (···) and the same form with a Gaussian-like tail (—).

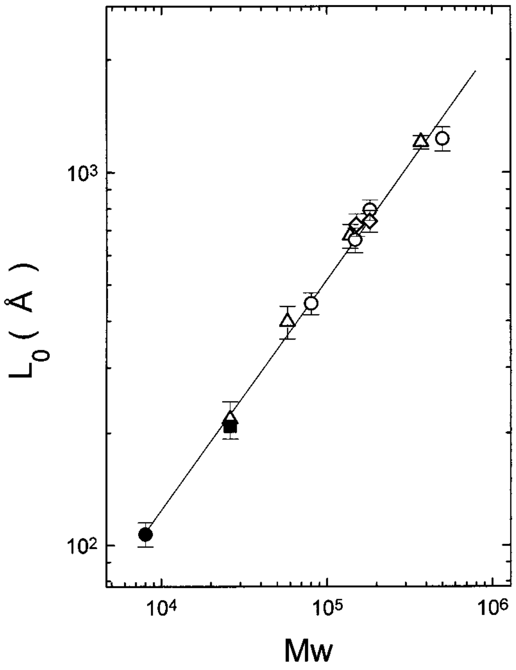

Figure 4. Scaling of the layer thickness L_0 with the molecular weight M_W. In the case of ABA telechelic polymers the effective molecular weight was taken to be equal to one-half the actual molecular weight, as described in the text. A gradient of 0.62 ± 0.02 is obtained from the plot. The data points represent results obtained from different techniques as follows: X−PS−X determined by neutron reflectivity (●) (present study), PEO−PS−PEO determined by neutron reflectivity (■) (present study), PS−X determined by surface forces measurements (△) (from ref 2), PS−PEO determined by neutron reflectivity (○) (from ref 4), PS−PEO determined by surface forces measurements (◇) (from ref 2).

These results clearly show that ABA type telechelic polymers adsorb predominantly in a loop conformation. The reflectivity profiles further demonstrate the presence of a substantial “tail” region in the outer extremity of the brush (also known as the “foot” of the brush) in these *loop*-forming end-attached chains as was found previously in the case of *tail*-forming AB type monochelic brushes.[4]

In conclusion, we have used neutron reflectivity to determine the volume fraction profiles of telechelic brushes and demonstrated that, to a very good approximation, ABA-type end-tethered chains behave in a manner equivalent to their AB-type counterparts of half their molecular weight. It would be of interest to extend this study to the case of multiarm telechelic star copolymers with the aim of exploring their volume fraction profile as a function of arm multiplicity.

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(20) The SCF treatment of Milner et al.[6,7] predicts a finite-chain correction to the parabolic profile such that in the vicinity of the outer extremity of the brush the volume fraction scales, to leading order, as $\varphi(z) \sim \exp(-{}^{2}/_{3}z^{3/2})$, where z is to be taken as the distance beyond the purely parabolic brush height.

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