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Communications to the Editor

Brush Formation in Middle-Adsorbing Triblock Copolymers

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Introduction. Polymer coils at the solid–liquid interface are of technological interest for many reasons. For example, they are used in the stabilization and flocculation of colloidal particles, for the enhancement of the biocompatibility of artificial implants, and for electrode modification.

Many studies have been made on diblock copolymers investigating their behavior at the solid–liquid interface.[1] Also, adsorption characteristics of end-attaching triblocks have been studied.[2] Scaling laws have been verified for the different symmetry regimes of diblock copolymers proposed by Marques and Joanny.[3] This scaling theory is consistent with the results of the self-consistent-field theory of Scheutjens and Fleer.[4]

In this study, we report on the adsorption behavior of middle-attaching triblocks. The materials employed consist of relatively short poly(ethylene oxide) (PEO) blocks capped by relatively long polystyrene (PS) blocks. The PEO block preferentially adsorbs to the surface, whereas the PS block remains dangling in solution. Denoting the adsorbing block by A and the buoy block as B, these copolymers are of the B–A–B architecture. Adsorption takes place from toluene, a good solvent, onto a well-characterized silicon oxide surface; this is a case of adsorption from a nonselective solvent onto a selective surface.

Experimental Section. The copolymers used in this study have the characteristics shown in Table 1. The triblocks were synthesized at the Technical University of Istanbul by a procedure described earlier.[5] It is seen that the compositions of the samples are such that the different regions of symmetry are covered (i.e., copolymers with $\beta < N_A{}^{0.5}$ lie in the symmetric to moderately symmetric regime and polymers with $\beta > N_A{}^{0.5}$ lie in the highly asymmetric regime, where β is the asymmetry factor given by the ratio of the block sizes of the nonadsorbing block to the adsorbing block and N_A is the number of poly(ethylene oxide) segments). The silicon wafers were obtained from Silicon Source Inc. (Phoenix) and treated as described in previous works.[2,6] The film thickness of the oxide layer is independently determined prior to the adsorption run using ellipsometry. HPLC-grade toluene (Aldrich Chemicals) was used after filtering three times through 0.2-μm Whatman filters. The adsorption experiments are all conducted at solution concentrations of 1.00 ± 0.01 mg/mL. Low-angle laser light scattering (Wyatt Technologies DAWN B) was used to measure weight-average molecular weights and the radii of gyration of the copolymer in solution; no evidence of micelle formation is present at the concentrations used in the experiments. Figure 1 shows a Zimm plot for the sample PS(107K)–PEO(20K)–PS(107K). The polydispersity was determined using gel permeation chromatography and seen to be less than 3.0 for all samples ($M_W/M_N < 3.0$). A specially modified rotating analyzer ellipsometer (Gaertner Scientific) is used to measure the adsorbed amounts.[7]

Data Analysis. The relationship of the measured ellipsometric angles (ψ and Δ) to the film parameters of a multilayer stack can be expressed as:

$$e^{i\Delta} \tan \psi = \frac{R_p}{R_s} = F(n_k,d_k) \qquad (1)$$

where R_p and R_s represent the overall reflection coefficients for the p (parallel) and s (perpendicular) basis waves, n_k and d_k refer to the indices of refraction and thicknesses of each layer present (denoted by the subscript k). Measurement of the two independent quantities, ψ and Δ, allows for the solution of two unknowns, a layer thickness, d_1, and a refractive index, n_1. In this study, the adsorbed layer thickness and refractive index are determined assuming a homogeneous layer for the polymer thin film; the adsorbed amount is insensitive to the layer model assumed.[6] The adsorbed amount is calculated as:

$$A = d_1c_1 = d_1(n_1 - n_0)/(\mathrm{d}n/\mathrm{d}c)_0 \qquad (2)$$

where n_1 and d_1 represent the refractive index and thickness of the adsorbed layer and c_1 is the mean concentration within the layer. Also, n_0 represents the refractive index of the copolymer solution, and $(\mathrm{d}n/\mathrm{d}c)_0$ is the change in refractive index of the solution with the concentration of the copolymer.

Knowing the adsorbed amount, the grafting density, σ, is calculated from eq 3.

$$\sigma\,(\text{chains/nm}^2) = \frac{A\,(\text{mg/m}^2)}{M_w\,(\text{mg/mol})} N_{AV}\,(\text{chains/mol}) \times 10^{-18}\,(\text{m}^2/\text{nm}^2) \qquad (3)$$

where N_{AV} is Avogadro's number.

The interchain spacing may then be calculated as:

$$D_{\text{int}} = (1/\sigma)^{0.5} \qquad (4)$$

The overlap spacing, which is the chain spacing at which coils on the surface first begin to touch, is taken as:

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Table 1. Triblocks Used in Adsorption Studies and Interchain Spacing Compared to Overlap Spacing

material (numbers in parentheses are block mol wts)	N_B (PS segments)	N_A (PEO segments)	$N_A^{0.5}$	β	D_{int} (Å)	D_{int}/D_{over}
PS(254K)–PEO(54K)–PS(254K)	4484	1227	35.03	1.97	284.8	0.5551
PS(59K)–PEO(1K)–PS(59K)	1134	22	4.7	9.16	138.5	0.3176
PS(22K)–PEO(1K)–PS(22K)	423	22	4.7	5.07	68.33	0.1927
PS(127K)–PEO(1K)–PS(127K)	2442	22	4.7	14.51	205.7	0.4552
PS(107K)–PEO(20K)–PS(107K)	2058	454	21.3	2.13	146.9	0.2929
PS(305K)–PEO(20K)–PS(305K)	5865	454	21.3	3.99	248.05	0.3942
PS(168K)–PEO(10K)–PS(168K)	3241	225	15	4.26	195.98	0.3242
PS(1045K)–PEO(10K)–PS(1045K)	20097	225	15	12.74	440.11	0.3492

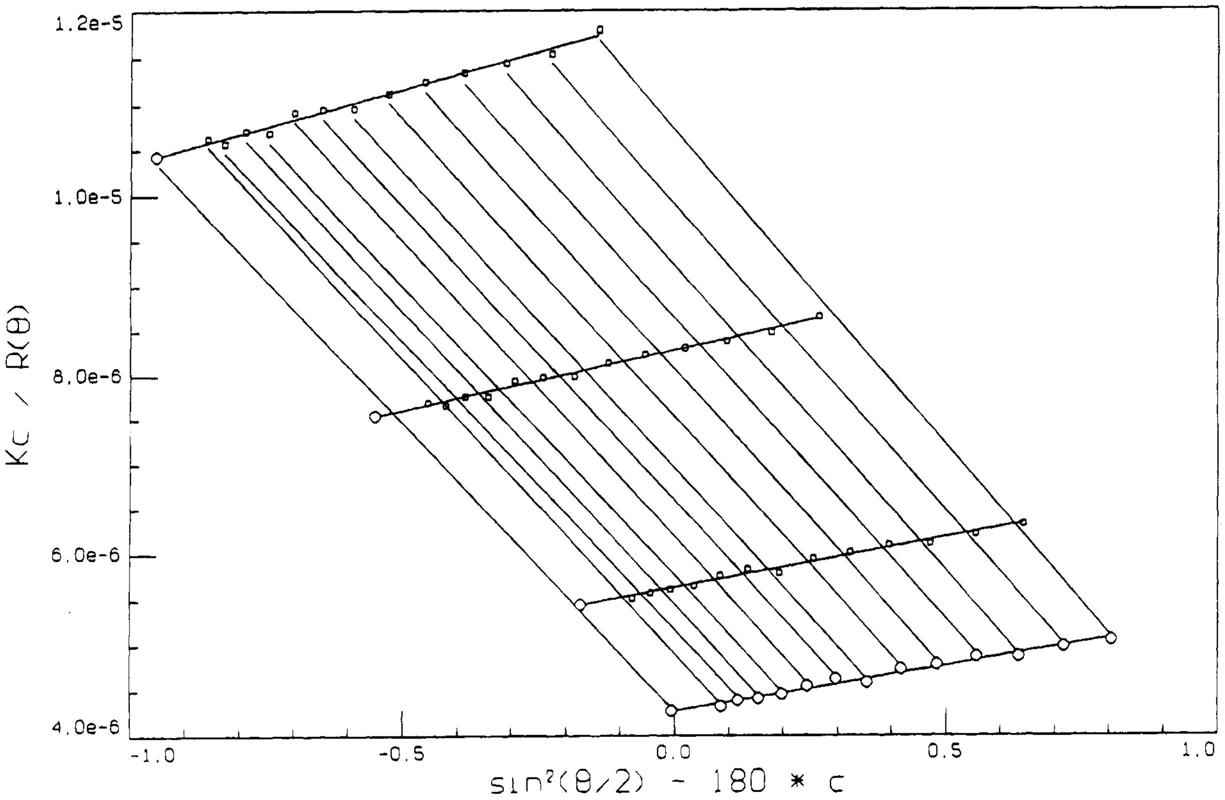

Figure 1. Zimm plot for PS(107K)–PEO(20K)–PS(107K). The molecular weight of the sample is 234 000 ± 20 000, and the free solution radius of gyration, R_{AB}, is 283 ± 6 Å.

$$D_{over} = (\pi R_B^{\,2})^{0.5} \approx (\pi R_{AB}^{\,2})^{0.5} \qquad (5)$$

where R_B represents the radius of gyration of the polystyrene blocks in solution and R_{AB} is the radius of gyration of the copolymer in solution, determined by using light scattering. Another important variable in the scaling description of copolymer adsorption is the asymmetry ratio, β.

$$\beta = a'(N_B/N_A)^{0.6} \qquad (6)$$

where N_B and N_A represent the number of polystyrene segments and the number of poly(ethylene oxide) segments, respectively. Also, a' is the ratio of the size of a single polystyrene segment to a single poly(ethylene oxide) segment and is taken as 0.87.

Results and Discussion. Results from the study are given in Table 1. It is clearly seen that the ratio of the interchain spacings to the overlap spacings (D_{int}/D_{over}) is less than unity, demonstrating that the triblock materials must be crowded at the surface and hence stretched away from the adsorbing surface. To our knowledge, this is the first report of brush formation in copolymers of the B–A–B architecture.

Figure 2 shows that the grafting density of the highly asymmetric triblocks scales with the reciprocal of the square of the asymmetry ratio ($\sigma \approx 1/\beta^2$). For the moderately symmetric to symmetric triblocks, the surface density scales with the reciprocal of the head size ($\sigma \approx 1/N_A$) as shown in Figure 3. Both these results

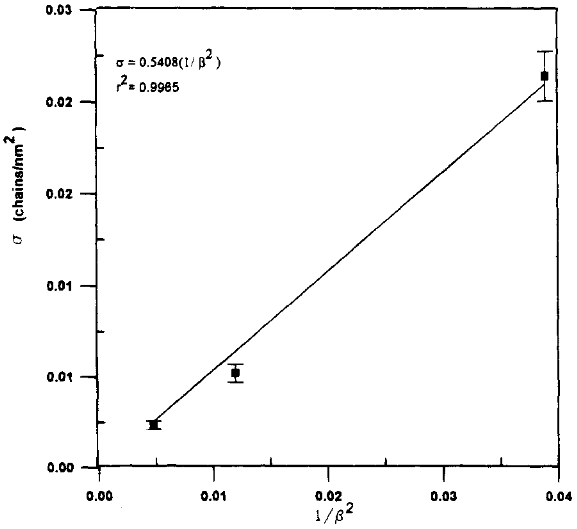

Figure 2. Scaling behavior of the highly asymmetric triblock copolymers. The grafting density scales with the reciprocal of the asymmetry ratio squared ($1/\beta^2$).

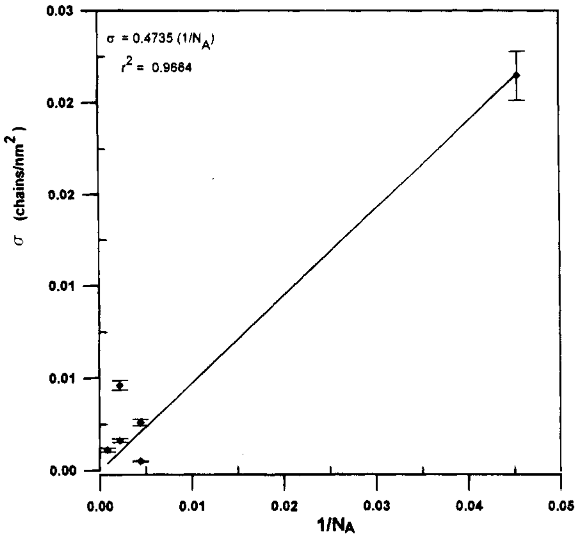

Figure 3. Scaling behavior of the symmetric to moderately symmetric triblocks. The grafting density scales with the reciprocal of the adsorbing block size, ($1/N_A$).

are consistent with the predictions of the scaling theory of Marques and Joanny for A–B diblock adsorption.[3] The B–A–B triblock materials are thus seen to behave similarly to diblock materials as far as the effect of chain composition on the structure of the adsorbed layers is concerned.

Conclusions. It is seen from the D_{int}/D_{over} values in Table 1 that the B–A–B triblocks are stretched, and hence it can be concluded that middle-adsorbing triblock materials can form a brush structure.

It can also be concluded that the middle-adsorbing triblock materials behave very similarly to diblock materials in terms of scaling behavior. The change in composition of the B–A–B copolymers produces changes in the structure of the adsorbed layer similar to changes in the A–B diblock layer. The surface density for the symmetric to moderately symmetric triblocks scales with the reciprocal of the head size ($\sigma \approx 1/N_A$). For highly asymmetric triblocks, we find that the surface density scales with the reciprocal of the square of the asymmetry ratio ($\sigma \approx 1/\beta^2$). As stated earlier, the materials under study are polydisperse. Though there is no conclusive evidence for the effect of this parameter on the scaling laws, Figures 2 and 3 seem to suggest that polydispersity does not have an appreciable effect on the scaling behavior for the grafting density. Also, it has been shown that mixing of chains of different lengths is entropically favored.[8] This would imply that the adsorbed layer itself is polydisperse, and apparently the scaling behavior can be described as long as an appropriate average molecular weight is used.

Computer simulation suggests that fewer B–A–B chains than other architectures are required to provide comparable surface coverage.[9] Hence, the efficiency of adsorption may be highest for this structure. As described by Uyanik et al.,[5] these block copolymers are fairly easy to synthesize from commercially available dihydroxy-terminated prepolymers, which can be made reactive and then used as free-radical initiators for the styrene polymerization. The adsorption efficiency coupled with the ease of synthesis could make such materials an optimum choice in steric stabilization applications.

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