2434 *Macromolecules* **1992,** *25,* 2434–2441

Role of Block Size Asymmetry on the Adsorbed Amount of Polystyrene-*b*-poly(ethylene oxide) on Mica Surfaces from Toluene

D. A. Guzonas, D. Boils, C. P. Tripp, and M. L. Hair*

Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, Ontario, Canada L5K 2L1

Received September 20, 1991; Revised Manuscript Received December 13, 1991

ABSTRACT: Surface force and IR data on polystyrene-*b*-poly(ethylene oxide) block copolymers adsorbed on mica from toluene are presented. The copolymers were selected to have a wide range of asymmetry radius ratio ($\beta = (R_{\mathrm{F,PS}}/R_{\mathrm{F,PEO}})^{3/5}$ as defined by Marques and Joanny. The extended length L of the block copolymers has been measured with the surface force apparatus and shown to scale as $L \sim N_{\mathrm{PS}}N_{\mathrm{PEO}}^{1/3}$ for moderately asymmetric copolymers ($1 \ll \beta < N_{\mathrm{PEO}}^{1/2}$). Deviations are observed when the nonadsorbing block is either much larger than the anchor block or approximately the same size. A general method using infrared spectroscopy has been developed which can measure the quantity of adsorbed polymers on mica. The Alexander–de Gennes scaling law for the surface density, $L \sim N_{\mathrm{B}}\sigma^{1/3}$, has been found to be roughly obeyed over a wide range of copolymer molecular weights and radius ratio β. The Marques and Joanny scaling laws for σ, $\sigma \sim 1/N_{\mathrm{A}}$, describe well the behavior of the moderately asymmetric materials. However, their model does not appear to predict the proper surface density for material at the crossover point between the 3D and 2D regimes, near $\beta \approx N_{\mathrm{A}}^{1/2}$.

Introduction

The steric stabilization of particle dispersions by polymer adsorption is of great technological importance. One method of steric stabilization uses block copolymer adsorption, and a great deal of attention, both experimentally[1–5] and theoretically,[6–9] has thus been focused on understanding the adsorption of block copolymers from solution. The usual model of block copolymer adsorption from a solvent pictures the adsorbed copolymer as consisting of an anchor block which has a strong interaction with the surface and a nonadsorbing buoy block which is soluble in the solvent. The anchor block can be either soluble or insoluble in the solvent. The buoy block extends into the solution up to as much as 10 times its normal radius of gyration in solution, and it is this brush layer which provides the thick steric stabilizing layer. Although adsorption of the copolymer takes place most frequently from a selective solvent, in which the buoy block is soluble but the anchor block is in a poor solvent, adsorption can also occur from a nonselective solvent, where both blocks are soluble. In the nonselective solvent there is less possibility of the association of the polymer in solution into micelles. As an example of adsorption from a nonselective solvent, both blocks of polystyrene-*b*-poly(ethylene oxide), abbreviated herein as PS/PEO, are soluble in toluene, but this material will adsorb strongly onto mica surfaces,[1,2] presumably due to a specific interaction of the PEO with the mica surface.

Diblock copolymer adsorption from both selective and nonselective solvents has been investigated recently using a variety of experimental methods which include SANS,[15] neutron reflectivity,[16] internal reflection interferometry,[6] and surface force measurements.[1–5] Hadziioannou et al.[5] have used the surface force apparatus to study the adsorption of poly(2-vinylpyridine)-*b*-polystyrene (PVP/PS) onto mica from toluene. Taunton et al.[3] have reported some force balance data for two PS/PEO copolymers adsorbed from toluene (a good solvent for both blocks) as part of a study of end-functionalized PS-X polymers. Marra and Hair[2] and Guzonas et al.[1] have conducted an extensive surface force study of PS/PEO block copolymers adsorbed on mica from toluene. Munch and Gast[6,7] have modeled block copolymer adsorption and have experimentally studied the adsorption of PS/PEO onto sapphire from cyclopentane using evanescent wave spectroscopy. At the same time a number of theoretical studies of block copolymer adsorption have appeared.[9–14] These use both mean field and scaling law approaches, and attempts have been made to reconcile the experimental data with these models. Thus, for example, Patel et al.[17] have proposed a model for the adsorption of block copolymers and have applied this with success to the surface force data on PVP/PS adsorption from the selective solvent toluene.

An important parameter in all models of copolymer adsorption is the surface density of adsorbed chains, or conversely the area per molecule on the surface. For example, the frequent starting point in scaling discussions is the Alexander–de Gennes[18,19] relation for the length L of a grafted polymer brush, namely

$$L \sim N_{\mathrm{B}}\sigma^{1/3} \qquad (1)$$

where N_{B} is the number of segments in the brush and σ is the surface density (number of chains per unit area) of the adsorbed polymer. The role of the sizes of the two blocks in determining the surface density is therefore important in understanding how the extended length of the brush, L, will scale with the sizes of the blocks. The length L can be readily determined using the surface force apparatus. However, as pointed out by Marra and Hair[2] and by Guzonas et al.,[1] the evaluation of σ using the surface force apparatus for these PS/PEO diblock copolymers is nontrivial. The small differences between the refractive indices of the solvent, toluene, and the copolymer means that the polymer volume fraction cannot readily be evaluated from the measured refractive index of the adsorbed layer. The method of Marra and Hair,[2] in which the polymer layer is collapsed by the addition of a nonsolvent heptane–toluene mixture, involves the assumption that there is no preferential uptake of one of the solvents of the mixture in one or both of the blocks. In spite of these difficulties, using the values of the adsorbed amount of the copolymers obtained with the surface force apparatus, Guzonas et al.[1] found the length of the adsorbed polymer layer to obey the Alexander–de Gennes scaling

0024-9297/92/2225-2434$03.00/0

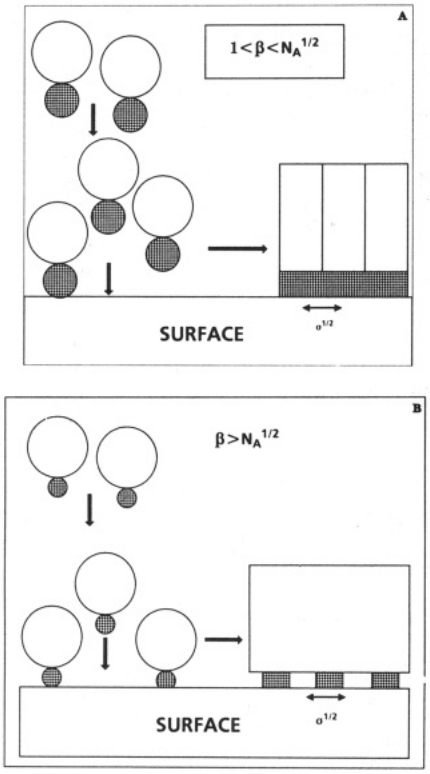

Figure 1. Structure of the adsorbed diblock copolymer layer from the model of Marques and Joanny: (A) continuous adsorbed layer; (B) thin layer (discontinuous regime).

law given by eq 1.

Parsonage et al.[8] have reported the adsorbed amounts of PVP/PS adsorbed from toluene solutions onto oxidized silicon and mica substrates, as measured by scintillation counting and by XPS. For this system toluene is a selective solvent, and they find that their results agree well with a recent model by Marques et al.[9] for copolymer adsorption from a selective solvent. Munch and Gast[7] have used an evanescent wave method to study the adsorption of PS/PEO on sapphire and have reported that the asymmetric materials require consideration of the molecular weight of the B block as well as the anchor block. Both Munch and Gast and Parsonage et al. have suggested that the size of both blocks is important in determining the adsorbed amount.

Recently, a theory of block copolymer adsorption from a nonselective solvent has been published by Marques and Joanny (MJ).[10] An important aspect of the MJ treatment is their derivation of scaling relations for the surface density in terms of the numbers of segments in the blocks. Thus the length of the stabilizing block can be calculated from basic polymer properties, without the need to experimentally determine the adsorbed amount. Depending upon the relative sizes of the two blocks, the anchor block may form either a thick, "fluffy", continuous adsorbed layer (Figure 1A) or a thin layer (thickness on the order of a monomer size) which may be continuous or discontinuous (Figure 1B). In keeping with the notation of MJ, the anchor layer thickness is d, the brush thickness is L, and we shall denote the total thickness as $D_0/2$, in accord with the experimentally accessible parameter from the surface force apparatus. (D_0 is the distance at which a force can be first noticed between the polymer chains.) The MJ model gives scaling laws both for a continuous adsorbed layer (which they denote the 3D regime) and for two cases where the anchor layer is on the order of a monomer size (the 2D regimes). If the anchor layer is continuous, then we have a 2D semidilute regime; if the anchor layer is no longer continuous, then the regime is 2D dilute. The scaling relationships for the 2D and 3D cases are quite different.

Our earlier work on PS/PEO has shown that the scaling approach of MJ is quite powerful for treating the adsorption of PS/PEO copolymers in toluene. We have therefore used a recently developed novel infrared spectroscopic technique using a dual-beam FTIR to measure the adsorbed amounts of PS/PEO copolymers on mica. This method is in many respects ideal for the study of adsorbed polymer layers because it requires no special preparation (e.g., labeling) of the polymers and, unlike reflectance methods, can be performed on a low-area surface of *any* reflectivity. Thus the adsorption can be carried out under conditions as similar as possible to those used in the surface force apparatus. In addition, the accuracy of this method is much better than the measurements using the surface force apparatus, as it involves no assumptions about solvent partitioning. A description of this instrumentation[20] and experimental details[21] of this method have been presented elsewhere. In this paper we present the results of quantitative IR measurements of the adsorbed amount of a series of PS/PEO copolymers adsorbed on mica from toluene and show how these results, particularly when combined with surface force data, can be used to test the limits of the scaling theory of Marques and Joanny. New length/adsorption data are presented for four new block copolymers of PS/PEO (500/4, 363/1, 770/1, and 65/0.7).

Experimental Section

Materials. The characteristics of the copolymers used in this study are listed in Table I. In this paper, we shall refer to the samples by the molecular weight of each block in thousands, as M_w(PS)/M_w(PEO). Thus, as an example, the sample labeled 334/19 has a measured M_w of 333 700 for the PS block and 19 200 for the PEO block. We will refer to the weight-average number of segments of polystyrene and of poly(ethylene oxide) as N_{PS} and N_{PEO}, respectively. Those labeled as XWRC were synthesized by anionic polymerization by T. W. Smith, J. Van Dusen, and D. J. Luca of the Xerox Webster Research Center, Webster, NY. The molecular weight and polydispersity of the samples (M_w/M_n) were determined by GPC measurements, while the PEO content was obtained by ^{1}H NMR analysis.

The other copolymers were obtained from Polymer Laboratories and were used without any further purification or characterization.

The solvents used were purchased from Aldrich as HPLC grade and were dried over molecular sieves and then glass-distilled immediately prior to being used.

Infrared Measurements. Infrared spectra were recorded on a Bomem 110-E FTIR modified for dual-beam operation (dbFTIR). The details of the equipment and the procedures used for obtaining spectra of adsorbed polymers are described in detail elsewhere.[20,21] Spectra were recorded at 4-cm^{-1} resolution, and 100 scans were coadded, requiring approximately 2 min.

Fresh copolymer solutions in toluene were prepared at a concentration of ~500 μg/500 mL. Adsorption was done in an all-Teflon trough over a period of 2–8 h. The mica sheets were rinsed thoroughly with toluene and allowed to dry before examination.

The surface density, σ, was calculated from

$$\sigma = \frac{s}{M_{PEO} + M_{PS}} \times 6 \times 10^{23} \times 10^{-18}\ \text{nm}^{-2} \qquad (2)$$

where s is the adsorbed amount in g/m^2.

Surface Force Measurements. This paper deals only incidentally with surface force measurements. The apparatus has been described in detail elsewhere,[2] and so only a brief description of the experiment will be given here. The force–

Table I
Characteristics of the Copolymers Used in This Study

PS/PEO	PS $M_w \times 10^{-3}$	PEO $M_w \times 10^{-3}$	M_w/M_n	N_B	N_A	V_A	N_T	β
100/4[a]	100	3.8	1.37	962	85	8	1047	4.28
62/4	61.6	4.1	1.27	592	93	14	685	3.03
2/4	2.33	4.34	1.07	22	99	35	121	0.4
334/19[a]	333.7	19.2	1.37	3209	436	11	3645	3.31
87/29[a]	86.6	28.8	1.27	833	654	44	1487	1.16
151/43[a]	151.3	42.7	1.57	1455	970	40	2425	1.28
148/2	147.8	2.25	1.16	1421	51	3.5	1472	7.4
500/4	502	3.84	1.13	4827	87	1.8	4914	11.1
123/25[a]	123	25	1.4	1183	625	34.6	1808	1.47
129/11[a]	129	11	1.4	1240	275	18.0	1515	2.47
343/27[a]	343	27	1.4	3298	675	17	3973	2.59
363/1	362.5	1.19	1.14	3486	27	0.77	3517	20
65/6	64.5	0.65	1.17	620	15	2.3	635	9.3
770/1	769.9	1.31	1.1	7404	30	0.4	7434	27.3

[a] XWRC.

distance curves were measured between two freshly cleaved, molecularly smooth mica surfaces which are silvered on one side and then glued, silver side down, onto cylindrically curved glass disks. These surfaces were mounted in the surface force apparatus in the crossed cylinder geometry. The measured forces were normalized by the experimentally measured radius of curvature (R) of the glass disks, to obtain the interaction energy $E(D)$ per unit area between two flat parallel surfaces according to the Derjaguin approximation,[22] $F(D)/R = 2\pi E(D)$.

The separation between the surfaces was measured interferometrically by analyzing fringes of equal chromatic order (FECO), the separation being measured to ±0.2 nm. The fringes were observed using a computer-interfaced image-intensified video camera which was mounted at the exit slit of the spectrometer.

At the start of each experiment, the surfaces were first brought together in an atmosphere of dry nitrogen, and this contact position is defined to be $D = 0$. The apparatus was then filled with dry toluene, and the force–distance profile was measured. The presence of an oscillatory profile as reported in the literature was considered to be a sign of surface and solvent cleanliness. Once the cleanliness of the system had been checked in this manner, the polymer was added to the apparatus.

Solutions of the copolymers in toluene were prepared such that the final concentration in the surface force apparatus was 4×10^{-8} mol/L in polystyrene. All polymer solutions were filtered before injection into the apparatus with Autovial syringeless filters (S.P.E. Ltd.) designed for organic solvents. The adsorption was found to be complete within 2 h as monitored by the changes in the range of the forces and the thickness of the layer upon compression. These observations are in agreement with the infrared measurements. Munch and Gast[6] have shown that adsorption of PS/PEO on sapphire is complete after 20 min.

Results

The values of the adsorbed amount, surface density, and area per molecule obtained using the dual-beam FTIR are presented in Table II, along with values of $D_0/2$ obtained using the surface force apparatus (SFA). The SFA data for the polymers 500/4, 363/1, and 770/1 have not previously been reported.

Some qualitative comments on the adsorbed amounts can be made. The measured values range from a low of 0.43 to a high of 2.3 mg/m^2. These values are of a similar magnitude to those obtained for PVP/PS copolymers adsorbed on silicon from toluene (a selective solvent for PVP/PS) by Parsonage et al.[8] It is interesting to compare the adsorbed amounts from the two types of solvent. Although most of their materials are more symmetric than ours, there are a few of similar molecular weight that can be compared. For example, for their PS/PVP 92/31 they obtain an adsorbed amount of 1.80 mg/m^2 which can be compared to 0.43 for our PS/PEO 87/29. Our PS/PEO 151/43 (1.0 mg/m^2) can be compared with their PVP/PS 152/30 (1.87 mg/m^2) or 152/60 (2.02 mg/m^2). Thus the amounts of similar molecular weight polymers adsorbed from toluene as a selective solvent are much higher than from toluene as a nonselective solvent. Munch and Gast[6] have reported the adsorbed amounts for two PS/PEO materials. For the material they denote as P170/1730 (180/7.5 in our notation) adsorbed on sapphire or glass from cyclopentane, a selective solvent, they report values between 8.4 and 16.2 mg/m^2, depending upon the bulk polymer concentration. It should be pointed out that the higher adsorbed amount was obtained at a bulk concentration (8.3×10^{-5} g/mL) below the cmc (1.2×10^{-4} g/mL), whereas the lower adsorbed amount was reached for a bulk concentration (5.5×10^{-4} g/mL) which is above the cmc. The adsorbed amount of P83/3470 (361/3.6 in our notation) was 8.4 mg/m^2 for a polymer concentration of 10^{-4} g/mL, which was below the cmc (1.75×10^{-4} g/mL). These adsorbed amounts are much higher than any values that we measured. However, it is pointed out that in their experiments cyclopentane (T_Θ = 19.5 °C) is a much poorer solvent for polystyrene at 23 °C. This is well-known to lead to higher adsorption. Taunton et al.[3] reported the adsorbed amount of an end-functionalized PS-X polymer of PS molecular weight 140 000 as 3.0 mg/m^2 using the refractive index method. This can be compared to our material labeled 148/2, for which we measure 1.9 mg/m^2 using the IR method.

Table II
Values of the Adsorbed Amount (s), Surface Density (σ), and Area per Molecule (A) Obtained by dbFTIR

	data from FTIR			data from surface
polymer	$s \times 10^3$, g/m^2	σ, nm^{-2}	A, nm^2	forces $D_0/2$, Å
100/4	1.5	0.0087	115	600
87/29	0.43	0.00224	446	400
148/2	1.9	0.0076	131	725
151/43	1.0	0.0031	322	488
2/4	1.2	0.108	9	75
334/19	1.4	0.0024	419	1050
62/4	2.3	0.0211	47.6	310
500/4	1.3	0.00155	646	1425
363/1	1.0	0.00166	604	1100
65/0.7[a]	0.0			
770/1	0.3	0.000234	4269	

[a] The polymer 65/0.7 did not absorb onto mica.

We were unable to detect *any* adsorption of 65/0.7 copolymer on the mica surface. This suggests that 15 PEO segments are too few to anchor a large polystyrene tail to the mica surface in a good solvent. Clearly the gain in enthalpy of 15 segments is too small to offset the loss of entropy required to constrain the PS tails at the surface and it is worth recalling that adsorption of end-terminated PS was very specific to the chemical functionality of the

Table III
Scaling Treatment of Marques and Joanny for the Surface Density and the Thickness of the Brush Layer[a]

β	3D regime $1 < \beta < N_A^{1/2}$	2D semidilute $N_A^{1/2} < \beta < N_A^{3/4}$	2D dilute $\beta > N_A^{3/4}$
$\sigma \sim$	N_A^{-1}	β^{-2}	β^{-2}
$L \sim$	$N_BN_A^{1/3}$	$N_B^{3/5}N_A^{2/5}$	$N_B^{3/5}N_A^{2/5}$

[a] Adapted from ref 10.

end group. Only the zwitterion termination gave rise to a polymer that would adsorb; OH, NH_2, and COOH terminal groups would not give an adsorbable molecule.

Discussion

The theory of Marques and Joanny[10] starts from the Alexander–de Gennes[18,19] scaling law for the brush length

$$L \sim N_B\sigma^{1/3} \tag{3}$$

and derives expressions for the surface density, σ, in terms of N_A, the number of segments of the anchor polymer (i.e., PEO), and N_B, the number of segments of the brush polymer (i.e., PS). This is done by introducing an asymmetry or radius ratio, β, which is defined in terms of the Flory radii of gyration:

$$\beta = R_{F,B}/R_{F,A} = (N_B/N_A)^{3/5} \tag{4}$$

where $R_{F,B}$ and $R_{F,A}$ are the Flory radii of gyration of the brush and the anchor layer, respectively. The models are as depicted in Figure 1, with the anchor layer adsorbing as a fluffy, self-similar layer which is either in the 3D or 2D region. MJ point out that the area/molecule occupied by the anchor polymer must equal that of the brush and, by minimizing the total energy they determine the scaling relations which are summarized in Table III.

An important test of the MJ model is to verify the proposed scaling laws for the surface density σ. These scaling laws are

$$\sigma \sim N_A^{-1} \quad \text{when } 1 \ll \beta < N_A^{1/2} \tag{5}$$

$$\sigma \sim \beta^{-2} \quad \text{when } \beta > N_A^{1/2} \tag{6}$$

In a previous paper we have indirectly verified the scaling law $\sigma \sim N_A^{-1}$, as it is substitution of this in $L \sim N_B\sigma^{1/3}$ that leads to

$$L \sim N_BN_A^{-1/3} \tag{7}$$

We reported surface force balance studies for six PS/PEO block copolymers and determined $D_0/2$ for those compositions. Provided d is small, then $D_0/2 \approx L$. These data taken along with results published previously by Marra and Hair[10] and Taunton et al.[3] fulfilled the relationship $L \sim N_{PS}N_{PEO}^{-1/3}$ over the range where $1 < \beta < N_{PEO}^{1/2}$. A number of PS/PEO polymers studied fell outside this criterion and for those polymers $D_0/2$ did not scale as expected.

The scaling treatment of Marques and Joanny, which is summarized in Table III, suggests a division into regimes based on the scaling law behavior. Since the scaling law behaviors of the 2D dilute and semidilute regimes are identical, we will combine them into one regime for the discussion of experimental results to follow. At the same time, implicit in Marques and Joanny and suggested by our previous work is a regime for which $\beta < 1$. We therefore introduce three regimes, which we denote as highly asymmetric (regime I), moderately asymmetric (regime II), and symmetric (regime III). The highly asymmetric regime corresponds to the combined 2D dilute and semidilute regimes of MJ, while the moderate asymmetric regime corresponds to their 3D regime. There is no correspondence in MJ theory for our symmetric regime. The three regimes can be illustrated by plotting a graph of N_B vs N_A, which will be referred to as N_B–N_A space. N_B–N_A space can be divided up as in Figure 2. The line $\beta = 1$ is the division between regimes II and III, and the curve $\beta = N_A^{1/2}$ forms the division between regimes I and II. β is defined as $\beta = (N_B/N_A)^{3/5}\,a'$, where $a' = a_{PS}/a_{PEO}$ and a is the monomer projection length. This ratio is taken to be 0.87.[24] A complete description as to how the diagram has been built is given in the Appendix. Due to the differences in the monomer sizes, an equal number of segments will lead to a value of $\beta = 0.87$. The line $\beta = 0.87$ has also been drawn in Figure 2. All of the polymers which are discussed in this paper are indicated on Figure 2, and it is apparent that we have polymers which fall in all three regimes.

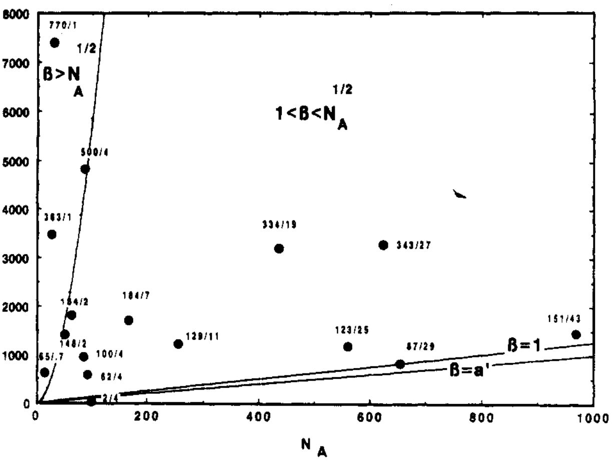

Figure 2. Regimes defined by the model of Marques and Joanny. The dividing lines between the regimes (β = 1 and $\beta = N_A^{1/2}$) were drawn according to the calculations in the Appendix.

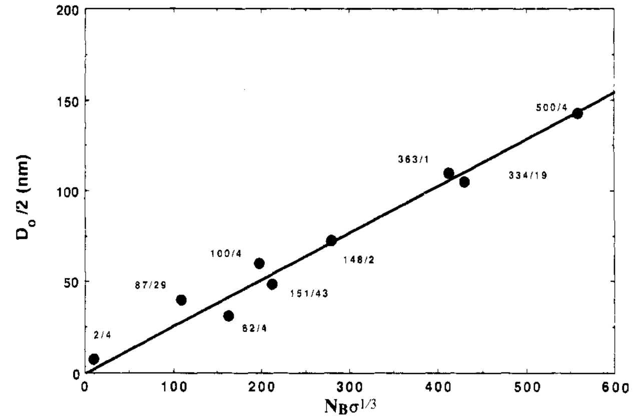

Figure 3. Measured thickness of the adsorbed layer as a function of $N_B\sigma^{1/3}$. The fit was obtained by drawing a line from the origin through the highest molecular weight copolymers (334/19 and 363/1).

To confirm the validity of the Alexander–de Gennes scaling law for these copolymers, the data from Table II are plotted in Figure 3, which shows a plot of the measured thickness of the adsorbed layer versus $N_B\sigma^{1/3}$ (eq 1). It is apparent that a reasonably linear relation is obtained for materials in all three regimes of Figure 2, with no significant deviations. Thus it appears that eq 1 is obeyed over a wide range of copolymer molecular weights and radius ratios. It is noted that the plot passes through the origin and that the materials containing the largest amounts of polystyrene show the best fit. These are not only the most accurate to determine in the SFA but will

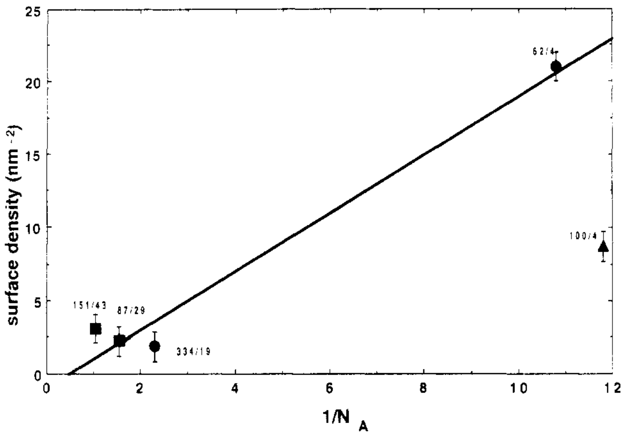

Figure 4. Actual surface density for polymers falling in regime I as a function of the inverse of the number of segments of poly(ethylene oxide).

Table IV
Values of the Area per Molecule (A) and the Overlap Area (A_{ov}) for All the Copolymers

polymer	A, nm^2	A_{ov}, nm^2	A_{ov}/A
100/4	115	386	3.4
62/4	48	216	4.5
2/4	9	4.3	0.6
334/19	419	1617	3.86
87/29	446	325	0.73
151/43	322	631	1.96
148/2	131	613	4.7
500/4	646	2629	4.07
363/1	356	1784	5
770/1	4269	4371	1.02

also be least susceptible to the value of d. The basic scaling law of Alexander and de Gennes (eq 1) has now received experimental verification both for grafted layer[3,23] and for adsorbed block copolymers.[1,17]

We can now examine the scaling relation for the surface density for the moderately symmetric regime. In this regime MJ predict that the surface density should scale as the inverse of the anchor block size, i.e.

$$\sigma \sim N_A^{-1} \tag{8}$$

The data in Table II for which $1 < \beta < N_A^{1/2}$ are plotted in Figure 4 as σ versus $1/N_A$. A linear least squares fit to all the data points except the 100/4 is shown in the figure; including the 100/4 in the data set lowers the correlation coefficient from 0.97 to 0.65. The large deviation of the 100/4 point from the rest of the data suggests that the 100/4 polymer is sufficiently asymmetric that it no longer follows the $1/N_A$ scaling law.

The polymers for which $\beta \approx 1$ also seem to scale reasonably well with N_A^{-1}. This, however, is not the case for the 2/4 material, which lies far off the top of Figure 4 (not shown). As β approaches 1, the large size of the poly(ethylene oxide) anchor block relative to the polystyrene block in these materials will cause the spacing between neighboring polystyrene chains to increase beyond the point at which they can overlap, and the strong stretching assumption will no longer be true. The area per molecule of a chain above which no overlap will occur, A_{ov}, can be modeled as

$$A_{ov} = \pi R_{PS}^2 \tag{9}$$

where R_{PS} is the radius of gyraton of the PS block in dilute solutions.

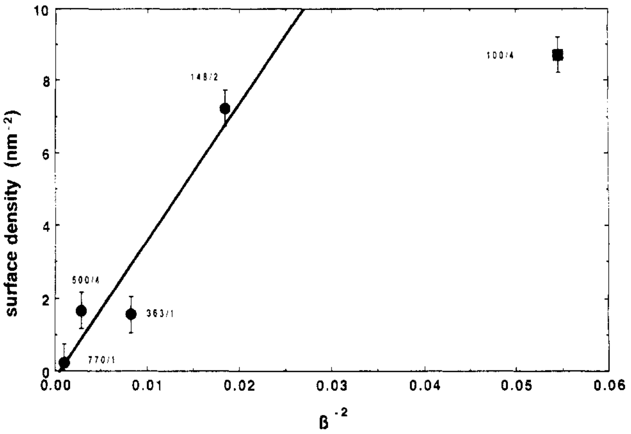

Figure 5. Surface density, as a function of β^{-2}.

Using the data for R_{PS} in toluene which has been reported by Parsonage et al.[8]

$$R_{PS} = 1.86 N_{PS}^{0.595} \tag{10}$$

we obtained the values of A_{ov} listed in Table IV. The material labeled 87/29 is below the area/molecule required for overlap of the tails, and the 2/4 copolymer is well into the regime where no overlap is possible. The adsorption behavior of the 2/4 material, in particular, is expected to be more like homopolymer PEO adsorption.

If we now consider the polymers which fall in the highly asymmetric regime, (i.e., $\beta > N_A^{1/2}$), we see that the size of the buoy block must also exert an influence on the adsorbed amount. Munch and Gast[6] have reported surface densities for PS/PEO copolymers adsorbed from a selective solvent, and their data suggest that the size of the PS block does influence the adsorbed amount. The data from Table II for the highly asymmetric polymers are plotted in Figure 5 as σ versus β^{-2} (filled circles). Again the best fit straight line is shown. The datum for the 100/4 polymer is also included in Figure 5 and is shown as a filled square. It was suggested earlier that the 100/4 material was too asymmetric to lie in the moderately symmetric regime II—but it is apparent that it does not fit here either.

Among the polymers studied in this report there is a series of four for which the size of the anchor block is constant: namely, 2/4, 62/4, 100/4, and 500/4. For this series, the mean value of N_{PEO} is 91. Using the scaling laws of MJ, it is easy to calculate the expected behavior of the surface density, adsorbed amount, and length as a function of the chain composition.

From MJ we have expressions for surface density, layer thickness, and adsorbed amount. When $\beta < N_{PEO}^{1/2}$ then

$$\sigma \sim N_{PEO}^{-1} \tag{11}$$

and

$$L \sim N_{PS} N_{PEO}^{-1/3} \tag{12}$$

When $\beta > N_{PEO}^{1/2}$ then

$$\sigma \sim \beta^{-2} \tag{13}$$

and

$$L \sim N_{PS}^{3/5} N_{PEO}^{2/5} \tag{14}$$

In both cases the adsorbed amount

$$s \sim \frac{\sigma(M_{PEO} + M_{PS})}{6.023 \times 10^{23}} \times 10^{18} \tag{15}$$

The two scaling behaviors cross over smoothly at $\beta = N_{PEO}^{1/2}$.

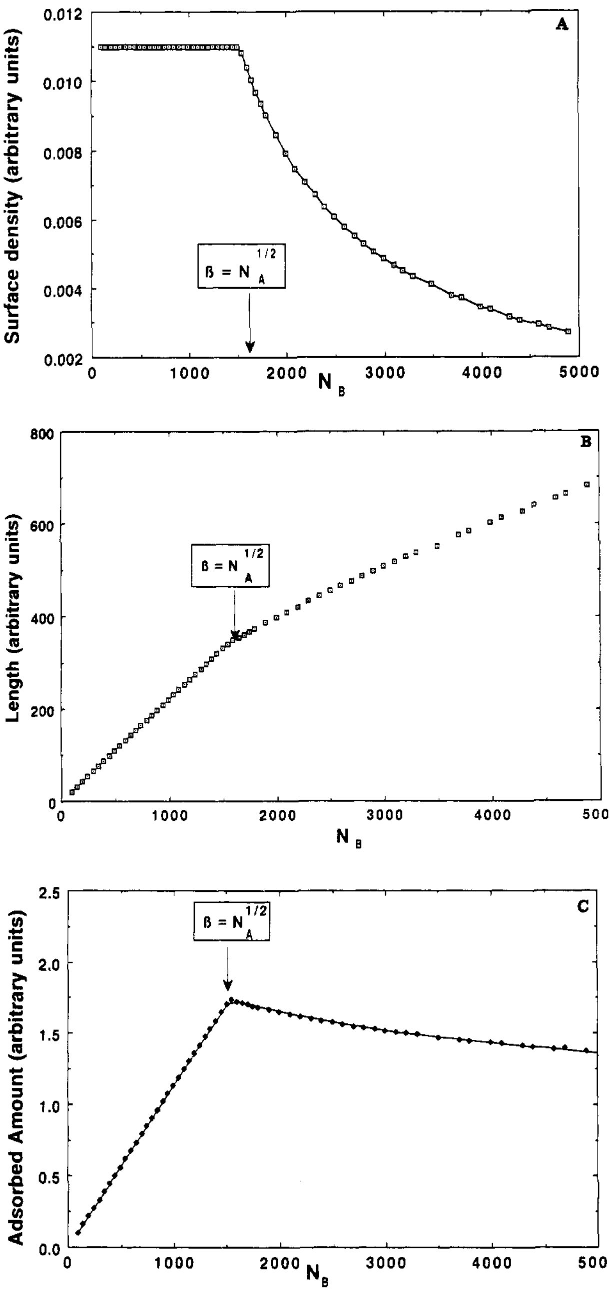

Figure 6. Surface density (A), length of the polymer brush (B), and adsorbed amount (C) as a function of the number of segments of the brush as defined by the MJ model at constant anchor block number of segments, $N_A = 91$.

Evers et al.[11-13] have recently published a mean field analysis of block copolymer adsorption in which they made detailed calculations of the behavior of the adsorbed amount, hydrodynamic thickness, etc. as a function of the fraction V_A of anchor block segments in a copolymer chain. Adopting their notation for the anchor block fraction we can compare our scaling calculations using the MJ model to their mean field calculations. It should be noted that their published calculations are for a case where the solvent is an athermal solvent for the buoy block but is a poor solvent for the anchor block. It is thus somewhat different from the nonselective solvent case of PS/PEO in toluene, which is discussed here, but the general trends are similar.

The surface density, the length of the brush, and the adsorbed amounts have been calculated at constant N_{PEO} as a function of N_{PS}. Results for σ, L, and s are shown in Figure 6 for an example where $N_{PEO} = 91$ and N_{PS} varies from 91 to 5000. For $\beta < N_{PEO}^{1/2}$, $\sigma = N_{PEO}^{-1}$, and we thus expect at constant N_{PEO} that the surface density will be constant. In this region the adsorbed amount is seen to increase linearly with N_{PS} (Figure 6C). At $\beta = N_{PEO}^{1/2}$ the two regimes cross over smoothly. For $\beta > N_{PEO}^{1/2}$ the surface density decreases and a maximum in the adsorbed amount is therefore predicted at $\beta = N_{PEO}^{1/2}$, i.e., at $N_{PS} = 1522$ when $N_{PEO} = 91$. Evers et al. have also shown from their mean field calculations that a maximum is expected in the adsorbed amount. The same behavior is expected for L, and it is apparent from Figure 6B that there is a change in the slope at $N_{PS} = 1500$ for the series of polymers where $N_{PEO} = 91$. In both MJ and Evers et al. the maximum adsorption occurs at a similar polymer composition, even though the Evers et al. model is for a selective solvent (Figure 7). As adsorption in good solvents is lower than in poor solvents, the relative difference between the two curves in Figure 7 is indeed expected to increase at higher V_A.

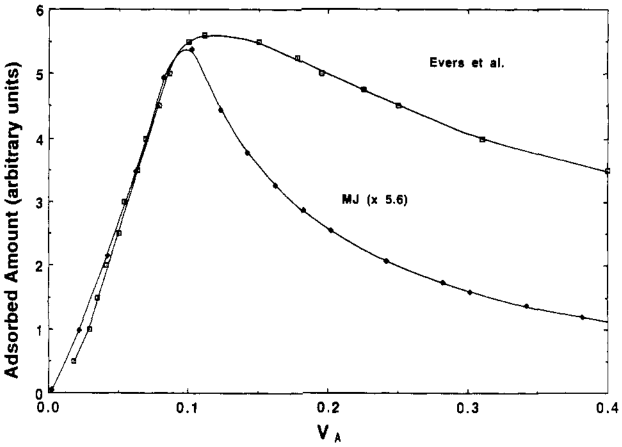

Figure 7. Comparison of the Evers and MJ models. The adsorbed amount is plotted as a function of the fraction of the number of PEO segments (V_A) in the polymer.

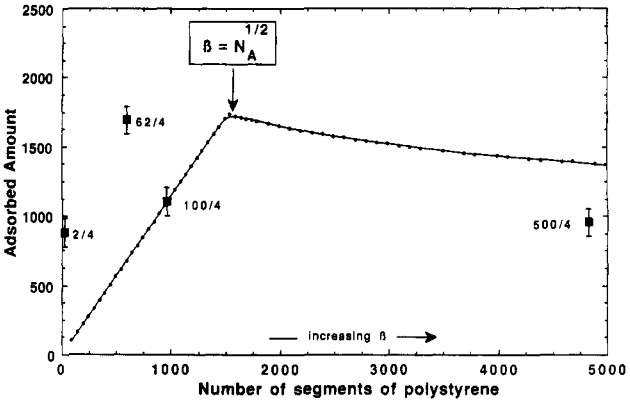

Figure 8. Comparison of measured adsorbed amount, as a function of the number of segments of polystyrene, with the predicted behavior for a series of polymers where N_{PEO} is constant.

A comparison of our measured values of the adsorbed amounts of the four materials with $N_{PEO} \sim 91$ with the predicted behavior is shown in Figure 8. (It should be recalled that the scaling predictions are to within a factor on the order of unity.) It is clear that no correction to the prefactor would be sufficient to bring the data onto the theoretically predicted curve, and although there is a maximum in the measured adsorbed amount, it does not occur at the composition predicted by MJ, but at a much lower value for N_{PS}. (The value of the adsorbed amount for the 62/4 material is larger than that of the 100/4 material.) Since MJ predicts that for $\beta < N_A^{1/2}$ the surface density is a constant ($\sigma \sim 1/N_A$), the model thus predicts

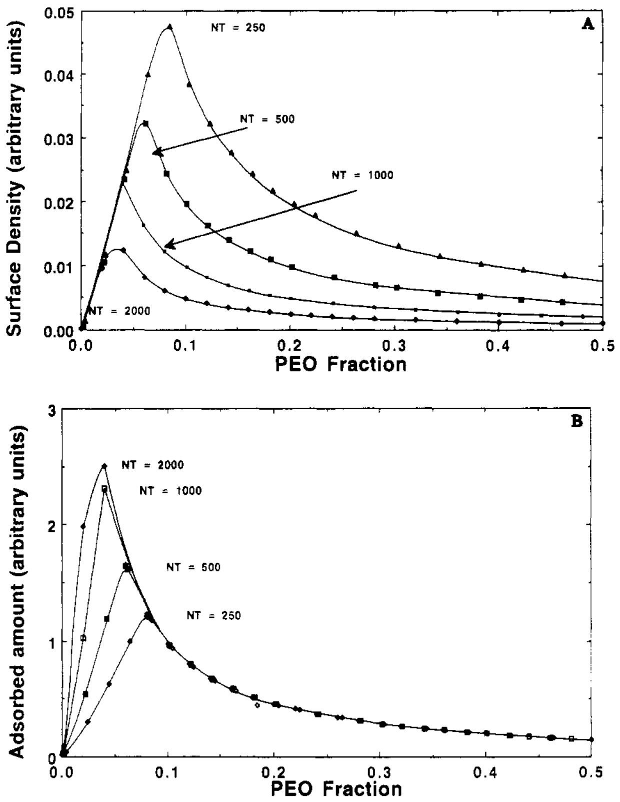

Figure 9. Model of MJ applied to the variation of the surface density (A) and adsorbed amount (B) with the PEO fraction for different constant total chain length, N_T.

that the 62/4 and 100/4 polymers should have the same surface densities. They clearly do not (see Table II) and the 100/4 polymer has adsorbed with a lower surface density than would be expected if the scaling approach were correct. If the 100/4 polymer adsorbed with the same surface density as the 62/4 polymer, i.e., at $\sigma = 0.021$ nm^{-2}, then the area/molecule would be 48 nm^2. From Table IV, the overlap area A_{ov} is 387 nm^2, which is ~8 times larger than 48 nm^2. The actual measured surface density shows an area/molecule of 115 nm^2, and A_{ov} is only ~3.4 times larger. Table IV lists the ratio A_{ov}/A for all the materials measured, and it can be seen that nowhere is this ratio larger than 5. As seen in Figure 6C, the model predicts that a material with $N_B = 1522$ for $N_A = 91$ would have the largest adsorbed amount. For such a polymer, A_{ov} would be 666 nm^2, and this is about 14 times as large as the area/molecule predicted for this polymer by MJ. The experimental data suggest that it is difficult to pack the PS chains any closer together than a surface density of ~5 times higher than that expected for chains which were just touching. This implies that the crossover between the 3D regime and the 2D semidilute regime occurs at value of β less than $N_A^{1/2}$ and suggests there may be an intermediate region which is governed by the enthalpy and elastic constants of the polymer. Parsonage et al.[8] have recently published values for the adsorbed amount of PVP/PS block copolymers on silicon and have noted that five of their polymers deviate from the theoretical exponent. These five polymers all have σ/σ_{ov} greater than 4.

The behavior of the adsorbed amount as well as the surface density can be modeled at constant total chain length, N_T. Figure 9 shows the surface density and the adsorbed amount plotted against the fraction of PEO in the polymer at various total chain lengths. Again a maximum in the surface density and adsorbed amount is found at low values of PEO fraction. Evers et al. also predict a maximum in the adsorbed amount at roughly similar chain compositions. Among all the polymers studied in this report there are three materials which have the same total chain length, namely, 148/2 ($N_T = 1450$), 125/11 ($N_T = 1468$), and 87/29 ($N_T = 1450$). Figure 10 compares the values of the adsorbed amounts found for these three materials to the theoretical curve for the adsorbed amount at $N_T = 1500$, using the expression $S = K\sigma_{calc}$ as one adjustable parameter (recall that the scaling law gives σ only to within a constant on the order of unity). It is apparent that the data can be fit by the scaling curve, but the lack of a data point near the peak of the curve makes this fit less than totally convincing. Also, the previous argument that the scaling model overpredicts the surface density at the crossover suggests that the fit near the peak in Figure 10 might also be poor for the same reason. Clearly it would be of value to examine a wider range of copolymers of both constant N_T and constant N_A to resolve these issues. In this respect we note that Wu et al.[25] have recently published data for a series of well-controlled block copolymers prepared by group-transfer polymerization. These were adsorbed onto silica particles from propyl alcohol (a nonselective solvent). Two series of data were obtained with constant N_T but varying N_A/N_B. As predicted from these theories, the adsorbed amount went through a maximum which was close to $N_A^{1/2}$ (A in that case being poly[(dimethylamino)ethyl methacrylate]).

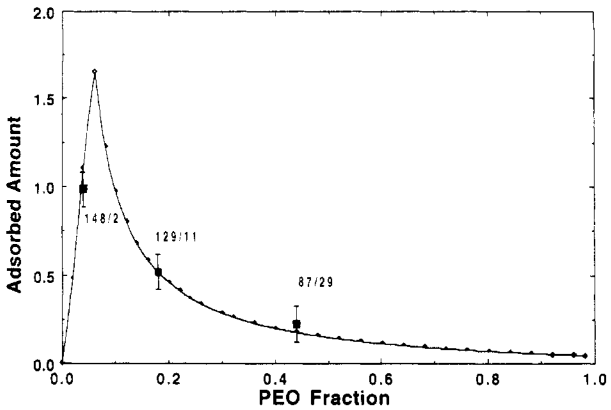

Figure 10. Comparison of measured values of adsorbed amount, as a function of the PEO fraction, with the predicted behavior by the MJ model for the adsorbed amount at a total chain length of $N_T = 1500$.

Conclusion

This report presents data for a series of PS/PEO block copolymers whose compositions range from symmetric to highly asymmetric. The experimental data can be fairly well accommodated within the scaling model of Marques and Joanny, although it appears that the model does not predict the proper surface density for materials at the crossover point between the 3D and 2D regimes, i.e., near $\beta = N_A^{1/2}$.

Appendix

The divisions between the different regimes in Figure 2 have been drawn from the conditions in the model of Marques and Joanny. The line $\beta = 1$ divides regimes II and III and the curve $\beta = N_A^{1/2}$ forms the division between regimes I and II. It is felt that the following derivation should be clarified.

In the MJ model, β is defined by the equation

$$\beta = \frac{a_B}{a_A}\left(\frac{N_B}{N_A}\right)^{3/5} \qquad (16)$$

where a_B and a_A are the monomer projection lengths. In their model, MJ assumed that the monomer sizes were identical, which means that the ratio a_B/a_A is equal to unity.

In practice, of course, this is never really true for block copolymers. In our case, the monomer size of the polystyrene is almost the monomer size of the poly(ethylene oxide). Therefore, this parameter has been taken into account when using eq 16 to draw the graph in Figure 2.

The division between regimes II and III is drawn by the line $\beta = 1$. Considering that

$$\beta = a'(N_B/N_A)^{3/5} = 1 \quad \text{where } a' = a_B/a_A \qquad (17)$$

we have

$$N_B a'^{5/3} = N_A \qquad (18)$$

By taking $a' = 0.87$,[24] the line $\beta = 1$ is drawn according to

$$N_B = 1.26 N_A \qquad (19)$$

i.e., by plotting $1.26N_A$ vs N_A. The division between regimes I and II is obtained by taking $\beta = N_A^{1/2}$. Considering that

$$\beta = a'(N_B/N_A)^{3/5} = N_A^{1/2} \qquad (20)$$

we have

$$N_B = N_A^{11/6}/a'^{5/3} \qquad (21)$$

a' being equal to 1.79. The line $\beta = N_A^{1/2}$ is drawn according to

$$N_B = 1.26 N_A^{11/6} \qquad (22)$$

and by plotting $1.26N_A^{11/6}$ vs N_A.

References and Notes

(1) Guzonas, D.; Boils, D.; Hair, M. L. *Macromolecules* **1991**, *24*, 3383.
(2) Marra, J.; Hair, M. L. *Colloids Surf.* **1988**, *34*, 215.
(3) Taunton, H. J.; Toprakcioglu, C.; Fetters, L. J.; Klein, J. *Macromolecules* **1990**, *23*, 571.
(4) Ansarifar, M. A.; Luckham, P. F. *Polymer* **1988**, *29*, 329.
(5) Hadziioannou, G.; Patel, S.; Granick, S.; Tirrell, M. *J. Am. Chem. Soc.* **1986**, *108*, 2869.
(6) Munch, M. R.; Gast, A. P. *Macromolecules* **1990**, *23*, 2313.
(7) Munch, M. R.; Gast, A. P. *Polym. Commun.* **1989**, *29*, 324.
(8) Parsonage, E.; Tirrell, M. *Macromolecules* **1991**, *24*, 1987.
(9) Marques, C. M.; Joanny, J. F.; Leibler, L. *Macromolecules* **1988**, *21*, 1051.
(10) Marques, C. M.; Joanny, J. F. *Macromolecules* **1989**, *22*, 1454.
(11) Evers, O. A. Ph.D. Thesis, Wageningen University, Wageningen, The Netherlands, 1990.
(12) Evers, O. A.; Scheutjens, J. M. H. M.; Fleer, G. J. *J. Chem. Soc., Trans. Faraday Soc.* **1990**, *86*, 1333.
(13) Evers, O. A.; Scheutjens, J. M. H. M.; Fleer, G. J. *Macromolecules* **1990**, *23*, 5221.
(14) Whitmore, M. D.; Noolandi, J. *Macromolecules* **1990**, *23*, 3321.
(15) Cosgrove, T.; Crowley, T. L.; Heath, T. G.; Ryan, K. *Macromolecules* **1987**, *20*, 2879.
(16) Cosgrove, T.; Heath, T. G.; Phipps, J. S.; Richardson, R. M. *Macromolecules* **1991**, *24*, 94.
(17) Patel, S.; Tirrell, M.; Hadziioannou, G. *Colloids Surf.* **1988**, *31*, 157.
(18) Alexander, S. *J. Phys. (Paris)* **1988**, *38*, 983.
(19) de Gennes, P.-G. *Macromolecules* **1982**, *15*, 492.
(20) Tripp, C.; Hair, M. L. *Appl. Spectrosc.* **1992**, *46*, 100.
(21) Tripp, C.; Hair, M. L. *Langmuir* **1992**, *8*, 241.
(22) Derjaguin, B. V. *Kolloidn. Zh.* **1934**, *69*, 155.
(23) Auroy, P.; Auvray, L.; Léger, L. *Phys. Rev. Lett.* **1991**, *66*, 719.
(24) Dondos, A. *J. Phys. (Paris)* **1987**, *48*, 1439.
(25) Wu, D. T.; Yokoyama, A.; Setterquist, R. L. *Polym. J.* **1991**, *23*, 709.

Registry No. PS/PEO (block copolymer), 107311-90-0.