Surface Force Measurements of Polystyrene-*block*-poly(ethylene oxide) Adsorbed from a Nonselective Solvent on Mica

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ABSTRACT: New surface force data are presented for six polystyrene-*block*-poly(ethylene oxide) block copolymers (PS/PEO) adsorbed onto mica from toluene. The polymers have been selected to have a low to moderate asymmetry radius ratio ($\beta = R_{F,ps}/R_{F,peo})^{3/5}$. The extended length L of the block copolymer layers has been determined and compared with data previously published on other PS/PEO copolymers adsorbed on mica. For moderate asymmetry ($1 \ll \beta \ll N_{peo}^{1/2}$) the extended length is shown to scale as $L \sim N_{ps}N_{peo}^{-1/3}$. Deviations are observed when the nonadsorbing block is either much larger than the adsorbing block or approximately the same size.

Introduction

The direct measurement of the forces between layers of adsorbed polymers on mica surfaces has been the topic of a number of studies in recent years. A comprehensive review of the literature on surface forces between adsorbed polymer layers has been published recently.[1] Although most of the early studies have dealt with homopolymer adsorption, more recently the force balance has been used to study the force–distance relationships between adsorbed diblock copolymers. Adsorption of polymeric amphiphiles can occur from either selective solvents, in which only one of the blocks is soluble in the solvent, or nonselective solvents, where both blocks are soluble. The former case is represented by, for example, polystyrene-*block*-poly(2-vinylpyridine), which has been studied by Hadziioannou et al.[2] An example of adsorption from a nonselective solvent is polystyrene-*block*-poly(ethylene oxide) (PS/PEO) diblock copolymers, from toluene, a good solvent for both blocks. Marra and Hair[3] have studied three PS/PEO copolymers adsorbed from toluene and Taunton et al.[4] included two PS/PEO polymers in their study of end-grafted polystyrenes adsorbed on mica from toluene. In all of the diblock copolymers studied, the observed force–distance curves exhibit an onset of the repulsive force at a distance many times larger than the radius of gyration of the unperturbed polymer in solution. This observation has been at least qualitatively explained as being due to the stretching out into solution of the nonadsorbing block, the so-called "brush" configuration.

More quantitative explanations in terms of the molecular weights of the blocks have also been given. For the PS/PEO diblock copolymers, which are of interest here, Marra and Hair[3] explained the range of the forces in their data by the following simple model: Scaling arguments[5,6] predicted that the length of the polymer brush scales as

$$L \sim N_{ps}\sigma^{1/3}a \tag{1}$$

where σ is the surface density, a is the length of a monomer segment, and N_{ps} is the number of segments of polystyrene.

Marra and Hair[3] assumed that the value of σ is determined by the value of R_g, the radius of gyration, of the anchor block, which for a good solvent is

$$R_g \sim N_{peo}^{3/5} \tag{2}$$

where N_{peo} is the number of segments of poly(ethylene oxide).

From this they derived

$$L \sim N_{ps}N_{peo}^{-0.4} \tag{3}$$

an equation that provided a good fit to their data.

Recently, Marques and Joanny[7] have considered the case of block copolymer adsorption from a nonselective solvent, using both mean field and scaling theories. The model assumes that the blocks are incompatible with each other but are both soluble in the solvent. The resultant polymer configuration at the surface is illustrated by Figure 1, where the adsorbed anchor layer A forms a fluffy, swollen layer against the surface and the B block is repelled from the surface and forms a brush layer. Their scaling treatment starts from a definition of the radius ratio β 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.

Two important assumptions are made for the derivation that follows: first, that the sizes of the two monomers are equal and, second, that the radius ratio β is much larger than unity. Following the model of Alexander,[5] they have used a blob model to calculate the free energy, F, of a grafted brush in a good solvent, with a chain density σ. This leads to

$$(F_B a^2)/T \sim N_B\sigma^{11/16} \tag{5}$$

where T is the temperature, and

$$L \sim N_B a\sigma^{1/3} \tag{6}$$

Using the modified free energy function of de Gennes,[6] which takes into account the concentration correlations induced by the excluded volume in an adsorbed layer, they obtain the concentration profile of the adsorbed layer by minimizing the free energy with respect to the local concentration of the A monomer. The concentration profile in the A layer is taken to be the same as for adsorbed homopolymer A except that the thickness of the anchor layer, d, is reduced by the confinement of the B chains.

The above argument is valid only if the adsorbed layer is continuous and can be considered to be locally semidilute. This is true if the radius ratio β is less than $N_A^{1/2}$, i.e., for moderately asymmetric polymers, and leads to the result

$$\sigma \sim 1/N_A \tag{7}$$

$$d \sim N_A^{1/2}/\beta \tag{8}$$

$$L \sim N_B N_A^{-1/3}a \tag{9}$$

For more asymmetric polymers, where $\beta > N_A^{1/2}$, the adsorbed layer can no longer be considered to be continuous but instead becomes a layer of individual isolated chains.

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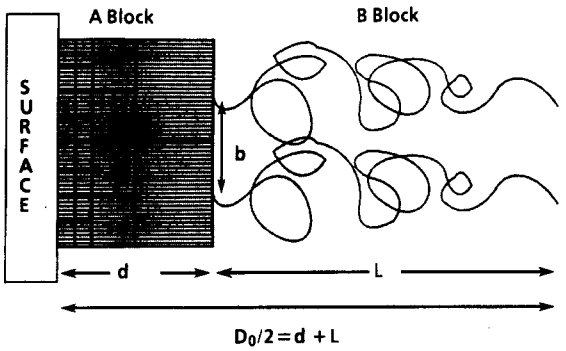

Figure 1. Model of AB block copolymer adsorbed from nonselective solvent (after Marques and Joanny[7]).

Table I
Characteristics of the Diblock Copolymers

PS/PEO	PS M_w × 10^{-3}	PEO M_w × 10^{-3}	M_w/M_n	N_B	N_A	% PEO
100/4	100	3.8	1.37	962	85	8
62/4	61.6	4.1	1.27	592	93	13.5
2/4[a]	2.33	4.34	1.07	22	99	35
334/19	333.7	19.2	1.37	3209	436	11
87/29	86.6	28.8	1.27	833	654	44
151/43	151.3	42.7	1.57	1455	970	40

[a] Supplied by Polymer Laboratories (U.K.).

Table II
Measurement of Adsorbed Amount[a] and Polymer Extension[b]

polymer	$D_0/2$, Å	adsorbed amt, mg/m^2	area/molec, nm^2
87/29	400	2.1	92
151/43	488	2.5	130
334/19	1050	2.6	212
2/4	75	2.7	4
100/4	600	2.8	60
123/25	300	0.73	210
129/11	425	2.1	75
62/4	310	4.0	26
343/27	950	2.2	190

[a] The amount of polymer adsorbed onto the mica is measured in situ from refractive index measurements as described in text. [b] D_0 is the distance between plates when repulsive force is first observed.

The thickness d of the anchor layer is then on the order of the monomer size and will scale as

$$d \sim N_B^{3/5} N_A^{2/5} a \qquad (10)$$

In this paper, we present surface force data on six PS/PEO diblock copolymers adsorbed on mica from toluene. These polymers have low to moderate asymmetries and include three for which β is close to unity and one where $\beta < 1$. We then discuss these data, as well as the previous data of Marra and Hair[3] and of Taunton et al.,[4] in terms of the model of Marques and Joanny[7] described above, and indicate the range of applicability of this model to the existing data on PS/PEO copolymers.

Experimental Section

Materials. Except where otherwise indicated, the polystyrene-*block*-poly(ethylene oxide) copolymers 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 copolymer statistics are listed in Table I. In ensuing discussions of the polymers we shall refer to the samples by listing the molecular weight of each block, M_w(PS)/M_w(PEO), in units of thousands. Thus, for example, 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

Table III
Calculated and Measured Values of the Polymer Parameters Needed To Study the Relation $D_0/2$ versus $N_{ps}N_{peo}^{-1/3}$ When $\beta \ll 1.5 \ll N_A^{1/2}$

PS/PEO	β	$N_A^{1/2}$	$D_0/2$, Å	d[a]
2/4	0.4	9.95	75	25
87/29	1.16	25.6	400	22
151/43	1.28	31.1	488	24

[a] d is given by eq 8.

Table IV
Calculated and Measured Values of the Polymer Parameters Needed To Study the Relation $D_0/2$ versus $N_BN_{peo}^{-1/3}$ When $N_A^{1/2} > \beta > 1.5$

PS/PEO	β	$N_A^{1/2}$	$D_0/2$, Å	d
123/25[a]	1.56	22.9	300	15
129/11[a]	2.58	15.9	425	6
343/27[a]	2.72	24.2	950	9
62/4	3.03	9.42	310	3
334/19	3.31	20.3	1050	6
184/7[b]	4.04	12.9	750	3
100/4	4.28	9.0	600	2

[a] The D_0 value has been taken from ref 3. [b] The D_0 value has been taken from ref 4.

Table V
Calculated and Measured Values of the Polymer Parameters Needed To Study the Relation $D_0/2$ versus $N_{ps}N_{peo}^{-1/3}$ When $\beta \geq N_A^{1/2}$

PS/PEO	β	$N_A^{1/2}$	$D_0/2$, Å	d
150/2[a]	7.4	7.1	725	1

[a] The D_0 values has been taken from ref 4.

weight-average number of segments of polystyrene and poly(ethylene oxide) as N_{ps} and N_{peo}, respectively. Values of β for all polymers can be found in Tables III–V.

The toluene and heptane used as solvents in the surface force experiments were purchased from Aldrich as HPLC grade. They were glass distilled, filtered, and dried over molecular sieves for several days before being glass distilled immediately prior to use.

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 with Autovial syringeless filtes (S.P.E. Ltd) designed for organic solvents before being injected into the apparatus.

Surface Force Measurements. Except for the addition of a video camera, the surface force apparatus used in these experiments has been described in detail in previous publications.[8,9] Only a brief description of the experimental arrangement will be given.

The force–distance curves are measured between two freshly cleaved, molecularly smooth mica surfaces, which are silvered on one side and then glued on to cylindrically curved glass disks. These surfaces are mounted in the surface force apparatus in the crossed cylinder configuration. The forces measured are then normalized by the measured radius of curvature R to obtain the interaction energy $E(D)$ per unit area between two flat parallel surfaces according to the Derjaguin approximation, $F(D)/R = 2\pi E(D)$.[10]

The separation between the surfaces is controlled by a three-stage mechanism consisting of a stepping motor for coarse (1 μm) positioning, a DC synchronous motor for positioning to within 20 Å, and a piezoelectric crystal, which allows positioning to within 2 Å. The outputs of these two devices are also fed into an A/D converter installed in the computer. The force is measured by the deflection of a double leaf spring of calibrated spring constant. The separation between the surfaces is measured interferometrically by analyzing fringes of equal chromatic order (FECO), and the distances can be measured to ±2 Å.[8] The fringes are observed on an image-intensified CCD video camera, which has been mounted at the exit slit of the spectrometer. The camera output is fed to a video monitor and to one channel of a MATROX IMAGER AT video processing board in an IBM-

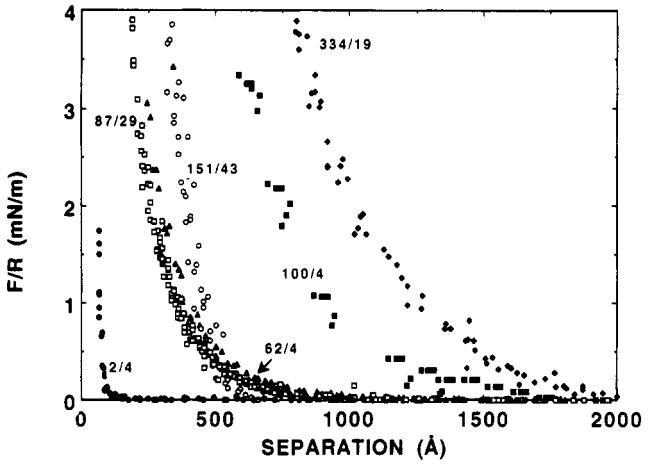

Figure 2. Measured force–distance curves for new polymers listed in Table I.

compatible AT computer. A mouse driven, C language software package is used to grab the video input for signal averaging and this provides instant output of the surface separation. The maximum distance resolution obtainable with this system is ±2 Å.

At the start of each experiment, the surfaces are first brought together in an atmosphere of dry nitrogen and this contact position is defined to be $D = 0$. The apparatus is then filled with dry toluene and the force–distance profile measured. The presence of an oscillatory profile as reported in the literature is a sign of solvent and surface cleanliness. Once the condition of the surfaces had been checked in this manner, the polymer was added to the apparatus. It was found by monitoring the surface forces that the adsorption was complete within 2 h for all the polymers studied, a result confirmed by infrared spectroscopy.[11] Munch and Gast[12] have independently shown that adsorption of PS/PEO on sapphire is complete after 20 min.

Results and Discussion

The results for the six copolymers studied here are presented in Figure 2. Each curve is a composite of a number of inward and outward force–distance measurements. In most cases, no difference was found between the force curve measured during the inward compression and that measured during the the outward movement. However, some hysteresis effects were noted for some of the symmetric materials listed in Table III. In all cases, the inward force curves were found to be highly reproducible over any number of cycles and at several contact points on the surface.

All of the force curves measured are purely repulsive, the range of the forces being dependent upon the molecular weight of both the polystyrene and the poly(ethylene oxide) blocks. For the three least symmetric copolymers (100/4, 334/19, and 62/4), it was found that as the molecular weight of the polystyrene block was increased, the distance at which a force could be first detected was found to increase. (This is most easily seen by comparing the pair 100/4 and 62/4.) If we include the results of Marra and Hair,[3] it is also found that an increase in the molecular weight of the poly(ethylene oxide) block decreases the range of the surface forces. The overall behavior of these three new copolymers thus corresponds very well to the previously reported data. The 2/4 copolymer also appears to follow this trend, viz., the series 100/4, 62/4, and 2/4; but the case of the 87/29 and 151/43 copolymers is more complex. Marra and Hair[3] report force curves for 343/27 and 123/25 (these polymers are labeled as 250/20 and 90/18 in their paper) and show the distances at which the repulsive forces are first measured (D_0) to be 1900 and 600 Å, respectively. Since our 87/29 copolymer has the same anchor block size, it would be expected that the

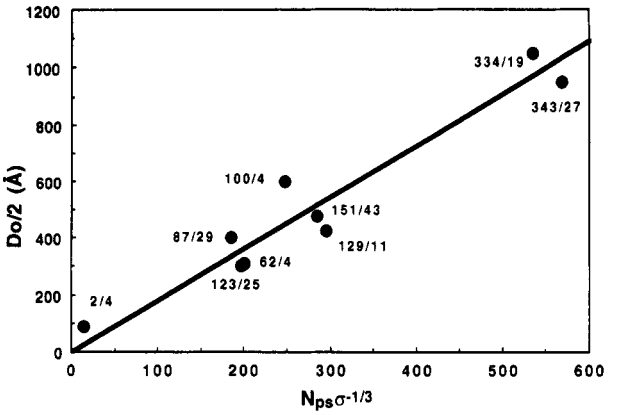

Figure 3. $D_0/2$ as a function of surface coverage and segment density of polystyrene. Data from Table II.

distance at which the force is first measured would be less than that measured for the 123/25 material. But this is not the case and D_0 is found to be 800 Å. In order to more closely examine the dependence of the range of the forces with the molecular weights, $D_0/2$ is tabulated in Table II for all of the copolymers studied to date. The errors associated with the length measurements are estimated as ±50 Å, in agreement with errors reported on similar systems by Taunton et al.[4]

In the derivation of the thickness of the adsorbed layer, all theories revert to the surface density. In the case of the polymer brush, scaling theories predict that

$$L \sim N_{ps}\sigma^{1/3} \tag{11}$$

Thus, a plot of L versus $\sigma^{1/3}$ should scale as the molecular weight of the polystyrene and be independent of the molecular weight of the poly(ethylene oxide).

The adsorbed amount, and hence the surface density, can in principle be determined from the surface force apparatus by measuring the refractive index of the medium between the surfaces. This measurement has been utilized by Taunton et al.[4] in the case of end-terminated polystyrene but is difficult because of the small differences in refractive index between toluene and both blocks of the copolymers. We have therefore used the method of Marra and Hair[3] in which the polymer layer is collapsed in a nonsolvent heptane–toluene mixture. Complications may arise from the presence in the system of a third component, but it is felt that thickness and refractive index measurements on the collapsed film are more accurate. Refractive index measurements on this collapsed layer indicated volume fractions of the adsorbed polymer between 0.6 and 0.8, in good agreement with data on precipitated PS.[3] The thickness of the collapsed layer is measured at a large compression. It is found that when the force is greater than about 4 mN/m there is little or no further inward compression and the adsorbed amount of the polymer can be estimated. The refractive indices of the solvent (1.496) and polymer (1.59) are such that the polymer volume fraction cannot be estimated better than 10%. Coupled with the average 5% error in the length measurements, the total accuracy is at best 15%. The copolymers with the largest polystyrene content will be the most accurate and the line in Figure 3 is drawn from the midpoint of 334/19 and 343/27 to the origin. The results are listed in Table II. In spite of the rather large errors associated with these numbers, the plot of $D_0/2$ versus $N_{ps}\sigma^{1/3}$ gives a relatively good linear relationship. It obviously would be of great value to have a more accurate value for the adsorbed amounts and Parsonage et al.[13] have recently reported the use of tritium-labeled polymers to quantify the adsorbed amounts of a large number of PVP/PS

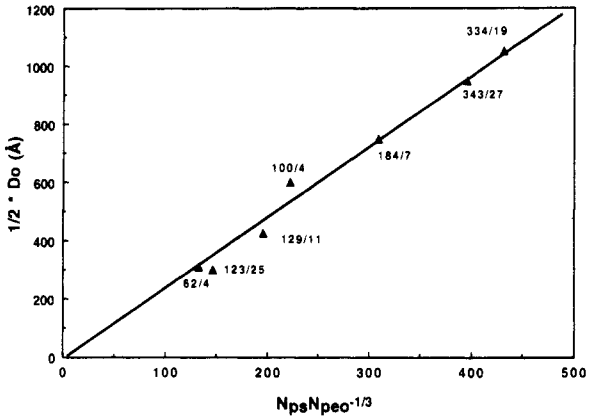

Figure 4. $D_0/2$ as a function of $N_{ps}N_{peo}^{-1/3}$ for polymers from Table IV. The straight line is drawn arbitrarily from the origin through 334/19.

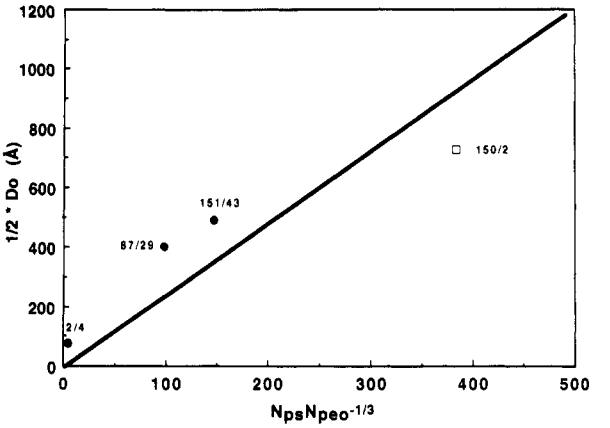

Figure 5. $D_0/2$ plotted versus $N_{ps}N_{peo}^{-1/3}$ for polymers in Tables III and V. The straight line is that shown in Figure 4.

diblock copolymers. They find values of the adsorbed amounts for all of their materials to be about 2 mg/m^2, and their surface density follows quite nicely the theoretical predictions of the theory of Marques et al.[14] for the adsorption of diblock copolymers from a selective solvent. We are currently developing a spectroscopic method for the determination of the adsorbed amount independent of the surface force apparatus.[11]

As noted earlier we will use the recent theory of Marques and Joanny[7] to interpret our results. For the purposes of the following discussion we must first clarify the relationship between the variables discussed in the theory and what is accessible from the surface force data. The surface force measurements give a value for D_0, the separation between the mica plates at which a force can first be measured. In the nomenclature used by Marques and Joanny[7] in their paper, this corresponds to $D_0/2 = d + L$. Thus, if the thickness of the anchor block is very small compared to the thickness of the buoy block, one expects that

$$D_0/2 \sim N_{ps}N_{peo}^{-1/3} \tag{12}$$

If d is large, a more complex relationship is anticipated.

All the data now available on PS/PEO block copolymers are listed in Table III–V in order of increasing asymmetry of the polymers. The data have been divided into three groups on the basis of the criteria set out by Marques and Joanny[7] for the limits of their model for a continuous anchor layer; viz., $1 \ll \beta \ll N_{peo}^{1/2}$, where $\beta = (N_{ps}/N_{peo})^{3/5}$, as discussed in the Introduction. We have rather arbitrarily set a value of $\beta \geq 1.5$ as fulfilling the condition $\beta > 1$. For the 11 polymers for which we have data, seven fall within the Marques and Joanny[7] conditions (Table IV), three have $\beta < 1.5$ (Table III), and one has $\beta \simeq N_{peo}^{1/2}$ (Table V). The copolymers in Tables IV and V are also expected to fulfill the condition that $d \ll L$. The data from Table IV are plotted as $D_0/2$ versus $N_{ps}N_{peo}^{-1/3}$ in Figure 4. It is apparent that the predicted scaling is followed quite well, a linear least-squares fit giving a slope of 2.4 ($R = 0.985$). This excellent accord with the predicted scaling relationship suggests first that the assumption that the thickness of the anchor block is small in comparison with the thickness of the brush was valid for these seven copolymers and second that the criteria of Marques and Joanny[7] for the validity of their model are also sound. Further evidence for both of these conclusions is found when $D_0/2$ is plotted versus $N_{ps}N_{peo}^{1/3}$ for the copolymers in Tables III and V (Figure 5). The solid line in this figure is the same line as was derived from Figure 4. The polymer with $\beta > N_{peo}^{1/2}$ falls below the line; i.e., the copolymer extension is shorter than predicted by the model. The three copolymers for which $\beta < 1.5$ fall above the line, with the deviation from the line increasing as β approaches unity.

It appears from Figure 5 that these three copolymers (for which $\beta < 1.5$) are longer than predicted by the simple scaling relation $L \sim N_{ps}N_{peo}^{-1/3}$. This result is not surprising when it is recalled that the measured onset of repulsion D_0 reflects not only the thickness of the brush layer but also the thickness of the anchor layer. Clearly, for these symmetric copolymers, the thickness of the anchor layer is playing a much greater role than merely determining the surface density; it also makes a contribution to the overall thickness of the adsorbed polymer layer that cannot be neglected. This behavior is, in fact, built into the model (Figure 1) and is a result of the fact that the PEO block is soluble in toluene and forms, a fluffy adsorbed layer rather than the compact, flat adsorbed layer, which has been suggested for PS/PVP on mica. This points out a major difference between the behavior of diblock copolymers adsorbed from selective versus nonselective solvents and suggests that for a given copolymer the repulsive forces will be of a longer range in a nonselective solvent.

The copolymer 150/2 was studied by Taunton et al.[4] In that case $\beta \geq N_{peo}^{1/2}$ and the polymer must be considered as a representative of the other extreme of very asymmetric copolymers. Here, the theory of Marques and Joanny[7] suggests the appropriate scaling relation is $L \sim N_{ps}^{3/5}N_{peo}^{2/5}$. The main thrust of the Taunton et al.[4] work was surface force data of a number of end-functionalized polystyrenes. For those polymers, they found a scaling relation for the onset of the repulsive force with $N_{ps}^{3/5}$, which is of course the limit of the above relation when N_{peo} approaches unity. Although they did not discuss the two PS/PEO copolymers in terms of the relationship $L \sim N_{ps}^{3/5}$, we find that these two copolymers fit this relationship reasonably well. We are currently in the process of exploring this region of the asymmetric ratio as well as the region where the crossover from a semidilute continuous layer to a layer of individual chains should occur.

The theory of Marques and Joanny[7] can further be used to try to bring all of the force–distance curves onto a "universal curve" in a manner similar to that derived by Patel et al.[15] for their PVP–PS data. From eqs 5 and 7, Marques and Joanny[7] derive an expression for the free energy, F, of the polymer brush

$$F_B a^2/T \sim N_{ps}N_{peo}^{-11/6} \tag{13}$$

Using the Derjaguin approximation,[10] the force $F(D)$ between two crossed cylinders of radius of curvature R

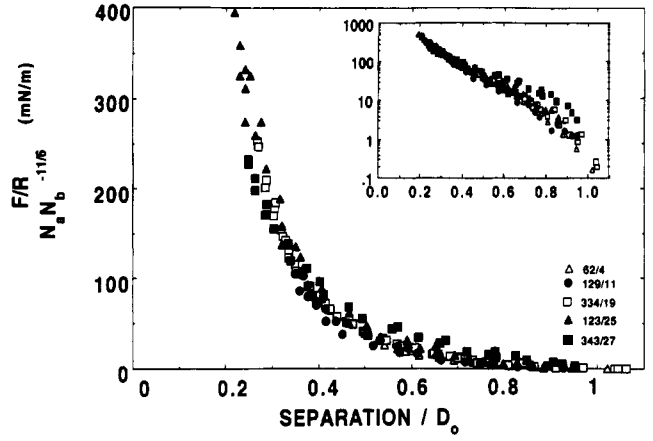

Figure 6. Universal force curve for the first five polymers listed in Table IV. F/R is scaled by $N_{ps}N_{peo}^{-11/6}$; separation of plates is scaled by distance at first contact. (Inset is a semilog plot.)

can be related to the interaction energy per unit area between parallel plates, $E(D)$, by

$$F(D)/R = 2\pi E(D) \tag{14}$$

as long as $D \ll R$, which is the case in our measurements. Assuming no interpenetration, but only mutual compression of the two layers, the free energy change associated with changing the length of the polymer brushes, and hence F/R, should scale as

$$F/R \sim N_{ps}N_{peo}^{-11/6} \tag{15}$$

Thus a plot of $(F/R)/N_{ps}N_{peo}^{-11/6}$ versus the normalized distance D/D_0 might be expected to reduce the data to a single curve.

The result of this scaling for two of the moderately asymmetric materials of this work and the three copolymers form Marra and Hair[3] is shown in Figure 6; a semilog version of the same curve is shown in the inset. It is apparent that this scaling is quite successful in reducing all the force–distance data to one curve. It was not possible to scale the 100/4 copolymer data exactly onto the universal curve.

We have so far avoided a discussion of the significance of neglecting the differences in the sizes between the PEO and PS monomers. That omission does not affect the scaling relationship $L \sim N_{ps}N_{peo}^{-1/3}$ since the ratio of the monomer sizes is a ratio that would be included in the neglected prefactors: but it does affect the value of β and thus it determines whether the copolymer falls inside the range of criteria of Marques and Joanny.[7] Indeed, for the 100/4 copolymer, if the differences in the monomer sizes are included, then this places the copolymer outside the criteria where the above scaling is applicable. It is thus suggested that the failure of this material to fall on the universal force curve in spite of its falling on the line in Figure 4 may be an indication that this is a borderline case, at the threshold of the noncontinuous regime.

The same scaling of the force by $N_{ps}N_{peo}^{-11/6}$, when applied to the three symmetric copolymers, is not successful in reducing these data to the "universal force curve", as shown in Figure 7. Here the data are presented in semilog form, and the solid line is the "average" (i.e., *not* a fit) line through the data points in Figure 6. Again, as in the plot of D_0 versus $N_{ps}N_{peo}^{-1/3}$, the three symmetric materials are seen to be "thicker" (i.e., shifted to the right on the distance scale) than the simple scaling relationship predicts.

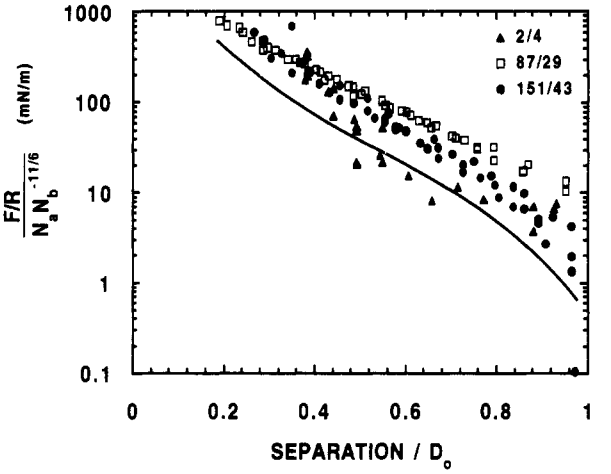

Figure 7. Scaling suggested by eq 15 applied to polymers in Table III. The solid line is the "average" from Figure 6.

Although Marques and Joanny[7] give a scaling relation for the thickness of the anchor layer, it is not possible to disentangle the effects of the dependence of d on the molecular weights from the dependence of L. This can be seen if one puts the proportionality constants into the scaling relations, to get an expression for the total thickness of the adsorbed layer. The resulting equation

$$D_0/2 = k_1 N_{ps}N_{peo}^{-1/3} + k_2 N_{ps}^{-3/5}N_{peo}^{-11/10} \tag{16}$$

cannot be used for the asymmetric polymer in the absence of values for the two proportionality constants. Thus it is difficult to decide from the experimental data presented here whether the data for the symmetric copolymers could be described by taking into account the thickness of the anchor layer predicted by Marques and Joanny[7] or if the model itself is no longer applicable for these cases where $\beta \leq 1$. This is clearly an area where future work would be of value.

This work shows, however, that for polymers of moderate asymmetry, $1 \leq \beta \leq N_A^{1/2}$, which fall within the regime of the Marques and Joanny theory,[7] the extended length of the polymer is satisfied by the relation $L \sim N_B N_A^{-1/3}$, which is proposed in that model.

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