Conformations of Block Copolymers Terminally Adsorbed at the Solid-Liquid Interface

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ABSTRACT

The conformations of end-adsorbed diblock and triblock copolymers of polystyrene (PS) and polyethylene oxide (PEO) adsorbed onto mica from toluene have been studied by the surface force method. The PS-PEO diblock copolymer system forms a semi-dilute brush with the non-adsorbing PS chains adopting an extended configuration away from the surface. Neutron reflectometry indicates that the volume fraction profile of such a system has a broadly parabolic shape, in agreement with theory. In contrast to PS-PEO diblock copolymers which adsorb only in a "tail" conformation, PEO-PS-PEO triblock chains form "loops" as well as "tails" on the mica substrate. Attractive forces are observed when an adsorbed layer of PEO-PS-PEO triblock copolymer is allowed to interact with a bare mica wall, due to the formation of polymer bridges between the two opposing surfaces.

INTRODUCTION

It is well-established that the conformations of macromolecules adsorbed onto a solid-liquid interface are generally rather different from those in the bulk solution. This is particularly true in the case of block copolymers with an amphiphilic character. Such macromolecules may consist of blocks with varying degrees of affinity for the solid substrate, which can profoundly affect the way the chains arrange themselves at the interface. The structural features of adsorbed block copolymers have been investigated by a variety of techniques including surface force measurements,[1-4] neutron scattering,[5,6] and more recently, neutron reflectometry.[7-9] Of particular interest is the case of diblock (AB) and triblock (ABA) copolymers containing adsorbing (A) and non-adsorbing (B) blocks in a good solvent.[3,4,10] At sufficiently high surface coverage such copolymers have been shown to form a semi-dilute polymer brush with the stretched B blocks extending away from the surface. This conformation is particularly suitable for applications in the steric stabilization of colloidal dispersions, since stability is greatly enhanced due to the stretched nature of the polymer chains in the adsorbed layer around the colloidal particles.   In the present paper we review some recent results on PS-PEO diblock copolymers and present new surface force measurements on PEO-PS-PEO triblock copolymers adsorbed onto mica from toluene. The use of a non-selective solvent, which is a good solvent for both components, may simplify the situation since it excludes self-association of the chains which could lead to micellization in the bulk, and similar aggregation phenomena at the interface. This makes toluene the solvent of choice for the copolymers of polystyrene and polyethylene oxide in this study.

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MATERIALS AND METHODS

The polystyrene-polyethylene oxide diblock copolymer (PS-PEO) and polyethylene oxide-polystyrene-polyethylene oxide (PEO-PS-PEO) triblock copolymer samples were purchased from Polymer Laboratories (U.K.) and have the molecular characteristics shown in Table 1. Spectroscopic grade toluene was obtained from Aldrich Chemical Company Ltd. All materials were used as supplied.

The surface force apparatus was used to measure the interaction between two adsorbed polymer layers as well as a single adsorbed polymer layer against a bare mica surface. Atomically smooth mica is used as a substrate, with two mica sheets mounted in a crossed cylinder configuration. The force, F, as a function of the separation, D, between the mica substrates is measured directly by observing the deflection of a leaf spring of known spring constant bearing one of the mica sheets. The surface separation is measured with the aid of interferometry. The results are presented in the form F(D)/R vs. D, where R is the geometric mean radius of curvature of the two mica surfaces. The value of F(D)/R gives the interaction energy per unit area of surface. The technique for measuring the interaction between two adsorbed polymer layers has been described in detail previously.[11,12] For force measurements with a polymer layer on one surface only, however, the normal incubation method of simply immersing the two mica sheets in the polymer solution simultaneously is not applicable. A literature survey shows that two different approaches have been devised to meet this requirement.[4,13] Both, however, require the removal of one of the surfaces from the apparatus during the experiment leading to a high failure rate due to possible surface contamination. Elsewhere,[10] we have reported a novel technique which allows the formation of a single clean adsorbed polymer layer on one of the mica surfaces only, while both of them remain in the force apparatus throughout the experiment. In what follows, we describe a brief outline of only the main procedures involved in this new method. To begin with, the lower mica surface only is allowed to incubate in a polymer solution in a stainless-steel bath within the force apparatus, whereas the upper surface is kept away from the polymer solution, but directly above the lower surface. Having incubated the lower surface in the polymer solution for a sufficient time to allow the formation of an adsorbed layer, a clean glass slip which can be moved laterally along the top of the bath is placed directly above the lower mica surface leaving a gap of ca.1mm between them. The polymer solution can now be drained and replaced by pure solvent while a small droplet which forms in this gap protects the polymer layer against any collapse due to drying. The glass slip is then removed and the interaction of the adsorbed layer against the bare upper mica surface is finally measured.

Typically, the lower mica surface was incubated in a PS-PEO or PEO-PS-PEO solution, according to the procedure described above, at a concentration of ca.2.4×10^{-3} (w/w) for about 20 hours before the force-distance profiles were measured with the surface force apparatus in its usual mode.[12] All the experiments were carried out at a temperature of $14\pm2°C$.

The neutron reflectivity measurements which were performed at the Rutherford Appleton Laboratory, UK, and at the Los Alamos National Laboratory, USA, have been described in detail elsewhere.[9] Optically flat single crystal quartz was used as a substrate in contact with a polymer solution in deuterated toluene. The neutron beam passed through the quartz crystal and was reflected from the face of the crystal bearing the adsorbed layer.

RESULTS AND DISCUSSION

The force-distance profiles of PS-PEO diblock copolymers adsorbed on mica are characterized by a long interaction range and the absence of hysteretic effects commonly observed in adsorbed homopolymers.[14] This is because in the good solvent toluene, PS does not adsorb onto mica while PEO adsorbs strongly.[4,14] Thus, the PS-PEO chains attach themselves terminally onto the substrate, and at sufficiently high values of the surface coverage they become fairly stretched. We are concerned here with the case where the adsorbing PEO block is rather small compared to the non-adsorbing PS chains (see Table 1). The self-

TABLE 1
Molecular Characteristics of the PS-PEO and PEO-PS-PEO Copolymer Samples

Sample	M_w	M_w/M_n	wt% PEO	$(PEO)_{x1}$ $(PS)_y$ $(PEO)_{x2}$		
				x1	y	x2
PS-PEO (80k)	80×10^3	1.07	5.0	0	730	90
PS-PEO (150k)	150×10^3	1.16	1.5	0	1420	51
PS-PEO (184k)	184×10^3	1.10	4.0	0	1700	167
PS-PEO (325k)	325×10^3	1.14	0.3	0	3115	22
PS-PEO (502k)	502×10^3	1.10	0.8	0	4788	91
PEO-PS-PEO (128k)	128×10^3	1.02	0.3	5	1225	5

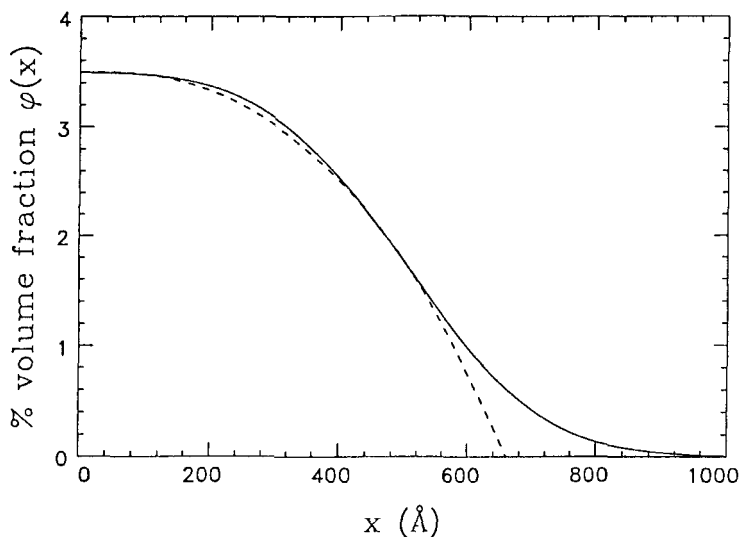x1, x2 and y are weight-averaged degrees of polymerization for each block.

Figure 1 Error function (———) and parabolic (------) polymer volume fraction profiles for the PS-PEO (150k) diblock copolymer determined by neutron reflectometry.[9] The curves were obtained from least squares fits of each model to the experimental reflectivity profile (not shown). The two profiles are essentially indistinguishable at short to intermediate distances from the surface, and differ only at large distances near the "height" of the polymer brush. The reflectivity data could not be fitted to exponential or power-law decay volume fraction profiles. The volume fraction of the polymer in the adsorbed layer is well-within the semi-dilute regime.
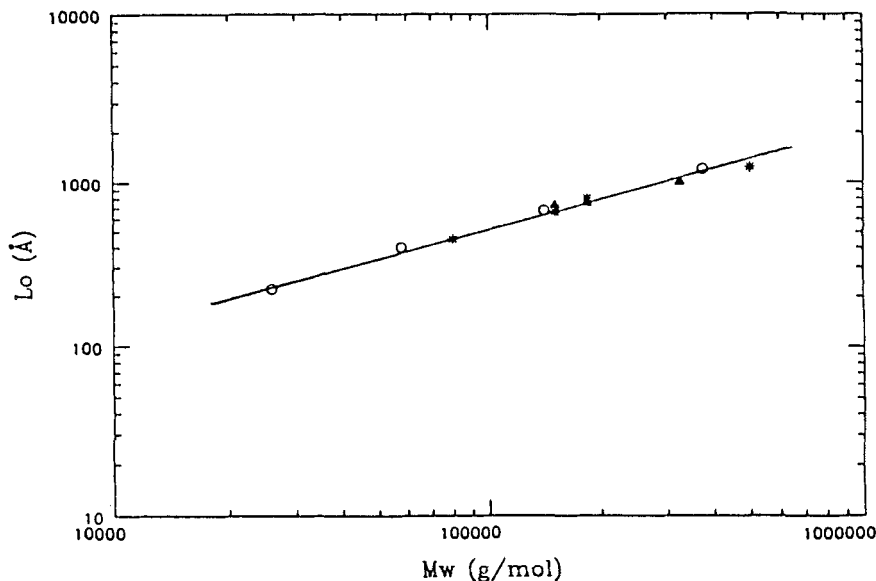
Figure 2 Variation of adsorbed layer thickness, L_0, with PS molecular weight M_w. The straight line has a gradient of 0.6. The layer thickness of the PS-PEO diblock copolymers (see Table 1) was determined both by surface force measurements (Δ)[4] and by neutron reflectometry $(*)$.[9] The PS-X data (o) were obtained from surface force measurements and are discussed in Ref.4.

consistent mean field theory of Millner et al[15] predicts a parabolic polymer volume fraction profile for such a system, while the thickness of the adsorbed layer, L_0, is expected to vary with the degree of polymerization of the non-adsorbing chain, N, and the surface coverage, σ, as $N\sigma^{1/3}$. We have used neutron reflectivity as a probe to investigate the polymer density profiles of end-adsorbed PS-PEO diblock copolymers at quartz-toluene interface.[9] It was found that the reflectivity profiles are well-described by a density profile of largely parabolic shape (see Fig.1), and are thus consistent with the theoretical prediction for a semi-dilute polymer brush.[15]

The values of layer thickness deduced from the parabolic profiles are in good agreement with those obtained from surface force measurements for the same polymer. Although the layer thickness, L_0, is predicted to scale linearly with the molecular weight of the non-adsorbing block at fixed surface coverage, it is not possible to keep σ fixed while N is varied for the *physically* end-adsorbed block copolymers (as opposed to *chemically* grafted chains) since by increasing the PS molecular weight the osmotic repulsions between neighboring chains are increased, leading to larger separations between anchor points and hence lower surface coverage. An "equilibrium" picture may, therefore, be envisaged where σ is determined by a
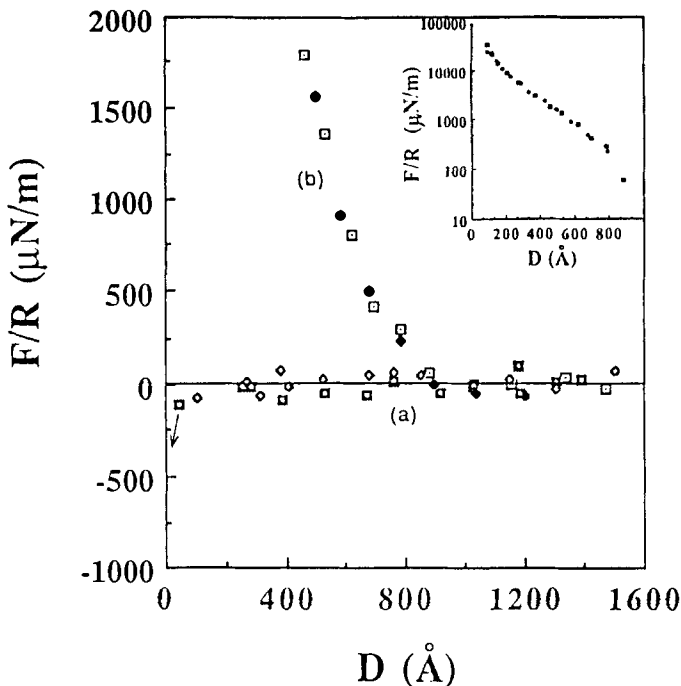
Figure 3 (a) Force-distance profiles between curved mica surfaces in pure toluene for two measurements on two different pairs of mica sheets. (b) Force-distance profiles for a single PS-PEO (150k) adsorbed layer against a bare mica surface in toluene; Inset shows the same curve as (b) on a log-linear scale. The solid and open symbols represent compressions and decompressions, respectively.

balance between the osmotic repulsion experienced by the non-adsorbing chains and the attraction of the sticking blocks to the interface, as appears to be the case in the present study. In such a system, if the strength of the attraction is fixed (possibly by keeping the size of the sticking block approximately constant) while N is allowed to vary, then L_0 is predicted[4] to scale with $N^{3/5}$. This is confirmed by the results shown in Figure 2. The agreement between the results obtained from surface force measurements and those measured by neutron reflectivity is particularly satisfactory.

From Figure 2, it is also noted that the behavior of the end-functionalised PS-X chains[4] where X is the zwitterionic group, $-(CH_2)_3N^+(CH_3)_2(CH_2)_3SO_3^-$, is described by the same line as that of the PS-PEO copolymers. Clearly, therefore, in the limit of a small anchoring block relative to the overall size of the copolymer, adsorption is mainly determined by repulsive

interactions between the non-adsorbing blocks. Thus both the form of the polymer volume fraction profile of end-adsorbed diblock chains, and the scaling of the adsorbed layer thickness with molecular weight are in reasonable agreement with theory.

While diblock copolymer and mono-end-functionalized chains can only adsorb onto a substrate in a "tail" conformation, ABA type triblock copolymers may also form "loops" with both A blocks sticking to the same surface. Furthermore, in contrast to diblock copolymers, such triblock chains may form polymer "bridges" by simultaneously attaching themselves to two opposing substrates if the surface separation is sufficiently small. In order to explore these interesting conformational features we have measured the interaction of a single adsorbed layer against a *bare* mica surface.

The results are presented in Figures 3 and 4. Figure 3(a) shows the interaction of two bare mica sheets in toluene. This is always measured before any polymer adsorption is allowed to occur, in order to check that the surfaces are uncontaminated. As expected, Figure 3(a) shows little interaction down to a separation, D≈150Å, followed by van der Waals like short-range attractions, which eventually cause the mica surfaces to jump into contact. This is in good agreement with the results reported previously for bare mica surfaces in toluene.[4,14] The jump is due to mechanical instability of the leaf spring which supports the lower mica surface.[14]

Figure 3(b) shows the interaction profile of a single adsorbed PS-PEO diblock layer against a *bare* mica surface in toluene. No attraction is observed at any separation of the surfaces, and strong repulsive forces are seen, commencing at D ≈ 900Å. In view of the fact that PEO segments can readily adsorb on the mica surface[14,16] whereas PS does not adsorb on mica from toluene,[4,14] we conclude that the PS-PEO chains have been terminally attached to the lower mica surface via the PEO segments, and that the polystyrene chains form a polymer "brush" which shows a repulsive interaction with the upper bare mica surface as it approaches. The force-distance profile given in the insert of Figure 3 is the same curve as Figure 3(b), but plotted on a log-linear scale over a wide range of separation, which shows clearly ca.4 decades of variation in force.

Figure 4 shows the evolution of the force-distance profiles with repeated compression-decompression cycles for a single adsorbed PEO-PS-PEO layer, formed under the same incubation conditions used for the diblock copolymer, against the *bare* mica surface. These reveal several interesting features:

Firstly, in contrast to the diblock behavior shown in Figure 3(b), all of the force profiles (Figure 4(a) ——— 4(c)) are characterized by a clearly detectable attractive minimum followed by monotonically increasing repulsive forces at smaller separations. It is important to note that the attractive forces seen in Figure 4 commence at large surface separations where van der Waals forces between bare mica surfaces are negligible. Having already established that only repulsive forces could be observed for the adsorbed PS-PEO diblock copolymer chains under the same experimental conditions (Figure 3(b)), we attribute the attractions seen in Figure 4 to polymer bridges formed by the PEO-PS-PEO chains with the two PEO blocks of a single chain simultaneously anchoring onto opposite surfaces.

Secondly, the magnitude of the attractive forces depends strongly on the number of compression-decompression cycles applied. While Figure 4(a) shows only a small attractive minimum, ca.100±20 µN/m, at D = 400±50Å for the first few compression-decompression cycles, Figure 4(b) gives a deeper attractive minimum at a similar surface separation after further compression-decompression cycles. This presumably suggests rearrangements of the PEO-PS-PEO chains in the adsorbed layer. It appears, therefore, that the adsorbed triblock copolymer layer contains not only fairly stretched "tail" chains which readily form polymer bridges, but also a significant number of chains adsorbed in a "loop" conformation which might be opened into a "tail" structure through repeated interactions with the upper bare mica surface. Thus, through compression-decompression operations the bridging attraction is gradually enhanced as
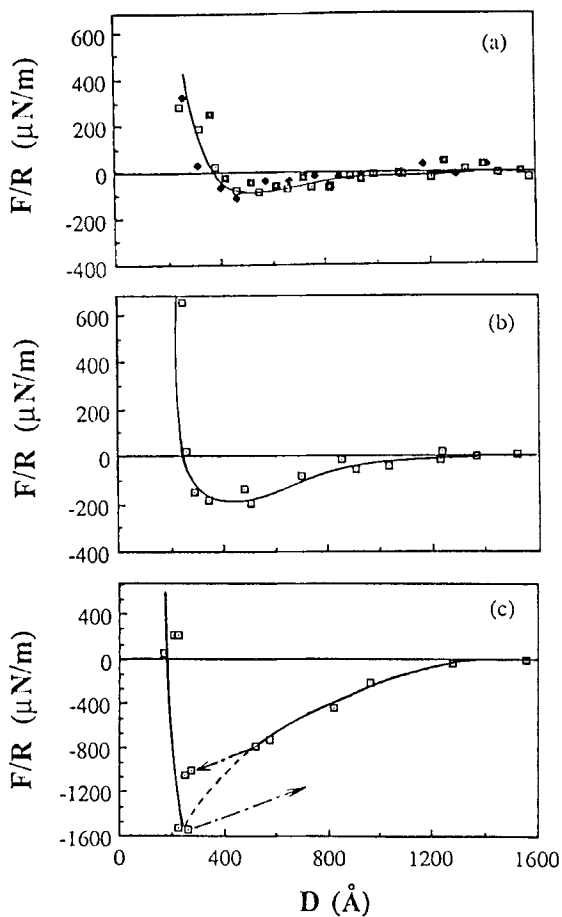
Figure 4 Force-distance profiles for a single PEO-PS-PEO adsorbed layer against a bare mica surface in toluene at different compression-decompression cycles. (a) 1st to 3rd cycles; (b) 6th cycle; (c) 15th cycle, note the scale of the force axis is different from those of (a) and (b), and the dashed line on the curve is experimentally inaccessible and schematic only. The broken arrows indicate inward and outward jumps as discussed in the text.

a result of an increase in the number of "tail" chains available for the formation of polymer bridges between the surfaces. As seen in Figure 4(c), if sufficient numbers of compression-decompression cycles are performed the depth of the attractive minimum may increase by a factor of up to about 15 relative to that seen in Figure 4(a), whilst a jump inward (compression) and a jump outward (decompression) are also observed. The inward jump provides additional evidence for the presence of polymer bridges, since it cannot be related to entanglement effects.[17]

Finally, with further compression-decompression cycles the attractive forces ultimately change into monotonically increasing repulsions due to intersurface migration of the adsorbed polymer chains between the mica surfaces under compression and the eventual attainment of a symmetric surface coverage on both mica sheets over the contact area. These effects are discussed in detail in Reference 10.

In conclusion, diblock and triblock copolymers consisting of large non-adsorbing chains and small "sticky" blocks with a high affinity for a substrate have been shown to adsorb terminally from a good solvent to form semi-dilute polymer brushes. Both surface force measurements and neutron reflectometry yield results consistent with this picture for PS-PEO diblock copolymers adsorbed onto mica or quartz from toluene, and in good agreement with the predictions of theoretical models. In contrast to a PS-PEO diblock copolymer brush whose interaction with a bare mica wall is purely repulsive, attractive bridging forces were clearly detected with PEO-PS-PEO triblock copolymers as the triblock chains were found capable of forming polymer bridges between the two mica substrates. Furthermore, pronounced conformational rearrangements were observed with the adsorbed triblock copolymers on repeated cycles of approach and withdrawal of the surfaces.

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