End-Adsorbed Triblock Copolymer Chains at the Liquid–Solid Interface: Bridging Effects in a Good Solvent

Liming Dai[*,†] **and Chris Toprakcioglu**[*,†,‡]

Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, England, and Institute of Food Research, AFRC, Colney Lane, Norwich NR4 7UA, England

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ABSTRACT: We report direct force measurements on the interactions of end-adsorbed diblock and triblock copolymer layers against a bare mica surface in toluene. Only monotonically repulsive forces are observed when a bare mica sheet interacts with a single layer of polystyrene (PS)–poly(ethylene oxide) (PEO) *diblock* copolymer, end-adsorbed at a toluene/mica interface. In contrast, clearly detectable *attractive* forces are found for PEO–PS–PEO *triblock* copolymers under similar conditions. The attraction is attributed to polymer *bridges* in which the two PEO end blocks of a single triblock chain simultaneously adsorb onto opposing mica surfaces. The experimentally detected evolution of the force profiles from attractive to repulsive with successive compression–decompression cycles reflects the dynamics of conformational rearrangements and the subsequent migration of chains between the surfaces. The results further indicate that the relative populations of chains adsorbed in a loop or tail conformation depend on the adsorption energy of the anchoring blocks, as does the degree of stretching of the bridging chains before rupture upon separation of the mica surfaces.

Introduction

The adsorption of polymers at interfaces is known to play an important role in various technological applications and in biological systems.[1] Examples include adhesion, lubrication, steric stabilization of colloidal dispersions, biological self-organization, and the interactions of cell membranes. Knowledge of the conformation and the intermolecular forces of polymer chains adsorbed at the interface is essential for a detailed understanding of these phenomena at the molecular level. The study of adsorbed polymer chains has attracted considerable attention, and significant advances in both the theoretical and experimental fronts have been achieved in recent years.[2,3] In particular, the surface force apparatus (SFA)[4] has been used to give information both on the intermolecular forces between adsorbed polymer layers and on the conformations of the adsorbed macromolecules at liquid–solid interfaces.[5–13] A comprehensive review article on studies of adsorbed polymer layers by the SFA technique has recently appeared in the literature.[14]

The use of the SFA technique to study interactions between adsorbed layers of homopolymers was pioneered by Klein.[5,15–17] Hadziioannou et al.[8] first reported force measurements using the same technique for adsorbed layers of *diblock* copolymer chains consisting of a nonadsorbing polymer chain chemically linked to an adsorbing block. Using polystyrene–poly(vinylpyridine) (PS–PVP) diblock copolymers with comparable molecular weight for each block, these authors demonstrated that the nonadsorbing PS block is held onto the mica surface in toluene by the strongly adsorbing PVP block and that the PS chains are stretched normal to the adsorbing surface forming a polymer brush at the liquid–solid interface.[8] In order to mimic a layer of end-grafted polymer chains more closely, Taunton et al.[10] investigated highly asymmetric diblock copolymers and demonstrated that polystyrene–poly(ethylene oxide) (PS–PEO) diblock copolymer chains with a *short* PEO block can be terminally anchored on mica through the adsorption of ethylene oxide segments on the mica surface with the polystyrene blocks dangling freely into the solvent (e.g., toluene). At high surface coverage the PS chains were found to be strongly stretched, and the monotonically repulsive interaction profiles of two such polymer "brushes" were in good agreement with theoretical predictions.[10,11] These results indicate that end-adsorbed PS–PEO and similar diblock copolymers might be good candidates as steric stabilizers for dispersed particles.

While end-attached diblock copolymers form polymer brushes in which the chains can only exist in a "tail" conformation, ABA *triblock* copolymer chains (where the A blocks represent short "sticking" segments, while the B block does not adsorb) may form both "loops" and "tails", whose relative fraction depends on the sticking energy of the A blocks. Moreover, *bridging* effects may be expected to occur with ABA chains, when the A blocks of the same triblock chain attach simultaneously onto opposing surfaces. Thus, triblock copolymers are more versatile in their adsorption behavior in comparison with their diblock counterparts, and in applications related to colloidal stability they might be used both as effective stabilizers and as flocculants, depending on the choice of system and experimental conditions. Hence, the adsorption of triblock copolymers and the interactions between such adsorbed layers merit closer attention. In this paper we explore the properties of adsorbed *triblock* copolymer chains at the mica/toluene interface by directly measuring the force, F, as a function of distance, D, between a *single* end-adsorbed poly(ethylene oxide)–polystyrene–poly(ethylene oxide) (PEO–PS–PEO) triblock copolymer layer and a *bare* mica surface in toluene. Preliminary experimental results have been published elsewhere,[18] while theoretical calculations connected to some of the experimental data are currently in progress.

Experimental Section

(a) Materials. The PS–PEO and PEO–PS–PEO copolymers were synthesized by Polymer Laboratories (U.K.). The weight-average molecular weight and molecular weight distribution of the samples were determined by gel permeation chromatography (GPC) measurements, while the PEO content was measured by ^{1}H NMR and checked by infrared spectroscopy and elemental analysis. The molecular characteristics of the copolymer samples are listed in Table I. For the force measurements, spectroscopic-grade toluene from Aldrich was used as solvent without further purification in each case.

† University of Cambridge.
‡ Institute of Food Research, AFRC.

Table I
Molecular Characteristics of the Copolymer Samples Used in This Study[a]

sample	M_W	M_W/M_N	wt % PEO	x_1	y	x_2
PS–PEO (150K)	150×10^3	1.16	1.5	0	1420	51
PEO–PS–PEO (128K)	128×10^3	1.02	0.3	5	1225	5
PEO–PS–PEO (49K)	49×10^3	1.09	7.6	42	435	42

[a] x_1, y, and x_2 refer to the polymerization index of the block copolymer $(PEO)_{x_1}(PS)_y(PEO)_{x_2}$.

(b) Force Measurements. The use of the SFA technique to measure forces between two adsorbed polymer layers has been described in detail elsewhere.[5,10,16,19] For force measurements of a *single* polymer layer against a *bare* mica surface, however, a departure was required from the normal incubation method of simply immersing the two mica sheets simultaneously in the polymer solution. In order to meet this requirement in an effective and reproducible manner, we have recently developed a new technique,[18] which is described in detail below: The force–distance profiles are measured between two thin, molecularly smooth mica sheets, which are silvered on one side and mounted on cylindrically curved glass disks (mean radius of curvature $R \approx 1$ cm). The glass disks are, then, assembled in the SFA in a crossed cylinder configuration, and the shortest distance, D, between the two curved mica surfaces is determined by use of multiple-beam interferometry through the observation of fringes of equal chromatic order (FECO)[20] to an accuracy of about ± 3 Å. The force, F, between the two curved mica surfaces is measured as a function of D by monitoring the deflection of a leaf spring supporting the lower mica surface, with a resolution of ca. 10^{-7} N.

At the commencement of each experiment, the bare mica surfaces are brought into direct contact in air to measure the thickness of the mica sheets and to ensure that a strong, smooth adhesion occurs, which indicates no contamination of the surfaces. Thereafter, toluene is injected, by a syringe through a 0.2-μm Millipore (FG grade) filter, into a stainless-steel bath (volume ca. 25 mL), which contains the mica surfaces. Then, the bare mica surfaces are brought together again in toluene as a check that no contamination arises from the solvent, and the upper surface is subsequently "pulled" away from the solvent by lowering the stainless-steel bath to which the lower mica sheet is attached by means of a leaf spring. It is at this stage that a predetermined amount of the polymer sample is introduced into the pure solvent, and the lower mica surface only is allowed to incubate in the polymer solution. In order to prevent the adsorbed polymer layer from any possible collapse due to drying, a clean glass slip having a width of about 1 cm which can be moved horizontally along the top of the solution bath is placed above the lower mica surface, forming a small gap (ca. 1 mm) between them. When the bath is emptied, this gap holds a droplet of the solvent due to capillary effects.

Following incubation of the lower mica surface in a polymer solution, according to the procedure described above, at a concentration of ca. 2.4×10^{-3} (w/w) for about 20 h, the polymer solution is then replaced by pure solvent, after thoroughly washing the solution bath with pure toluene several times, and the glass slip removed. Finally, the upper mica surface is allowed back into the pure solvent, and the interaction of the adsorbed polymer layer against the bare upper mica surface is investigated.

All force–distance profiles reported in this paper are based on at least two independent measurements (different pairs of mica sheets or different contact positions) made at a temperature of 14 ± 2 °C.

Results and Discussion

Interaction between the PS–PEO (150K) Layer and a Bare Mica Surface. As mentioned above, the interaction between bare mica surfaces in pure solvent is always measured, as a check that the surfaces are uncontaminated, before any polymer adsorption is allowed to occur. Figure 1a shows typical curves of F/R vs D for the bare
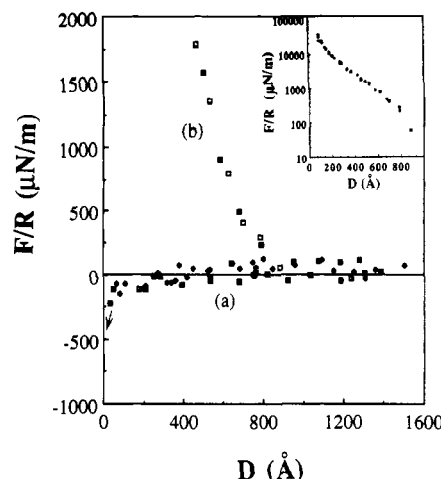

Figure 1. (a) Force–distance profiles between curved mica surfaces in pure toluene. The results are shown for several measurements on two different pairs of mica sheets. The force axis is normalized as F/R (here $R \approx 1$ cm is the mean radius of curvature of the mica) to yield the corresponding interaction energy per unit area, E, between flat plates of the same nature and at the same separation, D, via the Derjaguin approximation (i.e., $F(D)/R = 2\pi E(D)$).[21] The arrow indicates an inward jump due to mechanical instability and is expected whenever $\partial F(D)/\partial D \geq K$ where, K is the spring constant of the leaf spring supporting the lower mica surface.[7] (b) Force–distance profile for a single PS–PEO (150K) adsorbed layer against a bare mica surface in toluene. The solid and open symbols represent compression and decompression, respectively. Inset: The full range of interaction is shown on a log–linear scale for b.

mica surfaces immersed in pure undried toluene, which agrees well with results reported previously.[7,10]

As seen in Figure 1a, there is little interaction down to a separation $D \approx 150$ Å. At somewhat smaller separations van der Waals-like attractions are observed, which cause a jump of the surfaces into contact. The jump is due to mechanical instability and is expected whenever $\partial F(D)/\partial D \geq K$ (here, K is the spring constant of the leaf spring supporting the lower mica surfce).[7]

It is appropriate to mention here that the short-range (typically <60 Å) oscillatory structural forces, characteristic of mica/mica interaction in dried organic solvents (including toluene), reported previously by other investigators[12,22–24] are unobservable in this study. The absence of these oscillatory structural forces in *undried* organic solvents (e.g., toluene) is well documented[5,7,10,22,23] and has been widely attributed to trace amounts of water inevitably present in pure but undried solvents. As reported by various authors,[12,22–24] however, the range of the structural forces in most organic solvents, including toluene, is on the order of a few nanometers only, which is much shorter than the range of the forces arising from adsorbed polymer layers (typically, ca. 15–160 nm, as we shall see in the following sections) investigated in this study. Therefore, such short-range oscillatory forces have negligible influence on the form of the polymer-based force profiles, unless the presence of trace amounts of water in the undried toluene greatly affects the binding energies of the PEO anchoring segments to the mica surface. Our results and those of previous studies,[7,10,15,18,25] however, have clearly shown that PEO adsorbs strongly onto mica from *undried* toluene, whereas PS does not adsorb (it is known that water and certain organic impurities can displace adsorbed polystyrene segments from the mica/solvent interface).[26,27] Nevertheless, in order to minimize any possible effects due to varying amounts of water in different batches of toluene, we have used the same undried toluene for all of the experiments.

Figure 1b (and inset) gives the force–distance profile for a single adsorbed PS–PEO (150K) *diblock* copolymer layer against a *bare* mica surface in toluene, which shows typical monotonically repulsive forces commencing at $D \approx 900$ Å, in agreement with the results reported by Taunton et al.[10] We conclude, therefore, that the PS–PEO diblock copolymer chains have been terminally anchored on the lower mica surface via the sticking PEO segments, whereas the nonadsorbing PS blocks dangle freely into the solvent, leading to a long-range repulsive interaction with the upper bare mica surface as it approaches.

Interaction between the PEO–PS–PEO (128K) Layer and a Bare Mica Surface. The results for a single adsorbed PEO–PS–PEO (128K) *triblock* copolymer layer against a *bare* mica surface in toluene are shown in Figure 2. The salient features are as follows:

First, most of the force profiles (Figure 2a–d) show the same general shape of a clearly detectable attraction minimum followed by monotonically increasing repulsive forces at small separation distances. The attractive forces extend to distances far beyond the range where van der Waals forces between bare mica surfaces are of any significance. Clearly, attractions from the negative free energy of mixing[5] can be ruled out in this study, since toluene is a good solvent for the PEO–PS–PEO chains and the interaction is against a bare mica surface. Furthermore, as noted previously, while PEO segments can readily adsorb on the mica surface,[7,15] PS does not adsorb onto mica from toluene.[7,10] Having already established that only repulsive forces are seen for an end-adsorbed PS–PEO diblock copolymer layer under the same experimental conditions (see Figure 1b), we attribute the attractive forces seen in Figure 2 to polymer "bridges" formed by the PEO–PS–PEO chains between the mica sheets through simultaneous anchoring of the two PEO end blocks of a single triblock copolymer chain onto opposing surfaces.

Second, the depth of the attractive minimum depends on the number of the compression–decompression cycles applied. As seen in Figure 2, the force profiles recorded during the first few compression–decompression cycles (Figure 2a) show a small attraction minimum, $F/R = -100 \pm 20$ μN/m, at a separation $D = 400 \pm 50$ Å (where repulsions from osmotic and excluded-volume interactions counterbalance the "bridging" attraction) and no detectable difference is observed on the force profiles whether the surfaces are approaching (compression) or are being separated (decompression), whereas Figure 2b gives a deeper attractive minimum. Further compression–decompression cycles cause the depth of the attractive minimum systematically to increase by a factor of up to about 15 relative to that seen in Figure 2a, but its position remains essentially unchanged to within the experimental error (Figure 2c). This is evidence that the conformation of polymer chains in the adsorbed layer has undergone rearrangement under compression. We propose that the adsorbed PEO–PS–PEO layer initially contains *both* fairly stretched tail chains which readily form polymer bridges, as well as loops or "dangling" chains (i.e., chains with their free end in the inner region rather than the extremity of the polymer brush),[18,28,29] which might be gradually opened into a tail conformation through repeated attractive interactions with the upper bare mica surface. In fact, the spatial distribution of free chain ends in a polymer brush is known to be rather broad.[30,31] Thus, compression may be expected to enhance bridging, because as the upper bare surface moves into the brush region it "captures" dangling chains through their PEO end blocks. It is
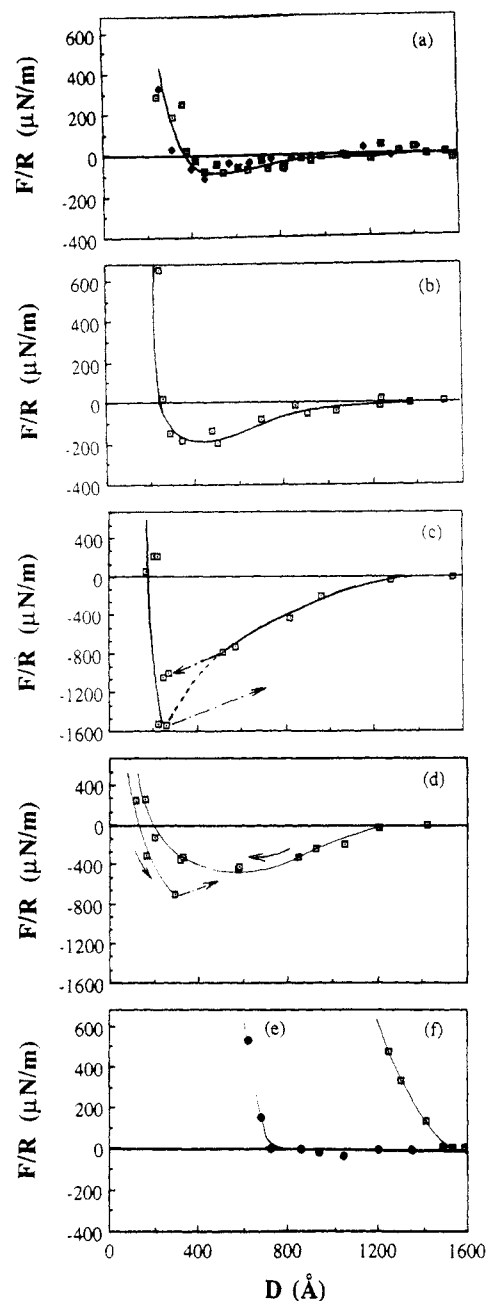

Figure 2. Force–distance profiles between a single PEO–PS–PEO (128K) adsorbed layer and a bare mica surface in toluene at different compression–decompression cycles: (a) 1st to 3rd cycles; (b) 6th cycle; (c) 15th cycle; (d) 20th cycle, note the hysteresis between the compression and decompression profiles (indicated by small arrows along each curve); (e) 33rd cycle; (f) 48th cycle. The solid curves are meant to guide the eye. The dashed line on curve c is experimentally inaccessible and schematic only. The broken arrows indicate inward and outward jumps as described in the text. Approximately 32 h have elapsed between the measurement of the first and last force–distance profiles. Most force profiles corresponding to intermediate numbers of the compression–decompression cycles have been omitted for reasons of clarity. Note the difference in force scales between (c, d) and (a, b, e, f).

important to point out that strong compression may enhance bridging even further, due to desorption of one of the chain ends belonging to a "loop" during compression (typically, the compression-enhanced osmotic repulsion amounts to energies of ca. 50–$100kT$ per chain) and its subsequent readsorption on the opposite surface. Enhanced bridging also increases the onset distance for attraction as seen in Figure 2a–c. On withdrawal, these additional bridges which formed during compression

should lead to a stronger attraction. The hysteresis seen in Figure 2d where the decompression curve shows a deeper attractive minimum may to some extent be attributable to this effect. The jump inward (compression) and the jump outward (decompression) shown in Figure 2c are another distinguishing feature of the force–distance profile. The inward jump further supports the presence of polymer bridges, since unlike its outward counterpart it cannot be related to entanglement effects.[6] These jumps are expected to occur whenever the magnitude of the gradient of the $F(D)$ curve exceeds the spring stiffness constant and follow the line of the local gradient of the $F(D)$ curve.[6] Thus, while the inward jump extends only over a small distance from ca. 550–250 Å, the outward jump comes to rest at about 2000 Å (Figure 2c).

We note that over the time scale of successive compression–decompression cycles (several hours) most of the triblock chains, which were opened into a tail conformation during compression, do not appear to return to a loop conformation when the surfaces are separated. This is evidenced by the gradual increase in the attractive force from parts a to c of Figure 2, indicating that the tail population increases with the number of compression–decompression cycles. This apparent reluctance of the perturbed triblock brush to return to its original equilibrium conformation may be attributed to kinetic factors. The dynamics of the conformational changes involved in the transformation from a tail to a loop for the PEO–PS–PEO (128K) chains are likely to be very slow compared to our experimental time scale.

When the compression–decompression cycles are repeated further, the attractive minimum continuously shifts outward and becomes less strong (for instance, it is found at $D_{min} = 600 \pm 50$ Å and $(F/R)_{min} = -430 \pm 20$ μN/m in Figure 2d). These changes can be rationalized by considering what might happen to a bridging chain during decompression. As the surfaces are pulled apart, the bridging chain becomes overstretched, and a stage is eventually reached when the adhesive force between the PEO blocks and the mica surfaces can no longer sustain the tension along the chain. Thus, the bridge is "broken" at one of its anchor points (the sticking energy, being on the order of a few kT only,[10] is much weaker than the chemical bonds linking the monomer units in the polymer chain, so "chemical breakage" is unlikely). This implies that some of the bridging chains will be pulled away from the lower mica surface and remain on the (initially) bare upper surface in predominantly a loop conformation as the local polymer concentration on the upper surface is to begin with rather low. Each compression–decompression cycle, therefore, results in more chains being transferred to the upper mica surface. As a consequence, on the one hand, the bridging attraction is weakened by the reduction in available free surface on which the PEO blocks from the lower surface can adsorb, and, on the other hand, the position of the attractive minimum is found to move outward due to an increase in the interaction range of repulsion. The hysteresis and the outward jump only seen in Figure 2d reflect, at least in part, additional attractive forces arising, upon separation, from entanglements between the adsorbed chains of the lower mica sheet and the newly formed loop chains on the upper surface.

Finally, if sufficient numbers of compression–decompression cycles are performed, the attractive forces ultimately change into monotonically increasing repulsions which commence at progressively larger onset distances until a limiting value of ca. 1400 $\pm$ 50 Å is approached (Figure 2e,f). This presumably indicates that, at this stage,
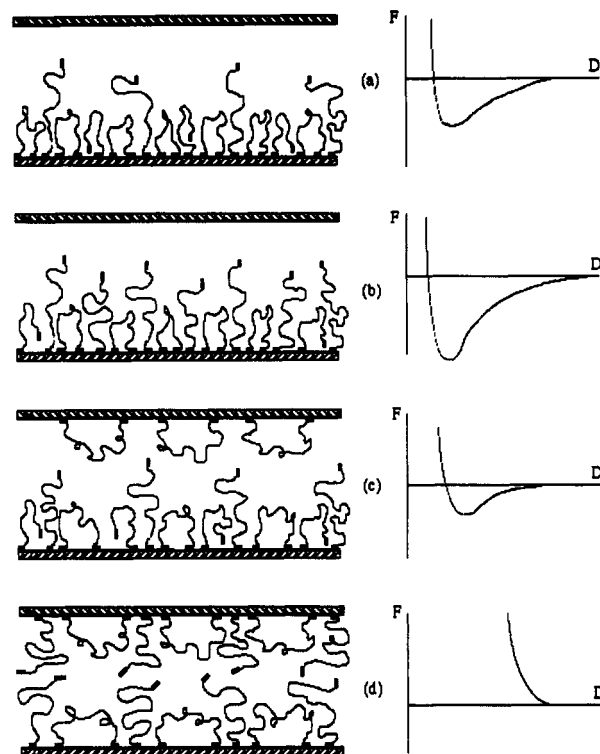

Figure 3. Schematic representation of the molecular organization of the PEO–PS–PEO (128K) triblock copolymers at the mica surfaces *before* each successive compression (left) and the corresponding force–distance profile (right) upon compression. (a) Before the 1st compression, the upper surface is bare, while the lower surface carries an adsorbed layer in which loops and tails coexist in equilibrium, their relative populations being a function of the sticking energy (see text). On initial compression, the tails readily form polymer bridges with the upper surface, and this leads to an attraction in the force–distance profile. (b) As additional bridging occurs on compression due to the opening of dangling chains and/or loops into tail structures, the population of tails is increased after separation of the surfaces. Thus, on subsequent compression the attractive force increases due to the availability of a larger fraction of tails which readily form bridges. (c) On separation of the surfaces following compression, some of the bridging chains remain on the *upper*, initially bare, mica surface. Thus, on further compression the presence of these chains on the upper surface tends to limit the extent of bridging, and the magnitude of the attractive forces is reduced. (d) As more chains are transferred to the upper surface with each successive compression, the coverage of the two surfaces eventually becomes equal, the formation of bridges on the experimental time scale of a compression–decompression cycle is severely curtailed, and the attractive forces disappear altogether. Note that the situations represented by diagrams b and c may be nonequilibrium because in each case the time scale of the force measurement and the time allowed between successive compression–decompression cycles are very short in comparison with the relaxation time required for the attainment of equilibrium.

a symmetric surface coverage has been achieved on both mica sheets under the contact area.

In light of the above results we propose some schematic ideas in Figure 3 for the rearrangement of the end-adsorbed PEO–PS–PEO chains between the mica surfaces over compression–decompression cycles.

While conformational rearrangements within the single adsorbed layer schematically shown in Figure 3a,b are clearly evidenced by the corresponding changes on the force–distance profiles seen in Figure 2a–c, the intersurface migration of the adsorbed chains represented by Figure 3c,d is most vividly suggested by the evolution of force–distance profiles given in Figure 4, which shows force–distance profiles over a much wider force range than that seen in Figure 2, where the main emphasis was on
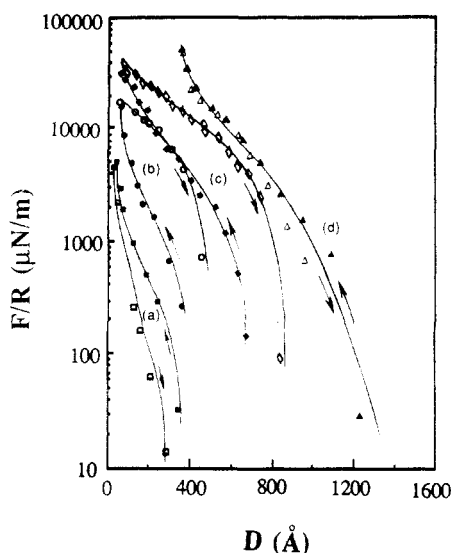
Figure 4. Force–distance profiles between a single PEO–PS–PEO (128K) adsorbed layer and a bare mica surface in toluene at different compression–decompression cycles on a log–linear scale: (a) 26th cycle; (b) 32nd cycle; (c) 33rd cycle; (d) 34th cycle and thereafter. The solid and open symbols represent compression and decompression, respectively. The solid lines are best-fit by eye.

attractive forces only. As seen in Figure 4a, the decompression curve gives a weaker repulsion than the corresponding compression, presumably indicating additional attractive forces arising, upon separation, from entanglements and/or the compression-enhanced bridging effect, as demonstrated already by Figure 2d. Parts b and c of Figure 4, however, reveal another interesting feature: the decompression curve moves outward, as compared with the corresponding compression data (or at a constant separation distance the force increases), to the extent that it overlaps partially with the subsequent compression profile. Such unusual behavior persists until a symmetric surface coverage is achieved on both mica sheets under the contact area, as indicated by the same force law for both compression and decompression seen in Figure 4d. The remarkably quick expansion of the decompression profiles to larger separations seen in Figure 4b,c unambiguously suggests a significant migration of the adsorbed polymer chains between the mica surfaces even within a few of the compression–decompression cycles. At first sight, the compression–decompression cycles of Figure 4b,c seem to indicate an apparent thermodynamic impossibility since the system appears to give back more work with decompression than the work performed upon it during compression (the work in question is, of course, represented by the area under each force–distance curve). Note, however, that in such a cycle the initial and final states are not one and the same, since at the end of the cycle polymer chains have been transferred to the upper surface. The extra work done by the system is associated with the energy released as a result of the redistribution of adsorbed chains between the two surfaces. A trivial explanation of the results of Figure 4 related to additional adsorption of polymer chains from the liquid medium can be ruled out, because *not only* the abnormal hysteresis seen in Figure 4b,c is observable even in an experiment where the surface separation was always kept at less than 20 μm to limit the diffusion process *but also* the attractive forces seen in Figure 2 can be reestablished by changing the contact position even after such monotonically repulsive forces as shown in Figure 2e,f have been observed at a certain (different) contact. We note, however, that the rate of the intersurface migration depends also on how

close the surfaces were brought together at the end of each compression and on how long they have been kept at the smallest separation each time. Consequently, the evolution of the force–distance profiles with successive compression–decompression cycles is subject to some variability, although the general patterns shown in Figures 2 and 4 are reproducible.

Interaction between the PEO–PS–PEO (49K) Layer and a Bare Mica Surface. A recent computer simulation[28] shows that competition between ABA triblock chains for free surface, on which A may adsorb, leads to different average conformations depending on the surface concentration. Thus, under conditions where adsorption depends on the availability of free surface, loops are expected at low surface coverage, while tails are predominant at high surface concentrations. Under the conditions of our experiments, however, it is more appropriate to consider an "equilibrium" picture for an unperturbed PEO–PS–PEO adsorbed layer, where surface coverage is determined primarily by a balance between the sticking energy of the PEO blocks of a given triblock chain and the osmotic repulsion experienced by the nonadsorbing PS block due to being end-attached to the mica surface (and hence surrounded by other terminally adsorbed chains). Under these conditions, one may expect, to a good approximation, a picture dominated by loops. Note, however, that tails can be neglected only in the limit of strong sticking (i.e., a high interaction energy between the PEO moiety and the surface).[32,33] Thus, two triblock copolymers of ABA and A'BA' with the same nonadsorbing block B but different sticking blocks A and A' may be expected to form different brushes in which the fraction of loops and tails differs depending on the discrepency in the affinity of A and A' for the surface.

An ABA type triblock copolymer system in which the adsorption energy of the A block is high has been studied by Patel et al.[34] These authors measured the interaction of two adsorbed layers of PVP–PS–PVP triblock copolymer in toluene using the surface force technique and found strongly repulsive forces. In this system, the chains are expected to form predominantly loops due to the high affinity for mica and low solvency in toluene of the PVP blocks.

In view of the above considerations, force measurements were made on a single adsorbed PEO–PS–PEO (49K) layer against a bare mica surface to try to demonstrate the effect of the sticking energy of the PEO end blocks. We chose a PEO–PS–PEO triblock copolymer with a much higher ethylene oxide content than the PEO–PS–PEO (128K) copolymer (see Table I) to ensure a stronger adsorption of the PEO block onto mica.[35] Typical results are shown in Figure 5. The significant feature to note is that, in contrast to Figure 2a–d, Figure 5 exhibits neither attractive forces nor inward jumps on *compression*, but otherwise the general patterns of Figure 2 are observable. The absence of any detectable attractive force during the compression clearly suggests that the number of tail chains in an unperturbed adsorbed PEO–PS–PEO (49K) layer is very small, which, in turn, is consistent with the expectation of the higher sticking energy for the larger PEO end blocks in this copolymer leading to the predominance of loops. Obviously, therefore, the attractive forces and outward jumps, on *decompression*, seen in Figure 5a, arise, most probably, from polymer bridges and possible entanglements resulting from chain rearrangements between the surfaces under compression. The absence of attractive forces for those compressions which are carried out even immediately after decompressions
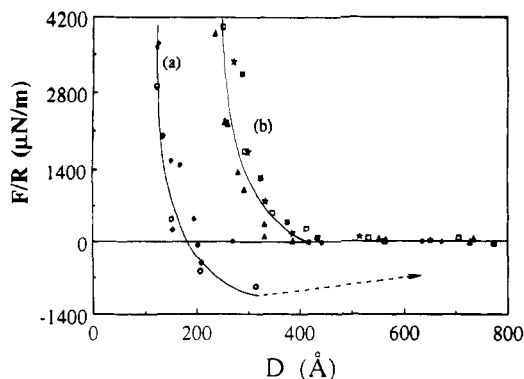
Figure 5. Force–distance profiles between a single PEO–PS–PEO (49K) adsorbed layer and a bare mica surface in toluene at different compression–decompression cycles: (a) 2nd and 3rd cycles; (b) 68th cycle and thereafter. The broken arrow indicates an outward jump as described in the text. Most force profiles corresponding to intermediate numbers of the compression-decompression cycles have been omitted to enable a clear presentation. The solid and open symbols represent compression and decompression, respectively. The solid curves are best-fit by eye.

suggests that most of the adsorbed chains remain in, or rapidly return to, a loop conformation after the intersurface chain rearrangements. This behavior is in contrast to that observed for the PEO–PS–PEO (128K) triblock copolymer where successive compression–decompression cycles were found to increase the number of chains remaining in a tail conformation, presumably because of the very slow rate of rearrangement of such tails to their original loop conformation upon separation of the surfaces. The predominance of loops and the rapid transformation of bridging tails into loops, after withdrawal of the surfaces, in the PEO–PS–PEO (49K) triblock copolymer (which has a much larger PEO block than its 128K counterpart) layer may thus be attributed to its higher adsorption energy. The number of polymer bridges and entanglements thus formed (hence, the outward jump) depends, of course, on the extent of compression—i.e., how close the surfaces were brought together at the end of each compression and for how long they have been kept at the smallest separation each time (normally a compression-decompression cycle takes about 20 min to complete).

Finally, as noted previously for the PEO–PS–PEO (128K) system, repeated compression–decompression cycles can also ultimately bring the force–distance profile of the adsorbed PEO–PS–PEO (49K) layer to a limiting behavior, characterized by a monotonically repulsive interaction commencing at ca. 400 Å with no hysteresis (Figure 5b), indicating the attainment of a symmetric surface coverage on both mica surfaces under the contact area, although the rate of the intersurface migration of the adsorbed PEO–PS–PEO (49K) chains, during the time scale of our compression–decompression cycles, is seen to be much smaller than that for the adsorbed PEO–PS–PEO (128K) chains. The slow rate of intersurface migration for the PEO–PS–PEO (49K) system may again be attributed to its higher adsorption energy, while the limiting onset distance (ca. 400 Å) observed after many compression–decompression cycles is consistent with the attainment of a loop conformation on both adsorbing surfaces.

Recently, the effect of bridging due to end-attached chains has been investigated theoretically by Johner and Joanny,[29] who used self-consistent mean-field theory and generalized their results to take into account the excluded-volume correlations in a good solvent. These authors considered the case of nonadsorbing chains which are

irreversibly end-grafted to one surface, while their free ends are allowed to adsorb on an opposing surface. The free ends are not, however, allowed to adsorb on the same surface on which the chains are grafted, so that loops are not permitted in this model. Nevertheless, the model may be sufficiently close to our experimental conditions on the first few approaches of the surfaces (i.e., before any significant transfer of chains to the bare mica surface has occurred) and at large to intermediate separation distances. This is because at such separations it is only chains in a tail conformation that contribute to the interaction over the time scale of our measurements. Before any attempt is made to quantitatively compare our experimental data with the theoretical results, however, one must recognize that most of the force–distance profiles measured in our study may correspond to a system which is not strictly at equilibrium, as the experimental time scale is—for practical reasons—much shorter than the relaxation times required for the system to reach equilibrium at any given separation distance between the surfaces. This situation is in contrast to that of end-adsorbed *diblock* copolymers where such equilibration appears to be very rapid,[10] and the difference is clearly due to the possibility of formation of loops and bridges in the *triblock* system. Conformational transformations between these structures in the adsorbed triblock copolymer layer greatly slow down the attainment of equilibrium.

Despite all the discrepancies mentioned above between the experimental conditions and the theoretical model system, Johner and Joanny's calculations[29] may to some extent serve as a useful approximation for describing the behavior of the PEO–PS–PEO end-adsorbed layers. For instance, in agreement with our experimental findings, the model calculations show that compressional forces enhance bridging, while pulling forces reduce the fraction of bridges and eventually lead to rupture. Furthermore, the force–distance profiles predicted by the theory for the crossed cylinder configuration show an attractive minimum whose magnitude is in the same range as that found in our experiments (see Figure 2).

Preliminary force measurements on a *single* adsorbed PVP–PS–PVP (30K–180K–30K)[36] triblock copolymer layer, a polymer which has an even stronger affinity for the toluene/mica interface than the PEO–PS–PEO (49K) due to the nonsolubility of PVP in toluene and its much higher molecular weight, show similar behavior as in Figure 5, but the adsorbed polymer chains are found, as expected, to be significantly stretched beyond their unperturbed layer thickness before any outward jump occurs. The stretching of the adsorbed polymer brush is currently a subject of considerable theoretical interest.[37-39] Our experimental results on interactions between a single adsorbed PVP–PS–PVP layer and a bare mica surface will be reported in detail elsewhere.[40]

Conclusions

We have demonstrated experimentally, through direct force measurements, that PEO–PS–PEO triblock copolymer chains with short PEO sticking blocks form a mixed population of loops and tails at the mica/toluene interface by adsorbing to the mica surface via one or both PEO blocks of a single polymer chain. Similar triblock chains which contain longer PEO sticking blocks are almost totally bound in a loop conformation at the mica/toluene interface. These observations are in good agreement with theoretical predictions. Furthermore, we have shown experimentally for the first time that the formation of polymer bridges is possible by ABA triblock copolymer chains in a good

solvent with both of the A sticking blocks in a single polymer chain simultaneously anchoring on opposing surfaces. Upon separation of the surfaces the bridging chains become overstretched and eventually break free at one of their anchor points. This results in the redistribution of chains betwen the two surfaces. The degree of stretching before breakup depends on the interaction energy between the A moiety and the surface. For a sufficiently high interaction energy between the A blocks and the surfaces, the adsorbed polymer chains can be stretched considerably beyond their equilibrium dimensions in the layer.

These results have potential implications for the use of triblock copolymers either as steric stabilizers (while in a loop conformation) or as flocculants (while in a bridging tail conformation) for dispersed particles and could also serve as a basis for elucidating interactions between various other polymer-coated surfaces.

References and Notes

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