Conformational Transitions of End-Adsorbed Copolymer Chains at the Liquid/Solid Interface

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ABSTRACT: Using the surface force apparatus, the conformational rearrangements of end-adsorbed diblock and triblock copolymer chains at the liquid/solid interface have been investigated. While the end-adsorbed poly(ethylene oxide)–polystyrene, PEO–PS, diblock copolymer "brushes" at a toluene/mica interface were seen to collapse upon the replacement of toluene by cyclohexane, rapid conformational transitions between "loops" and "tails" were observed for the end-adsorbed poly(2-vinylpridine)–polystyrene–poly(2-vinylpridine), PVP–PS–PVP, triblock copolymer chains at the toluene/mica interface during compression–decompression cycles. It was demonstrated for the first time that the newly formed tail-like triblock copolymer chains could be mechanically stretched beyond their equilibrium dimensions, a process which to some extent can be described by Rabin and Alexander's scaling model. The dynamics of the conformational rearrangements was followed by surface force measurements at the molecular level.

Introduction

Conformational transitions of individual macromolecular chains play an important role in many technological applications and biological systems. While conformational transitions are known to be responsible for thermochromic, solvatochromic, and piezochromic properties of certain conjugated polymers,[1–3] they are also shown to have a great influence on the stability of colloidal dispersions[4,5] and on the life processes such as the permeability of a cell membrane, metabolism, and the transmission of information.[6–8] Therefore, the investigation of macromolecular conformation and its conformational transition in solution and at the liquid/solid interface is the subject of considerable interest to both experimentalists and theoreticians.[9–17] Generally speaking, the conformation of polymer chains adsorbed at the liquid/solid interface differs from that in bulk solution.[10,18] This is particularly true in the case of end-functionalized homopolymer or diblock copolymer chains being preferentially adsorbed by their end group or end block from a good solvent, where random coils of the macromolecules in solution may become highly stretched polymer "brushes" of the nonadsorbing chains at the liquid/solid interface.[18–20] While end-adsorbed homopolymer and diblock copolymer form polymer brushes in which the chains can only exist in a "tail" conformation, end-adsorbed triblock copolymer, ABA (the A blocks represent short "sticking" segments, whereas the B block does not adsorb), has an additional degree of freedom at the liquid/solid interface, as it can form either a "loop" or a "tail" depending on the sticking energy of the A block and the surface coverage.[21,22] In the case where the ABA triblock copolymer chains exist as a tail structure, bridging effects may also be expected to occur when the A blocks of the same triblock chain attach simultaneously onto opposing surfaces.[22]

The importance of adsorbed polymer chains in mixed solvents to systems of practical interest such as liquid chromatography[12,23] has also stimulated many experimental and theoretical investigations on the effect of the solvent quality on conformations of adsorbed polymer chains.[12,14,15,23–26] However, experimental results are sometimes controversial. For instance, Marra and Hair[14] have recently measured the force–distance profiles as a function of the solvent quality for the interaction between *two* adsorbed polystyrene homopolymer layers in toluene–heptane mixtures at different mixing ratios of the solvents. One of the main features of their results is that the separation distance, at which the attractive interactions commence, decreases with decreasing solvent quality (i.e., increasing the volume fraction of heptane—worse solvent—in the mixture), whereas the adhesion force increases. This indicates that the extent to which the adsorbed polymer layers are collapsing increases as the solvency of the solvent mixture decreases. Meanwhile, a similar investigation has been carried out by Johnson et al.[15] for polystyrene homopolymer in cyclopentane and *n*-pentane with the latter being the worse solvent. In contrast to Marra and Hair's results, these authors found that both the adhesion force and the range of the force increase systematically with an increasing proportion of *n*-pentane in the solvent mixture. As has been suggested by Johnson et al.[15] the increase in the range of the forces with decreasing solvent quality is most probably due to additional adsorption of the polymer from the poor solvent, as most of their force measurements were carried out in a medium containing polystyrene in solution. More recently, Auroy et al.[12,24] have investigated, using the small-angle neutron-scattering technique, the collapse–stretching transition of terminally anchored polymer brushes in mixtures of a good and a poor solvent. In qualitative agreement with theoretical calculations,[23,25,26] these authors found a strongly nonlinear dependence of the layer thickness on the solvent composition. On this basis, they proposed to use the terminally anchored polymer chains for development of new filtration processes.[12,23] However, the dynamic and/or kinetic characteristics of the collapse–stretching transition have not been discussed, although they certainly have an important impact on the performance

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Table 1. Molecular Characteristics of the Copolymer Samples Used in This Study[a]

sample	$10^{-3}M_W$	M_W/M_N	wt % PS	$x1$	y	$x2$
PS–PEO (150K)	150	1.16	98.5	0	1420	51
PEO–PS–PEO (128K)	128	1.02	99.7	5	1225	5
PVP–PS–PVP (240K)	240	1.22	75	286	1730	286

[a] $x1$, y, and $x2$ refer to the polymerization index of the block copolymer: $(PEO)_{x1}(PS)_y(PEO)_{x2}$ or $(PVP)_{x1}(PS)_y(PVP)_{x2}$.

of the end-adsorbed polymer chains for the practical applications. In order to further clarify the above-mentioned controversy and to demonstrate some of the dynamic/kinetic aspects for the collapse–stretching transition, we have carried out surface force measurements on the end-adsorbed PEO–PS diblock copolymer chains in a good as well as a poor solvent.

Although most of the early studies focus on adsorbed homopolymer or diblock copolymer layers, the bridging effects and the adsorption behavior of the PEO–PS–PEO triblock copolymer chains have been reported in detail in our previous publications.[22,27] In this paper, we present results from direct force measurements on the end-adsorbed PEO–PS–PEO and PVP–PS–PVP *triblock* copolymer chains, together with those from the PEO–PS diblock copolymer, to demonstrate conformational transitions of the end-adsorbed copolymer chains in response to various external stimulations. As we shall see later, a solvent-induced, reversible, collapse–stretching transition was clearly seen for the end-adsorbed diblock copolymer chains upon changing the solvent quality, while a rapid conformational transition between loops and tails was observed for the end-adsorbed triblock copolymer chains during consecutive compression–decompression cycles, and the newly formed tail-like chains were experimentally seen for the first time to be *mechanically* stretched far beyond their equilibrium dimensions.

Experimental Section

(a) Materials. The PEO–PS and PEO–PS–PEO copolymer samples were purchased from Polymer Laboratories (U.K.), while the PVP–PS–PVP copolymer was anionically synthesized. The method used for anionic copolymerization of styrene and 2-vinylpridine has been previously described,[28] and details of the molecular characteristics of the diblock and triblock copolymers, supplied by the manufacturer and/or determined by GPC and NMR measurements, are listed in Table 1. Spectroscopic grade toluene and cyclohexane (Aldrich) were used as the solvents without further purification.

(b) Force Measurements. The force–distance profiles, $F(D)$, between two adsorbed polymer layers, and those of a single adsorbed polymer layer against a bare mica surface were measured by the surface force apparatus (SFA) at room temperature (ca. 20 °C) according to the published procedures.[21,22]

For force measurements on two adsorbed polymer layers, the adsorbed layers were constructured by the conventional incubation method of simply immersing the two mica sheets simultaneously in a polymer solution contained in a stainless-steel bath (ca. 25 mL in volume) within the SFA at a predetermined concentration, C, for about 16 h at ambient temperature. To measure the interaction of a single adsorbed polymer layer against a bare mica surface, however, the conventional incubation method was not applicable, and the technique described in our previous publications[21,22] was adopted, which allows the formation of a single clean adsorbed polymer layer on the lower mica surface only while both of the mica sheets remain in the SFA throughout the experiment. In the cases where a change of solvent was required, the polymer solution or solvent to be changed was replaced by a pure solvent of choice *after* having thoroughly washed the solution bath with the pure solvent for several times.

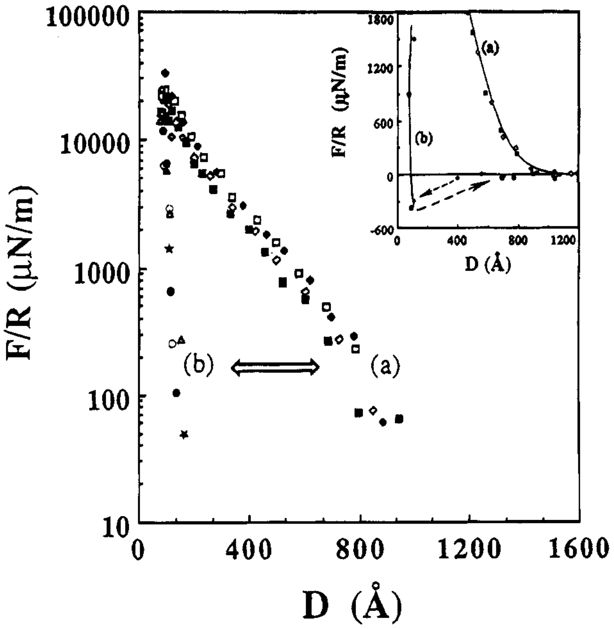

Figure 1. Force–distance profiles for an end-adsorbed PEO–PS (150K) diblock copolymer *single* layer against a bare mica surface during the first few compression–decompression cycles: (a) in toluene before (diamonds) and after (squares) having been immersed in cyclohexane; (b) in cyclohexane. The solid and open symbols represent compression and decompression, respectively, and the open double-arrow indicates that the transition between (a) and (b) is practically reversible. The inset shows the corresponding force–distance curves as (a) and (b), respectively, on a linear–linear scale. The broken arrows in the inset indicate inward and outward jumps, as described in the text. The solid lines are meant to guide the eye. The force axis is normalized as F/R, with $R = 1$ cm being the mean radius of curvature of the mica, to yield the corresponding interaction energy per unit area between two flat parallel surfaces of the same nature and at the same separation distance, D, via the Derjaguin approximation.[31] The copolymer was adsorbed from a toluene solution of bulk concentration $C = 2.4 \times 10^{-3}$ w/w (i.e., the weight ratio of polymer to solvent).

Results and Discussion

I. Diblock Copolymer Chains at the Liquid/Solid Interface. Collapse–Stretching Transition of the End-Adsorbed PEO–PS (150K) Chains. In order to avoid the preferential solvation (i.e., preferentially uptaking the good solvent) of an adsorbed polymer layer in mixtures of a good and a poor solvent[12,24] and any possible changes of the surface coverage with the compositional change of mixed solvents,[14,15] we have used the SFA technique to investigate interactions of a *single* layer of end-adsorbed PEO–PS diblock copolymer chains against a bare mica surface in *pure* toluene (good solvent) and *pure* cyclohexane (poor solvent with the Θ temperature being 34 °C),[29] respectively, at ambient temperature according to the procedures reported elsewhere.[21,22] In such a system, the adsorbed amount of the copolymer is held constant, through the strong sticking interaction between the PEO anchoring block and the mica surface, even in the case where the polymer solution, in which the polymer-bearing mica sheet was originally immersed, was replaced by pure toluene and subsequently replaced by the worse solvent cyclohexane, as to be demonstrated below.

Figure 1a shows the force–distance profiles on a log–linear scale for a single adsorbed PEO–PS (150K) diblock copolymer layer against a bare mica surface in toluene. No attraction is observed and strongly repulsive forces are seen, from which an effective layer thickness of ca. 1000 Å was deduced by estimating the onset distance for the repulsive forces.[19] This is in good agreement with similar results reported previously[19,22] and indicates that the PEO–PS (150K) chains are terminally attached to the mica surface via the short PEO segments with the polystyrene chains extending into the solution to form a polymer brush, as it is known that PEO segments adsorb strongly onto mica from *undried* toluene, whereas PS does not adsorb.[10,19–22,30] Figure 1b gives the force distance curve that was measured on the same end-adsorbed polystyrene layer after the toluene was thoroughly replaced by pure cyclohexane. In comparison with Figure 1a, Figure 1b shows a steeper repulsive wall commencing at a much shorter separation distance, which unambiguously suggests that the end-adsorbed polystyrene brush has collapsed in the poor solvent to form a more compact polymer layer at the cyclohexane/mica interface. Any possible desorption or additional adsorption in this study can be ruled out, since upon further replacing the cyclohexane with pure toluene the range of repulsive interactions seen in Figure 1a can be fully recovered. The complete overlap of the force–distance profiles for the end-adsorbed polystyrene layer in toluene before and after having been immersed in cyclohexane indicates not only that no additional adsorption or desorption occurs within the experimental time scale but also that the intersurface migration of the end-adsorbed chains is practically negligible during the first few compression–decompression cycles in cyclohexane (*vide infra*). Furthermore, it is important to note that transitions between Figure 1a and Figure 1b are practically complete within minutes after changing the solvents in each case. This indicates that the collapsing and stretching (structurally) of the end-adsorbed polystyrene brush with changing solvent quality are characterized by fast dynamics presumably due to the relative ease with which the end-adsorbed diblock copolymer chains can adjust their conformation in response to sudden changes of the solvent.[19,22] Whereas on the one hand the rapid response of the end-adsorbed polymer layer to changes of the solvent precludes the possibility of a detailed kinetic study on the conformational rearrangement by the SFA, on the other hand it indicates that the measured forces are most probably associated with equilibrium states at a fixed amount of adsorbed polymer.[14] Thus, the reversible collapse–stretching transition with fast kinetics found in this study ensures, at least in principle, the use of end-adsorbed polymer chains for such applications as proposed by Auroy et al. (*vide supra*).

The inset of Figure 1 shows the corresponding force–distance curves plotted on a linear–linear scale to highlight the region of weak interactions. The salient feature seen in the inset is the appearance of clearly detectable attractive forces for interactions between the end-attached polystyrene brush and a bare mica surface in *cyclohexane* (curve b). This is in contrast to the corresponding results obtained in toluene (inset, curve a), which shows no attractive forces at any separation distance. As seen from curve b in the inset of Figure 1, the separation distance at which attractive forces are first clearly detectable upon compression (ca. 400 Å) is far beyond the range of the van der Waals forces between bare mica surfaces (typically, <100 Å)[22] but is much smaller than the effective layer thickness deduced from Figure 1a. We attribute the attractions shown in curve b in the inset of Figure 1 to polymer "bridges" formed by the *collapsed* PEO–PS chains, since polystyrene is known to readily adsorb onto mica from *cyclohexane*.[32] Curve b in the inset of Figure 1 is also characterized by an inward jump (compression) and an outward jump (decompression). These jumps are known to occur whenever the magnitude of the gradient of the *F(D)* curve exceeds the spring stiffness constant of the force-measuring spring which supports the polymer-bearing mica surface.[22,29] The inward jump provides additional evidence for the presence of polymer bridges, for unlike its outward counterpart it cannot be related to entanglement effects. The absence of any detectable hysteresis in curves b of Figure 1 indicates that during the first few compression–decompression cycles in cyclohexane most of the bridging chains are "broken" at their attachment points on the upper, initially bare, mica surface, which, in turn, is consistent with the high affinity of the PEO end blocks for the mica surface.[22] Numerous compression–decompression cycles in cyclohexane, however, may lead to redistribution of the adsorbed chains between the two surfaces.[22] Nevertheless, successive compression–decompression measurements in cyclohexane are not our intention to carry out this study, which, as mentioned already, aims at exploring conformational transitions between different states.

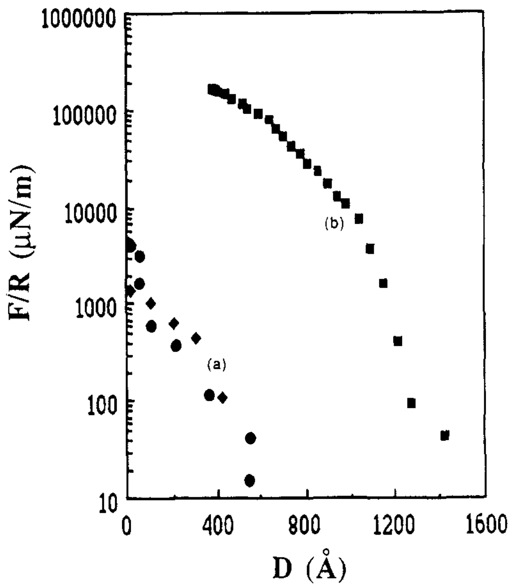

Figure 2. Force–distance profiles for the interaction of *two* end-adsorbed PEO–PS–PEO (128K) triblock copolymer layers. The copolymer was adsorbed from toluene solutions of different bulk concentrations: (a) $C = 1.5 \times 10^{-4}$ w/w; (b) $C = 2.4 \times 10^{-3}$ w/w. The force profiles corresponding to intermediate incubation concentrations have been omitted for reasons of clarity.

II. Triblock Copolymer Chains at the Liquid/Solid Interface. (a) Conformations of the End-Adsorbed PEO–PS–PEO (128K) Chains: The concentration dependence of the force–distance profiles for the interaction between *two* PEO–PS–PEO (128K) adsorbed layers shown in Figure 2 provides structural information for the end-adsorbed triblock copolymers at the toluene/mica interface. The remarkable increase in the effective layer thickness from Figure 2a to Figure 2b indicates a significant change in structure for the end-adsorbed triblock copolymer chains with a change of the incubation concentration. Our measurements on the PEO–PS (150K) end-adsorbed layers and those of previous studies,[19,22] however, show that the force–distance profile for the diblock counterpart is independent of the incubation concentration. Therefore, it is logical to conclude that the end-adsorbed PEO–PS–PEO (128K) triblock copolymer chains from solutions with a low incubation concentration form predominantly a loop conformation at the toluene/mica interface. The

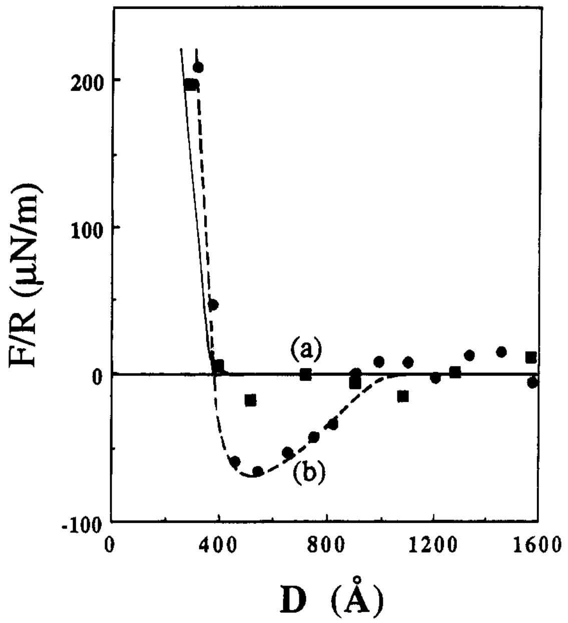

Figure 3. Force–distance profiles, recorded during the first compression, for the interaction of an end-adsorbed PEO–PS–PEO (128K) triblock copolymer *single* layer against a bare mica surface in toluene. The dashed and solid curves are best-fits by eye. The force–distance curves were plotted on a linear–linear scale to highlight the region of weak interactions, and the copolymer was adsorbed from toluene solutions of different bulk concentrations: (a) $C = 1.5 \times 10^{-4}$ w/w; (b) $C = 2.4 \times 10^{-3}$ w/w.

tail population, however, increases with the incubation concentration, leading to an outward shift for the force–distance profiles. The change in conformation of the end-adsorbed triblock copolymer chains is apparently driven by a corresponding change in the surface coverage, as a monotonic increase in adsorbed amount with the incubation concentration has been experimentally observed for a very similar triblock copolymer (i.e., PEO (220)/PS (125K)/PEO (220)) under similar conditions.[27] As the surface coverage increases with the incubation concentration, the repulsive forces from osmotic and excluded-volume interactions within the adsorbed layer are enhanced, which should "stretch" more chains into a tail-like structure at a higher surface coverage (i.e., a higher incubation concentration in this particular case).[18,22,27,33] This process continues until the adsorption energy is eventually balanced by the interchain interactions, leading to an equilibrium state for the adsorbed polymer layer.[18,22,34] The full-range interaction with an onset distance of ca. 1400 Å for repulsive forces shown in Figure 2b suggests that the PEO–PS–PEO (128K) adsorbed layer formed at the high incubation concentration contains a significant fraction of stretched tail chains at equilibrium.

Further evidence for effects of the incubation concentration on macromolecular conformations at the liquid/solid interface comes from the force measurements on a *single* adsorbed PEO–PS–PEO (128K) layer against a bare mica surface. Curves a and b of Figure 3 show such interactions for unperturbed end-adsorbed PEO–PS–PEO (128K) layers, incubated at a polymer concentration of 1.5×10^{-4} and 2.4×10^{-3} w/w, respectively, against bare mica in pure toluene. As can be seen, an attractive profile is observed in Figure 3b, in contrast to the monotonic repulsion in Figure 3a. The attraction seen in Figure 3b indicates, again, the presence of a significant amount of tails in the end-adsorbed PEO–PS–PEO (128K) layer formed at a high incubation concentration, as only the free PEO end blocks of the tail-like chains can adsorb onto the approaching bare mica sheet, forming polymer "bridges" between the two mica surfaces. The absence of any detectable attractive force, within experimental error, in Figure 3a confirms that the end-adsorbed PEO–PS–PEO (128K) chains from the solution of a low polymer concentration form dominantly a loop conformation at the toluene/mica interface. The similar onset distance of repulsion, together with the similar overall shape of the repulsive wall, seen in Figure 3a,b presumably implies that while the end-adsorbed PEO–PS–PEO (128K) layer from the solution of a high polymer concentration contains predominantly the stretched tail-like chains, there is also a considerable amount of the triblock macromolecular chains bound in a loop conformation. While the onset distance of repulsion of ca. 400 Å in Figure 3a can be taken as the effective layer thickness of the PEO–PS–PEO (128K) loops formed at the low incubation concentration, the corresponding onset distance seen in Figure 3b merely represents a separation distance at which the "bridging" attractions are just counterbalanced by repulsions from the osmotic and excluded-volume interactions. This is because the actual location for the repulsive wall of the loops corresponding to Figure 3b may have been shifted inward by the "bridging" attractions associated with those PEO end blocks distributed in the crossover region between the "inner" loop and "outer" tail layers, as might be predicted by a bimodal brush theory developed by Dan and Tirrell.[35]

(b) Loop–Tail Transition and Stretching of the PVP–PS–PVP (240K) Tail-like Chains. As can be seen from the foregoing discussion, for the end-adsorbed PEO–PS–PEO (128K) triblock copolymer chains at the toluene/mica interface either a loop or a tail conformation can form depending on the incubation concentration. While the incubation concentration may have a strong influence on the conformation formed by a *given* end-adsorbed triblock copolymer at a particular liquid/solid interface, the adsorption energy plays an important role in control of macromolecular conformations at the liquid/solid interface for different pairs of adsorbed polymer and interface. Thus, a triblock copolymer, ABA, which has a stronger affinity for the toluene/mica interface than PEO–PS–PEO (128K), may form predominantly a loop structure even at a high incubation concentration. This is exemplified by the end-adsorbed PVP–PS–PVP (240K) triblock copolymer chains, which have much stronger affinity for the toluene/mica interface than the PEO–PS–PEO (128K) triblock copolymer due to the nonsolubility of PVP in toluene[22] and its much higher molecular weight than the PEO block (Table 1). Figure 4a shows no detectable attractive force for the interaction of a *single* layer of PVP–PS–PVP (240K) against bare mica in toluene upon *compression*, which clearly demonstrates that tails, and consequently bridging chains, can be neglected in an *unperturbed* end-adsorbed PVP–PS–PVP (240K) layer formed in a solution of polymer concentration, C, as high as 2.4×10^{-3} w/w. This is consistent with a previous study on the interactions between two end-adsorbed PVP–PS–PVP layers, in which only loop conformations were observed.[36]

Clearly, therefore, the attractive forces and outward jumps seen in Figure 4b are mainly due to the formation of polymer "bridges" under strong compression and the subsequent *stretching* of the bridging chains on *decompression*. The attractive forces shown in Figure 4b extend to about 2000 Å, a separation distance which is much larger even than a putative layer thickness for

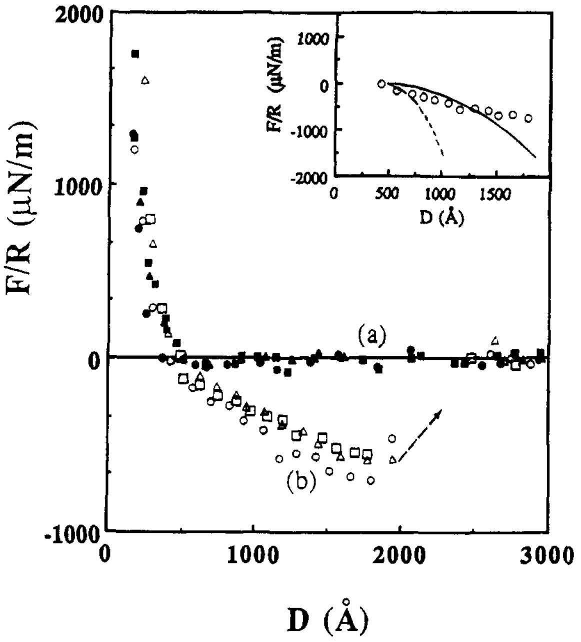

Figure 4. Force–distance profiles for an end-adsorbed PVP–PS–PVP (240K) triblock copolymer *single* layer against a bare mica surface in toluene during the first few compression–decompression cycles: (a) compressions (solid symbols); (b) decompressions (open symbols). The broken arrow indicates an outward jump. The inset shows the comparison of the experimental stretching forces with theoretical calculations: the dashed and solid curves correspond to $s = 100$ Å and $s = 200$ Å, respectively (see text and ref 42). The copolymer was adsorbed from a toluene solution of bulk concentration, $C = 2.4 \times 10^{-3}$ w/w.

an unperturbed *single* polystyrene brush with an equivalent polystyrene molecular weight (typically: 800–1000 Å).[19,28] This unambiguously suggests that the end-adsorbed PVP–PS–PVP (240K) chains were *mechanically* stretched significantly, before any outward jump occurs, during decompression. The absence of attractive forces for *subsequent* compressions (Figure 4a), which were carried out immediately after each decompression, clearly suggests that most of the stretched chains rapidly return to a loop conformation after separating the surfaces. The rapid transformation of the stretched PVP–PS–PVP (240K) tail-like chains into loops after withdrawal of the upper surface can be attributed to the strong affinity of the PVP end blocks for the toluene/mica interface.[22] A similar rapid transformation of bridging tails, though without being overstretched, into loops has been observed for the end-adsorbed PEO–PS–PEO copolymer chains with relatively large PEO blocks (i.e., PEO–PS–PEO (49K) in ref 22), and the dynamics of conformational changes involved in the transformation from a tail to a loop for the end-adsorbed PEO–PS–PEO triblock copolymer chains was found to become faster for the macromolecular chains with larger PEO blocks (i.e., higher adsorption energy).[22] Although numerous strong compression–decompression cycles could reduce, or even eliminate, the attractive forces due to redistribution of the adsorbed chains between the two surfaces, as is the case for the end-adsorbed PEO–PS–PEO triblock copolymer chains,[22] the intersurface chain migration seems not to be a serious problem for the relatively few compression–decompression cycles carried out in this study, as evidenced by Figure 4. As a working hypothesis, therefore, one can assume that the strong affinity of PVP blocks for the mica may firmly bound some of the end-adsorbed PVP–PS–PVP (240K) chains in a loop conformation even under strong compressions, which preferentially hold, possibly through entanglement effects, the overstretched bridging chains on the lower mica sheet upon separating the surfaces.

The observation of the mechanical stretching of the end-adsorbed polymer chains deserves further discussion since stretching of polymer chains has recently received some theoretical attention,[37–39] but no such experimental result has previously been reported except that Klein et al.[40] have experimentally observed a lateral stretching of the zwitterion-terminated polystyrene chains in toluene when two mica surfaces bearing such end-anchored polymer layers shear rapidly past each other. A current theory on stretching of end-grafted polymer layers in good solvents makes it possible to qualitatively compare our experimental results on stretching of the end-adsorbed PVP–PS–PVP (240K) triblock copolymer chains with the theoretical predictions.[37] Very recently, Rabin and Alexander extended the scaling arguments to the case of grafted polymer chains stretched beyond their equilibrium dimensions and obtained a simple expression for the stretching force per unit area (in simplified form):[37]

$$f = (kT/A^{3/2})[(L/L_0)^{3/2} - (L/L_0)^{-3/2}] \qquad L/L_0 > 1 \qquad (1)$$

where k and T are the Boltzmann constant and the absolute temperature, respectively, A is the area per polymer chain, L is the thickness of the stretched polymer layer, and L_0 is the equilibrium thickness of the grafted polymer layer.

Our experimental results are presented in terms of $F(D)/R$, which corresponds to the interaction energy per unit area, E, between two flat parallel surfaces of the same nature and at the same separation, D, via the Derjaguin approximation:[19,31]

$$F(D)/R = 2\pi E(D) \qquad (2)$$

$E(D)$, on the other hand, is related to the force per unit area, f, as follows:

$$E(D) = \int_{L_0}^{D} f \, \mathrm{d}L \qquad (3)$$

Thus, we finally have

$$F(D)/R = (4\pi kTL_0/A^{3/2})\{(1/5)[(D/L_0)^{5/2} - 1] + [(D/L_0)^{-1/2} - 1]\} \qquad (4)$$

Therefore, our experimental results may be directly compared with the theoretical prediction of eq 4.

In order to limit the number of free parameters, the onset distance (ca. 500 Å) at which attractive forces are first seen in Figure 4b can be taken as an effective equilibrium thickness, L_0. This is because the end-adsorbed triblock copolymer layer is apparently subjected to mechanical stretching over this separation distance during decompression although a polystyrene brush resulting from the *fully-opened loops* could have a maximum equilibrium thickness of about 630 Å. (The aforementioned putative layer thickness of 1000 Å for a corresponding unperturbed polystyrene brush with an equivalent polystyrene molecular weight must be scaled by a factor of $2^{-2/3}$ as the scaling relationship between the equilibrium thickness, L_0, and the anchoring distance, s, is given by[16,19] $L_0 = Ns^{-2/3}a^{5/3}$, and the s is expected to increase by a factor of 2 upon the opening of loops into tails). The slightly shorter onset distance, 500 Å, for stretching seen in Figure 4b than the expected equilibrium thickness, 630 Å, for the newly formed polystyrene brush may be attributed to possible normal and tangential deformations of the polymer layer due to strong entanglements between the loops and newly formed tails (*vide supra*).[41] The value of A may be calculated from experimental adsorption data previously reported and found to be in the range between 10^4 and 4×10^4 Å^2 for a nominally all-loop and all-tail conformation, respectively.[42] Thus, with *no* adjustable parameters the representative model fitting is given in the inset of Figure 4. Generally speaking, the discrepancy between the experimental data and the theoretical predictions increases with an increase in D. The higher degree of the superposition between the experimental data and the theoretical calculations with $A = 4 \times 10^4$ Å^2 (i.e., the solid curve in the inset of Figure 4) indicates that there are a significant number of loops being opened into tails upon decompression.[42] We note, however, that Rabin and Alexander's theoretical model assumes that the chains are permanently grafted onto the solid substrate, while in our experiments the chains are *physically* adsorbed on the mica surface where the grafting density of the polymer "bridges" on the upper surface may gradually decrease during decompression due to the "breaking" of the physically adsorbed bridges as they become overstretched. This may, at least partially, rationalize the substantially negative deviations between the experimental data and the calculated results at high D, as seen in the inset of Figure 4. Therefore, despite all the discrepancies mentioned above between the experimental conditions and the theoretical model system, Rabin and Alexander's theory may to some extent serve as a useful approximation for describing the behavior of end-attached polymer layers under stretching. This will certainly encourage and stimulate further experimental work on stretching of polymer chains by using better defined macromolecules such as polymeric *bridging* chains *covalently* double-end attached onto opposite surfaces.

Conclusions

In summary, we have studied the conformational rearrangements of the end-adsorbed PEO–PS diblock as well as PEO–PS–PEO and PVP–PS–PVP triblock copolymer chains at the liquid/solid interface. While a reversible collapse–stretching transition is observed for the end-attached diblock copolymer layer whenever replacements are made between a good and a poor solvent, a similar conformational transition between loops and tails is clearly demonstrated to occur for the end-adsorbed triblock copolymer chains at the toluene/mica interface during compression–decompression cycles. It is demonstrated for the first time that under certain circumstances the newly formed tail-like chains can be mechanically stretched far beyond their equilibrium dimensions before rupture. The force–distance profile obtained from the stretching measurements on the end-adsorbed PVP–PS–PVP (240K) chains at the toluene/mica interface qualitatively agrees with predictions from a scaling model proposed by Rabin and Alexander.[37]

Furthermore, both the collapse–stretching and loop–tail transition are shown to be characterized by fast kinetics. This finding could have important implications for the use of end-adsorbed polymer chains in the development of new separation processes, as previously proposed by others.[12,23]

References and Notes

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(42) The adsorbed amount of 1.82 mg/m^2 for the PVP–PS (31K–92K) diblock copolymer layer reported by Parsonage et al. (see: Parsonage, E.; Tirrell, M.; Watanabe, H.; Nuzzo, R. G. *Macromolecules* **1991**, *24*, 1987, Table III) provides an estimate for the mean anchoring distance, s (note $A = s^2$),[19] of ca. 100 Å. By assuming that equilibrium properties of an adsorbed PVP–PS–PV (30K–180K–30K), i.e. PVP–PS–PVP (240K) (see Table 1), layer with all chains in loop conformation resemble those for the adsorbed PVP–PS (31K–92K) diblock layer,[36] we can reasonably predicate that the value of s for the adsorbed layer of PVP–PS–PVP (240K) lies between 100 and 200 Å in our experiments due to the possible opening of loops into tails during compression–decompression cycles.

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