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Interaction between Adsorbed Polystyrene Layers in Acetone–Heptane Solvent Mixtures. Effect of Segment–Surface Adsorption Affinity

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ABSTRACT: A report is given of the direct measurement of surface forces between mica plates bearing polystyrene (M_w = 300 000) in acetone–heptane solvent mixtures. Part of this study is to address the effects of changes in the effective segment–surface binding affinity on the conformation of the adsorbed chains while the solvent quality is kept as much as possible unchanged. To this end, a layer of PS was adsorbed on mica from toluene–heptane mixtures and collapsed on the surfaces by exchanging these mixtures for pure heptane. A large extension of the PS layer is experienced when small quantities of acetone are introduced and the adhesion markedly increases. A desorption of this PS layer occurs when progressively more acetone is added. Also, in parallel PS adsorption does not occur from pure acetone, but it increases rapidly when an excess of heptane is added. It is suggested that in heptane, a displacement of PS segments from the mica occurs through preferential adsorption of acetone molecules to the mica surface, leading first to an expansion of the polymer layer and gradually to desorption. The results highlight the dependence of the spatial extension of the adsorbed polymer layer and the force vs distance profile on the effective relative adsorption affinity of the segments for the surface. They identify the importance of the degree of mutual polymer layer interpenetration on the surface force and illustrate the important role that the periphery of the adsorbed layer has with regard to the attractive forces at large surface separations in poor solvents. It is furthermore shown that the surface forces in phase-separated systems only become clearly dominated through the presence of large polymer flocs when the adsorbed amount is high and a considerable surface "roughness" has been created.

Introduction

The measurements of forces between polymer surfaces in a solvent is of direct relevance to the understanding of phenomena in fields such as adhesion,[1,2] dispersion stabilization,[3,4] and dispersion rheology.[5,6] Adsorption or grafting of polymers to solid–liquid and liquid–liquid interfaces has long been used to (de)stabilize colloidal dispersions; however, it has only been in the past few years that direct force measurements between polymer bearing surfaces have been carried out systematically.[7-11] Together with more traditional techniques (such as ellipsometry,[12,13] hydrodynamic measurements,[14,15] and the more recent neutron scattering,[16] and fluorescence work[17]) they have substantially contributed to our understanding of adsorbed polymer layers on surfaces as a function of molecular weight and thermodynamic quality of the immersion solvent.

Direct force measurements have confirmed that for homopolymers, attractive forces can exist both above and below the Θ temperature (T_Θ) of the adsorbed polymers.[8,9] Above T_Θ, when the polymers are able to span the medium between and adsorb on both surfaces simultaneously, a "bridging" attraction results. Below T_Θ both bridging and the negative free energy of mixing between the two interacting polymer layers contribute to the attraction (in addition to the usual van der Waals attraction). The occurrence of bridging is correlated with the extent of polymer adsorption and becomes prohibited when the polymer adsorption reaches saturation. In better than Θ solvents, this makes the forces purely repulsive (steric stabilization).

A rapid progress in the formulation of polymer adsorption theories and their adaptation toward an explanation of forces between surfaces bearing adsorbed polymers has provided a potential tool to quantitatively analyze experimental data. In these theories, the usual input parameters are the number of segments per molecule, the solvent quality (usually expressed through the Flory–Huggins parameter χ), the adsorption affinity of the polymer segments to the surface relative to the solvent molecules (expressed through the parameter χ_s which gives the differential adsorption energy per segment in units kT), and the polymer concentration in solution.

The present study addresses the effects of changes in the effective χ_s on the conformation of the adsorbed polymer chains while the other parameters are kept as much as possible unchanged. Ideally a whole range of situations between a very strong adsorption affinity and no adsorption affinity at all should be covered. Of particular interest is how χ_s can affect the amount of adsorbed polymer and the spatial extension of the adsorbed polymer layers. Both matters can be investigated with the surface force technique. The surface separation at which the onset of a surface force is experienced provides an estimate for the adsorbed layer thickness, and the optical technique used to determine the surface separation can be applied to evaluate the total amount of adsorption.

We have chosen to work with polystyrene (PS) previously collapsed on the mica surfaces from the nonsolvent heptane and then exposed to small volumes of acetone (also a poor solvent). Since acetone is a polar molecule, it is expected to have a stronger affinity to the polar mica surface than PS segments, thereby decreasing the effective χ_s. In parallel, we have started with the clean mica surfaces in a PS/acetone solution and progressively added heptane. Adsorption from such a mixture amounts to adsorption of polymers aggregates from a phase-separated system. It is investigated at which adsorption levels the expected inhomogeneities in the created adsorbed layers begin to affect the surface forces as compared to those in a homogeneously adsorbed layer.

Experimental Section

Materials. Polystyrene (PS) homopolymer (M_w = 300 000; M_w/M_n = 1.06) was purchased from Pressure Chemical Co. (Pittsburg, PA) and further purified by several precipitations from THF into methanol.

All organic solvents used in the present study were obtained reagent grade from Aldrich Chem. Co. They were dried for several days over molecular sieves A_4 and distilled just prior to use. This procedure ensures a high solvent purity and minimal water content. The use of filters to purify these solvents was avoided after it was noted that many organic solvents, especially aromatic

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ones often leach out trace amounts of impurities from the filters which can adversely affect the experiments.

Surface Force Apparatus and Procedure. Direct force measurements were carried out by using an apparatus developed by Israelachvili and constructed at the Australian National University in Canberra, Australia. A detailed description of the technique has been given before,[22] and only a short summary will be given here.

A key requirement for the adequate measurement of surface forces is the availability of smooth surfaces. To this end we use mica that can be cleaved from the crystal in thin plates (3–10 μm thick) exposing a molecularly smooth surface. Cleaving was carried out in a high-efficiency laminar flow hood to prevent particle contamination. Furthermore, the whole laboratory was pressurized with air led through a double set of activated charcoal filters after it was observed that organic contaminants in air were able to readily contaminate the freshly cleaved mica surfaces. The mica plates were silvered on one side with a 480-Å thick silver layer and glued down on cylindrically curved glass disks (curvature radius $R \approx 1$ cm), silvered sides down, before mounting them into the surface force apparatus. All components of the apparatus were previously cleaned in a soap solution, copiously rinsed with distilled water, soaked in ethanol, and blown dry with filtered nitrogen before being assembled.

In the apparatus one of the glass disks is mounted on a rigid support, while the other, facing the first one in a crossed cylinder configuration, is positioned on a double cantilever spring with a known spring constant. The apparatus is then sealed and flushed with nitrogen before being transferred to a marble antivibration table. This table rests on four airmounts each with a resonance frequency of 3 Hz which ensures that most of the external vibration during an experiment is effectively dampened.

The measurement of the separation between the surfaces is carried out by using white light multiple-beam interferometry.[23] A parallel beam of white light (from a 100-W tungsten–halogen lamp) is transmitted through the half-silvered mica sheets, caught in the objective of a microscope above the apparatus, and focused onto the entrance slit of a spectrometer (Spex, Model 1870, 0.5-m focal length) where it is dispersed into a series of bright fringes of equal chromatic order (FECO) as observed through an eyepiece mounted on a stage translator at the exit of the spectrometer. From the wavelengths and shapes of the FECO fringes, it is straightforward to evaluate the distance D between the surfaces, the contact position between the surfaces (which defines $D = 0$), the mean refractive index $n(D)$ between the surfaces, and the radius of curvature R of the surfaces. Generally D can be measured to an accuracy of 1–2 Å.

When the separated surfaces experience a force from each other, the force is evaluated by measuring the deflection of the spring and multiplying this with the spring constant K. When the force $F(D)$ is measured as a function of D down to surface contact, the full force law is obtained.

The distance between the two surfaces is controlled by a three-stage mechanism of increasing sensitivity. The coarse control uses a stepping motor drive and allows positioning to within 1 μm; the medium control uses a DC synchronous motor drive and allows positioning to within 10 Å; and a piezo electric crystal (which expands or contracts vertically by ~7 Å per volt applied axially across the cylindrical wall of the rigid support) is used for the final positioning to about 1 Å.

When strong and smooth adhesion between the mica surfaces was observed in air, freshly distilled solvent was introduced through an inlet into the apparatus and the forces measured. When no evidence of contamination was present, a concentrated polymer solution was introduced into the apparatus to a final concentration of 10 ± 2 μg/mL. To establish polymer adsorption, the mica surfaces were widely separated (~5 mm) and left to equilibrate for periods between 1 and 24 h at 22 ± 0.5 °C, before surface forces were measured. Each experiment was at least repeated once and usually more times to ensure the reproducibility of the results.

The measured forces $F(D)$ were scaled by the mean curvature radius R of the cylindrically curved mica plates. Because the distance range of the forces (<300 nm) is far less than the radius R (~1–2 cm), we can then use the Deryaguin approximation[24] $F(D)/R = 2\pi E(D)$, where $E(D)$ represents the surface interaction energy per unit area between two flat surfaces separated by a distance D.

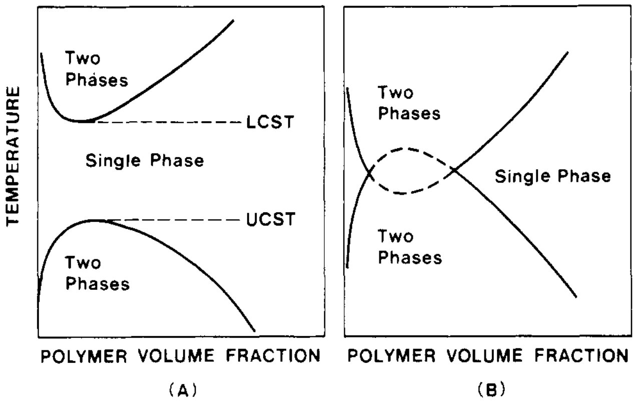

Figure 1. (A) Schematic representation of a polymer solution phase diagram when the two phase-separated regions are separated by a finite temperature interval. (B) The two phase-separated regions overlap leaving only a very dilute and a concentrated polymer solution to exist independently as single phases.

Results

PS in Acetone. Acetone is a poor solvent for PS. Its phase diagram represents a special case of the general type phase diagram (Figure 1a) where two regions of limited miscibility exist. One region lies below the upper critical solution temperature (UCST); the other above the lower critical solution temperature (LCST). For infinite molecular weight, the UCST becomes identical to the Flory Θ point. In the case of acetone, the two regions are known[25] to overlap each other (Figure 1B) and form an "hourglass" type phase diagram showing limited miscibility at all temperatures. It was noted, however, that a 10 μg/mL solution of PS ($M_w = 300\,000$) still forms a clear solution. This concentration must therefore be located in the dilute single-phase region of the phase diagram (at 22 °C). Furthermore, it provides evidence that acetone is a somewhat "better" solvent than heptane because in the latter solvent hardly any solubility of PS can be detected.

No adsorption of PS on mica from acetone could be detected, even after more than 20 h of adsorption time. Typically, below $D = 7$ nm an attractive van der Waals force was observed, merging into an oscillatory force vs distance below $D = 3$ nm, very similar to that reported by Christenson.[26] The oscillations reflect the layering of acetone molecules near the mica plates and were unaffected by the presence of PS in the solvent. Within our experimental accuracy ($\Delta F/R \approx 0.01$ mN/m), no attractive depletion forces could be observed in a 10 μg/mL PS solution. In previous work, this result was already anticipated by Luckham and Klein.[10]

PS Adsorption from Acetone–Heptane Mixtures. The solvent quality was worsened by the addition of heptane that is a nonsolvent for PS. Up to a volume ratio of 50/50 acetone–heptane no adsorption was detected. Only short-range oscillatory forces were present between the surfaces. At a volume ratio of 25/75 acetone–heptane, the solution has a turbid appearance indicating phase separation. However, due to the very low PS concentration, the polymer aggregates do remain dispersed for many hours. Between the bare mica surfaces in this solvent mixture (absence of polymer), the first adhesive minimum was located at $D = 1.2$ nm ($(F/R)_{\mathrm{adh}} \simeq -9$ mN/m) and a much deeper minimum at $D = 0.6$ nm, similar to what was observed by Christenson et al.[26] in n-octane.

After adsorption was allowed to proceed for 2 h, the onset of a long-range attraction was observed at $D = 12$

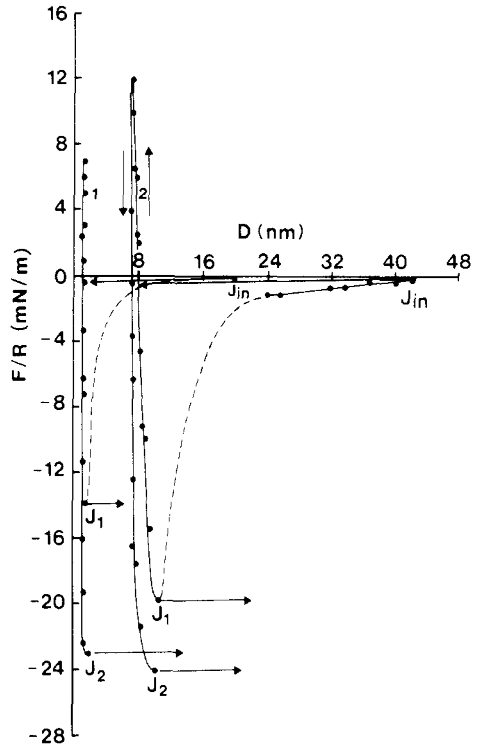

Figure 2. Curve 1: Force vs distance profile between mica surfaces on which PS has adsorbed from a 25/75 acetone–heptane mixture for a period of 16 h. Curve 2: Force vs distance curve when PS adsorption has proceeded for 3 h from a 12.5/87.5 acetone–heptane mixture. The positions (J_{in}) denote the surface separations from where an inward jump occurs. (J_1) denotes the outward jumps when no polymer layer compression has taken place; (J_2) denotes the outward jumps after a compression has been applied. The dashed regions of the curves are experimentally inaccessible.

nm. This onset gradually moved out to $D = 18$ nm after 16 h of adsorption. Curve 1 in Figure 2 represents the measured force law. At $D > 18$ nm, the magnitude of the attractive force is very small and is difficult to measure accurately. However, at $D = 18$ nm the gradient of the attractive force exceeds the spring constant K, creating a mechanical instability which causes the surfaces to suddenly jump into "contact" at $D = 1.5$ nm where they come at rest. Below $D = 1.5$ nm the force is steeply repulsive. Upon pulling the surfaces out of contact, an adhesive force had to be overcome whose magnitude (i.e., the minimum in the force vs distance curve) depended on the previous history. When the surfaces were separated immediately after an inward jump to $D = 1.5$ nm had occurred, an $(F/R)_{adh} = -14$ mN/m was measured, but when they were first compressed with a force up to $F/R = 5$ mN/m and then pulled apart, a greater $(F/R)_{adh} = -23$ mN/m was observed. On the basis of our observations in the absence of polymer, we expect an important contribution from the van der Waals forces to already exist at $D = 1.5$ nm. As soon as the surfaces were separated and brought into contact again, the strength of the adhesion again depended on whether or not a compression was applied on the polymer layer.

Curve 2 in Figure 2 gives the surface forces after adsorption of PS from a 12.5/87.5 acetone–heptane mixture had continued for 3 h. Here, the increased volume fraction of heptane has clearly led to an increase of the PS adsorption. It was noted that typically below $D = 60$ nm, the movement of the surfaces became quite sluggish as compared to the movement in polymer free solvent. This indicates an accumulation of polymer that restricts the drainage of solvent from between the surfaces.

When the surfaces were slowly moved together an attraction became apparent below $D = 44$ nm, though it was not a sudden jump into contact. The mica plates slowly but persistently drifted together until they came at rest at $D = 8$ nm; the whole process taking about 1 min. By applying an outward force during the inward drift, the inward movement could be halted and the surfaces separated again. This allowed the approximate forces also to be measured in a small region below $D = 44$ nm. The adhesion force was again to some degree dependent on whether the surfaces were separated immediately or first compressed. The adhesion measured in curve 2 is overall stronger than in curve 1. Clearly, also much more polymer is adsorbed. An estimate of the total adsorbed amount can be obtained by measuring the refractive index $n(D)$ between the surfaces. At $D = 7$ nm a value $n = 1.53 \pm 0.01$ was found. With the known refractive indexes $n = 1.59$ and 1.384 for bulk PS and the solvent mixture, respectively, it is easy to calculate that the polymer volume fraction ϕ at $D = 7$ nm must be about $\phi = 0.71 \pm 0.05$ (or equivalently, 2.7 ± 0.3 mg/m^2 PS on one surface). This volume fraction is quite comparable with polymer volume fractions found in the concentrated phase of a phase-separated polymer solution. It is noted that because PS is somewhat more soluble in acetone than in heptane, some preferential adsorption of acetone ($n = 1.359$) may have occurred in the adsorbed layer. With the present technique, it is not possible to quantify this matter but since the refractive index of acetone is close to that of the solvent mixture, the additional error in the estimated adsorbed amount is expected to be small.

On applying a surface compression for several minutes, no evidence of polymer desorption could be detected. Although the force is somewhat hysteretic during a compression–decompression cycle, these cycles were quite reproducible when the adsorbed layers were left to "relax" for a few minutes between cycles.

Figure 3 gives the forces after PS was allowed to adsorb for a further 20 h from the 12.5/87.5 acetone–heptane mixture. Clearly, the forces range much further out than in Figure 2 and the adsorption has drastically increased. It was observed that the FECO fringes, as viewed in the spectrogram, were no longer smoothly curved lines. Because the position of each point on the fringe line is a function of the refractive index of the medium between the surfaces, this points out that refractive index differences exist laterally across the surfaces. It shows that the polymer layer on the mica is nonhomogeneous in thickness and/or density, which is obviously the result of adsorption of large phase-separated PS flocs on the surface. Unfortunately, it is difficult to quantify this "surface roughness" because the lateral resolution of the FECO technique is about 4 orders of magnitude less than the depth resolution (which provides the surface separation). In any case we expect an effect of these inhomogeneities on the forces between the adsorbed layers.

The movement of the surfaces became very sluggish below $D = 300$ nm. When bringing the surfaces slowly together for the first time, the force was attractive below $D = 280$ nm (see inset Figure 3) and became repulsive at distances less than 70 nm. It was noted that when the surfaces were moved some distance toward each other, it always took a substantial amount of time to establish an equilibrium separation. For example, to bring the surfaces from $D = 160$ to 100 nm would take about 10 s, from $D = 70$ nm to 50 nm about 20 min, and from $D = 50$ nm to $D = 35$ nm would take more than 1 h. At the same time,

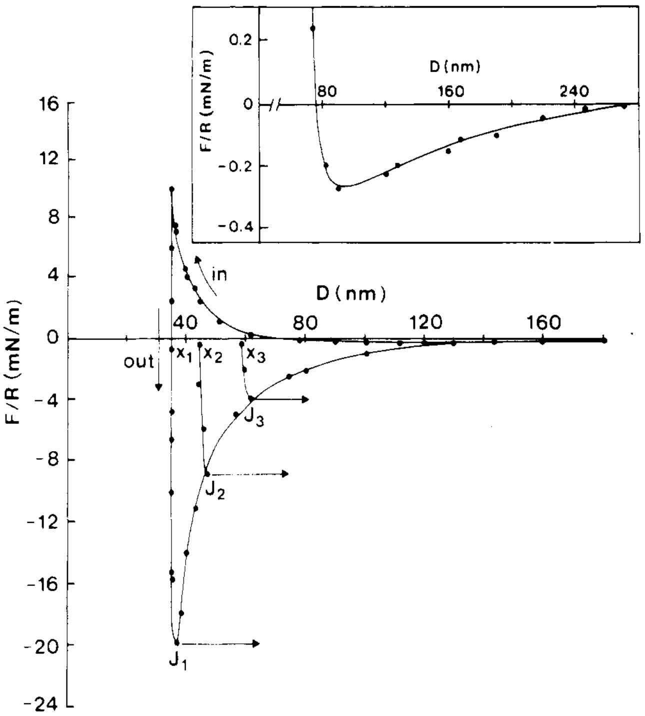

Figure 3. Forces vs distance when PS has adsorbed for 23 h from a 12.5/87.5 acetone–heptane solution. The inset shows the forces at large distances measured during the first approach of the polymer layers. At shorter distances, the forces follow the "in" and "out" arrows. The positions marked (x_1), (x_2), and (x_3) give the separations where the surfaces came at rest after an inward jump occurred at times 5 min, $1^1/_2$ h, and 12 h, respectively, since the first outward jump (J_1) had been completed. (J_1), (J_2), and (J_3) denote outward jumps obtained when the surfaces were slowly separated again from the positions (x_1), (x_2), and (x_3), respectively.

the fringes began to assume a more smooth profile, indicating that the adsorbed layers became more homogeneous when compressed. Clearly, surface compression causes an extensive, time consuming reorganization to occur in the polymer layers. This became even more evident when after compression up to F/R = 10 mN/m (reaching D = 35 nm), the polymer layers were pulled apart. (This caused most of the fringe blurring to reappear.) We take as the force of adhesion the force necessary to first initiate a slight outward movement of the surfaces. When such a "pull-off" force was established, the initially very slow outward movement (from J_1 in Figure 3) would gradually accelerate and eventually culminate into a fast outward jump. This whole process took about 30 min to be completed.

When, immediately after this first separation (decompression), the surfaces were brought together again, the forces were quite different. An attraction was again felt below D = 280 nm but now, below D = 150 nm instead of experiencing a repulsion, the surfaces kept drifting together, taking about 10 min before coming at rest at point (x_1) in Figure 3. This point is exactly at D = 35 nm where the minimum separation was reached during the first compression. Also, the same force $(F/R)_{\mathrm{adh}} = -20$ mN/m had to be applied to separate the surfaces again. (It should be noted that this adhesion force is quite similar to the value found for the adhesion in Figure 2 where altogether much less polymer was adsorbed.)

After waiting progressively longer times after surface separation had been established, attractive forces would still cause the surfaces to drift into contact, but the final "rest" position would progressively become located farther out (i.e. at (x_2) and (x_3)). A final separation at (x_2) was reached by waiting $1^1/_2$ h after completing the first decompression; separation (x_3) was reached after waiting 12 h. When the surfaces were pulled apart immediately after these positions were reached (i.e. no compression), the adhesion forces were also diminished (jumps from (J_2) and (J_3)). Extra compression applied, necessary to go from (x_3) down to D = 35 nm (x_1), would again lead to a much larger pull-off force needed to separate the surfaces, very similar to that found during the very first decompression (J_1). In this way, by measuring the adhesion force as a function of time after having the first decompression completed, a series of points (x_n) and (J_n) could be obtained. Eventually, after 24 h, the points (J_n) merged into the attractive part of the force vs distance curve given in the inset of Figure 3. Because the surfaces were always kept at a separation of less than 1 μm during the waiting periods, no extra adsorption from solution is likely to have taken place.

On the other hand, some polymer desorption probably occurred during surface compression. During the first compression–decompression cycle, the refractive index remained about the same (n = 1.52 ± 0.01) when the distance decreased from D = 50 nm to D = 35 nm. This indicates that some polymer has slowly been pushed away from the contact region laterally across the surfaces. It probably slowly returns after many hours because the original force vs distance profile could be re-established after about 24 h. It has already been mentioned that when the surfaces were pressed together, the fringes gradually became less "rough" in appearance and were completely smooth below D = 40 nm. Thus under a sufficient load, the compressed polymer layer becomes laterally homogeneous with regard to the mean polymer density whereas the free polymer layers possess inhomogeneities. These inhomogeneities are likely to cause a less "smooth" contact, equivalent to there being rough surfaces. The adhesion is then indeed less strong unless the adsorbed layers are firmly squeezed together before being pulled apart. The decrease of the adhesion force and the simultaneous outward shift of the positions (x_n) with time may well reflect a slow deformation and re-formation of local protruding inhomogeneities after an initial compression of the adsorbed layers to (x_1) is applied. Because the FECO technique only permits the measurement of an average refractive index between the surfaces, the precise spatial distribution of the inhomogeneities and their re-formation with time cannot be resolved.

PS Desorption from Acetone–Heptane Mixtures. As a starting point for the desorption studies we used a PS layer on mica that has been previously adsorbed from toluene–heptane mixtures and then collapsed on the mica by exchanging these mixtures for pure heptane. Details of the PS adsorption characteristics in toluene–heptane solvent mixtures will be published elsewhere.

Curve 1 in Figure 4 gives the surface forces between PS layers in pure heptane. The forces are attractive below D = 10 nm (the inward jump from J_{in} takes less than 1 s to complete) and become steeply repulsive below D = 5.2 nm. There was no evidence of hysteresis in the force law on approaching and withdrawing of the surfaces. At D = 5.2 nm, the refractive index between the surfaces was again found to be about 1.52 ± 0.01. Thus the PS (n = 1.59) can certainly not be considered as bulk polymer but still carries a considerable amount of solvent ($\phi_p \approx 0.65$). Part of this solvent may actually still consist of remaining toluene (preferential uptake). The amount adsorbed on one surface can therefore not accurately be calculated but is estimated to be about 2 mg/m^2. It should be noted that although this amount is of the same order as in Figure 2 (curve 2) for a 12.5/87.5 acetone–heptane mixture, the

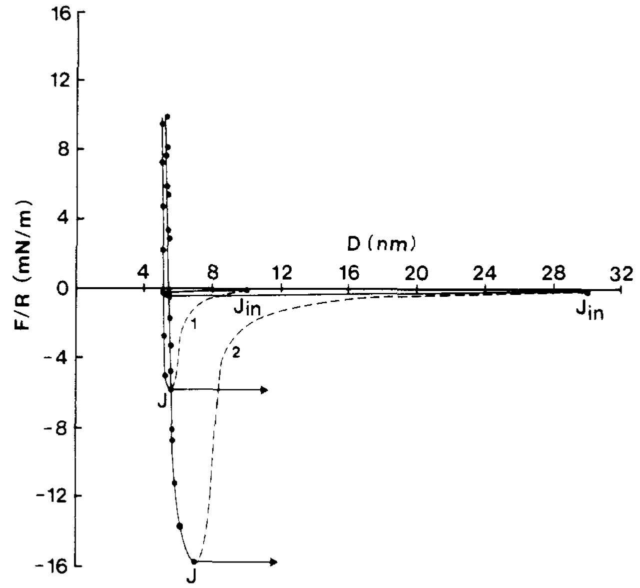

Figure 4. Curve 1: force vs distance profile between mica surfaces covered with PS in heptane. The PS was previously adsorbed from toluene–heptane mixtures. Curve 2: force vs distance profile measured after 3% acetone was added to the heptane. (J_{in}) denotes an inward jump; (J) denotes an outward jump. The dashed regions of the curves are experimentally inaccessible.

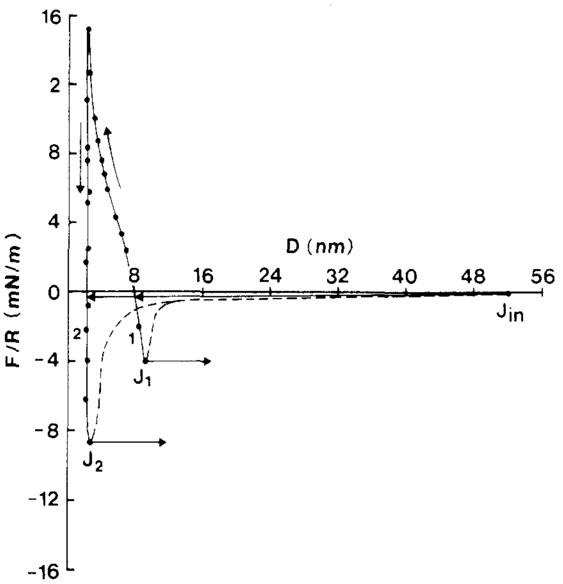

Figure 5. Forces as a function of distance when 25% acetone was added to the heptane. (J_{in}) denotes the position from where an inward jump occurred. (J_1) gives the outward jump when no compression on the polymer layer had been applied (curve 1); (J_2) gives the outward jump when previously a compressive force F/R = 15 mN/m had been applied (resulting in force curve 2). Force curve 2 does not "relax" back to force curve 1, but the position (J_{in}) remains approximately unchanged. The dashed regions of the curves are experimentally inaccessible.

attractive forces in that system extend much farther away from the mica surfaces and the adhesion is clearly stronger.

Curve 2 in Figure 4 shows the forces measured when acetone was added to the heptane to achieve a final volume fraction of 3%. The change is remarkable: The more so because it was established in less than a few minutes (the time it took to mix the acetone with the heptane in the apparatus). The attraction now extends many times further out, and the force of adhesion has become almost three times as strong. There is no hysteresis in the forces and also no evidence of polymer desorption. Hence it must be essentially the polymer configuration on the mica that has changed.

When the surfaces were moved toward each other, their rate of approach slowed down considerably below D = 50 nm. A similar phenomenon was found in the experiments described in the previous section and is probably associated with the hindered drainage of solvent from between the surfaces through the presence of polymeric material. It becomes more pronounced the further the polymer layer extends into the solution and is also expected to be a function of the local polymer concentration. However, when the surfaces were brought together slowly, the forces were attractive. The inward jump from (J_{in}) this time took about 30 s to be completed and was much slower than the jump measured in curve 1.

Figure 5 (curve 1) gives the initial force vs distance profile when the acetone content in the solvent was raised to 25%. The distance where the onset of attraction is felt has now shifted out to D = 50 nm. Another remarkable fact is that the inward jump from (J_{in}) was completed much faster (~1 s). When the polymer layers were separated, a smaller force of adhesion was measured ($(F/R)_{adh}$ = –4 mN/m) than in Figure 4 (curve 2). However, when the adsorbed layers were compressed first and then separated, the adhesion became about twice as strong (Figure 5 (curve 2)). At the same time the adhesive well in the force vs distance curve shifted further inward and did not "relax" back to curve 1. The onset of attraction remained at D = 50 nm. From refractive index measurements it was concluded that most of the adsorbed polymer had been displaced during compression. A similar compression could not significantly desorb polymer in Figure 4, indicating that as more acetone is added, the PS becomes more weakly bound to the mica. Stronger additional compression caused the adhesive minimum to even shift toward smaller separations, thereby increasing its depth.

No significant change in the force law was observed when the surfaces were left in the solution for several hours. Clearly, conformational changes in the adsorbed layers occur rapidly after solvent mixing has been established.

After the acetone content of the solvent was raised to 50%, long-range attractions were no longer observed. Instead, the force was zero down to about D = 6 nm where a weak attraction was found similar to the surface forces found between the clean mica surfaces in pure solvent. A solvation force was found below D = 1.4 nm, quite comparable to what was observed by Christenson et al.[26] in their study with *n*-octane, even though we now expect a preferential adsorption of acetone to the mica to occur. However, the solvation forces in pure acetone[26] below D = 1.5 nm are similar to those in octane, and we conclude that a presence of preferential acetone adsorption cannot simply be deduced from only the solvation forces. In any case a complete desorption of PS has now been established. Note that in the previous section it was shown that no adsorption of PS on mica could be established from a 50/50 acetone–heptane solution.

Discussion

Polymer adsorption on and desorption from mica surfaces, together with the accompanying changes in surface forces, have been studied within a small range of poor solvent qualities using a narrow molecular weight PS sample. Several interesting phenomena have emerged. It has clearly been demonstrated that the addition of small amounts of acetone drastically reduces the affinity of PS segments for the mica surface, first changing the conformation of the adsorbed molecules and finally giving rise to a complete polymer desorption, even though the solvent is always a worse than Θ solvent. Similarly, PS adsorption does not take place from a heptane–acetone solution unless the acetone content becomes less than 50%. The results strongly suggest that acetone molecules adsorb preferentially on the polar mica surface (an aluminosilicate) because of their polar nature, thereby displacing PS segments and lowering the effective differential adsorption affinity parameter χ_s.

Theoretically,[21] it is well-known that a certain minimum value of χ_s exists, dependent on the polymer molecular weight, below which no adsorption will occur. For a polymer chain to adsorb, a finite negative differential adsorption free energy has to exist (0.2–0.4 kT per segment) because the polymer chain loses configurational entropy once it becomes attached to a surface.

The distance where an attractive surface force becomes measurable increases dramatically when small amounts of acetone are added (see Figure 4), indicating an extension of the adsorbed polymer layer thickness. Whereas the thickness of the adsorbed layer can be defined in several ways (ellipsometry yields a root-mean-square thickness) in the present work, it is useful to define it as the distance where the onset of an attractive interaction is found. In most cases (except for the heterogeneous adsorption noted in Figure 3) this is near the distance where an inward jump originates.

Because the solvent quality has not been altered significantly (as in the preceding paper), the results shown in Figure 4 demonstrate that the force vs distance profile depends strongly on χ_s, given the presence of a fixed amount of adsorbed polymer. The same extended distance range where attractive interactions are found appears in Figure 2 which was measured after adsorption from a phase-separated solution had proceeded for several hours. Hence, although the results presented in Figure 2 refer to a nonequilibrium situation concerning the adsorbed amount of polymer (in principle it can reach infinite values from phase-separated systems), there is no evidence to believe that the spatial extension of the adsorbed layer responsible for the forces in Figure 2 and Figure 4 is a nonequilibrium profile. It shows that even in a poor solvent, absorbed polymeric material is able to extend far away from the surface (although we expect it to be very dilute) when the segment–surface adsorption affinity is lowered.

Recently, Scheutjens et al.[21,27] have pointed out that it is predominantly the tails of adsorbed polymers that are found in the periphery of the adsorbed layer and that they may well be of significant importance for the surface forces at long range. They also predict that when χ_s decreases, the average fraction of segments present in tails and loops increases, whereas the fraction of segments in trains (in direct contact with the surface) decreases. Given a constant amount of adsorbed polymer, a decrease in χ_s must always lead to an expansion of the adsorbed layer exactly as indicated in the force vs distance profiles in Figures 4 and 5. From the present results, there can be no doubt that the periphery of the adsorbed layers plays an important role with respect to the range and the onset of the attractive surface forces in a poor solvent. Segments in the tails of the adsorbed chains are the first segments able to interact with the polymer layer adsorbed on the opposite surface, and they very likely initiate bridging. PS adsorption experiments in toluene–heptane mixtures (preceding paper) have clearly shown that under better than Θ conditions, even when the adsorbed amount is very small, long-range weak attractions caused by polymer bridging clearly exist. Similar arguments were previously put forward by Israelachvili et al.[8] and Almog and Klein[9] working with single solvent systems.

Another important conclusion reached by Scheutjens et al.[27] was that it is the extension of the polymer tails from the surface that determines the "hydrodynamic thickness" of the surface. Within the hydrodynamic layer, the motion of solvent molecules is substantially suppressed, a situation analogous to the limited draining of free polymer coils. Recently, Israelachvili[28] has experimentally located the effective plane of shear (which bounds the hydrodynamic layer) near mica surfaces covered with PS in cyclohexane below T_Θ, using a dynamic technique. The result was that the sum of the hydrodynamic thicknesses of both polymer layers virtually coincided with the distance where an inward jump between the surfaces occurred in the surface force measurement. Thus the theoretical claim that a flow field near a surface is effectively prohibited from entering the periphery of a polymer layer seems justified. In most of the present experiments, although we can not quantify the results, it was also observed that a much more sluggish motion of the surfaces occurred near and especially just below the surface separation where an inward jump took place. This was most apparent when the adsorption was high (Figure 3). Also Klein[7] has suggested that the extended time it takes for an inward jump to be completed (often several minutes) can be completely accounted for by the restricted drainage of solvent through the adsorbed layers. On the other hand, there were two cases in the present study (Figure 2 (curve 1) and Figure 5) where inward jumps were completed quickly (~1 s) even though, especially in Figure 5, an extended polymer layer was present. In both cases, the adsorbed amount was low. Apparently, in these cases the segment density in the adsorbed layer is too small to severely retard solvent drainage but large enough to influence the force vs distance profile. A promising potential for future research clearly exists in this area. (Note that only thick adsorbed layers were studied in Israelachvili's hydrodynamic experiment.[28])

It is anticipated that when polymer adsorption proceeds with time from a phase-separated polymer solution, inhomogeneous multilayer adsorption soon occurs and not all adsorbed molecules have segments in actual contact with the surface. Given sufficient time, it might be expected that there will be essentially no limit to the amount of polymer adsorption since the surface acts as a nucleus for phase separation. This situation clearly exists in the experiments shown in Figure 3 where the adsorbed amount is estimated to be more than 10 mg/m^2 and where inhomogeneities in the adsorbed layers were evident. If some of the polymers are less strongly bound, it is easy to envisage their slow displacement from the contact zone between the surfaces after they have been compressed for a prolonged period of time. Together with the deformation of local protruding polymer layer inhomogeneities, this has resulted in a time-dependent hysteretic behavior of the surface forces. No such behavior was observed when smaller amounts were adsorbed though it cannot be excluded that a similar desorption could occur if the surfaces were to remain compressed for many hours or even days. Interestingly, although the adsorption in Figure 2 should also be primarily the result of the attachment of polymer aggregates to the surfaces, the main features of the force vs distance profiles are very similar to those between the homogeneous layers in Figure 4. We conclude that in Figure 2 the expected layer inhomogeneities do not as yet substantially affect the surface forces (apart from maybe the small degree of hysteresis), contrary to the situation in Figure 3 where much larger amounts are adsorbed. In particular, the adhesion force in Figure 2 is similar to the one in Figure 4 whereas in Figure 3 only a substantial compression of the adsorbed layer resulted in a strong adhesive force. Apparently, an initial "smoothing-out" or "wetting" of the polymer aggregates takes place on the surfaces.

A displacement of adsorbed polymer from between the surfaces due to compression is clearly apparent in Figure 5 (25% acetone) where the polymer is more weakly bound to the surface. Parallel to this observation is the result in Figure 2, curve 1, where after very long incubation times in a phase-separated system, only a very limited amount of adsorption had taken place. Evidently, in Figure 5 the notion of so-called restricted equilibrium, where the polymer cannot escape from the gap between the surfaces when they approach, holds less well when the polymer becomes more weakly bound (with an adsorption affinity close to the critical value of χ_s) or is phase separated onto the surfaces. In those cases, the applied compressive load and the time during which the adsorbed layers are compressed become important with regard to polymer displacement.

A final observation deserving attention is the large magnitude of the adhesion force when acetone is present, and its dependence on the amount of adsorbed polymer. The adhesion we have measured is about 20 times stronger than the adhesion between mica surfaces saturated with PS in cyclohexane below T_Θ, as reported by Israelachvili et al.[8] Figures 2,3, and 4 show that there is little variation of the adhesion force with the amount of adsorbed polymer. If polymer bridging had contributed significantly to the adhesion force then the adhesion would be expected to decrease with increasing adsorption until the bridging attraction became gradually eliminated. Clearly that does not occur in these experiments and thus the observed adhesion must be mainly the result of the negative free energy of mixing between the two adsorbed layers. Evidently, the extent of mixing and the resulting change in free energy depend a great deal on the extension of the adsorbed layers rather than on the amount of adsorption itself. This is already revealed in Figure 4 where the amount of adsorbed polymer has been kept constant. On addition of acetone in Figure 4, some acetone has probably preferentially adsorbed in the adsorbed layer but given that even small quantities of added good solvent toluene (preceding paper) are unable to substantially expand the adsorbed layer, the main reason behind the layer expansion must be the preferential adsorption of acetone to the mica surface, thereby lowering χ_s. When a *considerable* amount of adsorbed polymer has been displaced from the surfaces (Figure 5), the adhesion becomes weaker than in the previous cases, but then the amount of adsorption is also lower and this must have reduced the resulting free energy of mixing between the interacting adsorbed layers. From the observation that the minimum in the force vs distance curve shifts to shorter surface separations and becomes simultaneously deeper when desorption is induced, we conclude that a bridging attraction may be much more important in this case. Also the van der Waals forces should begin to contribute to the adhesion below $D = 3$ nm[26] but cannot account for all of the adhesion increase. Apparently, once the amount of adsorbed polymer drops below a critical level, the density of segments in direct contact with the surface becomes low enough to facilitate polymer bridging. A similar conclusion was reached by Klein and co-workers[9,29] concerning polymer layer interactions in better than Θ solvents.

The overall picture of polymer adsorbtion/surface forces in mixed solvents is complex and can, at this stage, only qualitatively be understood. It seems feasible to attempt a comparison with theory (for example, with the advanced lattice theory of Scheutjens and Fleer[21]) to see whether the main trends of the present investigation can be rationalized.

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