side-chain length for copolymers of approximately equal molecular weight.

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Registry No. IIa (9-anthrylmethyl ester sodium salt), 114956-82-0; IIb (9-anthrylmethyl ester sodium salt), 114956-84-2; IIc (9-anthrylmethyl ester sodium salt), 114956-83-1; sodium dodecyl sulfate, 151-21-3.

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Interactions between Adsorbed Polystyrene Layers in Toluene–Heptane Mixtures. Effect of Solvent Quality

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ABSTRACT: A report is given of the direct measurement of forces between mica surfaces on which PS homopolymer (M_w = 300 000) has been adsorbed from heptane–toluene mixtures. By changing the mixing ratio, polymer adsorption and the accompanying force vs distance profiles could be measured as a function of a broad range of effective solvent qualities. With PS on the surfaces, the forces at long range were always attractive independent of the solvent quality. The results point out that the forces at large surface separations are dominated by purely polymeric interactions originating from the dilute periphery of the adsorbed layers. These probably involve polymer bridging. For the bare mica surfaces there is clear evidence that below a surface separation of 5 nm, the surface-induced attraction becomes anomalously strong, leading to a stronger adhesion than expected from Lifshitz theory. A similar phenomenon may exist between polymer-bearing surfaces. As a consequence the force of adhesion becomes a function of the amount of adsorbed polymer, the solvent quality, and the surface separation at which the minimum in the force law is located. These three factors are not independent of each other, and the adhesion can be partly or totally the result of either the van der Waals attraction or the polymer bridging or the negative free energy of mixing between the interacting polymer layers. It is proposed that the sometimes observed hysteresis in the force vs distance profiles can be explained through the kinetics of the formation of polymer bridges. Although a quantitative comparison of the results with existing theories may be complicated because of the expected preferential uptake of the better solvent toluene in the adsorbed layers, the observed features are the first to illustrate the delicate interplay between mica-induced forces and polymer-induced forces.

Introduction

The technological importance of polymeric stabilization in colloidal dispersions has created a strong experimental[1-11] and theoretical[12-15] interest in the basic principles governing polymer adsorption on and polymeric interactions between interfaces. It is well-known that polymer adsorption profoundly modifies interparticle interactions.[16,17] An important application of this fact is encountered in nonpolar solvents. Due to the virtual absence of electrostatic interactions in those solvents, the adsorption or grafting of a polymer onto the surface of the particles is the only effective way to establish dispersion stability and prevent flocculation caused by the attractive van der Waals forces.

On the other hand, in paint, food, and ink technology there are applications for dispersions that are "weakly" flocculated. In these cases, the presence of an attractive interparticle interaction leads to weak particle associations that can easily be disrupted. Although such systems are usually the outcome of a complicated chemical engineering recipe, they can often be at least partly understood as dispersions in which the particles are stabilized by adsorbed or grafted polymer and suspended in a medium of moderately poor thermodynamic quality toward the stabilizing polymer. Attractive interactions between the polymers will always exist when the solvent is a worse than Θ solvent for that particular polymer. Napper[18] has formulated the general rule that the onset of dispersion flocculation coincides with the creation of Θ conditions in the solvent medium. (Exceptions to this are encountered when either the polymeric stabilizers are very short or when the particles become very small.) This proves that the solvent quality dependence of interactions between polymers in solution remains very similar when these polymers are attached to an interface, even though the chain conformations will generally be rather different.

In many cases it is the strength of the adhesion between aggregated particles that is of paramount importance. It is expected that the adhesion force between two polymer covered surfaces is a function of both the interparticle van der Waals force and the mutual polymeric interactions between the particle surfaces, both being dependent on the particle separation. The polymeric (or steric) interaction between surfaces is complex and is influenced by parameters such as solvent quality, polymer–substrate interaction energies, and polymer molecular weight. Scheutjens and Fleer[15] have recently incorporated all these parameters in an advanced lattice theory capable of predicting both polymer adsorption and polymeric interactions between surfaces. The van der Waals force is usually predicted on the basis of continuum Lifshitz theory[19-21] which has proven to work reasonably well for surface separations much larger than the dimensions of the mediating solvent molecules.[22,23] However, direct force measurements between molecularly smooth mica surfaces in organic solvents have recently revealed[22] that at surface separations comparable to a few times the size of a solvent molecule, the theory breaks down presumably through the inadequacy of the continuum approach under those circumstances.

In the literature several direct measurements of polymeric forces have been reported using a variety of techniques such as bulk compression experiments on stabilized lattices,[2,3] equilibrium thickness measurements of draining aqueous films in the presence of water-soluble polymers,[1] and, more recently, direct force measurements as a function of the distance between two polymer-bearing surfaces.[5-11] The latter measurements, mainly carried out by Klein and his co-workers, have greatly enhanced our understanding of polymeric interactions. However, these experiments have not specifically focused on polymer adsorption and polymeric interaction as a function of a broad range of solvent qualities or as a function of the segment–surface adsorption affinity. They were usually confined to a narrow range of temperatures around the Θ temperature in single solvent systems. Moreover, in their experiments the possible effect of the van der Waals forces originating from the mica surfaces on the observed adhesion has not been addressed. Although these are indeed not relevant when the polymer adsorption is high, they remain of paramount importance when the adsorbed amount is very low, as will be demonstrated in this paper.

The present study uses the direct force measurement technique developed by Israelachvili to address the problem of the forces between polymer-covered surfaces under a variety of conditions. Polystyrene (PS) $M_w = 300\,000$ was adsorbed on mica from toluene–heptane mixtures. Since toluene is a good solvent for PS and heptane is a nonsolvent (effective Θ composition in dilute solutions at 22 °C is about a 50/50 mixture), the mixing of those solvents allows the polymer adsorption and resultant surface forces to be studied as a function of a quite broad range of solvent qualities. Because of expected solvent partitioning in the adsorbed layers, together with a possible preferential adsorption of solvents on the mica, the solvent composition near the surfaces is probably different than in the bulk. Whereas on the one hand this is a complicating factor, on the other hand it reflects the situation in many systems of practical interest where one often deals with multicomponent solutions. By directly measuring the force of adhesion as a function of the adsorbed amount of polymer and then comparing with the force of adhesion between the polymer free surfaces, we have obtained direct information about the relative importance of the van der Waals forces at short surface separations. At the same time this procedure accounts for surface force modifications as a result of a possible preferential solvent adsorption to the bare mica surface.

In a parallel study (see following paper) the surface forces were furthermore studied as a function of the effective polymer–substrate interaction energy at (roughly) constant solvent quality.

Experimental Section

Polystyrene ($M_w = 300\,000$; $M_w/M_n = 1.06$) was obtained from Pressure Chem. Co. and purified by repeated precipitations from THF into methanol. Toluene and heptane 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.

Force measurements were made by using the apparatus developed by Israelachvili and constructed by Anutech Pty. Ltd. at the Australian National University in Canberra. This apparatus permits an accurate determination of both attractive and repulsive surface forces $F(D)$ as a function of the surface separation D. Prior to an experiment, two molecularly smooth mica sheets were cleaved from the crystal, silvered on one side with a 480-Å thick silver layer, and then glued (using a 50/50 anhydrous glucose–galactose mixture as the glue) on cylindrically curved glass disk that were mounted in the apparatus in a crossed cylinder configuration. The forces are determined by measuring the deflection of a spring on which one of the glass disks is mounted while the surface separations are measured with a resolution of 0.2 nm by using an optical interferometry technique. Details of these procedures have been described before.[24,25]

At the beginning of each experiment, the mica surfaces were brought into contact in an atmosphere of dry nitrogen, and this contact position, as measured by the interferometry technique, was then defined as $D = 0$. After the surfaces were separated, they were immersed in toluene and the force vs distance profile was measured. Subsequently, a concentrated PS solution in toluene was injected into the apparatus until a final polymer concentration of 10 μg/mL was reached. The mica surfaces were held widely separated and allowed to incubate in this solution for several hours. The solvent composition was changed by mixing the toluene stepwise with progressively larger volumes of heptane (thereby either keeping the PS concentration constant or completely removing it) until eventually pure heptane was present in the apparatus with all PS removed. After each step sufficient time was allowed for the mica surfaces to saturate with PS. Equilibrium adsorption was presumed to be established when no further changes with time could be detected in the surface force vs distance profile. All measurements were carried out at 22 °C. The reproducibility of the experimental results was guarded by repeating all experiments at least twice and usually more times.

The measured forces $F(D)$ are scaled with the mean radius of curvature R of the cylindrically curved surfaces. According to the Deryaguin approximation,[26] the ratio $F(D)/2\pi R$ is equal to the surface interaction energy $E(D)$ per unit area between two flat surfaces at a separation D. This equality is subject to the condition that the radius of curvature is much larger than the distance range over which interactions are measured. Since the typical radius of curvature was always between 1 and 2 cm and the interactions always had a distance range less than 30 nm, this condition is more than satisfied.

Results

Forces in Polymer-Free Solvents. Figure 1 gives the forces measured in pure toluene (Figure 1A), a 25/75 heptane–toluene mixture (Figure 1B), and a 50/50 heptane–toluene mixture (Figure 1C). At large separations (>6 nm), only attractive van der Waals forces are expe-

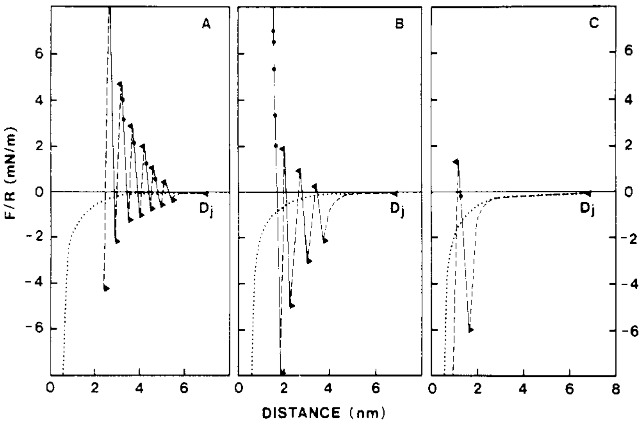

Figure 1. (A) Forces $F(D)/R$ as a function of the distance between two molecularly smooth mica surfaces in pure toluene. The dashed portions of the curve are experimentally inaccessible. The dotted line represents the theoretically predicted van der Waals force according to eq 1 using a Hamaker constant $A = 1.3 \times 10^{-20}$ J. Inward and outward jumps are denoted by "<" and ">" symbols, respectively. (B) Analogous to (A) but the toluene has been replaced with a 25/75 heptane–toluene mixture. (C) Analogous to (A) but the toluene has been replaced with a 50/50 heptane–toluene mixture. Most experimental points have been omitted for reasons of clarity.

rienced, but at shorter range it can be seen that the forces begin to oscillate with distance.

Since one of the mica surfaces is mounted on the end of a leaf spring, the system is mechanically unstable in regions where the slope $\partial(F(D)/\mathrm{R})/\partial D > K/R$. In the present experiments, the spring constant K was about 1.7×10^2 N/m, and the radius of surface curvature usually between 1 and 2 cm. Thus, because of the attractive forces, the surfaces jump inward from the positions D_j and come to rest at the surface separation where the force begins to oscillate with distance. The positions of D_j (generally between 6 and 7 nm, dependent on the value of K/R) are useful to evaluate the magnitude of the van der Waals attraction at long range. The (nonretarded) van der Waals interaction can be described with the Hamaker equation

$$E_{VdW}(D) = -\frac{A}{12\pi D^2} \tag{1}$$

where A is the (nonretarded) Hamaker constant. It is easy to show that a mechanical instability will occur at a distance D_j where

$$D_j = (AR/3K)^{1/3} \tag{2}$$

From the measured separations D_j in Figure 1, we typically obtain values $A = (0.7\text{–}0.9) \times 10^{-20}$ J. These are smaller than the expected nonretarded Hamaker constants calculated from Lifshitz theory, $A = 1.3 \times 10^{-20}$ J (heptane) and $A = 1.4 \times 10^{-20}$ J (toluene), which can be inferred from dielectric data obtained by extrapolation of refractive index measurements in the visible region.[19] However, the discrepancy can at least partly be removed when retardation is taken into account as this is known to reduce the magnitude of the van der Waals force. We will not further elaborate on this matter but merely state that in the present experiments the measured van der Waals forces at long range are roughly of the theoretically expected magnitude.

The period of the force oscillations at shorter range is about 0.5 nm. This is very close to the molecular diameter of the solvent molecules, and, in keeping with explanations given by other workers,[27] it is believed that the oscillations are related to the layering of solvent molecules near the surfaces giving rise to a solvation force. The decrease of the amplitude of the oscillations at large separations reflects the transition from an ordered structure near the surface to a random structure in the bulk of the solvent.

Christenson[27] has established that the distance range of the oscillations increases with the rigidity of the solvent molecules. Toluene is a rigid molecule, and it is seen from Figure 1A that the oscillations extend outward to about 5.5 nm. A very flexible molecule such as octane has been shown[27] to cause oscillations only below 2 nm and can be considered comparable to the heptane used in the study. Indeed, Figure 1 shows that the range and amplitude peaks of the oscillations decrease as more heptane is added, and Figure 1C is already similar to the data reported by Christenson[27] for pure octane. The flexible heptane molecules will certainly decrease the rigid ordering of the fluid close to the mica surfaces, but, in this case, the different packing parameters of toluene and heptane will also prohibit a molecular packing in well-defined layers near the surfaces.

The reduction in range and amplitude of the solvation forces with increasing volume fractions of a second solvent molecule is reminiscent of the behavior of solvation forces in nonpolar liquids on the addition of trace amounts of water:[27,28] Minute amounts of water were found to drastically reduce the range of solvation forces between surfaces. In the present experiments, the water content of the solvents was always less than 20 ppm and the data were reproducible. The authors do note, however, that when the surfaces were left in the solvents for many hours, a decrease in the height of the force barriers was observed. This may well be caused by small water concentration differences. It is likely that water molecules diffuse to the polar mica surfaces and preferentially adsorb, thereby reducing the molecular order near the surfaces. A reduced range of solvation forces in other miscible binary mixtures of nonpolar solvents has previously also been reported by Christenson.[29]

When Figure 1A is compared with Figure 1C, it is noted that the depth of the minima in the oscillations remained largely unchanged when heptane was added. Since it is the depth of these minima that is responsible for the surface adhesion, it is interesting to compare them with the theoretically expected magnitude of the van der Waals forces at short range. With the theoretical Hamaker constant $A = 1.3 \times 10^{-20}$ J, the full nonretarded van der Waals interaction has been drawn in Figure 1 as a dotted curve. It is clear that in the region where oscillations exist, the minima are deeper than the predicted attraction by almost an order of magnitude. This matter has been recognized before in other solvents[27] and points to the existence of anomalously high adhesion forces. The origin of the discrepancy is probably related to the breakdown of continuum Lifshitz theory at these short distances where the finite size of molecules plays a role. These effects are apparently less important beyond $D = 6$ nm where the van der Waals attraction is predicted much better.

Polystyrene Adsorption and Interactions in Heptane–Toluene Mixtures. When the mica surfaces were exposed to a 10 μg/mL solution of polystyrene in pure toluene, the PS did not adsorb and the surface forces remained similar to those shown in Figure 1A. A polymer segment will only adsorb when it has a higher affinity to the surface than the solvent: The differential adsorption free energy between a solvent–surface contact and a segment–surface contact (usually expressed through the parameter χ_s) must exceed a certain minimum value in order to compensate for the entropy loss of the polymer chain

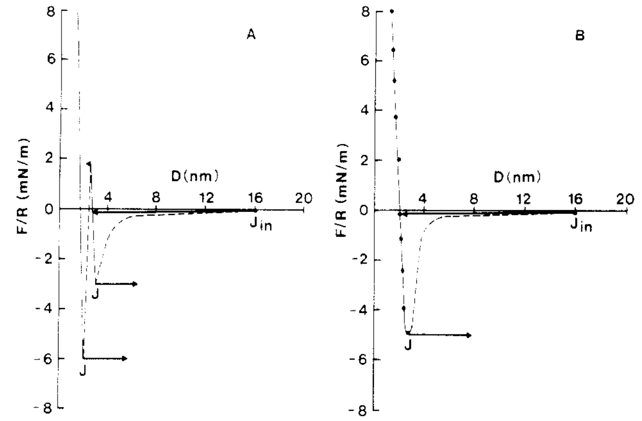

Figure 2. Force vs distance profile after equilibrium adsorption has been established from a 10 μg/mL PS (M_W = 300 000) solution in a 25/75 heptane–toluene mixture (A) or a 40/60 heptane–toluene mixture (B). J_{in} denotes an inward jump in the direction indicated by the inward arrow. The outward arrows denote outward jumps from an adhesive minimum. The dashed parts of the curves are experimentally inaccessible. For clarity, most experimental points have been omitted, but the forces were excellently reproducible in different experiments.

when it adsorbs.[15] Since toluene molecules are very similar to PS segments, it is not surprising that this condition is not met.

Heptane makes the solvent quality worse, and for dilute solutions, effective Θ conditions are attained in a 47/53 toluene–heptane mixture.[30] Figure 2A shows the force–distance curve that was measured after the heptane volume fraction was adjusted to 25% and the PS adsorption allowed to come to equilibrium. Comparison with Figure 1 shows that the attraction is of much longer range and a (slow) inward jump occurred from D = 16 nm (J_{in}). One oscillation in the surface force could be detected before a steep repulsion was encountered at D = 0.9 nm. Below D = 3 nm, the observed force is probably the result of both a polymeric interaction and a solvation force, but the very short range of the repulsion is evidence for very limited polymer adsorption. Given that the 25/75 heptane–toluene mixture is a better than Θ solvent, we do not expect attractive interactions to exist between polymer chains and the observed extra attraction at long range can therefore only be due to polymer bridging between the mica surfaces. This is reinforced by the observation that when the 25/75 mixture is replaced with a 50/50 mixture and immediately thereafter the surface forces are measured (thus without allowing further PS adsorption to occur), the position of J_{in} moved abruptly inward to D = 12 nm. The decrease in the solvent quality can be expected to limit the extension of the adsorbed chains from the surface, and this is consistent with a smaller separation of the surfaces below which polymer bridging can become effective.

Figure 2B gives the surface force after equilibrium PS adsorption had been established from a 40/60 heptane–toluene mixture. No oscillations in the surface force could be detected, and the forces were reversible both on surface approach and surface withdrawal without hysteresis. Polymer bridging was again observed below D = 16 nm. It should be noted in Figure 2 that the depth of the minima in the force vs distance profiles is very similar to those shown in Figure 1 at the same surface separation. Apparently, the extra bridging contribution to the adhesive forces is still relatively weak.

Figure 3 shows the forces measured in a 50/50 heptane–toluene mixture after PS adsorption (10 μg/mL concentration) had proceeded for $1^1/_2$ (Figure 3A) and 16 h (Figure 3B). The force profile is seen to be "farther out" in Figure 3B than in Figure 3A and indicates an increase in polymer adsorption with time. After 16 h (Figure 3B) the adsorption had come to an equilibrium and the force profile no longer changed with time. Also the positions J_{in} have now moved further away from the mica surfaces, and a slow inward jump occurred which took about 8 s to complete. Klein[5] has suggested that the slow surface motion is due to the restricted drainage of solvent from between the surfaces through the presence of polymeric material. Because the solvent quality is still better than that of a Θ solvent (although only slightly), it must again be polymer bridging that is responsible for the long-range attraction. Clearly, the distance range of the bridging attraction is enhanced by the presence of more polymer on the surfaces even though increased adsorption leads to a higher density of polymer (train) segments in actual contact with the surface, a factor which reduces the available surface area on which polymer segments from the opposite surface can adsorb.

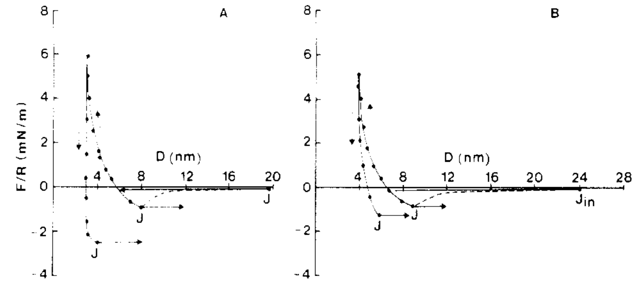

Figure 3. Force vs distance profiles after PS adsorption on mica from a 50/50 heptane–toluene mixture (10 μg/mL PS) has proceeded for $1^1/_2$ h (A) or 16 h (B). The latter profile is the equilibrium profile. In both cases, the forces are hysteretic during a compression–decompression cycle. A shallow adhesive minimum of −0.8 mN/m is measured when after an inward jump the surfaces are separated without first compressing the adsorbed layers. A deeper minimum closer inward is measured when the adsorbed layers are first compressed and then decompressed. Symbols have the same meaning as in Figure 2. Reproducibility between different experiments was excellent.

At shorter range, the surface force goes through a minimum before becoming monotonically repulsive. This minimum is located at D = 8 nm (Figure 3A) or 9 nm (Figure 3B) where the van der Waals attraction is very weak (cf. Figure 1), and we expect its location to be the result of a trade-off between attraction through polymer bridging and repulsion from osmotic and excluded volume interactions at shorter range.

The forces on approach and withdrawal of the surfaces are not reversible. The hysteresis results in a larger adhesion force after the adsorbed layers have been compressed but the extent of hysteresis decreases with increasing polymer adsorption. Possible reasons for this will be outlined in the Discussion and Summary. No evidence of polymer desorption during compression was found. After the surfaces were withdrawn and we waited for a few minutes, the previously measured forces were exactly reproducible.

The 10 μg/mL PS solution in a 50/50 heptane–toluene mixture of Figure 3B was then completely replaced by a polymer free 67/33 heptane–toluene mixture, and this in turn was replaced by pure heptane. The forces measured immediately after each solvent change are given in Figure 4A, curves 1 and 2, respectively. The force vs distance profiles essentially remained unchanged for several hours after the solvent change had taken place, and we conclude that the same amount of adsorbed polymer must be present as in Figure 3B. Due to the excess of heptane, the effective solvent quality is now well below Θ conditions.

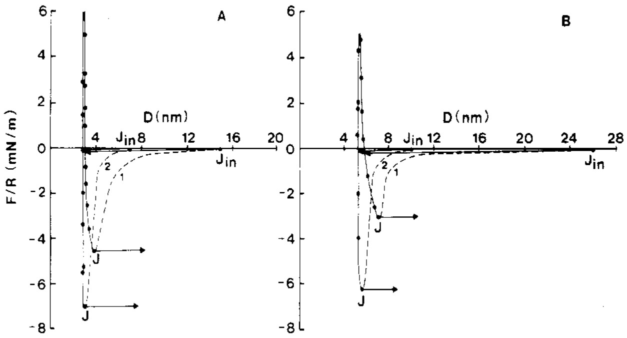

Figure 4. (A) Resulting force vs distance profile after the 50/50 heptane–toluene mixture in Figure 3B is replaced with a 67/33 heptane–toluene mixture (curve 1) or pure heptane (curve 2), leaving the amount of adsorbed PS the same as in Figure 3B. (B) Force vs distance profile after PS adsorption has proceeded from a phase-separated 3 μg/mL PS solution in a 67/33 heptane–toluene mixture for 16 h (curve 1). Curve 2 resulted when this mixture was replaced with pure heptane. Symbols have the same meaning as in Figure 2. All forces were reversible during a compression–decompression cycle. Similar as in Figures 1–3, only a few representative experimental runs have been presented.

This caused the distance range of the long-range attraction to decrease from 24 nm in a 50/50 heptane–toluene mixture (Figure 3B) to 15 nm in a 67/33 solvent mixture in curve 1 and 7 nm in pure heptane (curve 2). The inward jump was also much faster in the poorer solvents (<1 s). At D = 3 nm the force is steeply repulsive. These observations are consistent with there being a much less expanded, largely incompressible polymer layer on the surface. From Figure 4A it is furthermore clear that the adhesion force increases as the solvent quality decreases.

The optical interferometry technique that is used to measure D also permits measurement of the mean refractive index between the surfaces and hence can be used to estimate the amount of adsorbed polymer. In heptane (curve 2) a refractive index $n = 1.52 \pm 0.02$ was measured at D = 3.0 nm. One may compare this with the bulk refractive index of PS (n = 1.59), heptane (n = 1.388), and toluene (n = 1.496). Unfortunately, the experimental error in the refractive index measurements, together with the likely presence of some remaining toluene in the adsorbed layer, makes an accurate determination of the adsorbed amount impossible, but we estimate that the adsorbed amount is somewhat less than 1 mg/m^2 on each surface (volume fraction $\phi \simeq$ 0.5–0.7). The measurement in any case shows that there is a considerable amount of solvent in the adsorbed layer, similar to the swelling of a phase-separated polymer phase with solvent.

The adsorption of PS was then allowed to proceed for 16 h from a phase-separated PS solution (3 μg/mL) in a 67/33 heptane–toluene mixture, and the subsequent force measurements are given in Figure 4B, curve 1. Curve 2 results when the solvent is replaced by (polymer-free) pure heptane. From the distance range of the forces, it is clear that the amount of adsorbed PS has increased. From refractive index measurements, we inferred that about 1.7 $\pm$ 0.3 mg/m^2 PS has adsorbed. Again, this value only gives an upper estimate because small residues of toluene in the adsorbed layer would increase the refractive index, but we estimate that the adsorbed amount is now at least of the order of 1 mg/m^2. It is seen that the adsorption increase not only affects the short-range repulsion but also the extension of the adsorbed layers. The latter has shifted the onset of attraction out to D = 26 nm (J_{in}) from which distance a fast inward jump occurred. Replacement of the solvent with pure heptane reduced this extension and caused the position of J_{in} to move inward to D = 10 nm. In contrast with the data measured in 50/50 heptane–toluene (Figure 3), the forces in Figure 4 showed no hysteresis. When the PS bulk concentration is raised to 40 μg/mL, the adsorption increased much more rapidly, but this also appeared to make the adsorbed layer inhomogeneous in thickness and/or density as visualized by the interferometry technique which detects refractive index differences laterally across the surfaces. This is presumably the result of an adsorption of large polymer aggregates from solution. We did not elaborate on these phenomena but note that in a phase-separated system the adsorption is in principle never at equilibrium and can continuously increase because the surface acts as a nucleus for phase separation. However, judging from the fringe spectrogram and the obtained surface forces, the occurrence of adsorption of large polymer flocs was not apparent at a PS concentration of only 3 μg/mL and the obtained results in Figure 4B were excellently reproducible in different experiments.

A comparison between parts A and B of Figure 4 reveals that the adhesion forces measured in both heptane and a 67/33 heptane–toluene mixture decrease as the PS adsorption increases.

Discussion and Summary

Surface forces have been measured in heptane–toluene mixtures both with and without polymer on the mica surfaces. In the absence of polymer the force at long range is always attractive due to the van der Waals forces. At shorter range, below 5 nm, an oscillatory solvation force is found in toluene. The range of this force becomes less as heptane is added to the toluene. In this distance regime, the adhesion forces are much stronger than expected from continuum theory, presumably because the conventional approach to treat a solvent as a structureless medium breaks down at these short separations.

When the mixing ratio of a heptane–toluene mixture is less than 53/47, the solvent is a better than Θ solvent for PS. The amount of PS adsorbed on mica remains very limited and only clearly increases when the solvent quality is very close to Θ conditions. Adsorbed PS segments replace the ordered solvent molecules near the surfaces, and the oscillating solvation force is replaced by a polymeric interaction force. In these solvents, the forces at long range remain attractive due to polymer bridging and extend much farther than the van der Waals forces. This range is decreased by merely raising the heptane volume fraction but is increased when more PS is allowed to adsorb. At very small levels of PS adsorption, the forces at short range remain to some extent dominated by the solvation forces. The force of adhesion is then approximately the same as the adhesion forces between polymer-free surfaces. It is therefore concluded that under these conditions the forces at long range are dominated by polymeric interactions whereas the van der Waals forces remain chiefly responsible for the adhesion interaction.

In Figure 3 where the solvent has only a slightly better quality than a Θ solvent, the adsorption has increased. Here, the adhesion at D = 8 nm (Figure 3A) or D = 9 nm (Figure 3B) should be only the result of polymer bridging because at those distances, the van der Waals attraction is negligible (cf. Figure 1). With the value for the unperturbed radius of gyration of PS (M_w = 300 000) $R_g \simeq$ 15 nm,[30] we note that provided an equilibrium amount of PS has adsorbed, the attractive interactions commence at $D \simeq 1.6R_g$. The latter value is very close to $D \simeq 1.7R_g$ found by Almog and Klein[9] in PS solutions in cyclopentane under slightly better than Θ conditions, even though their equilibrium adsorbed amounts were clearly higher.

It may well be questioned whether the effective solvent quality near the surfaces in the adsorbed layers is the same as in the bulk solution. PS segments will have the tendency to surround themselves with toluene molecules, thereby causing a preferential uptake of toluene in the adsorbed layer. However, we recall that this effect has implicitly been accounted for in the bulk solution by determining an effective solvent quality. From data compiled by Napper,[18] it has become clear that the coagulation of dispersions stabilized by high molecular weight polymers through the addition of nonsolvent essentially parallels the establishment of effective Θ conditions for polymers in solution. The same was found when coagulation was established through temperature variation. Hence we conclude that there is no evidence which suggests that the local (i.e., effective) solvent quality (at least in the periphery of the adsorbed layers) is any different from that in the bulk solution. The situation becomes more complicated again when the adsorbed layers are compressed; however, the problem of a concentration-dependent effective solvent quality exists then equally well for single solvent systems.[18] Apart from this, the precise thermodynamic state in the gap between two surfaces is in any case extremely delicate and still rather controversial.[5,8,15,33]

The observation of hysteresis in Figure 3 which decreases with increasing adsorption deserves a discussion since it was not found in Figure 4 and also not in other reported studies[8,9] on PS-covered mica surfaces near Θ conditions. However, in the latter studies the adsorbed amount was higher than in Figure 3. Therefore, it seems logical to involve polymer bridging in the occurrence of hysteresis. It is well established[15] that the extent of polymer bridging decreases when an increased amount of polymer adsorbs, reaching zero when the surfaces become saturated. Moreover, polymer bridging increases when the adsorbed layers are compressed.[15] Taking these factors into consideration, hysteresis may well at least partly be related to the amount of time that is allowed to pass during a compression–decompression cycle (typically a few minutes); i.e., when the typical relaxation time of polymer bridges is clearly longer than the time scale used in our experiments, the bridging increase during compression would not immediately decrease on surface decompression and as such explain the hysteresis. Especially in Figure 3A, the adhesion found on decompressing the adsorbed layers is likely to also have a contribution from the van der Waals forces that cannot be ignored below $D = 4$ nm (cf. Figure 1). Whereas a similar phenomenon can be present in Figure 4, the (hysteretic) polymer bridging attraction may there have been overshadowed by the negative free energy of mixing and the van der Waals attraction. The kinetics of bridge formation has recently received some theoretical attention.[31]

In worse than Θ solvents (Figure 4B), the adsorption increases further. The forces at long range remain attractive but now originate from both polymer bridging and the negative free energy of mixing between the opposing polymer layers. From the force vs distance profiles in solvents with decreasing quality, it is evident that the adsorbed layers become thicker, lose their compressibility, and likely cover a larger fraction of the available surface area directly with train segments. It is expected that this will hinder and eventually, on reaching surface saturation, prohibit polymer bridging. If this is the case, it should lead to a decrease in attraction when an undersaturated adsorbed layer is allowed to thicken in the same solvent. It is indeed evident from Figure 4 that both in a 67/33 heptane–toluene mixture and in pure heptane, the force of adhesion decreases when adsorption increases. In a 67/33 mixture, the (reproducible) decrease of the adhesion following adsorption increase can be observed within one experiment and is therefore certainly not simply an artefact caused by experimental error. Unfortunately, this does as yet not provide conclusive evidence for a lesser extent of polymer bridging in Figure 4B as compared to Figure 4A. Between the bare mica surfaces (cf. Figure 1) in the region below 5 nm, we found that the surface-induced attractive forces were anomalously strong as compared to the theoretically predicted van der Waals forces. If the attractive forces measured in Figure 1 are subtracted from the adhesion forces found in curve 1 of parts A and B of Figure 4 (accounting for the differences in mica–mica separation), we come to a remaining attractive adhesion force in a 67/33 heptane–toluene mixture of about 3.0 mN/m in both cases. Provided this procedure is justified, the latter force should account for the polymeric contribution to the adhesion force. Similarly, in pure heptane (curve 2, Figure 4), the polymeric contribution is calculated to be 5.0 ± 1.0 mN/m and is independent of the adsorbed amount within experimental error. Nevertheless, it cannot strictly be excluded whether the differences in the adhesion in parts A and B of Figure 4 are not at least partly due to a decrease of the polymer bridging attraction as well, because we do not known whether the surfaces are fully saturated already. Figure 3 shows that the polymer bridging contribution to the adhesion force is about 0.8 mN/m. Since the latter contribution should in any case become less in worse than Θ solvents because of the increased coverage of the surfaces with train segments, it can thus be concluded that in Figure 4 the main contributor to the adhesion is the negative free energy of polymer mixing with a smaller contribution in Figure 4A from the van der Waals attraction and/or the bridging attraction. Strictly there is only unambiguous evidence for anomalously strong van der Waals forces in the case of pure liquids but from the present results, it can certainly not be excluded that the same phenomenon exists equally well between polymer-bearing surfaces.

All the force vs distance profiles presented in this work reflect the importance of the dilute periphery of the adsorbed layer in determining the onset of the surface forces. Using a lattice theory, Scheutjens et al.[15,32] have recently predicted that the outer part of the adsorbed layer consists mainly of the tails of the adsorbed chains. Tails have been ignored in previous polymer adsorption theories, but, as Scheutjens and Fleer pointed out, they govern the polymeric interactions at long range. A rigorous analysis of our data awaits a comparison with their (numerical)theoretical predictions. Similar force vs distance profiles as those in Figure 4 have also theoretically been predicted by Ingersent et al.[33]

From theory,[15] it is well-known that the differential adsorption affinity parameter χ_s together with the solvent quality parameter χ are determinants of the adsorbed amounts. By changing the heptane–toluene mixing ratio, we obviously change the effective solvent quality but most likely also the segment–surface binding affinity because of the change in solvent composition near the surface. However, it is difficult to say whether the latter change is substantial in terms of binding energies. We note that since the adsorption of nonpolar PS segments always occurs from a nonpolar solvent, the interaction of segments and solvent molecules should mainly be governed by nonspecific dispersion interactions. In this respect it is useful to compare the results in Figure 3B with those previously reported by Israelachvili et al.,[8] who studied PS adsorption from cyclohexane just above the Θ temperature and those of Almog and Klein[9] where PS was adsorbed on mica from cyclopentane under slightly better than Θ conditions. Overall, the evidence emerges that in those studies the equilibrium adsorbed amount was higher than in Figure 3B, thereby suggesting that under very similar solvency conditions a smaller segment–surface binding affinity exists in Figure 3B. Because of the similarity of toluene to the PS segments, toluene apparently acts as a displacer of PS segments from the surface and lowers the effective χ_s. Indeed, when pure toluene is present, PS adsorption is completely prohibited. We therefore expect the strongest segment adsorption affinity to exist in pure heptane. We note, however, that very small additions of toluene to heptane do not appreciably affect the force vs distance profiles measured in heptane in contrast with what happens when small amounts of acetone are added (see following paper). Thus we conclude that although some variation of χ_s must occur when the solvent mixing ratio is varied, the dominating influence on the level of PS adsorption and the resulting surface force profiles in Figures 2–4 comes from the change in the solvent quality. This is in particular the case in Figures 3B and 4A where the adsorbed amount is held constant.

Finally, these experiments show that conformational changes in the adsorbed layers respond very quickly to a sudden change in the solvent quality through the addition of heptane to toluene. Time-dependent rearrangement phenomena could not be detected once mixing of the solvents was established, and it is therefore believed that the measured forces are equilibrium forces related to a fixed amount of adsorbed polymer.

Registry No. PS, 9003-53-6.

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