(about 40 nm) and small size (about 10 nm). The particle size in *o*-xylene was about 20 nm, while that in *p*-xylene was about 75 nm. In valeric acid, dimethyl sulfoxide, and caproic acid, relatively larger palladium particles were obtained in the range 60~100 nm. Thus, the fact that relatively larger particles are prepared in organic solvents whose boiling points are much higher than that of methyl isobutyl ketone indicates the nucleation of palladium seems not to proceed rapidly, but the nuclear growth occurs in an organic solvent with a higher boiling point, resulting in a larger particle size of palladium.

Since very stable palladium particles were obtained in methyl isobutyl ketone, the effect of concentration of Pd(acac)$_2$ on the particle size of palladium was studied in methyl isobutyl ketone where the concentration of Pd(acac)$_2$ was between 0.1 and 1.0 mmol dm^{-3}. Figure 2 shows that the average diameter of palladium is nearly independent of the concentration of Pd(acac)$_2$ and ranges between 8 and 10 nm. The effect of refluxing time on the particle size of palladium was also studied. Figure 3a shows that the average diameter of palladium is almost constant in all the refluxing times studied. Further, Figure 3b shows that the absorbance of palladium particles in methyl isobutyl ketone increases with an increase of the refluxing time, suggesting that the number of palladium particles increases since the particle diameter is almost constant over a whole refluxing time.

It is concluded from the above results that the thermal decomposition of Pd(acac)$_2$ in methyl isobutyl ketone gives relatively monodispersed palladium particles whose stability is considerably high. The particle diameter ranges between 8 and 10 nm. Further, it is also expected that many organo precious metal particles can be prepared in organic solvents from decomposition of their corresponding organic complexes.

Registry No. MIBK, 108-10-1; Pd, 7440-05-3; Pd(acac)$_2$, 14024-61-4.

Influence of Solvent Quality on Surface Forces between Polystyrene Layers Adsorbed onto Mica

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Force–distance profiles were strikingly sensitive to small differences in temperature and solvent composition. Surfaces forces were measured at 18 and 28 °C between mica surfaces bearing polystyrene (M_w = 490 000 g·mol^{-1}) adsorbed from dilute cyclopentane solution (Θ temperature T_Θ = 19.5 °C). Forces at long range were monotonically repulsive at 28 °C and mildly attractive at 18 °C provided that a cyclopentane containing 5% linear pentanes was used. This contrasts with experiments in 99% pure cyclopentane, in which the range of detectable forces was (2–3)R_G (unperturbed radius of gyration) at 18 °C and (5–6)R_G at 28 °C, and the forces at long range were strongly attractive at 18 °C and weakly attractive even at 28 °C. A change of sign of the long-range interactions between adsorbed homopolymers, over a small range of temperature, does not appear to have been reported previously.

Introduction

Interfaces between adsorbed polymer and polymer solution have been of recent interest. These zones of nonuniform concentration are far thicker than those characteristic of small molecules, and their physical behavior is believed in many respects to be uniquely owing to the presence of long chains.[1-4] It must be acknowledged that experiments seldom have been able to do justice to the elegant and detailed theoretical predictions. By the same token, it has been difficult to assess the restrictiveness of various theoretical assumptions.

Among recent theoretical predictions to be observed experimentally have been the force–distance profiles between adjoining layers of homopolymer adsorbed from dilute solutions.[5-9] At full equilibrium, forces at long range are expected to be zero or attractive—migration of polymer out of the zone of interaction would dissipate a momentary repulsion. Forces under a "restricted" equilibrium, i.e., a fixed quantity of polymer present, are believed to better represent usual practice. They can be attractive or repulsive at long range, depending on the strengths of osmotic and bridging interactions. Osmotic interactions are expected to be repulsive above the Θ temperature T_Θ and attractive below it, while interactions resulting from bridging of single chains between two surfaces are expected to be attractive regardless of solvent quality. In this argument, T_Θ is presumed to be the same near a surface as in unbounded solution.

Previous experimental investigations in the vicinity of T_Θ have concerned polystyrene (PS) adsorbed onto mica from cyclohexane[10-13] (T_Θ = 34.5 °C) and cyclopentane[14] (T_Θ = 19.5 °C) dilute solutions. In both liquids, forces have

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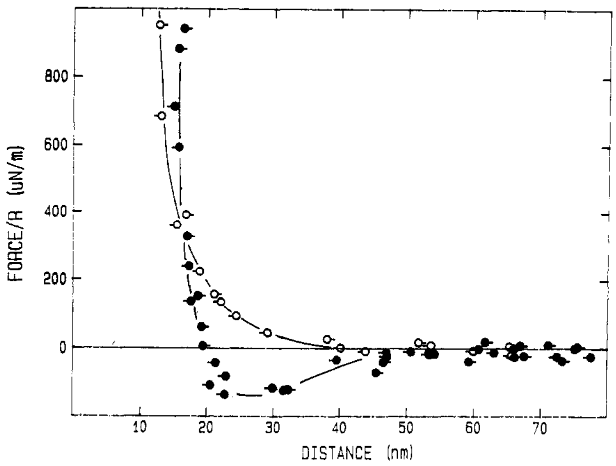

Figure 1. Force normalized by local radius of curvature of the mica surfaces, plotted against separation, for polystyrene adsorbed from liquid A as described in text. Two repeated runs at 18 °C are shown: pip left, compression; pip right, expansion; (○) 28 °C; (●) 18 °C.

developed at separations within about $(2\text{–}3)R_G$ (unperturbed radius of gyration) or even less if coverage of the surfaces by polymer was less than saturated.[12,14] In cyclohexane, forces were found to be attractive in the initial experiments at ca. 10 °C less than T_Θ.[10,11] Later, substantial attraction was observed to develop even at ca. 3 °C above T_Θ, and this was interpreted to suggest that bridging is a significant part of the total interaction on the time scale of this experiment.[12] However, other experiments in cyclopentane,[14] performed at ca. 3 °C above T_Θ in this system, found that long-range attraction during the early stages of adsorption evolved, with increasing mass of polymer adsorbed, to monotonic repulsion. This discrepancy in sign of forces in near-Θ solvents, at similar temperatures of corresponding states, motivated the present investigation.

Experimental Section

We have constructed a surface forces apparatus of Israelachvili type.[15] The experimental protocol was essentially as described previously.[10-15] Polystyrene (Polymer Laboratories) had M_w = 490 000 and $M_w/M_n < 1.08$. The unperturbed radius of gyration was calculated[16] to be R_G = 20 nm. The mica surfaces were incubated in PS solution (150 $\mu g \cdot mL^{-1}$) for at least 1 day at large separation, at the temperature of subsequent measurements, before measurements were begun. It was verified that force–distance profiles did not change after 1 day of incubation under these conditions. In the experiments reported below, temperature was well-controlled during each run but may have differed by ±0.5 °C between repeat runs. Experiments were performed in a room where the relative humidity was controlled to <20%.

Cyclopentane, the solvent in these experiments, was stored over type 4A molecular sieves and was freshly distilled before use. Two sources of cyclopentane were used: Aldrich reagent grade (95% cyclopentane by GLC, approximately 5% linear pentanes) and Eastman Kodak (99% cyclopentane by GLC). In the discussion below, these will be denoted as liquid A and liquid B, respectively. Linear pentanes are nonsolvents for PS and may be expected to raise T_Θ. Although we have not measured T_Θ for these liquids, we have measured the critical temperatures T_c for the solution concentration used in these experiments. The critical temperature T_c was 15.4 and <4 °C for liquids A and B, respectively. To confirm that this difference reflected the presence of linear pentanes, linear pentane was added to liquid B. When 5% *n*-pentane was added to a solution of PS in liquid B, its critical temperature rose from 4 to 15–16 °C.

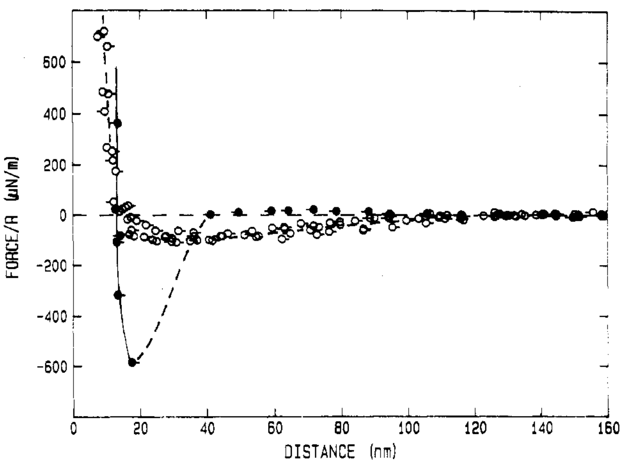

Figure 2. Force normalized by local radius of curvature of mica surfaces, plotted against separation, for polystyrene adsorbed from liquid B as described in text. Three repeated runs at 28 °C are shown. Symbols same as in Figure 1.

In measurements for mica immersed in polymer-free cyclopentane, we observed no detectable interaction at separations larger than 2–3 nm. At lesser separations, the oscillatory structural forces characteristic of dry liquids[17] appeared. Such forces have been studied in detail.[17] In our experiments, their presence served as a qualitative check, before adding polymer solution, that the mica surfaces were clean.

Results and Discussion

Figure 1 shows force–distance profiles between mica covered by PS adsorbed from liquid A. Force, normalized by the local mean radius of curvature of the surfaces, is plotted against separation of the mica. The force profile at 28 °C is monotonically repulsive starting at approximately 40 nm. This is in qualitative agreement with previous findings at 23 °C obtained by using a PS of similar molecular weight[14] but apparently different purity.[18] Note that at 18 °C the sign of the interaction at long range *switches* to a weak attraction developing at approximately the same separation. Although weak, the attraction is clearly larger than the experimental uncertainty. Such a change in the sign of long-range forces, over a small range of temperature, has been observed for layers of poly(vinylpyridine)–polystyrene diblock copolymers under conditions where bridging was believed to be severely impeded.[19] It has not been reported previously for adsorbed homopolymer.

The corresponding measurements for PS adsorbed from liquid B are shown in Figure 2. Long-range forces at 28 °C are now weakly *attractive*, and their range has more than doubled. The range of forces, $(5\text{–}6)R_G$, is close to that observed for homopolymer in good solvent conditions (poly(ethylene oxide) in aqueous salt[20] and in toluene[21]

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(18) The reason why previous experiments with the polystyrene–cyclopentane system[14] gave results more akin to those measured in our liquid A than liquid B is not known. The previous work used spectroscopic grade cyclopentane, a grade which should be equivalent to our liquid B. J. Klein has noted (private communication) that the experiments may not be strictly comparable because in the previous work the cyclopentane was not dried, whereas experiments in the present work were performed in a room of low humidity using dried solvents. The possible presence of other impurity is under investigation.

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solutions); but in those experiments the forces were repulsive unless the mass adsorbed was restricted, and pronounced hysteresis was observed. Within the experimental uncertainty, hysteresis was not observed over the experimental time scale in the present experiments. (An equilibration time of 2–3 min was allowed between measurements in the region of separations where forces were observed.) The behavior at 28 °C in Figure 2 is thus a curious hybrid of behavior previously observed in good and poor solvent conditions.

However, measured at 18 °C in this liquid, classical behavior[10-13] is recovered. Attractive forces leading to a deep attractive well develop at 40 nm. At 17 nm, there is a pronounced minimum, and at 13 nm the onset of a steep repulsion. Gauging the mass adsorbed by the thickness of the layers in the region of strong repulsion and assuming the density of undiluted PS,[12] we estimate an adsorbed mass of 6 $\mathrm{mg\cdot m^{-2}}$ (an upper bound) from this thickness. The same estimate is not possible for the data at 28 °C since the zone of repulsion is slanted, but insofar as the thickness is appreciably less at 18 °C, the mass adsorbed appears to be less at the higher temperature.

We consider the main feature of the findings in liquid B to be that the range of interaction more than doubled upon raising the temperature by only 10 °C. The corresponding increase in the unperturbed radius of gyration for PS of this molecular weight in cyclopentane is only approximately 10%;[22] it cannot explain this increase in the range of interaction. Measurements of the ellipsometric thickness of PS layers adsorbed onto chrome plate from cyclohexane[23] have also shown an expansion factor over this temperature range of only approximately 10%.

Quantitative comparison with theory is not possible because of the sensitivity of predictions[5-9] to the mass adsorbed, a number that we are only able to estimate. However, such a gross increase in range of interaction at equilibrium does not appear to be consistent with well-known theory based on mean-field considerations.[7,8,24]

The degree to which this unexpected long-range attraction could reflect incomplete equilibration is difficult to assess. Recent scaling theory,[9] as well as previous theory,[7,8] predicts that coverage less than the coverage at thermodynamic equilibrium should result in attractive forces at large separation. An operational definition of whether equilibrium is attained in an actual experiment is a delicate matter, however. In adsorption in a different polymer system, direct measurements of the mass adsorbed showed that the achievement of steady-state mass adsorbed occurred on a logarithmic time scale stretching to very long times.[25] While it is true that the coverage in the present study appears to have been less at 28 °C than at 18 °C, which might promote bridging (see below), it is also true that (as discussed above) the data were taken after the forces measured appeared to have stabilized. At any rate, questions of equilibration should be common to all surface forces experiments on adsorbed homopolymer layers.[10-15,20,21] Note also that it is not clear why an effort to explain in these terms the attraction observed in liquid B at 28 °C should not also apply to liquid A, where it was not observed.

In the experiments in liquid B, why were attraction interactions observed at longer range at 28 °C than at 18 °C? It is true that 18 °C is close to T_Θ, where binary interactions are zero, but enhanced binary interactions above T_Θ should show up as an interaction of the opposite sign as that observed, i.e., as enhanced repulsion. It is reasonable to postulate, as has become traditional, that attraction at a temperature higher than T_Θ arises from bridging of chains between the solid surfaces. As yet there appears to exist no detailed molecular theory of the phenomenon of bridging. Physically, we picture that chains that are adsorbed to one surface adventitiously penetrate the opposing layer by Brownian diffusion, with the result that they come to adsorb to two solid surfaces at once. The resulting entropic attraction may be expected to reflect Brownian excursions of chains beyond their mean positions, although the mean thickness of two layers is only ca. $2R_G$, as discussed above. We conjecture that the increased range of interaction at 28 °C, relative to 18 °C, could in part be due to increased range in the *fluctuations* of each layer's concentration profile beyond the mean value. A mean field theory could describe such excursions poorly.

The experiments with polymer in 95% cyclopentane (Figure 1), showing repulsion rather than attraction at 28 °C, suggesting that in ternary solution such bridging is restricted. More systematic experiments to explore this phenomenon are in progress.

The striking experimental finding in this liquid A is attraction at 18 °C combined with repulsion at 28 °C, precisely the qualitative change which would be expected for osmotic interactions in a binary solution. The magnitude of the attraction (approximately 100 $\mu\mathrm{N\cdot m^{-1}}$) is even similar to that predicted by theories which do not explicitly bring bridging into the model.[5-9] In fact, as noted above, these experiments were performed in ternary solution (95% cyclopentane), not the binary solution of theoretical models.[5-9] Ternary solutions are poorly understood and are difficult to characterize even in the isotropic state.[26]

However, the present system is particularly simple considering that it is ternary. Linear and cyclic pentanes may be expected to mix quasi-ideally and to have similar surface interaction parameters,[7] but cyclopentane is the far better solvent for PS. One would expect that the better solvent tends to segregate within the adsorbed polymer layers, so that its concentration there should be higher than in the bulk solution. Although the physics of this situation is surely complex and must await more exhaustive experiments for its elucidation, the present experiments suggest that the surface forces technique may serve to study not only surface problems but also solvent segregation and polymer–polymer interactions in ternary solutions.

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Registry No. Polystyrene, 9003-53-6; cyclopentane, 287-92-3; pentane, 109-66-0.

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