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Direct measurement of intermolecular forces between a polymer layer and mica

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Attractive forces that can develop between two adsorbed layers of polymer on mica sheets immersed in solvent brought to separations within about $3 R_g$ (unperturbed radius of gyration of polymer) depend on the quality of the solvent for the adsorbed polymer and on the coverage of the mica surfaces by polymer.[1–6] Lower temperature and lower adsorbed amount promote attraction.[4–6] The former strengthens the attractive osmotic forces between polymer segments; the latter facilitates bridging (simultaneous adsorption on both surfaces by one polymer). It has been demonstrated[4,5] that attraction can develop even above the theta temperature T_θ for the polymer in the immersion solvent. Above T_θ, osmotic forces are repulsive, so bridging is the only available mechanism of attraction between adsorbed layers above T_θ.

Recently, theories have been advanced for the forces between polystyrene layers immersed in solvents near T_θ.[9,10] While the positions of onset of detectable forces, and of minima are reasonably well-predicted, the magnitudes of the forces are considerably underestimated. Understanding the respective contributions from osmotic interactions and from bridging may provide a route to theoretical improvements.

Here, we attempt to measure the bridging part. When an adsorbed monolayer of polymer is brought into contact with a *bare* mica sheet and the mica–mica separation compressed to within $1 R_g$, many of the polymers bridge the surfaces. We present data on the magnitude of the resulting adhesion and on the kinetics of its evolution.

The technique is essentially as described previously.[1–8,11,12] It enables measurement of force-separation $F(D)$ profiles between smooth, curved (radius of curvature $R \cong 1$ cm) mica surfaces with a precision of about 0.1 μN in F at the lowest values of force measured and about 0.2–0.3 nm in D. In these experiments, with polymer on one surface only, a departure was required from past practice[1–6] of simply submerging the two mica sheets simultaneously in polymer solution. The two clean, dry mica sheets were brought together

in the apparatus to determine that the surfaces were clean. One surface was then transferred out of the apparatus, incubated a sufficient time in a polymer solution (150 μg/mL) for saturated adsorbance, then transferred back into the apparatus. All cyclohexane used was thoroughly dried. Experience indicates that no permanent collapse of polymer layers occur under the circumstances of our experiment. Finally, the apparatus was reassembled and filled with pure cyclohexane (freshly distilled). The polymer we used is poly(α-methylstyrene) (PαMS) from Pressure Chemical Co. with $\bar{M}_w = 90\,300$, $\bar{M}_w/\bar{M}_n < 1.10$. The theta temperature for PαMS is nearly the same as that for PS in cyclohexane (34–35 °C).[13]

Figure 1(a) shows representative data for two identical PαMS layers brought together at 25 °C. The forces shown are those observed after equilibration, which required 5–10 s in regions where the force was small and up to several minutes where the force was appreciable. The data of Fig. 1(a) are very similar to the data on PS near T_θ.[4] The attractive minimum at 7.0 $\pm$ 0.3 nm is near R_g for this polymer[14] and the onset of detectable attraction is about $3 R_g$. Attraction persists above T_θ.[4] From refractive index measurements in the gap,[7,8,12] we estimate the adsorbed amount of PαMS as 3.0 $\pm$ 0.3 mg/m^2, similar to PS of similar molecular weight.[1,2,4] Similar too, is the magnitude of the attraction.[2]

The data of Fig. 1(a) are reversible on change from approach to separation and repeatable over periods of a few hours, provided the surfaces are not left in close contact. Figure 1(b) shows measurements after the layers of Fig. 1(a) were left in contact for 12 h under compression of about 1000 μN/m. The attractive minimum has moved inward from 7.0 $\pm$ 0.3 to 2.5 $\pm$ 0.3 nm and its depth has increased about 70%. This is evidence that the polymer layer has rearranged under compression. Some polymer has left the gap (supported by refractive index measurements) diminishing the range of the repulsion and enhancing the role of bridging. These observations are qualitatively similar to our previous
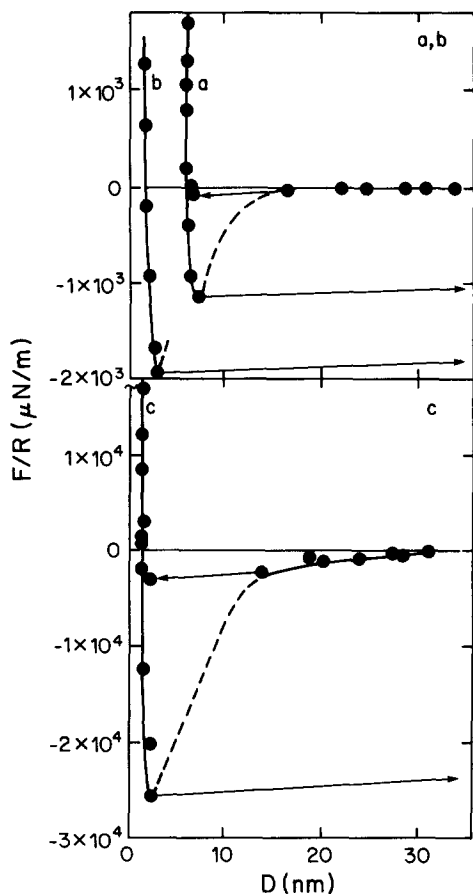
FIG. 1. Force-separation profiles between two curved mica surfaces immersed in cyclohexane at 25 ± 0.5 °C. The force scale is normalized as $F(D)/R$ to give the surface energy per unit area between flat parallel plates obeying the same force law, in the Derjaguin approximation (Ref. 15). (a) Each mica sheet bears 3 mg/m^2 of PαMS. (b) After leaving sheets of (a) in contact under approximately 1000 μN/m at an initial $D \cong 5.5$ nm for 12 h. (c) One mica sheet bearing 3 mg/m^2 of PαMS brought into contact with a bare mica sheet in pure cyclohexane. Adhesion measured after 2 min of contact at $D \cong 2.5$ nm. Arrows represent jumps that result from mechanical instability when $\partial F(D)/\partial D > K$. Slopes of the arrows drawn are K/R, where K is the spring constant of the force measuring spring. For curves a and b $K = 1.0 \times 10^2$ N/m, $R = 1.13$ cm; for curve c $K = 7.2 \times 10^2$ N/m, $R = 0.57$ cm.

observations with submonolayer coverage of the PS.[4] The new observation here is that coverage can diminish *during* time in contact.

Figure 1(c) shows data obtained with PαMS on one mica surface only. We now find the attractive minimum at 2.8 ± 0.3 nm, roughly the factor of 2 reduction in D expected with half the polymer in the gap relative to Fig. 1(a). Most significantly, the attractive minimum of 25 mN/m is a factor of 25 deeper than in Fig. 1(a).

When this curve is retraced repeatedly with the same layer, it is found that the depth of the adhesion measured depends on time up to about 10 min in contact. For longer contact times, a stable adhesion of 36 mN/m is attained, a factor of 36 greater than when the polymer is brought into the gap on two surfaces. This value is measured even after multiple contacts as long as the contact time exceeds 10 min.

The important fact revealed here is the large strength of the bridging interaction. This suggests that even a small amount of bridging could produce a strong, even dominant, attraction when two opposing polymer layers interact. We have previously shown[11] that the osmotic attraction, even 15° below T_θ, is weak, of order 100 μN/m or 10% of the adhesive minimum in Fig. 1(a).

The forces reported here are stable over the periods necessary to measure them, but *they clearly are not equilibrium forces*. The evolution of Fig. 1(a) into Fig. 1(b) shows that migration along the surface occurs. If true equilibrium were attained in these experiments, Figs. 1(b) and 1(c) should be identical.[10] We have essentially the same amount of polymer in the gap in the two experiments, as evidenced by the similar positions of the attractive minima and the repulsive barriers. When the polymer is brought into the gap all on one surface, favoring bridging, there is a more than 20-fold enhancement of the adhesion that persists for hours and over multiple contacts.

Rearrangements of macromolecules in these dense, intertwined surface layers are evidently very slow.

Finally, we can make an estimate of the segmental sticking energy of polymer to mica. Adhesion of $F/R \cong 40$ mN/m between orthogonal cylinders corresponds[15] to interaction energy of 6.7 mJ/m^2 between two parallel plates at the same separation. Estimating the area per PS segment as 20 Å^2 and *assuming* that polymer completely covers the opposing bare mica surface where they contact, the interaction energy per segment is 1.3×10^{-15} μJ/segment, or $\frac{1}{3}$ kT, which is in the range expected for dispersion forces.[16]

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