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 demonstrated4−5 that attraction can develop even above the theta temperature $T_\theta$ for the polymer in the immersion solvent. Above $T_\theta$, osmotic forces are repulsive, so bridging is the only available mechanism of attraction between adsorbed layers above $T_\theta$.

Recently, theories have been advanced for the forces between polystyrene layers immersed in solvents near $T_\theta$ 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 $R \approx 1$ cm) mica surfaces with a precision of about 0.1 $\mu$N 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 practice1−6 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 $\mu$g/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-(a-methylstyrene) (PzMS) from Pressure Chemical Co. with $\overline{M_w} = 90000$, $\overline{M_w}/\overline{M_n} < 1.10$. The theta temperature for PzMS is nearly the same as that for PS in cyclohexane (34−35 °C).13

Figure 1(a) shows representative data for two identical PzMS 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 $T_\theta$.4 The attractive minimum at $7.0 \pm 0.3$ nm is near $R_g$ for this polymer14 and the onset of detectable attraction is about 3 $R_g$. Attraction persists above $T_\theta$.4 From refractive index measurements in the gap,7,8,12 we estimate the adsorbed amount of PzMS as $3.0 \pm 0.3$ mg/m², 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 $\mu$N/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
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\textsuperscript{11} that the osmotic attraction, even 15° below $T_\theta$, 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 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.\textsuperscript{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 $F/R \approx 40$ mN/m between orthogonal cylinders corresponds\textsuperscript{15} to interaction energy of 6.7 mJ/m² between two parallel plates at the same separation. Estimating the area per PS segment as 20 Å² and assuming that polymer completely covers the opposing bare mica surface where they contact, the interaction energy per segment is $1.3 \times 10^{-10}$ μJ/segment, or $\frac{1}{kT}$, which is in the range expected for dispersion forces.\textsuperscript{16}

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