Interactions between Mica Surfaces in Solutions of Linear and Cyclic Polystyrene Chains: The Effect of Topological Selectivity

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ABSTRACT: We have measured the forces between mica surfaces immersed in cyclopentane (CP) in the presence of linear (LPS) and cyclic polystyrene (CPS) chains of similar molecular weights, a few degrees above the Θ-point of the LPS/CP system: while LPS adsorbs (in accordance with earlier studies), CPS does not adsorb under the same conditions. This is likely to be due to differences in the thermodynamics induced by the different topologies of the two types of polystyrene chains.

1. Introduction

Polymer chains that are adsorbed or grafted onto surfaces from solution strongly modify surface forces.[1,2] The interactions between smooth solid surfaces in liquid media bearing adsorbed linear polymers have been extensively studied in recent years, using the mica force measurement approach, as a function of solvent quality, chain microstructure, degree of polymerization, and the extent of surface excess or adsorbance of polymer. The experimental results have recently been reviewed.[2] The overall interactions between polymer-bearing surfaces display great richness of behavior but may be largely described by a combination of bridging forces and osmotic effects.[1,3] The former are due to a given chain or chains spanning the gap between the surfaces while being quasi-irreversibly adsorbed on both: such forces are always attractive.[3] The osmotic forces arise from the overall segment–segment interactions between the opposing adsorbed layers and depend on the goodness of the solvent medium.[4-7] The net forces between surfaces depend on the adsorbance and on their relative separation. At low adsorbance, even in Θ[5] and good solvent[8] conditions, bridging attraction dominates at large separations; as the surfaces approach, with no desorption of polymer, the segmental concentration in the gap increases, and eventually the osmotic interactions dominate and result in an overall repulsion.[8] This has considerable implications, since en route to a high-surface-excess, sterically stabilized situation, interacting surfaces need to pass through a low-adsorbance regime, which can result in net attraction (and, for colloids, aggregation and flocculation).[1]

Since bridging is primarily due to tails of the adsorbed chains, it is of interest to consider the behavior of adsorbed cyclic polymers. Such chains have no free ends, so one expects only *loops* to extend from each adsorbed layer. While loops may also bridge the intersurface gap, its likelihood and the rate at which they will do so are expected to be lower than for tails under the same conditions, and thus bridging effects with loops will be less marked, especially over finite measuring times. This is partly because the largest loop sizes are intuitively expected to be smaller on average than the longest tails and also because of kinetic effects. In order for a loop to interpenetrate from one surface through the opposing adsorbed layer to the other surface, it must adopt entropically unfavorable configurations ("hair-pin bends"); this is expected to considerably suppress both the equilibrium number of bridging loops and also the rate at which bridging in a "tailless" system will take place.[9]

The motivation for the present study derived from the assumption that the absence of tails would drastically affect the bridging phenomena. We investigated the interaction forces between two mica surfaces in solutions of both linear polystyrene (LPS) and cyclic polystyrene (CPS) in cyclopentane (CP), slightly above the Θ-temperature of the LPS/CP system. The interaction between mica sheets in PS/CP solutions has been extensively studied,[5,6] and in the present investigation we used the LPS with a molecular weight similar to that of the CPS as a control.

Section 2 describes the experimental procedure and the materials used. The results of our force measurements are given in Section 3, while in Section 4 we discuss the results and their implications.

2. Experimental Section

We measure the force $F(D)$ acting between two curved mica sheets (mean radius R) in a crossed-cylinder configuration as a function of their separation, D. The apparatus and general approach have been described in detail previously.[4] In essence, the deflection of a leaf-spring on which one of the mica sheets is mounted is measured as a function of D; force profiles $F(D)$ are thus determined. The optical technique may also yield[10] the refractive index $n(D)$ at the separation D.

After $F(D)$ is determined in the polymer-free cyclopentane (equilibrated with water vapor), the mica surfaces are separated to $D \cong 0.5$ mm and polymer solution is injected into the cell to final concentrations in the range 10^{-5}–10^{-4} g/mL (see individual captions). These concentrations are appreciably lower than the overlap concentration for either the LPS or CPS samples. The solution is stirred by a few rapid cycles of approach and separation of the mica surfaces. The surfaces are then left to incubate in the polymer solution, and $F(D)$ is measured by following progressively longer incubation times. All experiments were carried out at 24 ± 1 °C.

Materials. Table I shows the molecular characteristics of the two samples used.

The CPS sample was a cyclic polystyrene synthesized by an anionic polymerization process, in a moderately good solvent medium,[11,12] using dimethyldichlorosilane as a linking agent. The same sample (designated 83R) was studied by McKenna et al.[12] in the context of an extensive investigation of the viscoelastic and rheological properties of CPS melts. Its integrity as an uncatenated, ring polystyrene free of linear polystyrene

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Table I
Molecular Characteristics of Polystyrene Samples[a]

polystyrene	M_w, g/mol	M_w/M_n	R_g, Å
linear (LPS)	3.5×10^5	<1.07	168
cyclic (CPS)	3.91×10^5	<1.05	127[17]

[a] LPS was obtained from Toyo Soda Co. Ltd. (Japan) and used as received.

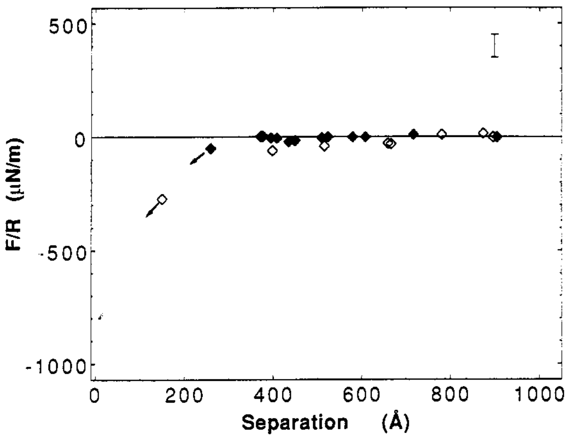

Figure 1. Interaction (F/R) as a function of separation (D) between mica surfaces in pure cyclopentane. Different symbols represent results from experiments with different mica sheets. The arrows indicate a jump to the air contact separation.

traces was thoroughly considered by these authors.

The apparatus was cleaned by using distilled water and analytical grade solvents as earlier described.[4] The solvent for the PS solutions was a spectroscopic grade cyclopentane (Fluka). Both solvent and solutions were filtered prior to use through a 0.2-μm Millipore (type FG) PTFE filter. The filter was prewashed by passing 50 mL of the pure solvent through it. The mica sheets were glued onto the cylindrical lenses by using *sym*-diphenyl carbazide, as in previous studies with cyclopentane.[5]

3. Results

The force profiles are normalized by the mean radius of curvature R of the mica sheets, following the Derjaguin approximation:[4,10]

$$F(D)/R = 2\pi E(D)$$

where $E(D)$ is the interaction energy per unit area acting between flat parallel plates a distance D apart and obeying the same force law.

Polymer-Free Solvent. In order to ensure a reproducible water content in the organic solvent, the cyclopentane was equilibrated with water in the force-measurement apparatus for 12 h before measuring $F(D)$ (water was placed in the cell in a separate small beaker). The water content of the solvent is an especially important parameter in these experiments, due to the combination of the hydrophilicity of the mica together with the very weak adsorption characteristics of the polystyrene. This will be considered in more detail in the Discussion section. Saturation or near-saturation with water vapor is the practical situation in most experiments with organic solvents, so this configuration was chosen in preference to the "dried solvent" limit used in other studies.[6] Figure 1 shows a typical profile: little interaction is noted down to $D < 150$ Å, where jumps (due to mechanical instability) occur into air-contact position. Profiles as in Figure 1 were reproducible (within a ±30-Å variation in the "jump" position and a threefold variation in the mean adhesive energy of contact of around 10^3 μN m^{-1}) over a period of up to 3–4 days. Thus, experiments—with added polymer—could be carried out over comparable periods and changes in $F(D)$ attributed to the polymer alone.

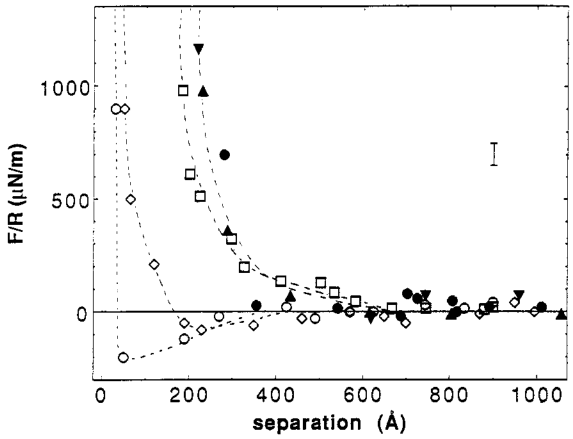

Figure 2. Interaction (F/R) as a function of separation (D) between mica surface, in a solution of LPS, concentration 1.5 × 10^{-4} g/mL in cyclopentane. Different symbols refer to different incubation times in the solution: (○) 5 h; (◇) 7.5 h; (□) 24 h; (●) 26 h; (▲) 40 h (approach/separation). Empty symbols and filled symbols are from two different experiments.

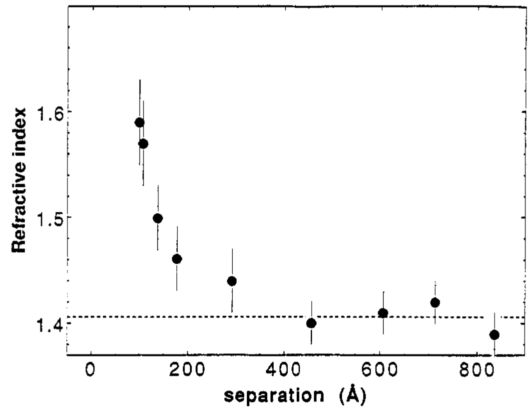

Figure 3. Refractive index of medium separating mica sheets, following adsorption of LPS. The profile was measured following 40 h of incubation in a solution of LPS, concentration 1.5 × 10^{-4} g/mL.

Linear Polystyrene. Force profiles with LPS are shown in Figure 2 and exhibit the general trend observed in the earlier LPS/CP studies.[5] At short incubation times, the polymer adsorbance is low: there is a relatively strong attraction on approach of the surfaces, and a repulsive regime at smaller separations, while at longer times the attractive minimum becomes shallower, and the repulsive regime shifts to larger D values. This pattern was reproducible for several different pairs of mica sheets. A marked feature of these experiments is the much slower rate of adsorption of polymer, relative to earlier studies. To achieve equilibrium adsorbance (beyond which little further changes were noted in $F(D)$) in reasonable times, it was necessary to work at concentrations > 10^{-4} g/mL. Thus, at a concentration of 1.5 × 10^{-4} g/mL the adsorbance reaches its limiting value after some 24 h. The kinetic aspects are considered in more detail in the Discussion section.

For better characterization of the adsorption of the LPS sample, refractive index $n(D)$ profiles were determined as described in earlier work,[4,10] with a view to estimating the adsorbed amount. Figure 3 shows the $n(D)$ profile following adsorbance to equilibrium of the LPS sample. The corresponding adsorbance is estimated from the somewhat noisy $n(D)$ data as $\Gamma = 2.5 \pm 1$ mg·m^{-2} of polymer on each mica surface.[23]

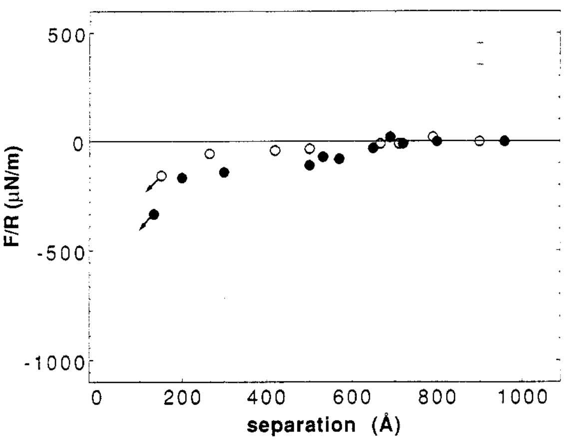

Figure 4. Interaction (F/R) as a function of separation (D) between mica surfaces following 12 h of incubation in pure cyclopentane (○) and following and additional 24 h of incubation in cyclic polystyrene solution (●) at a concentration of 1 × 10^{-4} g/mL. Arrows indicate jumps to the air-contact separation.

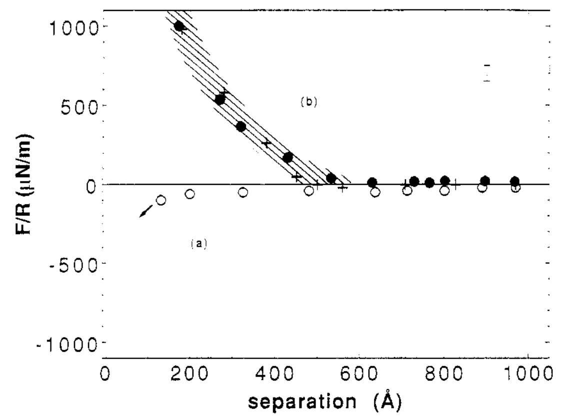

Figure 5. Interaction (F/R) as a function of separation (D) between mica surfaces. (a) Following 24 h of incubation in a solution of 1.5 × 10^{-4} g/mL cyclic polystyrene, CPS (○). The arrow indicates a jump to the air-contact separation. (b) As in a, but following addition of LPS to a concentration of 2 × 10^{-4} g/mL and an additional 24 h of incubation in the resulting mixed solution of CPS and LPS (symbols + and ● are for approach of surfaces in two consecutive runs at the same contact point). The shaded band covers the equilibrium force-distance data from Figure 2.

Cyclic Polystyrene. Figure 4 shows the interaction profile between two mica surfaces in H_2O-equilibrated cyclopentane prior to addition of polymer and 24 h after adding the CPS sample to an incubation concentration of 1 × 10^{-4} g/mL. Within the scatter, the force profiles without polymer and following 24 h of incubation in the cyclic polymer are identical. This tells us unambiguously that the CPS does not adsorb onto the mica surfaces from the cyclopentane. This result was quite reproducible in several other experiments and also at times shorter than 24 h.

As a second stage after incubation, following the observation of the nonadsorbance of CPS, LPS was added to the CPS solution, also to a concentration of 10^{-4} g/mL. The subsequent $F(D)$ behavior was very similar to that of Figure 2: i.e., the LPS sample adsorbed onto the mica in the presence of the nonadsorbing cyclic chains as revealed by the progressive change in $F(D)$. This is illustrated in Figure 5, where the open circles show the interaction following 24 h in the 10^{-4} g/mL CPS solution (a different experiment to that shown in Figure 4), while the solid circles and crosses show the effect of a further 24 h (in the same experiment) following addition of the LPS. The shaded band in Figure 5 corresponds to the $F(D)$ profile following equilibrium adsorbance of LPS, taken from Figure 2. Within the scatter, the data and the broken curve (corresponding to adsorbance from a LPS solution without the CPS) match closely. This behavior demonstrates that, in identical conditions, linear polystyrene adsorbs on the mica substrate, while the cyclic polystyrene does not. The absence of linear polystyrene contaminant in the CPS sample is in agreement with the conclusion reached by McKenna and co-workers[12] on the basis of recoverable compliance behavior of this sample.

4. Discussion

The main finding of this study is the effect of cyclization on the adsorbance of the polystyrene, in experimental conditions which provide a slightly better-than-Θ environment for the PS. From previous investigations, it is known that polystyrene adsorbs very weakly onto mica. This is indicated by several observations: (a) the polymer partially desorbs from mica when the immersing solution is slightly warmed following adsorption both from cyclohexane[13] and from cyclopentane,[6] (b) polystyrene partially desorbs from mica on dilution of the incubating solution following adsorption from cyclopentane,[5] (c) polystyrene does not adsorb at all from the good solvents toluene[7] and xylene.[14] These observations suggest that the net styrene-monomer/mica sticking energy is very weak; the polymer adsorption is clearly marginal, and it is important to bear this in mind when comparing different studies of the PS/mica system. In the present experiments, the equilibration of the cyclopentane with H_2O is an additional related factor: because the mica is hydrophilic, the competition with the water molecules may reduce the overall affinity of the PS chains to the mica surface even further.

It is of interest to compare our results for LPS with the earlier study by Almog and Klein of linear PS adsorption onto mica from cyclopentane and the resulting $F(D)$ curves between two surfaces.[5] The general trend, as shown in Figure 2, is very similar to the earlier data, with the lower adsorbance values (at shorter incubation times) corresponding to stronger bridging attraction. The final equilibrium profile (Figure 2 and also Figure 5) shows monotonic repulsion—within the scatter—with the onset of interaction between the plates at a separation of ca. 2.5–$3R_g$ of the LPS, somewhat larger than the onset of ca. $2R_g$ observed for the linear polystyrene samples of the earlier study.

The much slower rate at which the limiting adsorbance was attained in the present study was very marked. Thus, for the incubation concentration of 1.5 × 10^{-4} g/mL shown in Figure 2 the limiting behavior was reached after some 24 h, while for incubation concentrations of ca. 3 × 10^{-5} g/mL (not shown) the time required was some 40 h. This compares with ca. 16 h required for equilibrium adsorbance for the M = 6 × 10^5 linear polystyrene sample from a 10^{-5} g/mL solution in cyclopentane used in the study by Almog and Klein.[5] The longer times in the present study may be due to a number of factors, including (a) the different size of chains and (b) the higher H_2O content in the cyclopentane, which was equilibrated with water inside the cell, in contrast to the earlier study where the cyclopentane was merely used undried, in equilibrium with atmospheric H_2O.[21] As noted above, H_2O molecules compete with the polymer for the mica surface sites; thus, the slow attainment of the final adsorbance may be due to the correspondingly smaller sticking probability on approach of a PS chain to the mica surface in the water-saturated cyclopentane. This is because when a polystyrene molecule contacts the surface, it will adsorb only if it is in a configuration where enough monomers are adsorbed on the mica so that the overall sticking energy is high enough to prevent quick thermal desorption. Clearly, the adsorbance rate here is no longer diffusion-limited,[22] as the LPS sample has a lower molecular weight (and hence has a larger diffusion coefficient) than the faster adsorbing PS samples used in ref 5. The final overall adsorbance, however, as indicated by the refractive index profile, is comparable with the earlier values estimated, though within the uncertainty in both values a considerable difference is possible.

Finally we consider the main—and unexpected—qualitative result of this work: the nonadsorbance of the cyclic polystyrene CPS in conditions where the LPS undergoes adsorption. Since the microstructure of both molecules is identical, this difference must be due to the cyclic nature of the CPS. The thermodynamics of cyclic chain molecules is subtle and has been considered by Frank-Kamenetskii and others.[15] Essentially, the topological transformation of an open, linear chain into a ring creates an additional constraint on the equilibrium state of the rings: some configurations which are available to the open chains are excluded for the rings. Phenomenologically, this results in a *lowering* of the temperature at which the second virial coefficient disappears for cyclic relative to linear polystyrenes[12,16,17] (by some 6–7 °C in cyclohexane, for example). Theoretically, this has been considered by Iwata and Kimura[18a] and more recently by Tanaka.[18b] One may expect that a similar effect applies also for the case of cyclic relative to linear polystyrene chains in cyclopentane, so that at the temperature of our experiments (24 ± 1 °C) in the cyclopentane the second virial coefficient is slightly higher for CPS than it is for LPS (for which it disappears at the Θ-temperature of 19.6 °C). It is this effect, then, taken together with the small sticking energy of the PS monomer onto mica discussed above, which may enable the LPS to adsorb (i.e., a net overall sticking energy per chain) but not the CPS. It is appropriate to note that any depletion forces due to the nonadsorbing CPS are expected to be below the detection limit of our experiment at these low polymer concentrations.[7]

The one published theoretical treatment of ring adsorption onto surfaces is based on a mean-field, numerical, lattice approach.[19] This treatment predicts that under otherwise identical conditions, and for a given finite molecular weight, rings will adsorb to a similar (even slightly higher) adsorbance as the analogous linear chains. This clearly does not happen in the present study, where the linear chains adsorb but the cyclic ones do not. This may be due to the fact that the model does not take into account the effect of the different topology on the second virial coefficient, as discussed above and as revealed by the more detailed calculations.[18]

We also note that the observed nonadsorbance of the CPS is likely to be a thermodynamic effect rather than the manifestation of extremely slow adsorbance kinetics. The latter case, while possible in principle, would imply that over the times of our measurements (24 h) the amount of polymer adsorbed is so small that the forces $F(D)$ are unperturbed relative to those in polymer-free solvent. In addition, the adhesive force for pulloff after jumping into contact following incubation in the CPS solution (arrow, Figure 4) is within the range observed for adhesion between the mica surfaces in the polymer-free solvent; this again indicates that the surface coverage—if any—is extremely low.

In conclusion, our investigation, which was aimed at measuring surface forces between surfaces bearing adsorbed polystyrene rings and thus elucidating the effect of the absence of tails, revealed instead that cyclic polystyrene does not adsorb onto mica from cyclopentane in conditions that linear polystyrene does. This is probably due to the marginal adsorption characteristics of polystyrene in these circumstances, on the one hand, together with subtle topological effects which enhance the solvent quality for the cyclic relative to the linear chains. Our results suggest that a topological selectivity effect of this sort could provide a delicate analytical tool and, in addition, may enable separation—via selective adsorption—of cyclic from linear chains in a mixture of the two.

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(21) We note also the somewhat larger range of jump into contact in the present study under the capillary H_2O condensation forces (Figure 1), relative to earlier investigations, e.g., ref 5.

(22) We note in this context that for a linear PS sample of molecular weight 190 000 (not shown) the time for adsorbance to equilibrium was even longer than for the LPS sample.

(23) The adsorbance was estimated by using $n(D)$ values for $D >$ 200 Å, rather than the closest points ($D \cong 100$ Å). This is because for the smallest gaps the segmental anisotropy of the highly compressed PS chains may lead to deviations from the refractive index of bulk polystyrene, which are difficult to account for. The procedure for estimating the adsorbance is given in ref 4.