Macromolecules 1992, *25*, 2062-2064

Modification of Long-Ranged Forces by Surface Exchange of Polymeric Amphiphiles

Jacob Klein,*,†,‡,§ **Yoichiro Kamiyama,**‡,∥
Hisae Yoshizawa,‡ **Jacob N. Israelachvili,**‡
Lewis J. Fetters,⊥ **and Philip Pincus**†

Materials Department and Department of Chemical and Nuclear Engineering, University of California at Santa Barbara, Santa Barbara, California 93106, Department of Materials and Interfaces, Weizmann Institute, Rehovot 76100, Israel, and Corporate Research Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801

Received December 17, 1991
Revised Manuscript Received February 7, 1992

Flexible macromolecules at interfaces control phenomena ranging from adhesion, through lubrication, to the wettability of solid surfaces.[1] In particular, steric interactions beween polymer chains attached at the solid–liquid interface frequently determine the stability of colloidal dispersions, in both natural and synthetic systems.[2] In the case of adsorbed polymers—that is, where any of the segments along the chain may adhere to the solid substrate—such interactions display a broad spectrum of behavior.[3,4] A characteristic long-ranged attraction between the surfaces, due to bridging, is dominant at low coverage of polymer (and can lead to aggregation in colloidal dispersions[5]); while at high coverage, surfaces normally repel each other, providing steric stabilization. The case of polymers that do not adsorb but are chemically grafted or physically attached by one end only onto the surfaces (polymeric surfactants or amphiphiles) is of special interest. At dense coverage such tethered chains extend normal to each surface, forming a brushlike layer whose thickness, for a given degree of polymerization, considerably exceeds that of adsorbed chains.[6-10] And, in contrast to adsorbing chains, the forces that act between two brush-bearing surfaces across a good solvent medium are repulsive at all coverages,[7,8] with obvious implications for their steric stabilization properties. The structure and the long-ranged interactions between brush layers have only recently been studied: they reveal that, once formed, these layers are remarkably stable with respect to compression,[8] shear,[11] and the dilution of the surrounding solution.[8] An outstanding issue is how such layers may be modified, or "tailored", in order to control their structure and the related interfacial properties.[10] Such modification must depend on the behavior of the brushes at equilibrium and on the molecular relaxation mechanisms as they approach it: the ground rules in this case may be very different from those applying to adsorbed chains, whose properties have long been established.[2,12-14] We have now examined this question by direct measurement of the forces between two surfaces bearing tethered polymeric amphiphiles.

Two monodispersed polystyrene (PS) samples of widely different molecular weights were used, each terminated by the zwitterionic group $N^+(CH_3)_2(CH_2)_3SO_3^-$ (designated X). The molecular characteristics of the samples (designated PS–X(26) and PS–X(375)) are given in Table I. The properties of these model polymer amphiphiles have been widely investigated using the mica force balance.[7,8] While functionalized polystyrene does not adsorb onto mica from good solvents such as toluene, the PS–X chains attach densely via the zwitterion onto mica to form extended brushlike layers. In the present study the forces $F(D)$ between mica sheets a distance D apart were measured using a surface force apparatus,[15,16] first in pure toluene and then following addition of the longer amphiphiles PS–X(375) to a concentration 1.0×10^{-4} g/mL. Typical force profiles are shown in Figure 1 and are closely similar to data reported earlier with the same samples.[8] The force profiles show a monotonically increasing repulsion commencing at a surface separation of some 230 nm, corresponding to a thickness of each PS–X(375) layer of 115 nm. At this point the surfaces were widely separated and the shorter chains (PS–X(26)) were introduced into the solution containing the longer amphiphiles. On remeasuring the force profiles within 2 h of adding the shorter chains a sharp decrease in the range of the repulsive forces from 230 to some 80 nm is noted, as shown in Figure 1. After overnight incubation, an additional slight decrease in the range was observed, which did not change further over 5 days. The force profiles and the adsorbed amounts at this point were closely similar to those observed in earlier studies[8,17] between mica surfaces to which PS–X(26) had attached from a toluene medium. These results show unambiguously the replacement of the long-ranged surface forces characteristic of the end-tethered PS–X(375) chains by the much shorter-ranged repulsion due to the PS–X(26) layers.

In a different experiment, the order was reversed: the shorter amphiphiles were first added to the pure toluene to a concentration 1.0×10^{-4} g/mL, resulting in the characteristic force–distance profiles shown in Figure 2. These profiles were identical (within scatter) to the final profiles—following addition of the PS–X(26)—shown in Figure 1. At this point the surfaces were widely separated and PS–X(375) was added to the solution. Force–distance profiles were measured at several subsequent times over a 2-day period but showed no change; i.e., addition of the longer amphiphiles had no effect on the force profiles (within the estimated uncertainty in the data) once the shorter chains had attached to the mica surfaces—the exchange works in one direction only.

Our results show that, for a given end-anchoring group, shorter polymeric amphiphiles that end-attach onto a surface may rapidly replace previously-attached longer amphiphiles from that surface. This behavior contrasts diametrically with that of *adsorbing* homopolymers, where the number of segments that may attach at the interface depends on the length of the chains: in this case it has long been known[12-14] that, in equilibrium, longer polymers replace shorter ones on an adsorbing substrate, due to their greater overall sticking energy. The different behavior of the end-anchored chains may be understood as follows: in equilibrium, the adhesion energy tethering each chain is balanced by the repulsive osmotic interactions that the chain experiences due to its neighbors.[6] This balance determines the mean spacing between the end groups anchoring the chains.[8] The overall free energy per unit area ΔF is then lower for layers of shorter chains: a simple calculation[18] indicates that

$$\Delta F \propto -(\gamma^{11/5} k_B T)/(N^{6/5} a^2)$$

here $\gamma k_B T$ is the adhesive energy anchoring each amphiphile to the substrate,[19] k_B and T being Boltzmann's

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* Address correspondence to this author at the Weizmann Institute.

† Materials Department, University of California at Santa Barbara.

‡ Department of Chemical and Nuclear Engineering, University of California at Santa Barbara.

§ Weizmann Institute (permanent address).

∥ On leave from Fuji Photo Film Co., Ltd.

⊥ Exxon Research and Engineering Company.

0024-9297/92/2225-2062$03.00/0

Table I
Molecular Characteristics of PS-X Polymer[a]

sample	M_w	M_w/M_n	R_F, nm
PS-X(26)	26 500	1.02	12.2
PS-X(375)	375 000	1.03	57.5

[a] The samples were synthesized as described in ref 8. Weight- and number-average molecular weights M_w and M_n were determined by size-exclusion chromatography. R_F is the root-mean-square end-to-end dimension of the chains in toluene.[8]

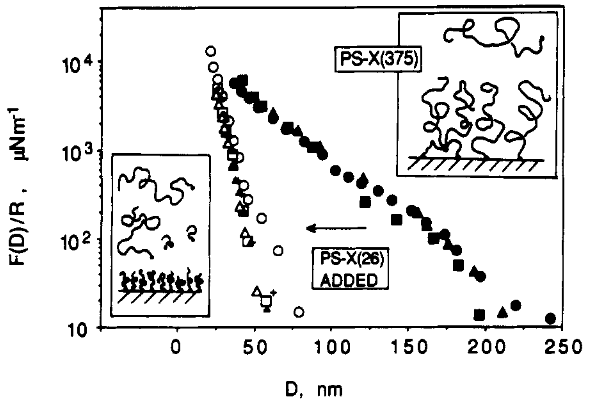

Figure 1. Reversible force ($F(D)$)-distance (D) profiles between curved mica sheets (mean radius of curvature $R \sim 1$ cm) immersed in solutions of the PS-X polymeric amphiphiles in toluene (Fisher HPLC grade) at 25 ± 0.5 °C, a closest distance D apart. Data are shown for several different contact positions. The force axis is normalized as $F(D)/R$ to yield the corresponding normalized interaction energy profile in the Derjaguin approximation:[15,16] (●,▲,■) force profiles following addition of PS-X(375) to the toluene to a concentration 1.0×10^{-4} g/mL; (○) 2 h after adding PS-X(26) to the solution to a concentration 1.0×10^{-4} g/mL; (△,▵,+) 14-26 h following addition of the PS-X(26); (□) 4.8 days following addition of the PS-X(26). The cartoons illustrate schematically the surface coverage in the presence of PS-X(375) and following addition of the PS-X(26) and their displacing of the longer amphiphiles from the surface.

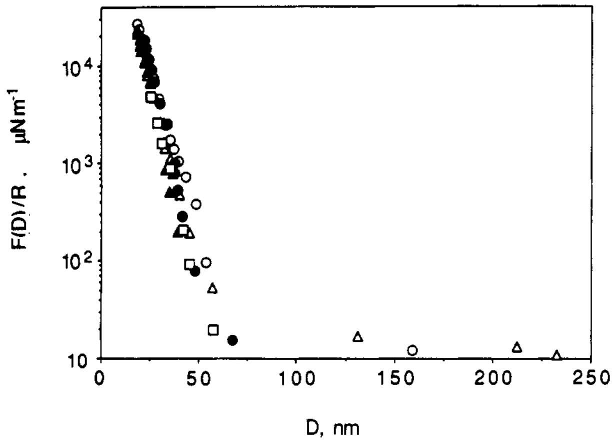

Figure 2. Force-distance profiles (as in Figure 1) between curved mica sheets in a PS-X/toluene solution a closest distance D apart: (●,▲) following addition of PS-X(26) to the toluene to a concentration 1.0×10^{-4} g/mL and its attachment to the mica; (○,△) profiles at different contact points taken 39-40 h following addition of PS-X(375) to the solution to a concentration 1.0×10^{-4} g/mL; (□) data taken from Figure 1 (same symbol), for a force profile taken 4.8 days after addition of PS-X(26) to a solution of PS-X(375). The estimated uncertainty in the data is ±10 μN m^{-1}.

constant and the absolute temperature, respectively, and N is the number of monomers, each of size a, per chain. Thus at lower N values ΔF is more negative: in the present study the specific surface free energy of a PS-X(26) brush layer is expected to be negative and some 20-fold larger than that of a PS-X(375) layer. It is this difference that drives the shorter amphiphiles to displace the longer ones from the surface. In our experiments the shorter surfactant is added to the solution to a monomer concentration equaling that of the longer one (Figure 1), and hence to a higher molar ratio: calculations (to be published) indicate that complete displacement of longer surfactants from the surface should occur even at very low relative molar concentrations of the shorter chains in the bulk solution. By varying the value of γ and its ratio for the chains, as well as the relative polymer lengths and concentrations, interesting possibilities for tailoring of surfactant monolayers,[10] and the related long-range surface interactions, are immediately indicated.

The characteristic time indicated for the exchange process shown in Figure 1 deserves comment. This time—some 2 h in our system—is very comparable with the times (2-3 h) for formation of brush layers from PS-X solutions onto initially bare mica in an identical configuration.[8] This qualitative observation suggests that the existing brush of the longer amphiphiles does little to delay the formation of the shorter brush which displaces it. There appear to be a number of reasons for this. The effective pore size within the PS-X(375) brush[20] is larger than the coil size of the shorter chains, so that diffusive transport of the latter, as they penetrate this layer, is relatively unhindered. In addition, the density of PS-X(26) chains on the surface at equilibrium is much higher than that of the longer polymers,[8,20] thus, for the shorter surfactants, the PS-X(375)-covered surface appears relatively "empty" and they readily attach to it. Finally, the displacement of PS-X(375) from the surface by the shorter surfactants must take place over a similar time, despite the zwitterion-mica adhesion energy of ca. 6-8 k_BT anchoring each of the longer amphiphiles to the surface.

To summarize, in the case of polymers that attach densely from solution onto a surface via a given functional group at one end, shorter chains may displace longer ones from the substrate, in contrast to the behavior of adsorbed homopolymers. Within the range of our experimental parameters this displacement is complete and rapid. This phenomenon has implications where grafted polymer layers are used to modify surface characteristics and colloidal behavior and suggests also an efficient approach for separating polymeric amphiphiles from populations of mixed lengths.

Acknowledgment. J.K. thanks NCRD (Israel), J.N.I. and H.Y. thank DOE, and P.P. thanks BP (America) for financial support of this work.

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(17) From the magnitude of the repulsive interactions at high compressions for the two force profiles, values of 3.0 ± 0.5 and 2.2 ± 0.4 mg/m^2 may be estimated (as described in detail in ref 8) for the adsorbance of polymer from the PS–X(375) solution and following addition of the PS–X(26), respectively. These compare with previously determined[8] values of 3.2 ± 0.5 and 2.0 ± 0.4 mg/m^2 for pure PS–X(375) and PS–X(26) brushes, respectively.

(18) This expression is derived as follows. The free energy per unit area of a polymer brush consisting of N-mers, monomer size a, is first minimized with respect to the brush thickness at a fixed spacing of chain ends s on the surface to yield the Alexander result[6] for the equilibrium brush thickness $L_0 = (\text{const})Ns^{-2/3}a^{5/3}$. The resulting free energy per unit area using this value of L_0 but now with s variable and an additional adhesive energy contribution, $-(\gamma k_B T/s^2)$, per unit area[19] is then minimized with respect to s to yield ΔF as appears in the text. This result is derived more generally by including the chemical potential contribution of the polymeric surfactants (in preparation).

(19) For the PS–X/mica/toluene system the zwitterion–mica interaction energy has been estimated[8] as $\gamma k_B T \approx 6\text{–}8\ k_B T$.

(20) The mean spacing s between chain ends on the surface is evaluated from the absorbance of polymer[16] and its molar mass. For PS–X(26) and PS–X(375) this yields $s = 4.5 \pm 0.5$ nm and $s = 14.5 \pm 1.5$ nm, respectively, in these experiments. The mean pore size may be approximated as the segment–segment correlation length ξ within the brush,[6] where $\xi = s$. For the PS–X(375) brush, ξ (=14.5 nm) compares with the PS–X(26) coil size $R_F = 12.2$ nm (Table I).

Registry No. Polystyrene, 9003-53-6.