Interaction Forces between Adsorbed Layers of Associative Polymer

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ABSTRACT: We have measured normal quasi-equilibrium forces between adsorbed layers formed on hydrophilic surfaces in aqueous solutions of telechelic poly(ethylene oxide) end-terminated with octadecyl groups. At low polymer concentrations, c_{pol}, a monolayer adsorbs, which has properties similar to the monolayer of adsorbed nonhydrophobized poly(ethylene oxide). At moderate concentrations of ca. $c_{pol} \approx c_{cmc}$, a multilayer adsorbs onto the surface, which is presumably formed by micelles adsorbed onto the top of a monolayer. The adsorbed layers exhibit repulsion on approach and attraction on separation of the surfaces; the latter evolves after several/decompression cycles. The adhesion energy increases with the time that the compressed layers are maintained in contact and with the extent of compression of the adsorbed layers. We attribute the attraction between the adsorbed layers to bridging between the hydrophobic groups of molecules adsorbed onto opposite surfaces.

Introduction

Over the past decade, water-soluble polymers containing hydrophobic substituents have been extensively studied in aqueous solutions[1−5] where they show strong association. With an increase of polymer concentration in the solution, individual molecules assemble into supramolecular structures varying from micelles to physical gels. The extent and the type of association are determined by polymer concentration, $c_{pol,}$ in the solution and chemical composition of macromolecules, i.e., the degree of polymerization, the nature and the length of hydrophobic constituents, and the fashion in which hydrophobic groups are attached to the polymer backbone.

To date, the hierarchy of association is best understood for linear flexible water-soluble polymers bearing two terminal hydrophobic end groups.[2] At very low c_{pol}, isolated macromolecules exist in a bulk polymer solution. Pairs of end groups either stick together or are exposed to the solution depending on the competition between the loss in configurational entropy and gain in energy due to association. Above a threshold concentration, c_{cmc}, telechelic molecules self-assemble in flowerlike micelles with a hydrophilic corona and a hydrophobic core formed by the end groups. The aggregation number is determined by the balance between the steric repulsion of water-soluble chains in the corona and the surface energy gain due to association of the hydrophobic groups. As c_{pol} further increases, telechelic molecules form bridges between the micelles. Ultimately, a physical network is produced by micelles bridged together.

Less attention has been attracted to the interfacial properties of associative polymers (AP's) although almost all practical applications of these polymers, e.g., stabilization, flocculation, and modification of the rheology of colloid dispersions, depend critically on various aspects of polymer−surface interactions. The amphiphilic nature of the AP's causes their affinity to a variety of surfaces. This feature may lead to a substantial modification of the properties of a bulk system. For example, in dispersions containing an AP in a liquid phase, polymer adsorption on the surface of colloid particles changes rheological properties of the system.[6] In concentrated dispersions, bridging of particle surfaces or polymer phase separation will affect the stability of the system.

Recently, a few experimental studies of the telechelic hydrophobically modified poly(ethylene oxide) (PEO) have shed light on the interfacial properties of this polymer.[6−8] Pham et al.[6] examined adsorption of octadecyl-modified PEO onto poly(methyl methacrylate) colloid particles and its effect on the viscosity of dispersions. The authors suggested that when polymer concentration in the solution increases, macromolecules adsorbed on the surface of particles undergo a transition in conformation from moderately stretched macrochains anchored to the surface by two hydrophobic groups to macrochains attached to the surface with only one end group. Under these conditions, the other end of the chain becomes incorporated in micelles in the solution phase. Bridging of polystyrene surfaces bearing adsorbed dodecyl end-terminated PEO was studied by Courvoisier et al.[7] using atomic force microscopy. At polymer concentrations below the threshold of association, a long-range attraction of the polymer-covered substrates was observed, whereas repulsion forces dominated at short distances. Studies of octadecyl end-capped poly(ethylene oxide) in monolayers formed at the air−water interface were carried out by Muller at al.[8] The authors suggested a model based on a brush theory, which accounted for the exchange between anchoring of one or two hydrophobic groups at the interface and a possibility of desorption of the polymer chains from the interface.[8]

These experiments along with extensive information about the properties of hydrophobized PEO in bulk aqueous solutions[4,9−11,16] motivated us to explore molecular interactions between the adsorbed layers of this polymer. We employed the surface-forces balance technique[12] to measure normal quasi-equilibrium forces

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acting between the adsorbed layers of PEO end-capped with octadecyl groups. The range of polymer concentrations in aqueous solutions examined in the current work covered concentration regimes examined for bulk systems: from dilute solutions where little association occurs to moderately concentrated solutions with c_{pol} just below the threshold of bulk phase separation.[6]

Experimental Section

Materials. The associative polymer with a formula

$$C_nH_{2n-1}-NH-CO-(OCH_2CH_2)_x-O-CO-NH-C_nH_{2n-1}$$

where $n = 18$, $x = 800$ was synthesized at Rohm and Haas. The synthesis and purification of the polymer are described elsewhere.[6,16] Briefly, poly(ethylene oxide) (Fluka Chemicals) with the molecular weight 35 000 and a polydispersity index 1.2 was end-capped by reaction with excess of octadecyl monoisocyanates in toluene. The degree of end group termination was measured by ^{1}NMR, mass spectrophotometry, high-pressure liquid chromatography, and gel permeation chromatography and was found to be very close to 2.0 octadecyl groups per polymer chain. In this work, we refer to octadecyl-terminated poly(ethylene oxide) as ODU-35K. Before the experiment, the hydrophobized polymer was additionally purified by twice dissolving it in methanol, filtering the solution through a 0.2 μm filter (Acrodisc 13 CR PTFE, Gelman Sciences), and drying under vacuum. Aqueous ODU-35K solutions were prepared at least 12 ± 3 h before introducing them into the surface-forces apparatus.

Potassium nitrate (purity > 99.99%) was purchased from Sigma-Aldrich Canada Ltd. Deionized water was passed through a Milli-Q water system and then distilled. Methanol was A.C.S. Spectroanalyzed, Fisher Scientific. Mica was first grade muscovite mica purchased from S&J Trading (U.S.A).

Methods. In the surface-forces balance technique, the normal forces acting between the surfaces are measured as a function of the surface separation.[12] Mica surfaces were back-silvered, glued with the silver side down onto cylindrical silica glass lenses, and mounted in the surface-forces apparatus in a crossed-cylinder configuration. The distance between the surfaces, D, was measured using an interferometric technique from the relative position of the fringes of equal chromatic order. Normal forces between the mica surfaces were measured by detecting the deflection of a flexible spring supporting the lower lens. The results of experiments were presented as force−distance profiles $F(D)/R$ where R is the local mean radius of curvature of the surfaces.

The measured force $F(D)$ normalized by the mean radius of curvature is related to the free energy of interaction per unit area between two flat surfaces, $E(D)$, by the Derjaguin approximation,[13]

$$F(D)/R = 2\pi E(D) \quad (1)$$

The experimental procedure was as follows. After measuring the position of the interferometric fringes in air and then verifying $F(D)$ in the electrolyte solution (0.1 M KNO_3), the surfaces were separated, and ca. 6 mL of the electrolyte solution was replaced with a solution of ODU-35K in 0.1 M KNO_3. After force profiles were measured, the polymer concentration in the experimental cell was increased by a consecutive replacement of the original polymer solution with a more concentrated solution. The time of incubation of the mica surfaces in each polymer solution prior to the surface forces measurements varied from 35 min to 72 ± 2 h. The separation between the surfaces during polymer adsorption was of ca. 2−3 μm. The repetitive approach and separation of the mica surfaces were carried with the rates varying from 10 min to 30 per run. The time that the surfaces were maintained under compression varied from ca. 20 s to 1 h.

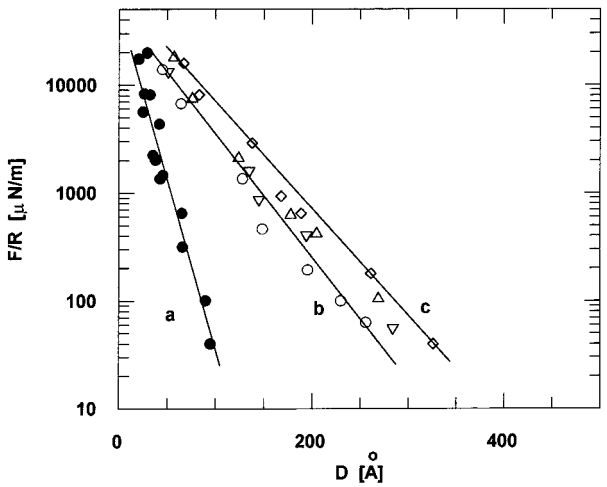

Figure 1. Force−distance profiles, F/R vs D, measured between the mica surfaces in compression experiments in (●) 0.1 M KNO_3 aqueous solution, 17 ± 1 h incubation; in 2.0×10^{-5} g/mL ODU-35K solution in 0.1 M KNO_3 following adsorption times: (○) 1 h; (▽) 2 h; (△) 5 h; (◇) 17 ± 1 h.

All results reported here are based on six independent experiments.

Experimental Results

In Figure 1, curve a shows the force profile measured for the bare mica surfaces in 0.1 M KNO_3 solution. The range and the value of the repulsive forces compare well with the electrostatic double-layer overlap repulsion expected from the DLVO theory for 1:1 electrolyte solution of 0.1 M concentration.

Low-Concentration Regime. Insertion of ODU-35K into the electrolyte solution to $c_{pol} = 2.0 \times 10^{-6}$ g/mL did not result in an appreciable change of the forces measured in the solution of KNO_3 prior to polymer addition. Further increase of c_{pol} to 2.0×10^{-5} g/mL shifted the onset of repulsion toward larger values of D. Curves b and c in Figure 1 outline the force profiles measured on a first approach of the surfaces following their incubation in the solution of ODU-35K for various time periods. All force profiles indicate repulsion monotonically increasing with decreasing D. The distance of the onset of repulsion slightly evolved with adsorption time: it increased from 260 Å after 1 h adsorption to 340 Å after 17 ± 1 h exposure of the surfaces to the polymer solution, whereas the thickness of the highly compressed layers remained at ca. 80 Å. For incubation longer than 17 ± 1 h no further changes were observed in the force profiles. For $D = 80$ Å, the mean refractive index n of the medium confined between the surfaces was 1.52 ± 0.01, i.e., close to the bulk refractive index of PEO. From this value of n polymer adsorption $\Gamma = 4.0 \pm 1.0$ was calculated as previously described.[14] Adsorbance did not change in consecutive compression−decompression measurements.

Intermediate Concentration Regime. Experiments in the intermediate concentration regime were carried out at $c_{pol} = 8.0 \times 10^{-5}$ g/mL and $c_{pol} = 6.1 \times 10^{-4}$ g/mL. At these concentrations, substantial association of ODU-35K occurs in bulk solutions.[1,2] The main features of the forces measured between the polymer-bearing surfaces in this concentration regime can be summarized as follows:

(i) In repetitive compression−decompression experiments, interactions measured between the surfaces on their approach featured only repulsion, independently

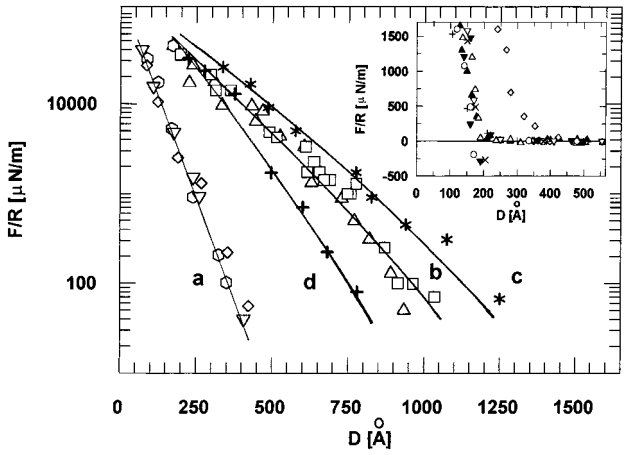

Figure 2. Force−distance profiles measured in compression runs between mica surfaces exposed to 8.0×10^{-5} g/mL solution of ODU−PEO following incubation times: (⬡) 1 h, (▽) 2 h, (◇) 5 h, (△) 17 ± 1 h, (∗) 34 ± 2 h. Force profiles following addition of ODU-35K to $c_{pol} = 6.1 \times 10^{-4}$ g/mL and incubation for 34 ± 2 h: (□). Force profiles following dilution of (□) to 2.0×10^{-5} g/mL and incubation for 17 ± 1 h: (+). Inset shows force−distance profiles on a linear scale measured in successive compression−decompression experiments following surface incubation in polymer solution for 5 h: (◇/△) 1st compression/decompression, (+/×) 4th compression/decompression, (▲/▼) 6th compression/decompression.

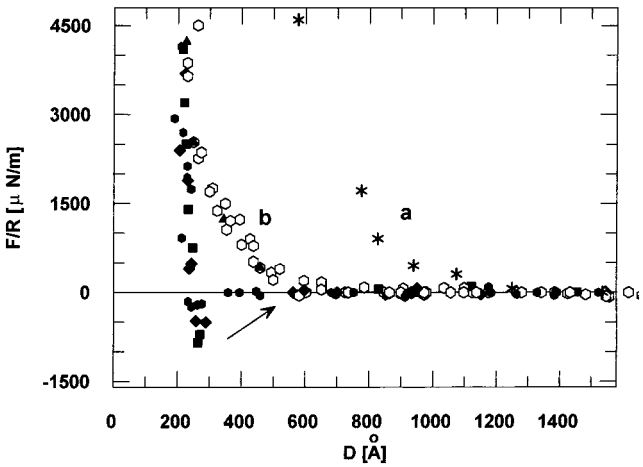

Figure 3. Force−distance profiles between mica surfaces exposed to 8.0×10^{-5} g/mL polymer solution in 0.1 M KNO_3 for 34 ± 2 h: (∗) first compression after equilibration; (▲) immediate decompression following (∗); (⬡) second compression following (▲); all subsequent compression profiles followed (⬡); (⬢) immediate decompression following (⬡); (◆) decompression succeeding (⬡) after 15 min in contact; (■) decompression following (⬡) after 30 min in contact.

of the time that the surfaces were maintained in contact under compression and the time of equilibration after decompression. This feature was similar to that observed in the low-concentration regime.

(ii) The magnitude and the distance range of the repulsion forces increased with the adsorption time (Figure 2). Exposure of the mica surfaces to the ODU-35K solution at $c_{pol} = 8.0 \times 10^{-5}$ g/mL for the time intervals varying from 2 to 5 h led to a small shift in the onset of the repulsion forces from 340 to 480 Å (Figure 2, curve a). Following 17 ± 1 and 34 ± 2 h exposure, the range of repulsion forces shifted from 480 to ca. 1040 Å (Figure 2, curve b) and then to 1250 Å (Figure 2, curve c). Longer incubation time did not result in a noticeable change of the force profiles.

(iii) Effect of the increase in c_{pol} was less significant. Addition of ODU-35K to $c_{pol} = 6.1 \times 10^{-4}$ g/mL did not cause significant change in the force profiles measured for $c_{pol} = 8.0 \times 10^{-5}$ g/mL (Figure 2). The dilution of the 6.1×10^{-4} g/mL solution to $c_{pol} = 2.0 \times 10^{-5}$ g/mL accompanied by 17 ± 1 h equilibration led to a relatively small shift of the normal force profile from ca. 1250 to ca. 870 Å (Figure 2, curve d). This distance range was substantially larger than 380 Å measured in the original polymer solution at $c_{pol} = 2.0 \times 10^{-5}$ g/mL (Figure 1, curve c).

(iv) The force profiles measured in the solution at $c_{pol} = 8.0 \times 10^{-5}$ g/mL featured hysteresis in compression/decompression experiments, which depended on the number of approach-and-separation cycles. Figure 3 summarizes the force−distance relations measured on approach and separation of the surfaces exposed to the solution of ODU-35K for various periods of time. For the 34 ± 2 h exposure, on a first approach, a monotonically increasing long-range repulsion was measured at $D = 1250 \pm 30$ Å (Figure 3, curve a). An immediate separation of the surfaces led to a shift in the onset of the repulsion forces to ca. 700 Å (Figure 3, curve b). On a second approach the force profile shifted toward substantially shorter values of D following curve b, whereas on a second separation measurable attraction appeared between the surfaces. The minimum in the force profile was located at a surface separation of 250 ± 25 Å. All subsequent compression profiles measured at $c_{pol} = 8.0 \times 10^{-5}$ g/mL featured repulsion commencing at $D \approx 700$ Å; all decompression profiles measured for the different contact time showed attraction between the surfaces at D of ca. 250 Å. Only after equilibration of the surfaces at $D \approx 3$ μm for about 3−5 h, the long-range force profile following curve *a* was restored. Similar interactions were measured following short-time exposure of the surfaces to the solution of ODU-35 (Figure 3, inset): after several compression/decompression cycles notable weak attraction occurred at $D = 180 \pm 20$ Å upon decompression of the surfaces, whereas on their approach repulsion was repeatedly measured.

The adsorbance of ODU-35K at $c_{pol} = 8.0 \times 10^{-5}$ g/mL and 34 ± 2 h exposure was estimated to be $\Gamma = (12 \pm 1.5) \times 10^{-3}$ g/m^2 in the first compression run for $n = 1.46 \pm 0.015$ at $D \approx 350$ Å. However, in the second compression to $D \approx 200$ Å the value of $\Gamma = (9.7 \pm 1.5) \times 10^{-3}$ g/m^2 was slightly smaller, indicating partial expulsion of the polymer from the surfaces.

The force−distance relations measured in compression/decompression experiments for $c_{pol} = 6.1 \times 10^{-4}$ g/mL exhibited similar features, i.e., long-range repulsion on a first approach of the surfaces, a shorter-range repulsion in the first decompression and subsequent recompressions, and attraction in the second and subsequent decompressions.

(v) The magnitude of attraction forces depended on the extent of the surface compression. In the second series of experiments, the surfaces were brought together to $D = 300 \pm 10$ Å, maintained at this distance for various periods of time, and then separated. The corresponding force profiles are shown in Figure 4. Again, attraction between the polymer-covered surfaces was measured upon their separation. For the 30 min contact time, the magnitude of attraction forces was on average 3 times lower than that measured for the compression to $D = 200 \pm 10$ Å.

When the surfaces were approached to $D \geq 420$ Å for the time periods varying from ca. 20 to 180 s, no

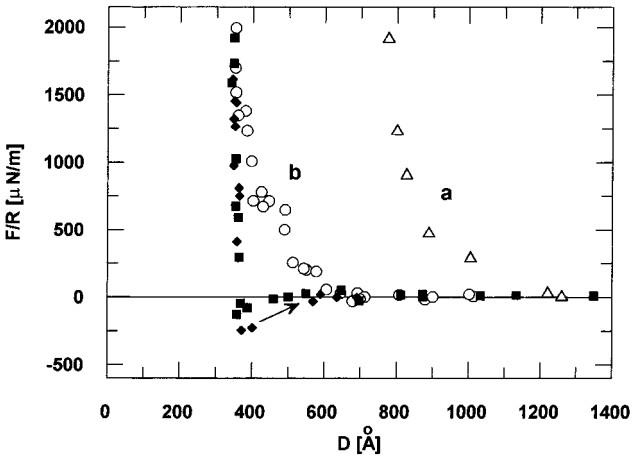

Figure 4. Force−distance profiles measured in conditions similar to those of Figure 3 for compression of the ODU−PEO layers to $D = 300 \pm 10$ Å: (△) first compression after 34 ± 2 h equilibration; (○) second and subsequent compressions; (■) immediate decompression; (◆) decompression following 30 min in contact.

noticeable attraction was measured upon their separation.

(vi) The attraction "pull-off" force needed to separate the polymer-covered surfaces in the second and subsequent decompression increased with the time that the surfaces remained in contact (Figures 3 and 4). This tendency was observed for the different extent of the layer compression; however, for weaker compression the difference in the magnitude of the "pull-off" force for immediate surface separation and separation following 30 min contact decreased.

Discussion

The experimental results shown in Figures 1−4 demonstrate two important features of the interactions between the hydrophilic surfaces covered with the associative polymer: (a) the dependence of forces acting between the surfaces on polymer concentration in the solution and (b) the different response of the adsorbed layers to compression and decompression.

Effect of Polymer Concentration in the Solution. In Figure 5 equilibrium force−distance profiles measured for ODU-35K in compression experiments are plotted on a linear−linear scale. Within the scatter of our measurements, the forces measured upon approach of the surfaces in different concentration regimes show interactions governed by the osmotic repulsion between ethylene oxide segments. Some increase in the onset of repulsion observed when c_{pol} increases from 2.0×10^{-5} to 8.0×10^{-5} g/mL (first hours of adsorption) can be caused by the formation of a dense adsorbed layer of ODU-35K. For comparison, a force profile measured by Klein et al.[15] for monolayers of nonhydrophobized PEO ($M_w = 40\,000$) is plotted on the same graph. This profile compares well with those measured in the solution of ODU-35K at $c_{pol} = 2.0 \times 10^{-5}$ g/mL (17 ± 1 h adsorption) and at $c_{pol} = 8.0 \times 10^{-5}$ g/mL (2−5 h adsorption). The thickness of the strongly compressed layer is also very close for ODU-35K and PEO.[15]

The onset of the long-range repulsion corresponds generally to twice the extension of the adsorbed macromolecules from the surface and thus gives twice the thickness d of the adsorbed layer. The value of $d = 240$ Å measured in our work for the layer of ODU-35K

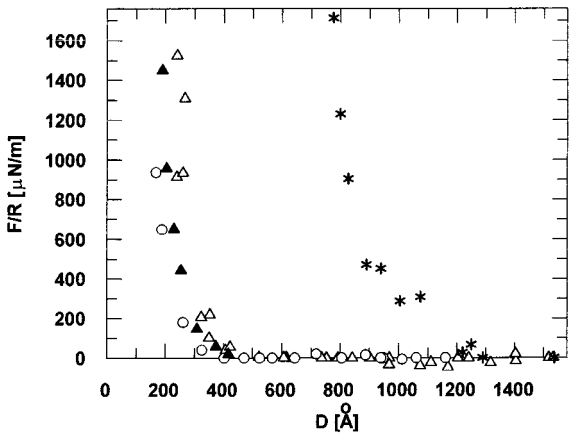

Figure 5. Force profiles measured in compression runs plotted on a linear−linear scale for various c_{pol}: (○) 2.0×10^{-5} g/mL; 17 ± 1 h incubation; (△) 8.0×10^{-5} g/mL, 5 h incubation; (∗) 8.0×10^{-5} g/mL, 34 ± 2 h incubation; (▲) indicates F/R vs D for PEO ($M_w = 4.0 \times 10^4$, $M_w/M_n = 1.03$) measured by Klein et al.[15] at $c_{pol} = 1.5 \times 10^{-4}$ g/mL.

adsorbed at $c_{pol} = 8.0 \times 10^{-5}$ g/mL after 5 h adsorption corresponds approximately to 3.5 unperturbed radii of gyration of PEO.[15] This value of d is close to 260 ± 50 Å obtained in the light scattering experiments for the adsorbed layer of ODU-35K on poly(methyl methacrylate) latex particles.[6]

It can be concluded from the comparison of the force profiles of nonhydrophobized and hydrophobized PEO that a monolayer of ODU-35K adsorbs onto the mica surface from a dilute polymer solution, which does not significantly change after its short time exposure to solutions at moderate c_{pol}. The properties of the ODU-35K and PEO monolayers do not notably differ as could be expected from a reduced quality of the solvent for the PEO end-terminated with hydrophobic groups. The reason for the similarity of the adsorbed layers of PEO and ODU-35K can be understood in terms of the molecular conformation acquired by ODU-35K on the mica surface (shown schematically in Figure 6a). In dilute polymer solutions and in the intermediate concentration regime after short-time incubation, adsorption of the polymer onto the hydrophilic mica surface is driven by interactions between the ethylene oxide segments and the substrate. In addition, a possibility of adsorption of the hydrophobic end groups should not be ruled out, since they are localized on the surface by the adsorbing PEO backbones and do not pay much entropic cost to stick to the surface. In both cases, the hydrophobic octadecyl moieties are located inside the adsorbed layer to reduce unfavorable interactions with water.

"Thickening" of the adsorbed layers of PEO-35K from $d \approx 240$ Å to $d \approx 625$ Å after long time adsorption from the solutions at $c_{pol} \geq 8.0 \times 10^{-5}$ g/mL indicates growth of the multilayers on the surface. Since $c_{pol} = 8.0 \times 10^{-5}$ g/mL is very close to c_{cmc} of ODU-35K of ca. 1.0×10^{-4} g/mL,[16] it can be expected that the multilayers are formed by adsorption of micelles. The thickness of the adsorbed multilayer of ca. 625 Å accounts well for the adsorption of a single layer of micelles with the diameter of about 380 Å onto the 240 Å thick monolayer of ODU-35K. This size of micelles of ODU-35K compares well with ca. 420 Å measured by Pham et al.[16] for ODU-35K with the dynamic light scattering technique.

The depiction of the structure of the ODU-35K multilayer shown in Figure 6b is based on current under-

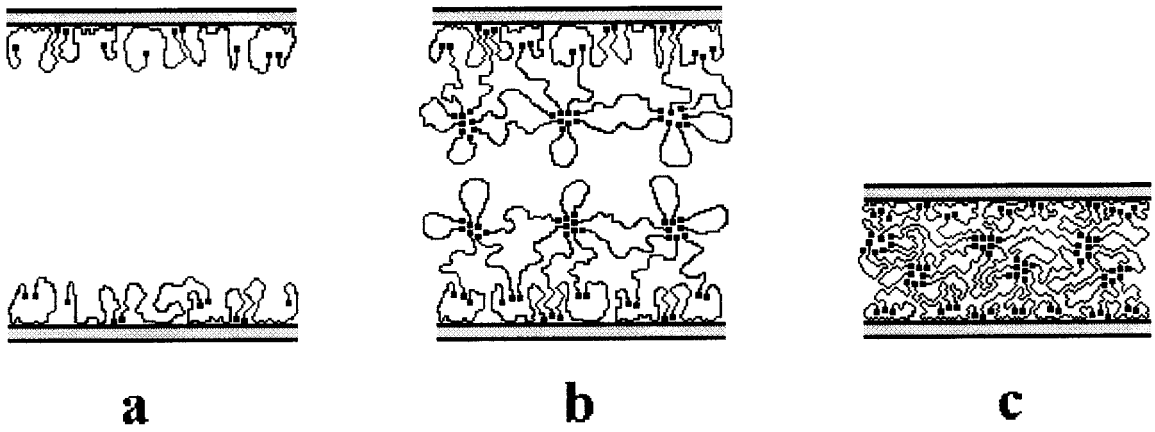

Figure 6. Schematic presentation of the adsorbed layers poly(ethylene oxide) end-capped with octadecyl groups: (a) monolayer adsorbed in dilute polymer solutions or in solutions of moderate concentrations following short time incubation; (b) polymer layer adsorbed from moderately concentrated solutions; (c) formation of bridges between compressed adsorbed layers of the telechelic polymer.

standing of the formation of networks in concentrated solutions of telechelic polymers.[1,2] For $c_{pol} > c_{cmc}$, the adsorption of micelles is driven by association of alkyl end groups of molecules residing in micelles and alkyl end groups that are attached to macrochains adsorbed onto the mica. The attachment of micelles to the surface is accompanied by the exchange of the hydrophobic groups between neighboring aggregates at the surface and the formation of a network. The multilayer can be thus pictured as a thin layer of a weak micellar gel adsorbed onto the surface.

The long time required to achieve the equilibrium adsorption of the multilayer can be expected from the lower value of the diffusion coefficient of single micelles of ODU-35K than that of isolated ODU-35K chains. The time, τ, required to attain equilibrium adsorbance of ODU-35K was calculated as $\tau = [2R(2\Gamma_{eq}/c_{pol} - D_0)]/\nabla$ where Γ_{eq} is equilibrium polymer adsorbance, D_0 is the surface separation during adsorption, and ∇ is the diffusion coefficient.[17] For $R \approx 10^{-2}$ m, Γ_{eq} of ca. 4 and 12 mg/m^2 for individual molecules of ODU-35K and for micelles of ODU-35K, respectively, $c_{pol} = 2.0 \times 10^{-5}$ and 8.0×10^{-5} g/mL, $D_0 \approx 3$ μm, $\nabla \approx 3.1 \times 10^{-11}$ m^2/s for isolated PEO chains ($M_w = 34\,000$),[9b,18] and $\nabla \approx 9.5 \times 10^{-12}$ m^2/s for single micelles of ODU-35K,[16] the characteristic time of equilibrium adsorption increases from $\tau \approx 30$ h for the solution at $c_{pol} < c_{cmc}$ to $\tau \approx 83$ h at $c_{pol} > c_{cmc}$. In our experiments, the value of τ for the adsorption of both individual chains and micelles was lower, perhaps because of additional stirring of the solution confined between the surfaces during compression/decompression experiments. Another factor that determines the rate of adsorption of micelles is the exchange of octadecyl groups between the micelles and the adsorbed monolayer. For the telechelic polymers with a low c_{cmc}, such as ODU-35K, the exit time of the hydrophobic ends from their multimer structures is long; thus, substantial time is needed for bridging of the micelles to the monolayers of ODU-35K and for the formation of a gel-like layer.

The network structure of the polymer layer accounts for the slow desorption process following dilution of the polymer solution to $c_{pol} = 2.0 \times 10^{-5}$ g/mL (Figure 2). Since in the gel-like layer the micelles of ODU-35K do not perform anymore as isolated entities, their diffusion from the surface upon dilution is suppressed, and 17 ± 1 h incubation of the layer in the dilute solution is not sufficient to achieve an equilibrium thickness of the adsorbed layer.

Hysteresis in Compression−Decompression Profiles. Repulsion measured on approach of the polymer-covered surfaces is consistent with the structure of the adsorbed layers schematically shown in Figure 6a,b. Since the exit time of the alkyl moieties is slow and the fraction of the free hydrophobic ends is small, on the time scale of the compression experiments the octadecyl substituents do not notably contribute to the surface interactions. These feature contrasts ODU-35K from the telechelic polymers end-capped with short solvated substituents, e.g., zwitterionic groups, for which a substantial fraction of free end groups leads to weak attraction of the polymer layers upon their approach.[19]

A shorter range of the repulsion forces measured on a first separation of the surfaces indicates that the decompression time is not sufficient for a complete relaxation of the adsorbed layers. In addition, decrease in polymer adsorbance implies that partial expulsion of weakly adsorbed ODU-35K occurs upon polymer compression.

The attraction between the polymer-bearing surfaces measured only after several approach/separation cycles, as well as the dependence of the adhesion force on contact time and the extent of compression, indicates that structural rearrangements occur in the adsorbed multilayers under their compression. Two latter features are demonstrated in Figure 7. Figure 7a shows the dependence of the adhesion energy versus the time of surface contact. The adhesion energy, γ, was calculated from the value of the "pull-off" force, F_s, measured upon separation of the surfaces as[20]

$$\gamma = -F_s/(3\pi R) \qquad (2)$$

The energy of adhesion between the layers of ODU-35K adsorbed from the solution at $c_{pol} = 8.0 \times 10^{-5}$ g/mL increases almost four times when the time of the molecular contact at $D = 200 \pm 10$ Å increases from ca. 10 to 1800 s.

In Figure 7b the value of the adhesion energy is plotted versus the extent of compression of the adsorbed layers of ODU-35K. The degree of compression, M, was determined as $M = (d - d_c)/d$, where d_c is the thickness of the adsorbed layer under compression and d is the equilibrium thickness of the layer that accounts for

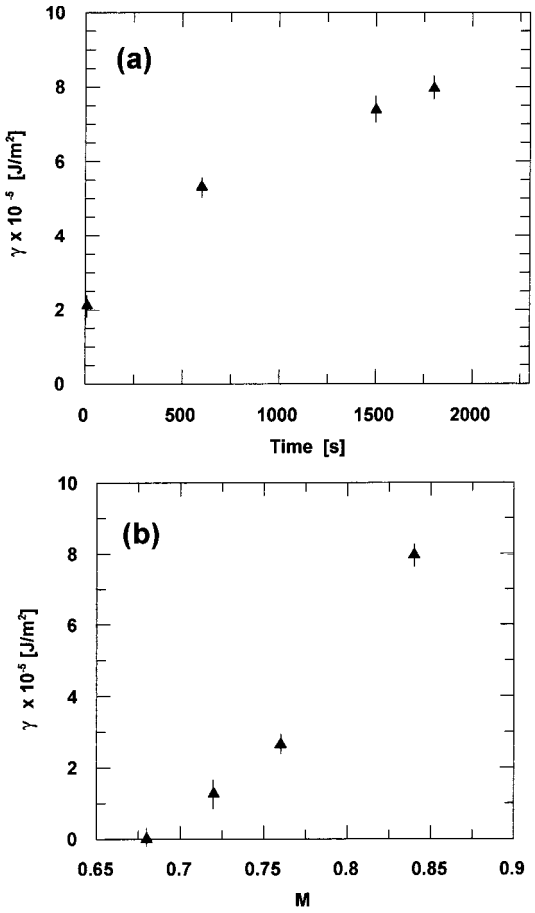

Figure 7. Adhesion energy as a function of (a) contact time and (b) extent of compression: (a) the surfaces were exposed to the solution of ODU-35K at $c_{pol} = 8.0 \times 10^{-5}$ g/mL for 34 ± 2 h, then brought to $D = 200 \pm 10$ Å in the second or successive compressions, maintained in contact for various times, and then separated; (b) the same multilayers as in (a) were compressed for 30 min to different D.

strongly and weakly adsorbed chains, $d \approx 625$ Å. Measurable attraction between the layers appears only when $M \geq 0.72$.

Compression of the polymer-bearing surfaces is equivalent to increasing polymer concentration in the gap between the surfaces. Under these conditions, attraction between the adsorbed layers of ODU-35K is generated by bridging between the compressed polymer micelles adsorbed onto two opposite surfaces. This situation is schematically shown in Figure 6c.

The bridging does not significantly affect the response of the adsorbed layers to compression since this response is dominated by the excluded-volume interactions. In contrast, the attraction of the surfaces upon their separation depends on the number of bridges formed between the micelles under compression.[21] When the surfaces are brought in contact and especially maintained in the compressed state for sufficient time, an exchange of octadecyl groups occurs between the two opposite layers. Long time contact and strong compression of the surfaces lead to increase in the number of bridges, which results in the growth of the adhesion energy. Upon surface separation, bridges transform into loops with hydrophobic groups residing in the cores of micelles. However, this conformation is not equilibrium, and a considerable period of time is needed to attain the equilibrium thickness of the adsorbed layer.

A theoretical model for estimating interactions between micelles in micellar gels of AP's was suggested by Semenov et al.[22] A reference system for a "flowerlike" micelle was a telechelic brush attached to the surface with two end groups. Although the description of molecules of ODU-35K aggregated in micelles with the brush model is rough (water is only moderately good solvent for PEO, $\chi = 0.45-0.48$[23]), some conclusions can be made by comparing our experimental results with predicted ones.

The magnitude of attraction between the surfaces bearing adsorbed micelles is proportional to the number of bridges formed per micelle and the number of micelles. For a particular telechelic polymer in a compressed micellar gel, the number of bridges per micelle, N_0, grows as $N_0 \sim (\phi/\phi^*)^{(1/9)[1-(3\nu-1)]}$ where ϕ is polymer concentration in the compressed gel, ϕ^* is a crossover concentration, and ν is the Flory exponent, $\nu = 0.588$.[22] Since in our experiments polymer adsorbance does not change significantly and $\phi/\phi^* \sim M^{-1}$, we were able to compare the experimentally measured and the estimated from the Semenov model effects of compression on adhesion between the polymer-covered surfaces. The comparison revealed a stronger than predicted effect of compression on the attraction between the surfaces. The difference can be ascribed to considerable interpenetration of micelles under strong compression. In this regime, almost all chains form bridges, the end group exchange occurs between both adjacent and distant micelles, and $N_0 \sim (\phi/\phi^*)^{(1/9)[1-(3\nu-1)]}$ is no longer valid.

Conclusions

We showed that adsorption of hydrophobically modified poly(ethylene oxide) from solutions below c_{cmc} produces monolayers similar to those of nonhydrophobized PEO. This similarity is unexpected and suggests that the hydrophobic groups at the chain ends are screened by the ethylene oxide segments exposed to the liquid phase. At moderate polymer concentrations which are comparable with a cmc threshold, a micelle-like layer adsorbs onto the surface. Polymer layers adsorbed from the low and moderately concentrated solutions exhibit different responses to compression and decompression: on approach repulsive forces are observed, whereas on separation attraction between the surfaces evolves after several compression/decompression cycles. The magnitude of attraction forces depends on the extent of the layer compression and on the time that the surfaces were maintained in contact before separation. The practical implication of this effect is that colloid particles bearing adsorbed layers of associative polymers will not immediately flocculate. However, if their surfaces remain in contact for a longer time, changes in the adsorbed layer will occur that facilitate flocculation.

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