Macromolecules 1988, *21*, 3333–3336

Table I
Equilibria between PE-3, PE-3-H$^+$CH$_3$SO$_3^-$, C$_8$H$_{17}$-3, and C$_8$H$_{17}$-3-H$^+$CH$_3$SO$_3^-$ in CH$_2$Cl$_2$[a]

[PE-3]$_0$/ [C$_8$H$_{17}$-3-H$^+$CH$_3$SO$_3^-$]$_0$	[PE-3-H$^+$CH$_3$SO$_3^-$]$_0$/ [C$_8$H$_{17}$-3]$_0$	$[K_{eq}]^{-1}$
1/1		4.0
2/1		3.6
10/1		10
	1/5	22
	1/1	3.6
	3/2	5.0

[a] Equilibria were measured at 25 °C in CH$_2$Cl$_2$ suspensions. Concentrations were determined after the suspensions were allowed to equilibrate until repetitive scans showed no further changes were occurring in the UV–visible spectrum. The values of ϵ for C$_8$H$_{17}$-3 and for C$_8$H$_{17}$-3-H$^+$ were 25 700 and 3990 L/(mol cm) at 435 nm and 2650 and 55000 L/(mol cm) at 520 nm, respectively.

values listed reflect the differing protonating ability of soluble **3** and polymer-bound **3** (i.e., $[K_{eq}]^{-1} = K_{a\,\text{PE-3-H}^+\text{CH}_3\text{SO}_3^-}/K_{a\,\text{C}_8\text{H}_{17}\text{-3-H}^+\text{CH}_3\text{SO}_3^-}$) and ranged from 3.6 to 22. The results in Table I show that the acidity of PE-3-H$^+$CH$_3$SO$_3^-$ was greater than that of C$_8$H$_{17}$-3-H$^+$-CH$_3$SO$_3^-$.

Determinations of the K_{eq} in Table I include several assumptions and are subject to some experimental limitations.[12] For example, attempts to measure equilibrium constants with a large excess of PE-3-H$^+$CH$_3$SO$_3^-$ or PE-3 relative to the soluble analogue were frustrated by the small amount of **3** in the polymer sample (typically 10^{-8} mol). Second, use of a large excess of soluble C$_8$H$_{17}$-3-H$^+$CH$_3$SO$_3^-$ or C$_8$H$_{17}$-3 relative to PE-3 or PE-3-H$^+$-CH$_3$SO$_3^-$ never produced a true equilibrium because diffusional limitations affected the access of the soluble azo dye to the polymer-bound analogue. Third, we assumed in these calculations of K_{eq} that the ϵ measured for the octyl ester in solution was valid in the polymer matrix and that the concentrations determined in a conventional way from the measured absorbance could be used to calculate a K_{eq} in CH$_2$Cl$_2$ suspension. Nonetheless, the data taken together clearly indicate that a protonated polyethylene-bound cationic azo dye is a stronger acid than its souble analogue. These changes in acidity presumably reflect the lower stability of ionic structures within polyethylene. We think such an effect should be a general phenomena for polyethylene-bound cationic acids. Such effects along with the kinetic effects of acid or base size and solvent polarity are important parameters which can govern proton transfers and related chemistry at polyethylene–solution interfaces.

Acknowledgment. Support of this research by the National Science Foundation (Grant DMR-8605941) and by the Texas Advanced Technology program is gratefully acknowledged.

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(9) The polyethylene used in these experiments was high-density polyethylene (M_w 180 000–200 000) and was obtained from Allied Chemical Corp. The powders prepared by these precipitation techniques appeared to exist as small platelets by light microscopy (dimensions of ca. 1 × 1 × 0.02 mm) and were uniformly colored with dye. The cast films were typically 0.5-mil thick.

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(11) The H_0 values cited are based on sulfuric acid–water solvent mixtures and thus are not transferable to a relatively nonpolar organic solvent systems like CH$_2$Cl$_2$. However, the relative basicity of a series of similar compounds like **4–8** should be unchanged.

(12) Frommer and Bergman (Frommer, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 5227–5234) discuss many of the problems encountered in measuring equilibrium constants in which one of the species is an insoluble polymer.

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Received June 7, 1988;
Revised Manuscript Received September 12, 1988

Direct Measurement of the Interaction between Mica Surfaces with Adsorbed Diblock Copolymer in a Good Solvent

The use of flexible polymers to stabilize colloidal dispersions is well established.[1] In choosing appropriate stabilizers a number of requirements must be met: the polymer should adsorb strongly, it should extend sufficiently far from the surface (to prevent particles from aggregating due to van der Waals attractions), and the polymer should be in good solvent conditions, to ensure repulsion between the segments in the absorbed layers. In recent years the important role of *bridging* has become apparent: even if the above conditions are observed, for undersaturated surface concentrations polymer chains may readily bridge the gap between the opposing surfaces, adsorbing quasi-irreversibly on both and leading to a net attraction.[2,3] This has been empirically overcome by using diblock copolymers where one block adsorbs while the other extends into the solution or polymers which are end-grafted onto the surface, where one end adsorbs while the rest of the polymer extends into the solution (under good solvent conditions). Recently, force measurements between mica sheets in a polystyrene–poly(2-vinylpyridine) (PS–PVP) diblock copolymer solution have been interpreted in these terms,[4] while very recently forces were measured between mica sheets bearing *end-grafted* polystyrene in toluene[5] (a good solvent for PS). The results of the two studies were rather different both in the range and in the relaxation properties of the forces reported. In this paper we report the measurement of forces between two mica surfaces in a solution of a diblock polystyrene–poly(ethylene oxide) (PS–PEO) copolymer in a good solvent and compare our results critically with the earlier studies.

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Table I
Molecular Characteristics of Polymers Used

polymer	M_w	M_w/M_n	PEO content, %	$(PS)_x(PEO)_y$ wt-av DP x	y
PS[a]	1.31×10^5	1.02		1310	
PS-PEO[b]	1.84×10^5	1.10	1.5	1810	63

[a] Kindly donated and characterized by L. J. Fetters. [b] Obtained from Polymer Laboratories (U.K.) and characterized by them.

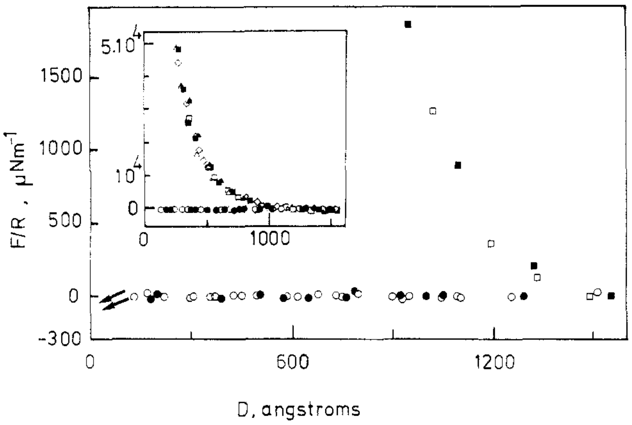

Figure 1. Force-distance ((*F*/*R*) versus *D*) profile between two curved mica surface a distance *D* apart. *R* is the mean radius of curvature of the mica sheets and *F*(*D*)/*R* gives the equivalent interaction energy per unit area between two flat parallel surfaces a distance *D* apart, obeying the same force-distance law, in the Derjaguin approximation.[7] (○) Surfaces immersed in pure toluene; (●) following addition of PS (Table I) and 12-h incubation (arrows indicate jumps into contact); (□, ■) 2 h after addition of PS-PEO (Table I). Inset: Data on a reduced linear-linear scale. Additional symbols are for different compression-decompression cycles following PS-PEO adsorption.

Previous experiments[6] have shown that PS does not adsorb onto mica from (undried) toluene whereas PEO adsorbs strongly. The molecular characteristics of the polymers used are given in Table I. The polystyrene-poly(ethylene oxide) diblock copolymer was synthesized by Polymer Laboratories (Shawbury, UK) and characterized by them, while the regular PS was synthesized, characterized, and kindly donated by L. J. Fetters.

Forces between the mica sheets were measured by using the approach described earlier.[7] At the start of each experiment the forces between bare mica sheets immersed in toluene (BDH analytical grade) were measured. No forces were detected (within the scatter) at intersurface separations *D* greater than about 200 Å, below which there was an attraction and the surfaces jumped together into adhesive contact from about 100 Å, as shown in Figure 1. This is in agreement with earlier studies,[6] the attraction being attributed to water bridging between the surfaces in the undried solvent. As a control, linear polystyrene (PS) was at this stage added to the solvent in which the mica sheet were immersed, to a final concentration of 10^{-4} g/cm^3 and 12 h were allowed for equilibration. No change in the force profile was detected (Figure 1), confirming that in these conditions PS does not adsorb onto mica from the toluene.

The diblock copolymer was then added to the cell, by replacing the PS solution by a PS/PEO solution, also at 10^{-4} g/cm^3 concentration. Within 1 h of adding the copolymer there was evidence of adsorption, with the previous short-range attraction being replaced by a longer ranged repulsion. Since the regular PS does not adsorb onto the mica, as indicated directly by our control measurement (Figure 1), we may conclude unambiguously that the PS-PEO diblock is anchored to each mica surface via the PEO block. Toluene is a good solvent for both PS and PEO, and we have observed no evidence of micellization, which might complicate the situation in cases where one block is insoluble or in poor solvent conditions.

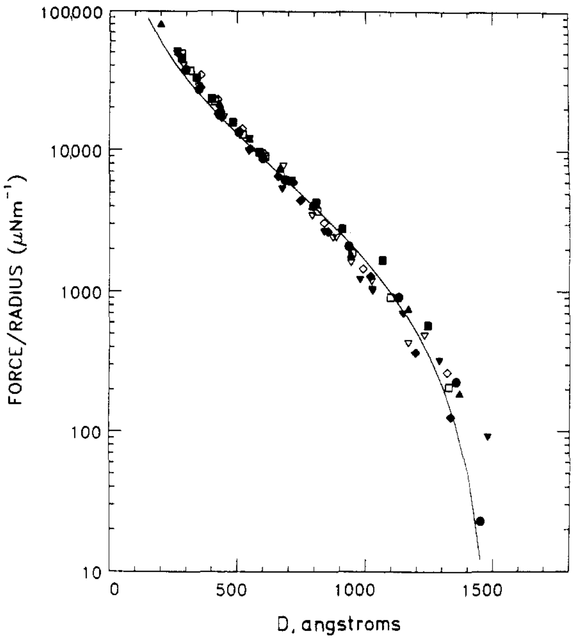

Figure 2. Forces following saturation adsorption of the PS-PEO. Solid symbols show forces measured on compression, (including compression following overnight adsorption) and open symbols the corresponding forces on rapid decompression. Different symbols are for different cycles of compression-decompression. The solid line shows the predicted variation with *D* of the energy *U*(*D*) per unit area between flat parallel plates a distance *D* apart, where $U(D) = \int_{2L}^{D} f(D')\,dD'$ and *f*(*D*) is given by eq. 1 in the text. 2*L* is taken as 1500 Å, from the experimental data.

We observe no evidence of bridging attraction even at the shortest accessible incubation times, indicating on absence of bridging.[13] The limiting force-distance profile (i.e., which does not change on further incubation) is generally achieved with 2 h of replacing the PS by the PS-PEO and is shown in Figure 2. The force axis is normalized to give the interaction energy per unit area between the mica sheets (see legend to Figure 1) and is plotted logarithmically to show clearly the 4 orders of magnitude variation in force. Repulsion is first detected systematically when the separation between the mica surfaces is some 1500 Å, corresponding to around 13R_g (unperturbed radii of gyration of the PS block). If we take the separation at onset of interaction as being twice the effective layer thickness of the PEO-anchored copolymer on each surface, this suggests an effective thickness of some 6-7R_g for the dangling PS block from each surface, compared to some 3-4R_g for adsorbed *homopolymers*.[6] We have also carefully measured force profiles at different rates of compression and decompression of the mica surfaces (shown by different symbols in Figure 2): we find that the force-distance law is essentially independent (within the scatter) of the compression-decompression rate, with no evidence of hysteresis even when compressing to 100 000 μN/m. This differs markedly from the behavior of layers of *adsorbed* homopolymers[6] where (both in organic[6a] and in aqueous[6b] good solvents) large nonequilibrium relaxation effects have been a characteristic feature, attributed to the higher-than-equilibrium number of monomers forced to adsorb onto the surface at high compressions. With the present *nonadsorbing* PS tails such effects, as well as the bridging attraction, are indeed absent.

The profiles we obtain are very similar to those found in a recent study[5] in which the forces were measured between polystyrene chains (PS-X) terminally anchored to the mica surface via a single zwitterionic end group X. This suggests that the interactions between layers of diblock copolymers, anchored by only a short length of one block, may be analyzed successfully in terms of the forces between end-anchored, nonadsorbing tails. The range of the forces in the earlier study, indicating a layer thickness for the end-adsorbed PS-X of ca. $6R_g$, and the absence of any hysteretic effect on rapid compression and decompression are especially reminiscent of the present data.

Our finding of rate-independent force laws with the PS–PEO diblock copolymer differs qualitatively from force profiles between mica sheets in PS–PVP solutions,[4] where hysteresis was reported at moderate compressions (>5000 μN m^{-1}). The thickness of the adsorbed layers, as measured by half the range for onset of repulsive interactions, is also very different for the two cases. Thus for the closely comparable cases of PS–PVP, with a PS block of $M = 1.85 \times 10^5$, and our present PS–PEO sample, with a PS block of $M = 1.81 \times 10^5$, the effective adsorbed layer thicknesses are ca. 1250 and ca. 750 Å, respectively. These differences between the two cases, which have practically identical PS blocks, may be due to a number of factors. First, the PS–PVP diblock copolymer is known to form micelles in toluene (a poor solvent for the PVP block) at concentrations similar to the incubation concentration in the force experiments,[8,9] and the presence (if any) of micelles may well complicate the interpretation of the data. Also, in the PS–PVP case the lengths of the two blocks are comparable; the large size of the PVP block may imply that it should not be considered as an anchor block of negligible dimensions normal to the surface, and it may thus exhibit the hysteretic behavior characteristic of adsorbed polymers.[6,14] In contrast, the rather short PEO moiety in the PS–PEO diblock ensures that we are dealing with a relatively small anchor group, reminiscent of the zwitterionic end-group in the recent[5] surface interaction studies on the end-grafted polystyrene chains. A third possibility,[4] which might explain the difference in range but not the hysteretic behavior, is that the surface coverage by the PS–PVP diblock is very much higher than for the PS–PEO. This is less likely, however, since the magnitudes of the repulsive interactions in both cases are similar in the region of high compression, which is dominated by the osmotic repulsion due to PS segments; this suggests that the overall adsorbed amounts of PS segments are similar in the two cases.

Our study shows that only very small lengths of the anchoring polymer (PEO in this case) are necessary in order to attach the polymers to the surfaces in what appears to be an irreversible manner: no desorption was detected in our experiments, as evident from the reproducibility of force profiles immediately following even very high compressions (>10^5 μN/m), much larger than the sort of surface forces one might expect in Brownian collisions between colloidal particles. Indeed, it is a little surprising that such large compressions do *not* force the small anchoring PEO moiety off the surface: we tentatively attribute this to kinetic factors. On the one hand, the effectively permanent (on our time scales) 2-D "network" formed by the highly compressed polymer layer is prevented from escaping by the confining mica surfaces; at the same time the diffusion of the copolymer chains within this layer is likely to be hindered by the tendency of the PEO moieties to stick to the mica surfaces.

A scaling model of chains adsorbed onto a surface by one polar headgroup in a good solvent has been proposed by Alexander[10] and further extended by de Gennes[11] to give a form for the force profile. The force is analyzed in terms of a repulsive osmotic term which comes from the increased polymer concentration in the intersurface gap as the surfaces approach, and which will dominate at very high compressions, and an elastic term in which the *reduction* in free energy, on compression of the over-extended tails, is taken into account. The total force per unit area, $f(D)$, between flat plates a distance D apart bearing a high coverage of terminally-attached chains is given in this model by

$$f(D) = kT/s^3[(2L/D)^{9/4} - (D/2L)^{3/4}] \qquad D < 2L$$

where L is the mean thickness of the polymer layer and s the average distance between anchor points. This expression, integrated appropriately to correct for the crossed cylinder configuration of our experiments, is plotted as the solid line in Figure 2. No unknown parameters are needed to make a fit, other than supplying an appropriate shift in the y-axis, as the scaling argument does not give the necessary prefactor. The fit is very reasonable. We note that the Alexander–de Gennes theory also provides a very good quantitative fit to the data of our earlier study with PS-X.

In summary, our study has shown directly that the interaction between surfaces bearing adsorbed block copolymers, with the anchoring block of a much smaller length than the nonadsorbing, stabilizing block, is monotonically repulsive, is of very much longer range than that for corresponding adsorbed homopolymers, and shows no measurable hysteresis. A comparison with previous experimental observations on end-grafted polymers,[5] and the quantitative agreement found with a scaling model of end-grafted chains, strongly indicates that such systems can be successfully analyzed in terms of layers of terminally anchored polymers.

Acknowledgment. We thank L. J. Fetters for providing the linear polystyrene sample, the SERC (U.K.) and Unilever plc for a CASE award (H.J.T.), and the Israeli Academy and Minerva Foundation for partial support. J.K. is the incumbent of the Herman Mark Chair in Polymer Physics at the Weizmann Institute.

Registry No. (S)(EO) (block copolymer), 107311-90-0.

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(13) Experiments (to be published) where only one of the mica surfaces was covered with PS–PEO diblock copolymer, while the other remained bare, also show purely repulsive forces, unambiguously indicating the absence of any bridging.
(14) It is of interest that in a recent force study[12] using PVP–poly(*tert*-butylstyrene) diblock copolymer where both com-

ponents were rather short (with the PVP assumed to be the anchoring block) no hysteresis was observed.

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Received July 12, 1988;
Revised Manuscript Received August 3, 1988

Viscoelastic Properties of Lipid Surfactant/Polymer Composite Films

Water-insoluble polyion complexes are formed from ionic lipids and ionic polymers with opposite charges.[1] By casting the solution of the polyion complexes in common halogenated organic solvents, lipid surfactant/polymer composite films are prepared. The aggregation state of the lipid in the films has already been examined by differential scanning calorimetry (DSC) and X-ray diffraction, and it was confirmed that the films are composed of lipid multilamellae, in which lipids aggregate in a manner similar to lipid bilayers (Figure 1).[1] For this reason, the composite films have been referred to as immobilized lipid bilayers. The films thus obtained are expected to exhibit unique properties based on the highly ordered structures similar to biomembranes. Membrane transport experiments were carried out for several solutes, and marked changes in permeation were observed near the phase-transition temperature of the lipid bilayers.[1b,c,e] However, the physical state of the lipid bilayers and the influence of ionic polymers on lipid bilayers are not fully known. In this paper, we report for the first time that dynamic viscoelastic measurement, which is effective to study the aggregation state and the phase state of polymers, is also very useful to know the fundamental properties of the lipid/polymer composite films. ESR studies of a spin probe incorporated into the films were also carried out to obtain information about molecular motion of the lipids.

According to the procedure of the previous reports,[1] the polyion complexes were obtained as precipitates by mixing a 2% aqueous dispersion of dialkyldimethylammonium bromide ($[CH_3(CH_2)_{n-1}]_2N^+(CH_3)_2Br^-$, $n = 14, 16, 18$) and a 0.5% aqueous solution of high molecular weight sodium poly(styrenesulfonate) (lipid/polymer repeating units 1. 5:1 (mol/mol)) and purified by reprecipitation twice from chloroform with ethanol (recovery 30–50%). Polyion complexes consited of almost stoichiometric composition of lipids and polymer as determined by elementary analysis.[3] About 5% chloroform solutions of the polyion complexes were cast on flat glass plates and were evaporated to dryness at room temperature. Transparent films with thicknesses of 200–300 μm were obtained after vacuum drying.

Dynamic mechanical measurements of the composite films were made with a nonresonance, forced vibration instrument,[2] Rheovibron viscoelastmeter Model DDV-II-C (Toyo Baldwin Co. Ltd.) in water at a heating rate of 0.5 °C/min at a frequency of 110 Hz after aging the films at 60 °C in water for 10 min.

DSC measurements were performed with a Du Pont DSC 9900 system at a scanning rate of 10 °C/min in the presence of a small amount of water.

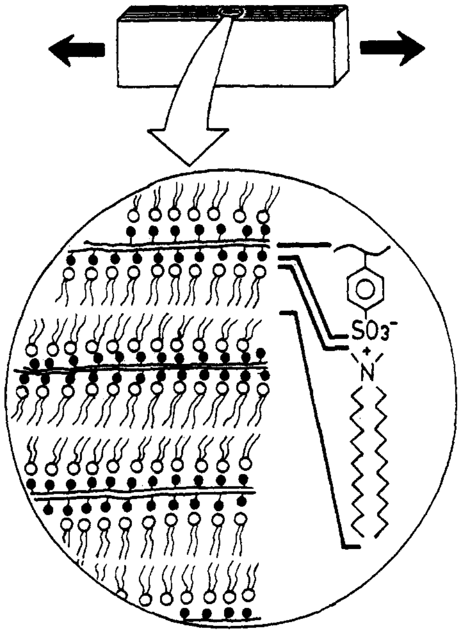


Figure 1. Schematic illustration of the structure of the lipid/polymer composite films. Arrows indicate the direction of oscillating stress and strain applied on the films. The specimen size was 5 mm in width, 10–15 mm in length, and 0.2–0.3 mm in thickness.

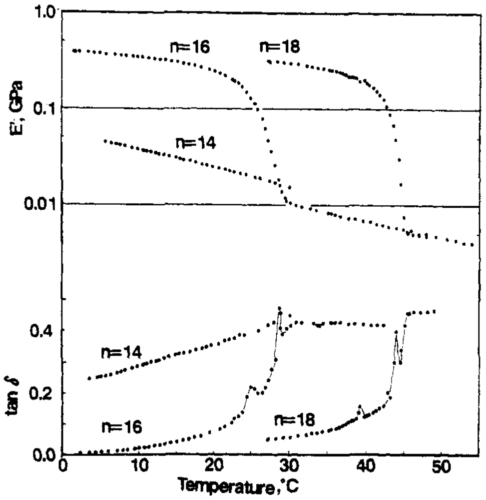
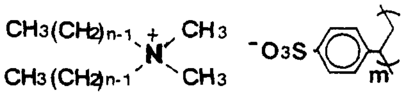


Figure 2. Thermomechanical behavior of the composite films, 2Cn2C1-PSS, n = 14, 16, 18.

The composite films for ESR measurement were prepared by casting the chloroform solutions of polyion complexes and 12-doxylstearic acid (spin probe concentration: 10^{-4} mol/1000 g of polyion complex). Samples were dried in vacuo and annealed in water at 60 °C prior to measurement. ESR spectra were recorded on a Varian E-line 9.5-GHz ESR spectrometer with a temperature control unit in the presence of a very small amount of water which does not interfere with measurement.

Figure 2 shows the dynamic mechanical storage modulus, E', and tan δ measured for the three composite films (2CnN2Cl-PSS, n = 14, 16, 18). These films have tensile



2CnN2C1-PSS n=14, 16, 18

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