Polymer-Surfactant Films at the Air-Water Interface. 1. Surface Pressure, Ellipsometry, and Microscopic Studies

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ABSTRACT: Mixed films formed by an insoluble polymer, poly(dimethylsiloxane) (PDMS), placed on the surface of aqueous solutions of two different soluble surfactants are studied by a variety of different methods: surface tension isotherms, ellipsometry complemented by the neutron reflectivity experiments presented in part 2, and direct observations of the surface via the Brewster angle microscope. A vertical separation into superimposing surfactant and polymer layers is exhibited, with mixing between the layers depending on the surfactant. On one but not the other of the surfactant solutions studied, a lateral separation of the polymer monolayer is also observed, into domains similar to those previously observed on pure water. The collapse of the monolayer into a three-dimensional state with increasing polymer concentration occurs more smoothly than on water.

Introduction

The presence of a polymer modifies the properties of surfactant systems. The polymer can thus stabilize or destabilize colloids and related, generally surfactant-based, compositions.[1] This certainly involves modification of the surface properties of the system, but while considerable effort is being expended in exploring the action of polymer and surfactant in the bulk liquid,[2] little is known of the result of the combined action at a surface. The configuration, dynamics, and thermodynamics of polymer and surfactant at an interface remain essentially open questions, experimentally and theoretically.

The action of a soluble polymer at an interface of a surfactant solution has recently been considered theoretically by de Gennes,[3] and further by Brooks et al.;[4] the presence of the polymer is expected to change such properties of the interface as the curvature elasticities and the surface viscosity. The latter may affect flow in such practical systems as soap films: The effect of such a polymer on the drainage of a soap film has been explored by Leonti-Addad et al.,[5] who find that the presence of the polymer can lead to slower drainage in the film, with stabilization of that film. In that particular case bulk properties may also be involved, though the presence of polymer at the interface has been deduced for a similar system;[6] any effect on surface properties must depend on the structure of the polymer-surfactant film, little known at present.

Here, we investigate an insoluble polymer, poly(dimethylsiloxane) (PDMS), placed at the surface of surfactant solutions. We treat solutions of two different surfactants with contrasting properties: aerosol OT (AOT), a double-chain anionic surfactant, and penta(ethylene glycol) mono-*n*-decyl ether ($C_{10}E_5$), a single-chain nonionic surfactant. Most of the work reported here concerns surfactant solutions above the critical micellar concentration (cmc), ensuring a maximum surfactant concentration at the interface on which the polymer is spread.

Even the conformation of polymer and surfactant at this interface is unknown. The polymer PDMS alone at the air-water interface forms a fairly dense, compact film with chains essentially parallel to the surface and little looping into the bulk, a long-standing hypothesis,[7] which has recently been verified by neutron reflectivity studies.[8] One can imagine several possibilities for the mixed film: one of the components may be excluded from the interfacial region, leaving a pure film; surfactant and polymer may mix to form a homogeneous film (Figure 1a); polymer and surfactant may segregate into patches to form a heterogeneous film (Figure 1b); or polymer and surfactant may segregate vertically, forming nearly separate layers at the interface (Figure 1c).

Preliminary studies (by means of surface tension measurements and ellipsometry)[9] comparing the behavior of the polymer on AOT and on pure water surfaces suggest both a vertical separation into surfactant and polymer layers and, within the polymer layer, a lateral separation into dense and dilute polymer domains, up to a saturation polymer concentration. On water this lateral separation has been confirmed by direct observation.[10] Similar surface tension and ellipsometric behavior on one surfactant solution suggests the extension of the direct visualization to this and other mixed systems, along with a more detailed exploration of the structure of the mixed film.

A series of different methods is used for the exploration: Thermodynamic indications to the state of the film are given by surface tension measurements, both as a function of surfactant concentration c_b (saturating the surface in polymer) and at fixed c_b (confined to $c_b >$ cmc by slow equilibration with more dilute solutions). Reflectivity experiments, both ellipsometry and neutron reflectivity (the latter presented in detail in part 2[11]), provide a direct access to the thickness and composition of the film on the saturated surface of surfactant solutions ($c_b >$ cmc). Brewster angle microscopy allows direct observation of any lateral inhomogeneities in the films.

Experimental Methods

Surface tension measurements were made by the Wilhelmy method using a platinum open-frame probe, a fine horizontal wire (0.19 mm in diameter and 20 mm long) fixed in a fine wire frame;[12] more usual probe shapes, the plate and the ring, yielded anomalies in measurements on the insoluble polymer layer.[9,13] The open-frame probe gave results in agreement with other methods and literature data for the insoluble monolayer on water and in agreement with the plate method, within the ±0.1 mN/m

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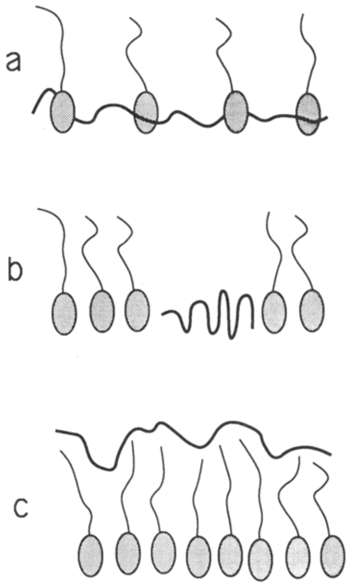

Figure 1. Possible configurations for a mixed polymer–surfactant film: (a) Monomolecular mixed film; (b) segregation in a monolayer; (c) vertical segregation into two layers.

precision of that measurement, for standard soluble surfactant solutions.[13] Reproducibility with the open-frame probe on a given surface is ±0.02 mN/m and overall accuracy estimated at ±0.2 mN/m.

Ellipsometry was performed on an in-house built instrument[14] using the phase modulation technique.[15] Measurements were taken at the Brewster angle where the ellipticity is very sensitive to any structure at the interface: the reflectivity $R_\parallel$ of light polarized parallel to the plane of incidence would be zero at this angle for the perfect plane, abrupt interface. The ellipticity $\bar{\rho}_B = \mathrm{Im}(R_\parallel/R_\perp)$, the imaginary part of the ratio between the reflectivities of light polarized parallel and perpendicular to the plane of incidence, at this angle is due to departures from this ideal: the roughness, thickness, and anisotropy of the interfacial region.

For small roughnesses, the ellipticity can be written as the sum of a roughness term and terms depending on the presence of the film:[16]

$$\bar{\rho}_B = \bar{\rho}_r + \bar{\rho}_d + \bar{\rho}_a \qquad (1)$$

Thermally-induced capillary waves yield a roughness term $\bar{\rho}_r$ depending on the surface tension and any bending elasticity of the interface. For an isotropic film, the thickness contribution is given by the Drude formula:[17]

$$\bar{\rho}_d = \frac{\pi}{\lambda}\frac{(n_1^2 + n_2^2)^{1/2}}{n_1^2 - n_2^2}\int_{-\infty}^{\infty}\frac{(n_1^2 - n(z)^2)(n_2^2 - n(z)^2)}{n(z)^2}\,\mathrm{d}z \qquad (2)$$

depending on the indices of refraction of the bulk phases, n_1 and n_2, and the index of refraction $n(z)$ through the interfacial region. Amphiphilic molecules are oriented with respect to the interfacial regions: the index of refraction may be different parallel and perpendicular to that interface, with the further possibility of orientation within the plane. In those cases, a correction for this optical anisotropy may be given by a term $\bar{\rho}_a$.

Because of the multiple factors involved, any attempt to go beyond an "optical thickness", to deduce quantitative information about the layer, involves the introduction of a model with multiple hypotheses. For condensed surfactant layers, with the head at the liquid surface and tail directed nearly vertically from it, significant optical anisotropy is expected; a simplified molecular model has been one choice for the treatment of this case.[18] Results less dependent on the particular model are in principle possible by comparisons with other experiments, as Paudler et al.[19] tentatively deduce an optical anisotropy in comparing ellipsometry results with those from neutron and X-ray reflectivity experiments.

For thin polymer layers, the optical anisotropy is usually assumed negligible.[20,21] A natural model, giving a first basis of comparison, is thus a thin isotropic layer with a density and index of refraction equal to that in the bulk polymer. It must be kept in mind that the ellipsometric data are not sensitive to certain of the hypotheses in this (or any other) model. One pertinent example of the difficulties involved is given by studies suggesting that certain insoluble polymer layers were not confined to the surface but rather dangled deep into the water;[21] it was later demonstrated that the ellipticity was sensitive only to the polymer surface concentration, not the disposition of the polymer chain with respect to the surface, as long as the chain dangled into the water rather than sticking out into the air.[20] Ellipsometry remains an interesting technique for the study of monolayers on a liquid surface in part because, if precise quantitative results are difficult to obtain because of ambiguities in interpreting the data, qualitative changes in the layer can be very clearly revealed. Ellipsometry provides a relatively simple, rapid, and precise technique allowing the extensive exploration of such behavior on the millimeter scale; the quantitative interpretation in terms of film and molecular configurations requires supplementary information.

The data obtained in ellipsometry may be expanded upon in two different ways. First, the ellipsometry gives a value averaged over the laser beam, about 2 mm in diameter. Where heterogeneities in the surface are suspected, the same surface-sensitive properties of $R_\parallel$ at the Brewster angle may be used to obtain a local image of the surface, using the Brewster angle microscope developed recently in this laboratory.[22] Here heterogeneities similar to those already observed on water[10] are expected on one but not the other of the surfactants. The microscope is used to explore this behavior, within the limits of the 1-μm resolution and the ~1-mm field-of-view.

Neutron and X-ray reflectivity experiments, unlike ellipsometry, are in principle sensitive to both the thickness and the index of refraction of thin surface layers, allowing for more quantitative data. X-ray reflectivity experiments have the advantage of much greater fluxes, but recent studies on polymer layers achieved insufficient resolution to distinguish more than their effect on the surface tension (and hence surface roughness); little information was obtained about the structure of the layers.[23] Neutron reflectivity has the advantage of allowing variation of the contrast between the substrate and the different elements of the film by the method of isotopic substitution: air contrast-matched water, for example, permits a signal due solely to the presence of the film. This recently allowed an exploration of the conformation of the polymer PDMS on pure water;[8] in part 2,[11] this study is extended to the mixed PDMS–surfactant layers.

For all experiments in part 1 of this article, the PDMS was of M_w = 10 000 (M_w/M_n = 1.13, a gift from L. Leger, or M_w/M_n = 1.8, Rhône-Poulenc 47v100 treated to remove low-weight oligomers, a gift from Rhône-Poulenc; no significant differences between samples were observed for the work reported here, though subtle differences were noted in other contexts.[10,13]). The surfactant AOT, a gift of Cyanamide (France), was purified according to Wong et al.[24] and dried in vacuo. The surfactant penta(ethylene glycol) mono-*n*-decyl ether ($C_{10}E_5$) was used as received from Nikkol. Exploratory experiments were also performed on sodium dodecyl sulfate (SDS, BDH "specially pure", used as received); these were not pursued because of the difficulties associated with the degradation of the surfactant into the very surface-active dodecanol.[25,26] The results on concentrated (~3 cmc) SDS solutions, where such problems are minimized, will be discussed qualitatively. The surfactants were dissolved in water taken from a Millipore MilliQ system; the solutions, or pure water, then served as surfaces for the deposition of the insoluble polymer.

The polymer was applied to the surfaces either pure, as a several microliter droplet, or for a controlled surface concentration, in a spreading solution, using the method of successive addition. The solvent for these solutions was hexane (Merck, for analysis) for all data presented here unless specified otherwise. Chloroform spreading solutions, more frequently used in the literature for the polymer on pure water substrates, do not spread the polymer on surfactant surfaces.

Experiments were performed at room temperature, 21.5 ± 1 °C for all except the ellipsometry experiments (at 24 °C). Various sample cells were used, adapted to the particular experiments:

for surface tension experiments on pure water or concentrated surfactant solutions (c_b > cmc), a solid Teflon trough with dimensions 350 mm × 70 mm × 5 mm; for surface tension experiments as a function of bulk surfactant concentration, deep glass dishes which could be tightly covered between measurements, taken over a period of 18 h (it should be noted that a fraction of the polymer adsorbs on the glass surfaces over long periods;[13] all data under these conditions were taken above saturation, in the presence of excess polymer); for the ellipsometry experiments, round polished glass or Teflon troughs, 60 mm in diameter; for the Brewster angle microscopy experiments, a round trough, 70 mm in diameter, with a polished glass botton and Teflon rim. These troughs were cleaned with alcoholic sodium hydroxide and sulfochromic acid solutions. It was verified that measurements on pure water agreed with literature values and changed insignificantly over the time periods involved. The troughs were protected by glass or Plexiglas covers, also promoting a high humidity.

Results

In pure amphiphilic systems, simple isotherm measurements of the surface tension as a function of surfactant concentration can give some access to the thermodynmic state of the surface. For a single pure soluble surfactant, isotherms in function of the bulk surfactant concentration c_b give the surface excess concentration of that surfactant or, equivalently, the surface area per molecule Σ, via Gibbs' law:[25]

$$\Sigma_G = -k_B T \frac{d \ln c_b}{d\gamma} \tag{3}$$

where $k_B T$ is the temperature in energy units and γ is the surface tension. For the true surface area per molecule, this value should be multiplied by a constant between 1 and 2 depending on the degree of surfactant ionization. This assumes a two-component surfactant–solvent system, the Gibbs convention for determining the position of the interface, thus defining the surfactant surface excess, and of course thermodynamic equilibrium. A second surface-active agent introduces a not-necessarily independent contribution to the surface tension decrease. Most often an ideal surface solution is assumed in order to disentangle the contributions,[25,27,28] but this hypothesis is not justified a priori; it does not hold for a system with at least partial separation into surfactant and polymer layers for example. The quantity Σ_G can be used as one basis for discussion of this case.

The surface tension is given as a function of c_b in Figures 2 and 3 for the two surfactants, alone and in the presence of a macroscopic (several microliters) drop of PDMS. This allows the surface to saturate in polymer (additional bulk polymer is observed either in lenses or partially spread on the surface, in a complicated fashion that depends both on the solution concentration and on time;[13] the measured values did not depend on the local state of the surface). In principle it would be interesting to introduce a second variable, the polymer surface concentration, but equilibration was slow for c_b < cmc (see Figure 4). Measurements in this region were thus taken at one easily-controllable polymer concentration (saturation), and measurements as a function of polymer concentration were confined to c_b > cmc where equilibration was rapid and results were independent of c_b; these data will be discussed shortly. The data presented here for less concentrated solutions were taken after a period of 18 h in the presence of the polymer droplet, after which no further significant changes in surface tension were observed.

The isotherms of the pure surfactants show contrasting behavior: γ is linear in $\ln(c_b)$ for AOT solutions above ~cmc/10 (Figure 2), demonstrating via Gibbs' law (eq 3) saturation of the surfactant surface concentration. For $C_{10}E_5$, the surface does not appear to saturate below the cmc (Figure 3, insert).

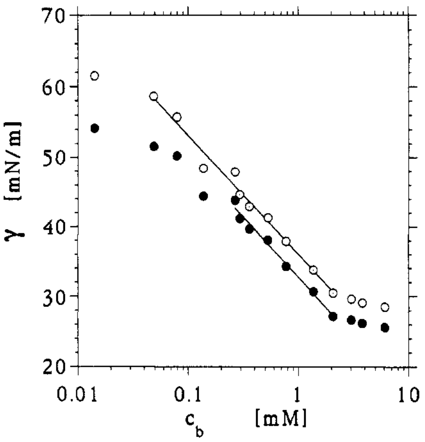

Figure 2. Surface tension of aqueous solutions of AOT, (○) pure and (●) after the addition of several microliters of PDMS (plus 18-h wait). The presence of a partically spread polymer film (present particularly at low surfactant concentrations; the polymer spreads on very clean water) may interfere slightly with the method of measurement. The constant slope above the cmc (solid lines) gives the area per molecule from the Gibbs equation (eq 3): Σ_G = 55 Å^2/molecule (Σ = 110 Å^2/molecule assuming completely ionized AOT molecules).

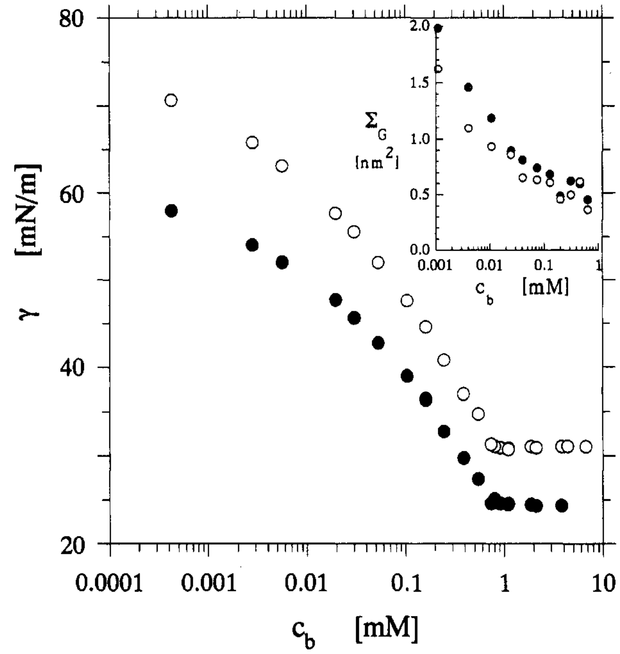

Figure 3. Surface tension of aqueous solutions of $C_{10}E_5$, (○) pure and (●) saturated in PDMS (18 h after the addition of a macroscopic (several microliter) droplet in PDMS). The inset gives the area per molecule, Σ_G, as calculated by the Gibbs equation (3); note that in the presence of a second species, here the polymer, this does not necessarily give the true Σ.

The presence of the polymer decreases the surface tension is every case, but without changing the cmc: the polymer does not affect the bulk surfactant at this level. The surface tension vs c_b curve simply shifts downward, changing slightly in shape. This information can be exploited in two different ways: one can compare the slope of the individual curves, that is Σ_G (Figures 2 and 3 (insert)), for information about the surface concentration of the soluble surfactant, and one can look at the change in surface tension due to the polymer (Figure 4) for information about the polymer, using for example standard isotherm models.[25,27,28] The two quantities are clearly not independent

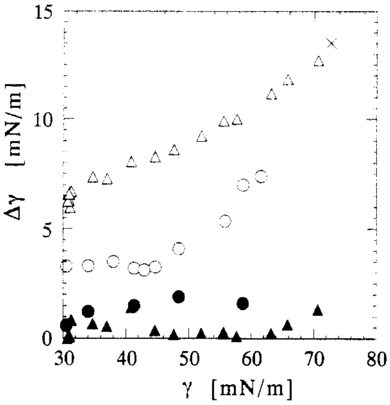

Figure 4. For two surfactant solutions (circles, AOT; triangles, $C_{10}E_5$) as a function of the surface tension γ of the pure solution: (open symbols) (and ×: pure water substrate) change $\Delta\gamma$ in surface tension after saturation in PDMS (18 h after a macroscopic drop is applied). (Filled symbols) change in $\Delta\gamma$ with time after application of the polymer, $\Delta\gamma|_{18\ h} - \Delta\gamma|_{2\ h}$.

in general; the interpretation is clear only when independence can be demonstrated, and some care should be taken.

On solutions of AOT, the presence of the polymer leaves Σ_G unchanged, in contrast to the behavior with $C_{10}E_5$ solutions as substrate. Where a change in Σ_G occurs, it is difficult to draw a conclusion: the surface concentration of the surfactant may change in the presence of the polymer, or the direct effect of the polymer on the surface tension may vary with surfactant concentration (as is quite likely where the surfactant surface concentration certainly changes with bulk concentration, as is also the case with $C_{10}E_5$ as opposed to AOT). Where there is no change in slope on the other hand, one can reasonably conclude that there is little change in surfactant surface concentration: this is the case for AOT for $c_b >$ cmc/5 (Figure 2). For the other surfactant, one cannot conclude more than that the change in surface surfactant concentration is probably minor ($\Delta\Sigma_G < 20\%$ for $c_b >$ cmc/5; Figure 3, insert); this is supported by ellipsometry studies to be presented shortly. In either case, the surfactant surface concentration changes little, suggesting a model in which the polymer clearly present at the interface (the surface tension changes) lies essentially above the surfactant layer (Figure 1c), perhaps mixing into the surfactant chains but without much affecting the headgroups. This picture is confirmed by the neutron reflectivity studies presented in part 2.[11]

Similar data have been obtained for alkane films on various surfactant solutions, including AOT.[28] As is indicated by the observation that Σ_G is nearly unchanged by the presence of the alkane (for c_b just below cmc), the alkane–surfactant films are also partially segregated vertically: Neutron reflectivity on the TTAB (c_b = cmc/2)–dodecane system demonstrates that the center of mass of the dodecane is significantly above that of the surfactant.[29]

The effect of the polymer can be explored more directly via the change in surface tension due to the presence of the polymer, $\Delta\gamma$: this is given in Figure 4 (as a function of the surface tension of the pure solution to allow comparison with the effect of the polymer on pure water on a convenient scale). Here it is clearly seen that the saturation value for $\Delta\gamma$ is independent of surfactant concentration for AOT with $c_b >$ cmc/5; at lower concentrations it varies continuously toward the value recorded for pure water, as it does for $C_{10}E_5$ at all concentrations $c_b <$ cmc.

Mixed films in the plane may be formed in the low c_b regimes, as has been suggested for the alkanes on various surfactants,[28] but slow equilibrium (also demonstrated in Figure 4 with the difference in $\Delta\gamma$ as measured 2 and 18 h after the polymer droplet is introduced) prevented systematic studies. These were confined to $c_b >$ cmc, where various parameters were studied as a function of polymer surface concentration c.

For a pure insoluble surfactant, isotherms are taken as a function of surface concentration. The decrease of the surface tension from that of pure water is equivalent to the surface pressure; this isotherm is then directly analogous to three-dimensional pressure–volume isotherms and such quantities as the static elasticity can be directly deduced, while any abrupt changes are taken as indicating changes in the surface state.

The data on the mixed system, where contributions from polymer and surfactant may be entangled, should be treated with caution. With concentrated solutions ($c_b >$ cmc/5) of AOT as a substrate, the presence of the polymer has no visible effect on the AOT surface concentration, and the change in surface tension due to saturation of the surface in polymer is independent of that AOT concentration. For such concentrated solutions, it is reasonable to treat independently the effect of the surfactant and the polymer on the surface tension, and to relate the decrease ($\Delta\gamma$) in surface tension from that of the surfactant substrate to a polymer surface pressure. This separation into surfactant and polymer contributions is no longer clear with the $C_{10}E_5$ solutions, but since the effect of the polymer on the surfactant surface concentration is relatively minor (probably <20%) for concentrated solutions, some comparison of $\Delta\gamma$ with a surface pressure can be made as a first approximation.

This change in surface tension $\Delta\gamma$ is given in Figure 5 for the three different substrates, pure water and concentrated ($c_b \sim 2.5$ cmc) solutions of AOT and of $C_{10}E_5$. The three curves show a certain resemblance: $\Delta\gamma$ reaches a plateau value in each case, and the increase can be defined as occurring around a characteristic concentration of similar order; here a value is selected out rather arbitrarily and called c_1 ($\equiv 0.75$ mg/m^2). Numerically, c_1 corresponds to saturation with a dense layer of monomers each adsorbed on the liquid surface (the exact value of this saturation would depend on the configuration of the monomer with respect to the surface: $c = 0.6$ mg/m^2 if both the silicon and oxygen atoms are adsorbed on the surface, $c = 0.8$ mg/m^2 for a zigzag conformation, with only the oxygen adsorbed on the surface[30]). The polymer has usually been assumed to take on these conformations on pure water, since the earliest surface tension studies 45 years ago.[7] Occasional doubt has been raised, suggesting the possibility of looping into the subphase,[31,32] but the model of chains lying essentially parallel to the surface was recently verified, with neutron reflectivity studies[8] which show a fairly dense layer of monomer thickness ($d = 0.8$ nm with a phase fraction $\phi_p = 0.85$) near c_1.

To compare the three sets of data further, it is natural to turn to the theory of two-dimensional polymer systems, using the concept of the surface pressure (remembering that this may not be exact for the mixed systems).

At sufficiently low concentrations that the individual polymer chains do not interact, one expects them to form an ideal gas, with pressure $\pi = c/M_wRT$. For the molecular weight considered here, M_w = 10 000, this would lead to surface pressures at the limit of measurability, $\pi \sim 0.1$ mN/m even for c approaching 0.6 mg/m^2; $\Delta\tau$ is at or below this limit for both the water and AOT substrates. On the water surface, a series of lower mass polymers has been studied;[32] the surface pressures were clearly lower than

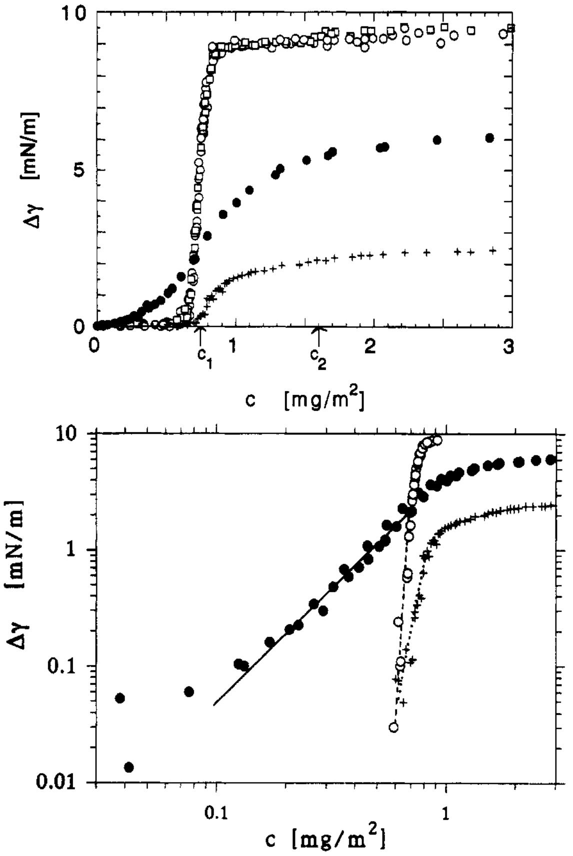

Figure 5. Change in surface tension as a function of polymer concentration, for three different substrates: pure water (○, hexane spreading solution; □, chloroform spreading solution); $C_{10}E_5$(●; $c_b \sim 2$ cmc); AOT (+; $c_b \sim 2$ cmc). (b) Log–log plot: (solid line) $\Delta\gamma \propto c^{2.07}$; (dashed line) $\Delta\gamma \propto c^{25}$; (dotted line) $\Delta\gamma \propto c^{10}$. (Best fits assuming uncertainties ±0.003 mg/m² on c and ±0.05 mN/m on $\Delta\gamma$, and not considering data above the obvious bends in the curves around collapse.)

those expected from an ideal gas. The second virial coefficient is certainly negative, indicating net attractive interactions between chains, and it was suggested that this regime represents phase coexistence between dense and very dilute polymer domains.[32] Such domains have been observed on water[10] and, in view of the similar isotherm behavior on the AOT substrate, might be expected in that case as well. On the other surfactant, $C_{10}E_5$, the change in surface tension is greater than that expected by the ideal gas law in the entire region below c_1; one may suppose repulsive interaction between polymer chains, though again the possibility of changes in the surfactant layer should not be forgotten.

As c_1 is approached, the individual polymer chains necessarily come into interaction. In this case, the natural comparison is with two-dimensional polymer theory. This predicts a semidilute regime above the concentration at which the macroscopic density is equal to the internal chain density; the polymer chains come into contact and interpenetrate, interacting through much smaller segments called blobs. The surface pressure is expected to be independent of molecular weight, following a scaling law $\pi \propto c^y$, where y depends on the balance of monomer–monomer and excluded volume forces.[33] These can be summarized by considering that the environment of the surface acts as a good, Θ, or poor solvent for the polymer.

For good solvent behavior, one expects $y \sim 3$; similar values have been found for a variety of different polymers on different substrates, for example $y = 2.70$ for PVAc on water[34] and $y = 3.5$ for PDMS on tricresyl phosphate.[32]

The behavior of a polymer in a two-dimensional Θ solvent has been more controversial, with difficulties introduced by the fact that in this case, the monomers within each polymer chain are relatively dense on the surface. Recently, however, a variety of different theoretical methods[33,35] have led to a common value for the radius of gyration of a single polymer chain, which in the simplest model also characterizes the overlap concentration and osmotic pressure in a collection of those chains,[33,34] leading to $y = 8$.

Known polymer systems tend to give much higher (or much lower as just cited) values, for example $y = 16.5$ for PMMA on water.[33] It is difficult to determine a value for y from our data for PDMS on water, given the restricted range available between the limits of the precision of the measurement and the effect of residual impurities at low surface pressures and the clear collapse of the polymer layer at higher surface pressures, but we find (Figure 5b) $y \geq 22$, consistent with the value $y \sim 50$ estimated by other groups.[32,36] This high value has been taken as the signal of poor solvent behavior, consistent with phase separation at lower average surface concentrations.

On solutions of $C_{10}E_5$ on the other hand, we find (below the clear onset of collapse; Figure 5b) $\Delta\gamma \sim c^{2.05\pm0.1}$, while on solutions of AOT the data over a very limited range (<1 mN/m) suggest intermediate behavior, $\Delta\gamma \sim c^{10\pm2}$. On $C_{10}E_5$, this dependence is even less than expected for the surface pressure of a two-dimensional polymer in a good solvent, but again $\Delta\gamma$ cannot be clearly related to a polymer surface pressure π, since the polymer may affect the underlying surfactant layer. Furthermore, the polymer may not be confined into two dimensions but rather change conformation with respect to a fictitious surface.

However, it is clear that the isotherms in the intermediate concentration regime near c_1 as well as at lower concentrations suggest poor solvent conditions, and the possible separation into domains at low concentrations, for the polymer on water and perhaps on AOT solution substrates, with no such separation on the $C_{10}E_5$ solution.

Other data are necessary for any firm conclusions. One possible source is ellipsometry: data for the three systems are given in Figure 6.

To compare the observations with possible configurations of the system, models must be introduced. As a first trial, consider an ellipticity of the substrate, $(\bar\rho_B)_{\text{substrate}} = (\bar\rho_r + \bar\rho_d + \bar\rho_a)|_{c=0}$ (eq 1), unchanged by the presence of the polymer. In fact, the roughness is expected[16] to increase slightly (<5%, $\Delta\bar\rho_r < 0.05 \times 10^{-3}$) with the slight surface tension decrease (<10%). This is insignificant on the scale of the precision of the measurement; the essence of the hypothesis is that the surfactant layer is unchanged by the presence of the polymer. The thickness of the polymer layer is then given by the Drude formula, eq 2, assuming an isotropic layer with the bulk density ($\rho = 0.98$ gm/cm³) and index of refraction ($n = 1.403$). This leads, under this restrictive model, to an ellipticity as a function of polymer concentration c:

$$\bar\rho_B = (\bar\rho_B)_{\text{substrate}} + 1.02 \times 10^{-3}\frac{c}{[\text{mg/m}^2]}$$

shown as straight lines on Figure 6. Many hypotheses were necessary to obtain this relation; changes in the surfactant surface concentration with addition of the polymer as well as any inhomogeneity or optical anisotropy in the polymer layer would lead to deviations from this prediction. The data would however be insensitive to any mixing of the polymer and surfactant layers, as it is

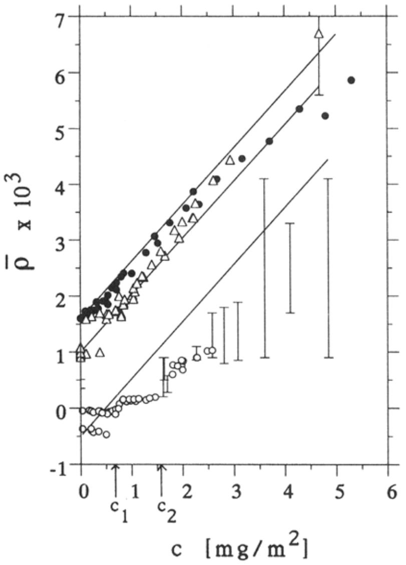

Figure 6. Ellipticity $\bar{\rho}_B$ as a function of polymer concentration, for three different substrates: pure water (○); AOT (Δ; $c_b \sim 2$ cmc); $C_{10}E_5$ (●; $c_b \sim 2$ cmc). Estimated errors are 10% on $\bar{\rho}_B$ and 5% on c, on the order of the data symbol size. Bars represent fluctuations in the ellipticity out of this range, as shown in Figure 7; the physical origin of these fluctuations is demonstrated in Figure 8b. Lines: $\bar{\rho}_B = \bar{\rho}_O + 1.02 \times 10^{-3}\, c/[\mathrm{mg/m^2}]$.

insensitive to mixing between a polymer and the water substrate for example.[8,20]

As can be seen, the ellipticity for the polymer on the two surfactant substrates is in reasonable agreement with the model, for moderate polymer concentrations. This should not be taken as indicating entirely separate surfactant and polymer layers: The agreement between model and data indicates rather that the surfactant surface concentrations is little changed by the presence of the polymer, in agreement with the surface tension data, without ruling out mixing between the polymer and the surfactant chains. Note also that the slope for the ellipticity vs concentration curve is about 15% less on the $C_{10}E_5$ than on the AOT substrate: this is at the edge of the ±10% experimental resolution but, like the surface tension data, suggests a greater effect of the polymer on the former surfactant substrate. This will be demonstrated much more clearly in the neutron reflectivity experiments.[11]

On the pure water substrate, the data are in striking disagreement with the simple model, showing considerable structure including plateaux as well as large fluctuations, with some indication of discrete values, at high polymer concentration (Figure 7a). In fact, domains of various discrete thicknesses have been observed on this substrate (Figure 8b).[10] These may represent either multilayers or monolayers in which the polymer chain takes on different configurations, with only a fraction of the monomers adsorbed directly on the surface. A "bilayer" for example may consist of two superimposed layers of stretched-out chains, or of a single layer in which only one oxygen in two is adsorbed on the surface, so that the polymer forms an extended zigzag, or as in the traditional models,[7,30] of the polymer in α-helix formation, with about six monomers per turn. Contrary to the traditional models,[7,30] the transition between configurations is clearly not continuous.

Data on the AOT, as opposed to the $C_{10}E_5$, substrate also show signs of fluctuations and possible discreteness at polymer concentrations equivalent to several monolayers (Figure 7b,c), but over a much reduced range in ellipticity (corresponding to one or two monomer thicknesses) compared to the fluctuations observed at these polymer concentrations on pure water surfaces. Microscopic observations exploring the irregularities on the AOT solutions at these polymer concentrations were unclear, with very large scale (>1 mm) domains observed in the period (~1 h) shortly after deposition, but with diffuse borders between regions. With both domains and domain borders on the scale of variations in the illumination of the field, and with little contrast between domains, these are clear only as they move across the field; no (still) images are presented. In some runs, a different kind of inhomogeneity was observed, in the form of small (<1 μm), slightly more brilliant points in the polymer layer; these correlate with slight impurities or dust evident in the initial surfactant layer.

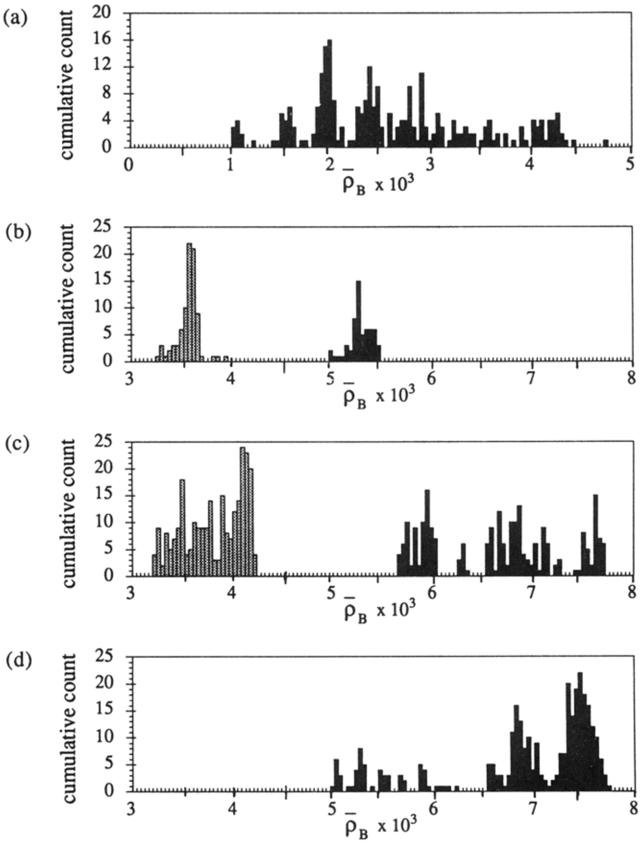

Figure 7. Histograms of ellipticity measurements of PDMS at moderate average surface concentration on various substrates (bin sizes correspond to the digitalization of the signal): (a) 3.6 mg/m^2 on water; (b) 2.1 mg/m^2 (gray) and 4.8 mg/m^2 (black) on $C_{10}E_5$ solution ($c > c_b$); (c) 2.2 mg/m^2 (gray) and 4.7 mg/m^2 (black) on AOT solution ($c > c_b$); (d) macroscopic drop on AOT solution ($c > c_b$).

For a pure polymer droplet placed on either surfactant substrate, a limit to spreading is observed, with the possibility of macroscopic drops, homogeneous thick films, and molecular films in coexistence, where on AOT these films may be as thin as about 5 nm (roughly seven molecular layers; Figure 7d). This spreading is quite complicated. On both substrates ($c_b >$ cmc) the polymer droplet initially spreads and then retracts into a lens, followed by the slow spreading of films from the droplet, for a surface as just described. However, the time scale varies markedly with the surfactant solution: On $C_{10}E_5$, the retraction occurs within ~1 s (depending on the surfactant concentration), with subsequent respreading within ~1 min; on AOT solutions, the time scale is on the order of hours.

A difference of behavior on the two substrates is also seen at less than monolayer polymer coverage. For $c < c_1$, the ellipticity on the AOT substrate (but not the $C_{10}E_5$

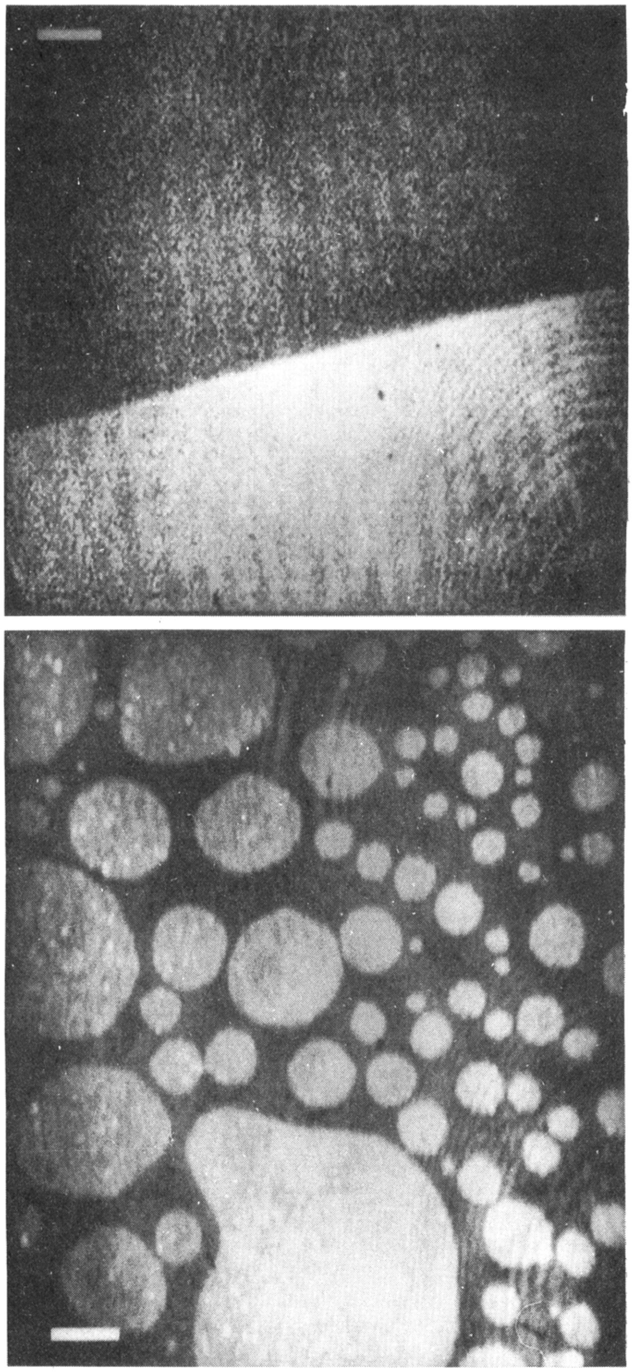

Figure 8. PDMS on water, Brewster angle microscopy. The Gaussian beam intensity is visible on the images. Bar: 50 μm. (a, Top) separation into domains for $c < c_1$ ($c \sim 0.3$ mg/m^2). (b, Bottom) domains in the collapse regime ($c \sim 4$ mg/m^2). Note the simultaneous presence of macroscopic droplets in the form of more brilliant points.

substrate) deviates from the simple homogeneous polymer–surfactant bilayer model: as on water, two ellipticity levels are seen over most of this range, one ellipticity characteristic of the substrate and one at a higher level, without fluctuations between the two. That these reflect a separation into very large (much larger than the 2-mm beam size) dense and dilute polymer domains has already been demonstrated[10] by Brewster angle microscopy on pure water substrates (Figure 8a) and confirmed here for the AOT substrate as well (Figure 9). On the other hand, the polymer film shows no sign of a division into domains on the $C_{10}E_5$ substrate, neither on the millimeter scale of ellipsometry nor on the micrometer scale of the Brewster angle microscope.

While the phase separation occurs on the two substrates, water and AOT, for $c < c_1$, a distinction should be made: the difference in ellipticity levels $\Delta\bar{\rho}_B$ between dense and dilute domains varies with the substrate. On AOT, $\Delta\bar{\rho}_B$ is that expected of a polymer monolayer, with optical thickness 0.7 nm, similar to that observed on low-energy solid surfaces.[37] The value for $\Delta\bar{\rho}_B$ on the pure water substrate, lower by half, could reflect a more stretched-out configuration of the polymer. This can be compared to the spreading of the polymer on high-energy solids, where the PDMS forms thicker than monomeric but less dense layers; it is suggested that monomers are trapped at specific sites on these solids.[37] Similar strong interactions between polymer and substrate could lead to a more stretched-out configuration on a liquid. The difficulty of interpreting the ellipticity is brought out in noticing that the same data would be retrieved on the water surface with a thicker, less dense layer, if the holes in this layer are filled with air rather than the more likely water. Further uncertainties are introduced with large uncertainties in the ellipticity of the water substrate, as well as, fundamentally, in considering more carefully the molecular origins of the ellipticity, which depend not only on the configuration of the polymer itself but also on its immediate surroundings, whether water or AOT.

The ellipsometry, while revelatory, clearly does not yield a quantitative response to questions about polymer–surfactant structure. It is necessary to turn to some other method; this is represented by neutron reflectivity, presented in detail in part 2 of this article.[11] Most relevant to the discussion here, the neutron reflectivity results both verify the vertical separation into predominantly polymer and predominantly surfactant layers with both surfactants and demonstrate a greater intermingling of polymer and surfactant when the surfactant is $C_{10}E_5$, as opposed to AOT.

Except for the initial isotherm data (Figure 2) where the bulk surfactant concentration was varied and which revealed slow equilibration at lower c_b, almost all data (including the neutron reflectivity data to follow in part 2) were taken at high surfactant concentrations, $c_b >$ cmc. In that case, the polymer appears to form a nearly separate layer on a dense surfactant substrate. As the surfactant surface density decreases, for $c_b <$ cmc, the polymer may penetrate more into the surfactant layer. Preliminary studies were made for $c_b =$ cmc/50, with both AOT and $C_{10}E_5$ solutions. On AOT, both ellipsometry and the microscopy indicate very inhomogeneous mixed films. On $C_{10}E_5$, ellipsometry data were very similar to those for c_b > cmc, except that the optical thickness of the substrate was about 40% less, in agreement with the thickness deduced from isotherms via Gibbs' law (Figure 3). For macroscopic quantities of the polymer, the spreading behavior is very complicated, depending both on the surfactant and on its concentration c_b and evolving with time.[13]

Discussion

A clear difference is seen in the behavior of the polymer on the different substrates. The origin of this difference can be considered from several different points of view.

The coexistence of (more than monomolecular) films and of macroscopic drops suggests recent theories of pseudopartial wetting,[38] where long-range interactions across the spread film limit its thickness, with excess liquid collecting in macroscopic liquid lenses. In the system at hand, van der Waals forces would in fact be expected to provide such a limit, assuming that the films spread at all,

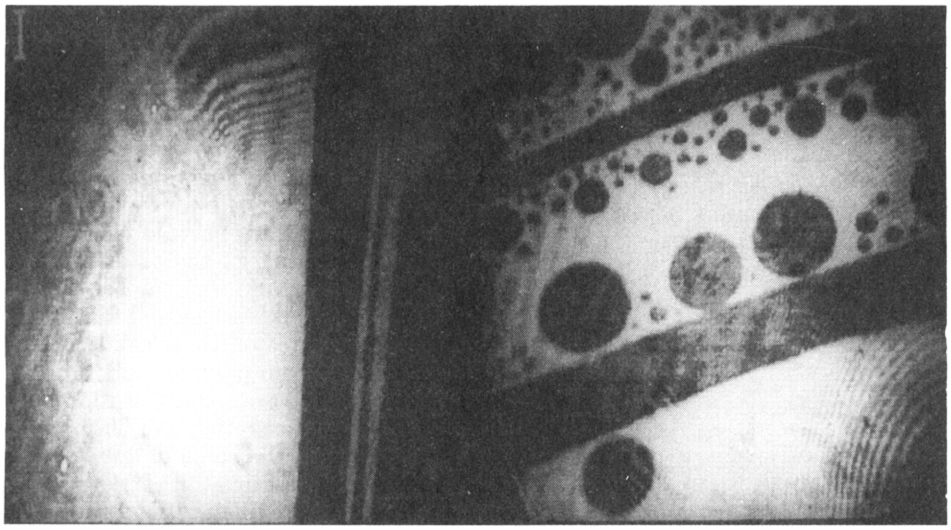

Figure 9. PDMS on AOT ($c_b \sim 2$ cmc): separation into domains for $c < c_1$ ($c \sim 0.3$ mg/m^2), Brewster angle microscopy. The Gaussian beam intensity is visible on the images. Bar: 50 μm. Domains may be very large, but as on pure water surfaces,[8] smaller domains are observed at bordering regions (b, right) in the absence of the protective cover consistently used in ellipsometric experiments. The cover ensures a high humidity and protects against air currents; while the origin of the effect is unclear, these variables clearly should be considered in careful monolayer work.

essentially because the polymer is more polarizable than either of the surrounding media[39] (water and air). (Slightly more refined models,[40] taking into account the polar nature of both water and the polymer, yield qualitatively the same result: a slight attraction between the two surfaces, leading to thinning of a thick polymer film. A proper estimate would require information about the dielectric response of the polymer at all frequencies, which is unavailable.) Unfortunately, a limiting thickness can be defined neither experimentally nor theoretically at this time: experimentally, no single limiting thickness is evident for any of the systems, while theoretically some knowledge of the various interactions over the film thicknesses of interest would be necessary. All that can be said is that the presence of the surfactant layer may change a delicate balance. However, molecular considerations clearly apply.

From the molecular point of view, different configurations of the polymer may be favored by direct substrate–polymer interaction. Hydrogen bonding, which on water favors a stretched configuration, is no longer available to the polymer on the surfactant layer: this is likely to change the molecular configuration both above and below monomer coverage. The collapse to a bulk configuration would be expected to be more continuous on the surfactant layer, with no need to take these interactions into account, as is indeed observed. A difference in molecular configuration between cases where the polymer does and does not penetrate into the surfactant layer also seems clear. Both the change in configuration and the direct interaction with the surfactant would change the effective interaction between monomers, as seen in the contrasting behavior, "poor" vs "good" solvent, for the partial monolayer on the three substrates.

One can also ask why there is such a difference in the penetration of the different surfactant layers, does it result from direct polymer–surfactant interactions or a simple steric effect? The difference does not seem to be a simple question of ionic vs nonionic surfactants. Preliminary surface isotherm and ellipsometry experiments[13] using concentrated surfactant solutions of SDS for the substrate suggest behavior similar to that on the nonionic $C_{10}E_5$: some penetration of the polymer into the surfactant layer and good solvent behavior for $c < c_1$. On the other hand, for the double-chained (and branched) AOT, it is mainly the chains which determine the molecular area, leading to a dense hydrocarbon film as the exterior surface of the AOT film: little penetration by the polymer would be expected, as little penetration is observed for such films in contact with the longer alkanes.[41] The more open chain geometry of the $C_{10}E_5$ and SDS films would allow for considerably greater penetration, with minor changes in the film itself.

Conclusions

Concentrated surfactant solutions ($c_b >$ cmc) appear to act primarily as a substrate for the polymer, which forms nearly separate layer, with a degree of mixing between layers that depends on the surfactant. The behavior of the polymer on this substrate depends on the detailed polymer–substrate interactions.

At submonolayer concentrations, the polymer separates into dilute and dense phases when deposed on the surface of both water and concentrated AOT solutions. Under controlled conditions of high humidity and a protected surface, these phases form very large domains, millimeters to centimeters across. In vivid contrast, on solutions of $C_{10}E_5$ the density of the layer increases continuously by all measurements, from the millimeter scale given by the field-of-view of the ellipsometer to the micrometer scale as revealed by the Brewster angle microscope to the molecular level revealed in the surface pressure isotherms. The analogy given by two-dimensional polymer theory is that the surface of these solutions acts as a relatively good solvent to the polymer compared to the poor solvent of the surface of AOT solutions and particularly of water.

As the surface concentration is increased out of the monomer monolayer range, forcing the layer to collapse toward a three-dimensional state, the ellipsometric behavior on AOT approaches that on $C_{10}E_5$: in contrast to the very inhomogeneous films seen on the water substrate at all polymer concentrations, the polymer forms a nearly uniform layer which thickens continuously. The average optical thickness of this layer is slightly smaller on $C_{10}E_5$, consistent with some mixing of the polymer into the surfactant layer as suggested by surface tension measurements and revealed unmistakably in the neutron reflectivity data.[11] Some signs of coexisting films of discrete thicknessses about 1 monomer apart are seen on the AOT substrate; on both substrates macroscopic spreading is limited and macroscopic drops of the polymer can coexist with both thick and molecularly thin films.

The greater penetration into the $C_{10}E_5$ layer correlates to both the greater homogeneity and the smoother, more rapid spreading of the polymer on this substrate. The underlying reasons for the striking differences between the two surfactant systems remain to be fully understood. A study of the behavior of the polymer on other surfactant solutions is indicated.

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