

POLYMERIC SURFACTANT STRUCTURE

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Abstract Polymeric surfactants are amongst the most widespread of all polymers. In nature, proteins and polysaccharides cause self organization as a result of this surfactancy; in industry, polymeric surfactants play key roles in the food, explosives and surface coatings sectors. The generation of useful nano- and micro-structures in films and emulsions as a result of polymer amphiphilicity and the application of mechanical stress is discussed. The use of X-ray and neutron small angle scattering and reflectivity to measure these structures and their dynamic properties will be described. New results on linear and dendritic polymer surfactants are presented.

Keywords Polymeric, Surfactant, Structure, X-ray, Neutron, Reflectivity, Film

INTRODUCTION

The focus of this paper is to explore ways in which thermodynamic and mechanical stress applied to polymeric surfactant systems produces new textures on the nanometer and micron scales. This application of stress is one of the ways in which nature produces functional patterns in biological systems and it is our hope to imitate some of these ways to make new materials for product and device applications. Well known to polymer scientists is the deployment of thermodynamic stress as measured, for example, by the Flory-Huggins parameter χ . The compatibility of polymers as measured by the χ parameter is a key factor in designing polymer blends. It is also a key factor in the behavior of block co-polymers and the recent work on patterning in tri-block co-polymers is a vivid example of what can be achieved on the micron scale.

Figure 1 shows three examples of polymeric surfactants under study in our laboratory. The simpler structures (a), (b) are atactic polystyrene and *cis*-1,4-polyisoprene, both terminated with a hydroxyl headgroup to make them surface active. These molecules are typical of those used in the stabilization of emulsions and some paints. The polymer tacticity, molecular weight and molecular weight distribution may be varied chemically to control key factors in their usefulness. Figure 1(c) shows a fourth generation monodendron, based on 3,5-dihydroxy benzyl alcohol. While the properties of the polystyrene and polyisoprene surfactants resemble those of normal hydrocarbon surfactants, the dendrimers show three-dimensional organization at interfaces. They have interesting properties for drug transport, micro-environment chemical reactors and photo-chemical reactivity. The surface chemical methods we use are one of the best ways of studying their structure since most of them cannot be crystallized.

Because of the highly controllable chemistry of anionic polymerization and "convergent" dendrimer synthesis all of these molecules can be prepared with precise molecular weights and so lend themselves to a detailed understanding by modern physical chemical techniques. For the linear species we could expect that as the chain length of the surfactant is increased the surface properties and the surface activity would undergo a

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transition to a state where the bulk properties of the polymer chain dominate the surface behavior. In this work we present a study of the interfacial properties of an oligomeric polystyrene surfactant as a function of increasing molecular weight. We show some aspects of the surfactant to non-surfactant transition that they undergo and illustrate the textures produced at interfaces as a result of thermodynamic and mechanical stresses on organized nano-molecular layers of the polymer.

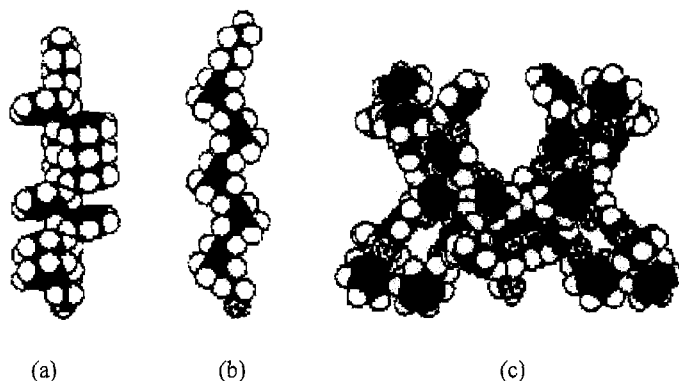


Fig. 1 Representative models of surfactants of (a) atactic polystyrene, (b) *cis*-1,4-polyisoprene and (c) the fourth generation monodendron, based on 3,5-dihydroxy benzyl alcohol

Thermodynamic properties of these polymers are conveniently studied by spreading dilute solutions in toluene at the air/water interface. The surface pressure, Π , - surface area, A , relationships of the resultant film were measured by the Langmuir trough method and reveal surprising differences in behavior^[1, 2, 3]. A structural understanding of this behavior, intrinsic to the useful properties of these materials, has been obtained using the new techniques of x-ray and neutron reflectivity^[4, 5].

EXPERIMENTAL

The synthesis of polyisoprene and polystyrene can be carried out by a number of methods. It is important, however, that the molecular weight distribution should be as narrow as possible for the experiments described in this paper. For this reason the polymers were made by anionic polymerization to produce controlled molecular weights with distributions, M_w/M_n of 1.1 or less. The other feature of this technique is the ability to functionalize the ends of the polymer^[6]. To ensure control of the polymer chain-length and efficient termination, all syntheses were carried out in the absence of oxygen. Vacuum distillation and outgassing of solvents and vessels to 10^{-5} to 10^{-6} torr were routine as was the manipulation of the products under dry nitrogen. Water was always removed by distillation over sodium and calcium hydride according to the solvent, the solvents and terminating species being degassed three times on the vacuum line by freeze pump thawing. After termination, e.g. with ethylene oxide to produce an alcohol headgroup, all polymers were washed with large volumes of distilled methanol to remove lithium salts arising from the tertiary butyl lithium initiator. Materials were fractionated by gel permeation chromatography against polystyrene and polyisoprene calibration standards using Waters ultrastaygel columns suitable for the molecular weight range studied. Proton and carbon 13 magnetic resonance was used to check the purity and to characterize the polymer structures. The dendrimer molecules were prepared for us by Dr Craig Hawker of the IBM Research Laboratories, California.

In an effort to produce a larger number of the low molecular weight PSEtOH's and to test the effect of molecular weight distribution, a sample of a 950 M_w PSEtOH was fractionated into narrower distributions by gel permeation chromatography. Inhibitorless THF was used to elute the sample which was passed down four Waters ultrastaygel (0.2×500 nm and 0.2×10^3 nm) columns. The molecular weight distributions were then determined by GPC and NMR was used to check the purity.

The Teflon Langmuir trough of area 222 cm² employed a modified Wilhelmy method^[7] to measure the

surface pressure. The substrate was Milli-Q water collected at 18 M Ohms cm. The surface was repeatedly swept and siphoned off until no change in the surface pressure could be observed. All measurements were performed at $20.0 \pm 0.1^\circ\text{C}$ and a compression rate of $0.2\text{ cm}^2\text{ s}^{-1}$.

Solutions of PSEtOH, of concentration about $1.0 \times 10^{-4}\text{ g/mL}$, were spread by allowing very small drops to completely evaporate before continuing with the next. Great care was taken to ensure small enough drops so that any film present was not over-compressed. The dropping rate was of the order of 0.15 mL per hour or less.

RESULTS

Thermodynamics of Polymer Surfactant Films

Figure 2 shows typical compression/expansion Π - A isotherms for as-prepared polystyrene surfactants at 20°C as a function of molecular weight. A progressive change in the surfactancy is observed. These data were produced by slow continuous compression/expansion of the spread film. We focus first of all on the case of the 950 M_w film. The isotherm can be divided into three regions; the first (at the highest surface area) is characterized by a slowly increasing pressure to a peak with decreasing area. This phase of the surfactant film is similar to a phase identified for phospholipids^[8] and will be designated a fluid or expanded phase^[9]. There is no indication of a gaseous region for these isotherms.

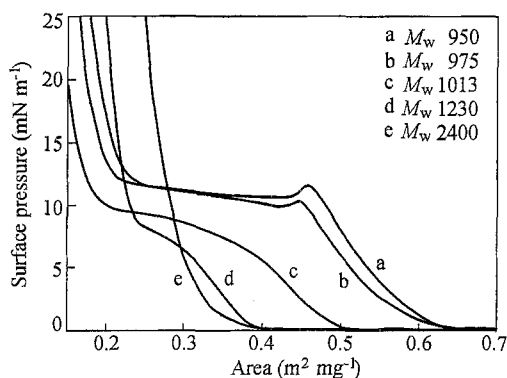


Fig. 2 Π - A compression isotherms of as prepared hydroxyl terminated polystyrenes as a function of molecular weight over the oligomer region

The second region occurs at higher compressions starting at ca. $0.48\text{ m}^2\text{ mg}^{-1}$ and here a further reduction of surface area does not give a significant increase in surface pressure. The peak in pressure, Π_{collapse} , and the subsequent collapse behavior are typical of a nucleating system^[10]. A new phase with an interesting surface texture has started to form. The peak in the isotherm marks the point where the change in area due to compression equals the extent of growth of the new phase. In this region, relaxation phenomena occurred when the compression was held at constant area for a period before continuing with the compression. The pressure was observed to decrease. On the reverse cycle, a similar process occurred for the expansion though in this case the pressure increased as the film relaxed — the film was viscoelastic. This relaxation phenomenon occurs as the system moves toward the equilibrium spreading pressure, Π_{esp} , for a monolayer in contact with the newly formed phase. Transformation of the monolayer fluid film by nucleation and growth into this second phase occurs at all pressures lower than Π_{collapse} but above the equilibrium spreading pressure.

It is this sort of transformation from a monolayer to some superstructure in response to the external mechanical stress that is of interest to us. A number of examples of interesting structures created at the air/water interface have been studied in our laboratory and our evidence so far also points to these structures occurring also at the oil/water interface in emulsions. These structures produce new rheological effects in surface films at interfaces. Below we show how the film response may be varied by changing the molecular weight of the surfactant.

The start of the third region in the Π - A isotherm is defined by the sharp increase in surface pressure at about $\Pi = 12 \text{ mN m}^{-1}$. This region of the isotherm is classified as a transition to a complete, solid film, of the newly formed phase. Extrapolating the initial rise in surface pressure to $\Pi = 0 \text{ mN m}^{-1}$ the limiting area for the fluid phase was found to be about $0.6 \text{ m}^2 \text{ mg}^{-1}$ while that for the solid phase was about $0.2 \text{ m}^2 \text{ mg}^{-1}$. Thus it is concluded that the completed solid film is a tri-layer^[11]. We show how the dimensions and time evolution of this structure may be measured by reflectivity methods.

There is a close analogy with similar results for the fatty acids at low pH and for liquid crystals. Given that the polymer chain lengths are short, equivalent to about C_{20} aliphatic chains, the consistency with the behavior of fatty acids and alcohols is understandable.

On expanding this completed trilayer film there is considerable hysteresis. The area of the hysteresis loop is a measure of the stored energy in the cycle. Again this is an interesting thermodynamic parameter (although not an equilibrium parameter) which can be controlled by the molecular architecture such as chain tacticity and overall conformation. For example, the behavior of M_w ca. 1000 *cis*-1,4-polyisoprene surfactant terminated in the same way as the polystyrene surfactant described here is quite different. This system shows almost no hysteresis loop, the polymer relaxation being so quick at the interface that the initially spread film structure is recovered upon expansion. Again, very distinctly different behavior is encountered for the dendrimers. For some of these^[5] a series of compression and expansion cycles leads to a "limit cycle" in the Π - A curves. A durable structure is produced at the air/water interface and there is little respreading. The structures formed have been investigated by the reflectivity techniques which have proved so successful for understanding the oligomeric polystyrenes^[1, 5].

Effect of Molecular Weight

Figure 2 shows the transition in isotherm properties as the length of the polymer molecules was increased for the unfractionated polymer with $M_w/M_n = 1.1$. The shape of the isotherms was expected to depend on the surfactant molecular weight in some systematic way that might allow a scaling relation to be derived^[12]. An increase in molecular weight was also expected to change the surfactant properties from a state for low molecular weight, where the Π - A isotherm reflects the cross sectional area of the molecules and their interactions with the substrate, to a state where the isotherms are dominated by bulk (hydrophobic) polymer properties.

The data for fractions taken from the nominal $M_w \approx 950$ polymer of Fig. 2 are shown in Fig. 3. The fractionated polymers have $M_w/M_n < 1.05$. The range of molecular weight represented in Fig. 3 (718 to 1230 g/mol) corresponds to the oligomer region for which there is a change in the polymer glass transition temperature from 22°C to 47°C with increasing chain length^[13]. In the oligomer region the polymer chains do not form Gaussian coils. For polystyrene a transition to the next region^[13] occurs at a molecular weight of about 1300 g/mol and T_g of 57°C , and so the surfactant with a molecular weight of 2400 g/mol with a T_g of about 67°C falls beyond the oligomeric region.

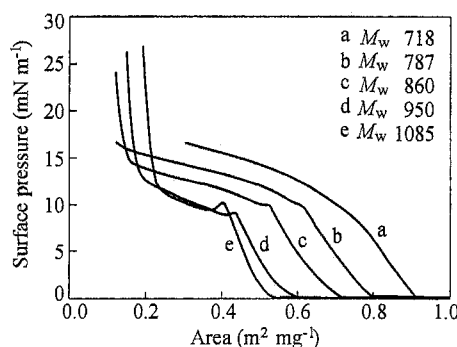


Fig. 3 Π - A compression isotherms of fractionated polystyrenes, as a function of molecular weight over the oligomer region

The narrow molecular weight distribution produced significant alteration of the isotherms. At the low molecular weight end, a broader Π - A distribution result was found accompanied by a larger area per molecule ($815 M_w$ compared to $787 M_w$, for example). At the higher molecular weight end, the plateau region becomes progressively shorter as the molecular weight increases, as was found for the unfractionated material (Fig. 2). This is indicative of a transition in the polymer conformation at the surface to the globular state.

Scaling of Polystyrene Isotherms as a Function of Molecular Weight

The limiting areas, A_0 in $\text{m}^2 \text{mg}^{-1}$, from the polystyrene isotherms are plotted as a function of the molecular weight. This is shown in Fig. 4. The linear relationship over more than four decades of the molecular weight demonstrates scaling and is believed to continue in like manner to infinite molecular weights. The plot contains data from both hydrophilic and hydrophobic^[14] polystyrenes and indicates that the properties of the polymer chain dictate the surface behavior of the polymer spread as a monolayer at the air/water interface. This line was found to follow the equation:

$$\lg A_0 = x \lg M_w + C$$

beyond a molecular weight of about 1300 g/mol. The slope was found to be unity as expected for a polymer chain in a theta state^[12, 14, 15]. Below a molecular weight of 1300 g/mol the oligomer region is entered where the chains no longer form Gaussian coils. The hydrophobic polystyrenes tend to multilayers when pressure is applied while the hydrophilic polymers tend to behave much more like surfactants. The insert shows that at low molecular weights the curve tends towards a limiting molecular area of about 0.95 nm^2 per molecule.

Temperature Effects

Decreasing the temperature of the substrate causes an increase in the surface pressure needed to produce collapse and a shortened collapse region as shown in Fig. 5. The highest graph is for the substrate at 1°C and the lowest 30°C . The data are for the fractionated surfactant of molecular weight 950. A decrease in the temperature results in slower collapse kinetics for the growth of the new phase and therefore allows the monolayer to be compressed to smaller areas and higher pressures before nucleation of the trilayer phase begins. The reduction of the length of the collapse region as the temperature decreases also suggests increasing rigidity of the film below room temperature. The exact morphology of the buckled states produced by the collapse process illustrated here is not yet understood although neutron reflectivity and other measurements should provide insight into this as they have done for the data at 20°C . It is to be noted that for collapsed fatty acid monolayers at high surface pressures long ribbons of collapsed film are formed^[11]. It is supposed that very little compression is required to form a bridge network which supports a resilient film. The changes in limiting areas of the oligomeric and long chain polystyrene surfactants with molecular weight (Figs. 2 and 3) are constant with the view and indicate that conversion to trilayer is more easy as the molecular weight increases.

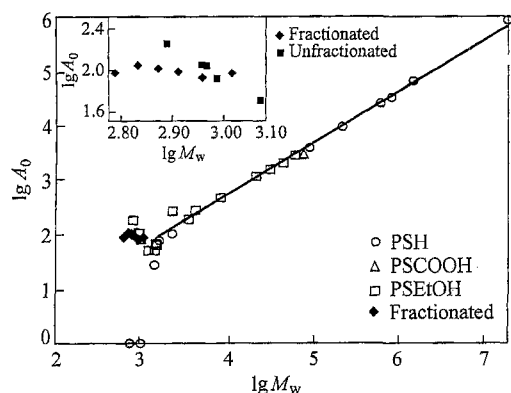


Fig. 4 lg-lg Plot showing the scaling relation of the limiting area to the molecular weight, and (inset) the behavior for the low molecular weight oligomer region

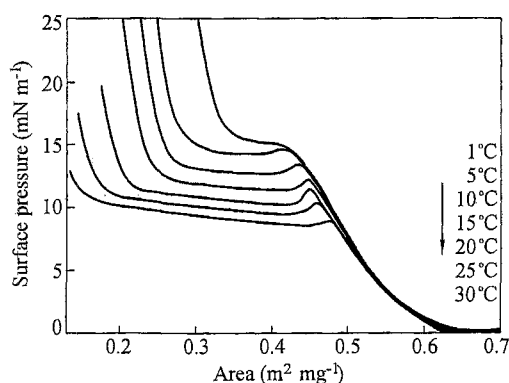


Fig. 5 Temperature dependence of isotherms of $950 M_w$ polystyrene surfactant at the air-water interface

The free energy in the films at the collapse point can be measured as the product of Π and A at this point. When these free energies at different temperatures are plotted as the function of temperature of the substrate a straight line dropping from about 6000 J/mol to 4000 J/mol between 0 and 35°C is obtained. The area, the surface tension, the entropy, temperature, pressure, volume and the number of moles present all enter the expression for the surface free energy. As the pressure, volume and the number of moles are constant and the surface tension changes from 75.6 mN m⁻¹ to 71.18 mN m⁻¹ over the temperature range from 0 to 30°C for water, the change in free energy at collapse point from about 6000 J/mol to 4000 J/mol between 0 and 35°C can be further understood.

Nanostructure and Texture

The structure of films and interfaces produced by polymeric surfactants can be determined at nanometre resolution from specular reflectivity measurements using neutrons and X-rays. The two methods are complementary. The X-ray method has the tremendous intensity now available from synchrotrons and the potential for anomalous contrast. The neutron method is indispensable because of the contrast variation available for hydrogenous systems by H/D isotopic replacement. Recent reviews of these rapidly advancing areas of research are available in the literature^[16, 17, 18].

The behavior of the polystyrene surfactant (PS-OH) with an average molecular weight of 975 g mol⁻¹ whose Π - A isotherm is shown in Fig. 2 illustrates some of the time dependent phenomena involved in respreading^[2, 3]. To establish structures at equilibrium, neutron reflectivity profiles were measured at a number of surface pressures for fully deuterated PS-OH spread on two different subphases: D₂O and air contrast matched water (ACMW, a mixture of D₂O and H₂O with scattering length density the same as for air).

Modeling of the data indicated that the film is initially composed of a monolayer of surfactant with a thickness of 1.33 nm at a surface pressure of 0.5 mN m⁻¹. As the film is compressed to higher surface pressures it becomes thicker as the polymer chains are forced to become closer packed and more linear in conformation. At a surface pressure of 10 mN m⁻¹ the film ruptures and undergoes a structural transition to a monolayer overlaid by islands of trilayer. When the reflectivity profiles were fitted for time intervals after the initial compression and the thicknesses of the various layers calculated, it was found that the trilayer hydrated over a period of about 100 minutes (Fig. 6). Faster kinetic phenomena on the time scale of seconds to minutes have also been identified^[2]. These will be studied using X-ray reflectometry in the millisecond reflectometer^[17] instrument proposed by us for the Chem Mat CARS beamline at the Advanced Photon Source, Argonne National Laboratory, USA. Neutrons may never achieve such a short time scale – once again we see complementarity.

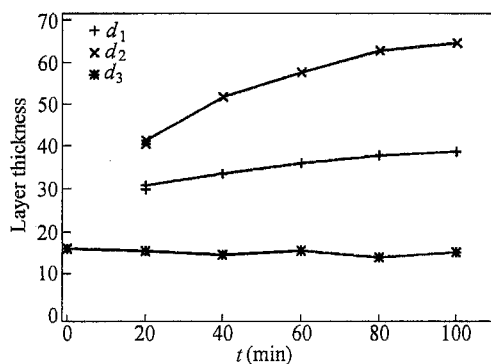


Fig. 6 Time dependence of the thickness of the three layers in the model for the polystyrene surfactant film after trilayer formation, d_3 head group layer in water, d_2 bilayer region, d_1 diffuse top layer

Texture on the micron scale in these compressed films is revealed by the “off-specular” scattering in neutron and X-ray reflectivity. This appears promptly as the nucleation point is reached in the film compression^[2] and can be modeled as the Fourier transform of the film height-height correlation function parallel to the surface, $C(X, Y)$

defined below^[19].

If the roughness of an interface is assumed to be Gaussian the standard deviation of the actual surface from the mean value is σ , $\sigma^2 = \langle [z(x,y) - z(x',y')]^2 \rangle$. If the surface roughness is assumed to be Gaussian in distribution and only depends on the relative position $(X,Y) = (x' - x, y' - y)$, then it can be described by a function:

$$g(X,Y) = \langle [z(x',y') - z(x,y)]^2 \rangle$$

where $g(X,Y)$ is a average over all pairs of points on the surface. Representations of $g(X,Y)$ have been described by Sinha^[20]. For a self-affine surface, the roughness can be expressed by:

$$g(X,Y) = g(R) = AR^{2h} \quad (0 < h < 1)$$

where $R = (X^2 + Y^2)^{0.5}$. This expression provides a good model for most surfaces with the value of h (representing the jaggedness of the surface, a smooth surface would have a value of $h = 1$) usually varying in the range of 0.5 to 0.7. $g(X,Y)$ can be expressed as:

$$g(X,Y) = 2\langle z^2 \rangle - 2\langle z(X,Y) z(0,0) \rangle$$

and in terms of the height-height correlation function $C(X,Y)$:

$$g(X,Y) = \langle z(X,Y) z(0,0) \rangle = \sigma^2 - 1/2 g(X,Y)$$

The formation of nucleated surface patches of the trilayer has also been detected^[19] by electron microscopy, the film being scooped off the water surface onto an electron microscope grid. As this procedure may lead to drying and other artifacts it is interesting to compare the "wet method" – looking at the unchanged film by the "off specular" scattering and the dry electron microscope result. This has been done by Saville^[19].

Electron Microscopy

Langmuir-Blodgett films, of the collapsed monolayer films at several compressions, were prepared for transmission electron microscopy, TEM, studies. Copper transmission electron microscopy grids, 400 mesh, were coated with a formvar film prepared from 0.5% formvar in chloroform. Initial tests on picking the surfactant films up onto the grids by a vertical method failed to produce adhesion of the film to the formvar surface. Also no attachment was found for plasma etched formvar surfaces which were noticeably more hydrophilic than the formvar films as prepared from chloroform. As a result, a horizontal dipping method, as illustrated in Fig. 7, was used. This involved contact of the formvar coated surface of the micrograph grid to the multilayer film coated air-water interface. The grid was then withdrawn, Fig. 7(b), and usually parted from the water surface with a droplet adhering to the grid's surface, Fig. 7(c), except at very high compressions.

This method may produce two possible surfaces. The first will be referred to as a type I film. Figure 7(f) shows this, and consists of the original monolayer on top of the islands of the new phase which are themselves the layer which initially comes into contact with the formvar coated grid. Type I films occur when the rupture of the meniscus does not completely coat the grid with a second layer of film. A type II film, Fig. 7(g), has been observed and this occurs when a second layer of the film attaches itself back to back (monolayer to monolayer) with the type I film initially formed on contact with the formvar.

In the next step of preparing the films for study, they were inserted into a chamber which was then evacuated before shadowing the films with 10% Pt/C. It was found that pumping down the shadowing chamber to the recommended pressure of 10^{-6} torr resulted in dewetting of the polymer films from the formvar. This was avoided by shadowing the films as soon as the pressure had reached 10^{-4} torr. The Pt/C gun was aligned at the grids at an angle of 10 degrees and run for a few seconds.

The electron micrographs in Fig. 8 are presented as representing the two types of film structure which can result from the horizontal lifting technique. Figure 8(a) is a very clear image of the circular island domains resulting from monolayer collapse. This image represents a type II film, as per Fig. 7(g). Figure 8(b), represents a type I film, as per Fig. 7(f), where a slumping process reveals the underlying structure of the domains. In this image, the islands are also visible as circular domains (these appear as very coarse grains in comparison to the

islands of Fig. 7(a) though they are blanketed by the remains of the monolayer. In some parts of this image, the blanketing monolayer appears to have collapsed down onto the formvar, being visible as non-circular grainy areas. It is also possible that the monolayer has dewetted in these regions.

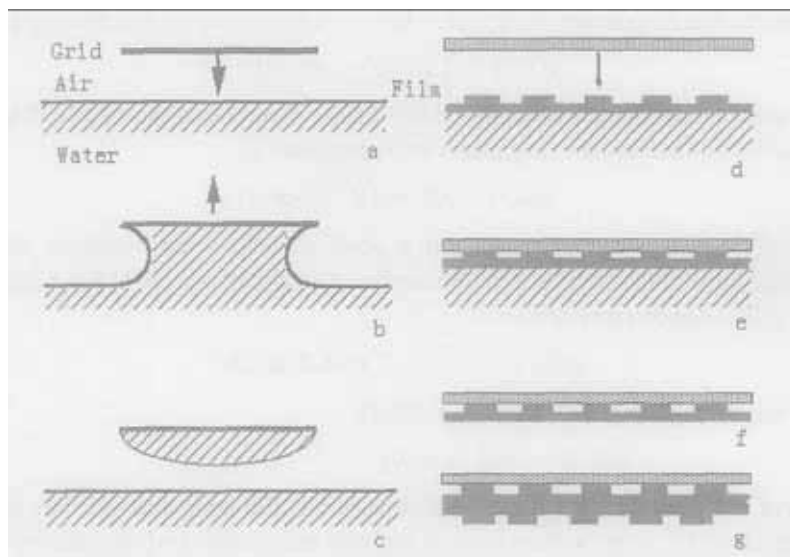


Fig. 7 Horizontal dipping method used for picking up Langmuir-Blodgett films for electron microscopy work

The grid is brought up to contact the surface, 7(a) and 7(d), after contact the grid is withdrawn from the surface, 7(b) and 7(e), the meniscus breaks leaving a droplet attached to the grid surface, 7(c). The two possible surfaces resulting from this contacting method are seen in 7(f) and 7(g) and will be referred to as type I and type II films, respectively.

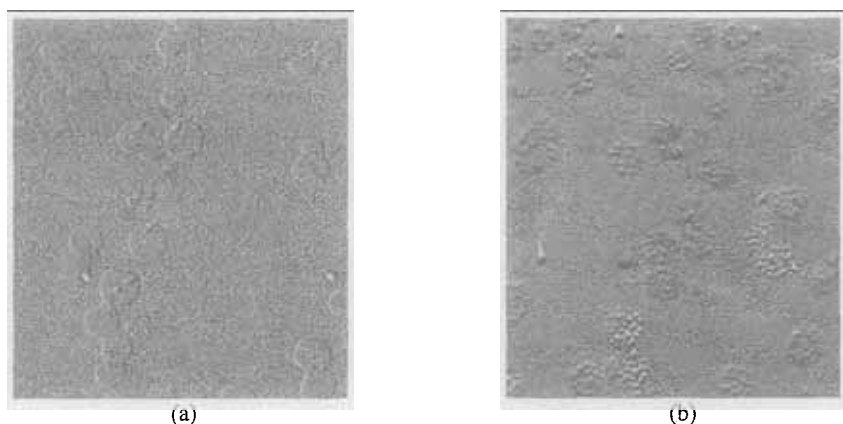


Fig. 8 Images depicting a type II film (a: $\times 4000$) and a type I film (b: $\times 5000$)

Mechanism of Nucleation and Growth of Trilayer

Models of the mechanism of nucleation and growth of the trilayer can be quantitatively tested against measurements of the relaxation rates of the surface area (at constant surface pressure) and island growth as a function of time at fixed surface pressure. These data are given in Saville's thesis^[19] and only a summary can be given here together with the technique of comparing electron microscopy with "off specular" scattering on the same film. Inspection of the electron micrographs as a function of time shows that the growth of disc-like nuclei can be schematically represented as shown in Fig. 9.

After the initial nucleation and growth of the new phase, the island domains grow along their surface tension minimized circumference until overlap occurs with a neighboring domain. At this point the area from which monolayer can be transformed into the new phase is reduced and the surface pressure increases. It is observed that even in the early stages of the collapse region overlap of the growing centers has already occurred.

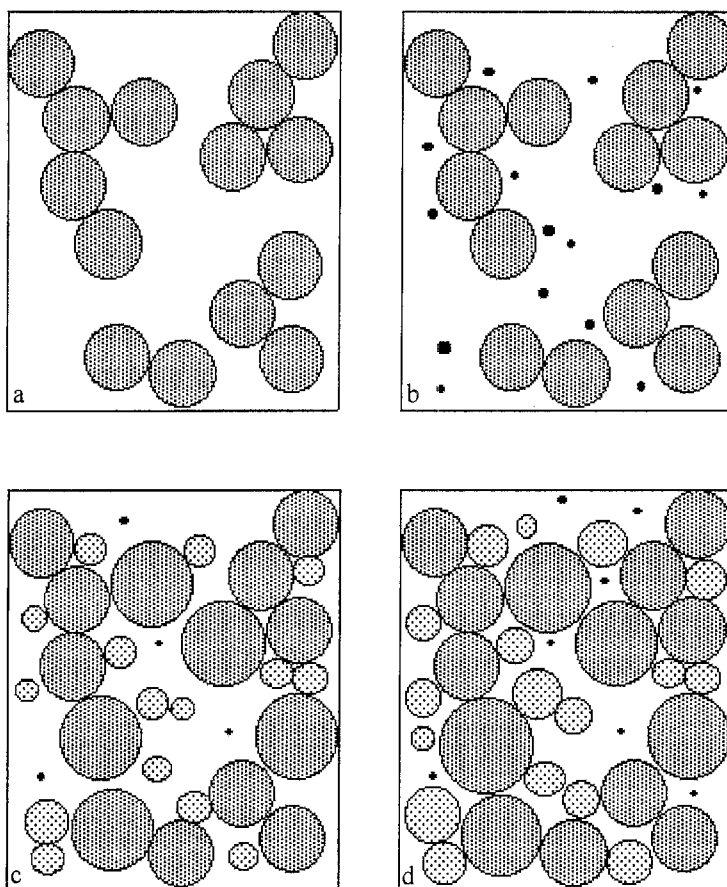


Fig. 9 Partial mechanism of film collapse

Initial nuclei grow into domains until overlap results (a). New nuclei, black dots, form when the pressure rises above the nucleation pressure again due to the reduced area from which the monolayer can transform to the new phase (b). This process continues (c) until the surface is no longer compressible; the isotherm enters the solid region (d), region III of Fig. 2.

The isotherm, Fig. 2, also shows an increase in the surface pressure after only a few percent conversion of the monolayer to trilayer. When the surface pressure is again high enough, new nuclei can form, and so the process repeats. At the end of the compression, the new phase has formed a "solid" if incomplete film, which spans the trough. New nuclei can form to fill in the remaining "holes" in the film.

Simulation of the Off-Specular Scattering

Having obtained electron micrograph images of the films in different states of compression, the negatives were digitized. The digitized images were then processed using NIH Image to highlight the domains and create binary images, such as that seen in Fig. 10. Figure 11 is a plot of the correlation function $g(r)$ as a function of the radius, obtained from the image in Fig. 10 by comparing the distance from every black pixel to every other black pixel (this procedure is rather time consuming even for 11% coverage).

The validity of the correlation function, $g(r)$, was tested for the following necessary features; at $r = 0$, $g(0) =$

α^{-1} , where α is the surface coverage, while as $r \rightarrow \infty$, $g(\infty) = 1.0$. This plot has been normalized by dividing by the surface coverage so the first condition is met. The contribution to the function in the region of 0 to 1 μm comes from the domain size. It is noted that the rest of the correlation function drops off below 1.0 as the radius increases, which is indicative of the sample size being too small to give good statistics for the function in this region. However, qualitatively there are weak correlations between the domains giving rise to the peaks at about 3.8 and possibly 6 μm , which are not unreasonable values.

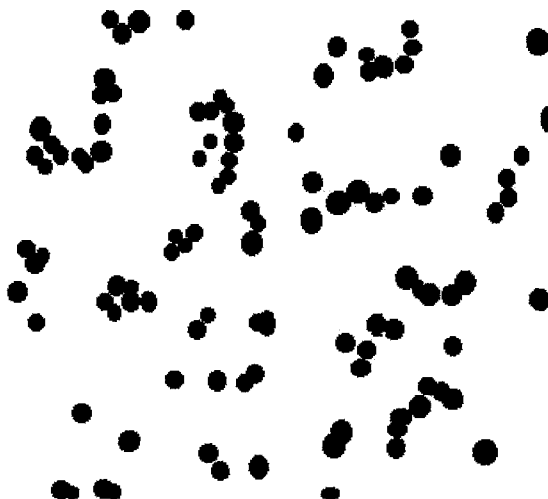


Fig. 10 Binary image of collapsed film at 11.4% coverage, 4000 $\times$ magnification

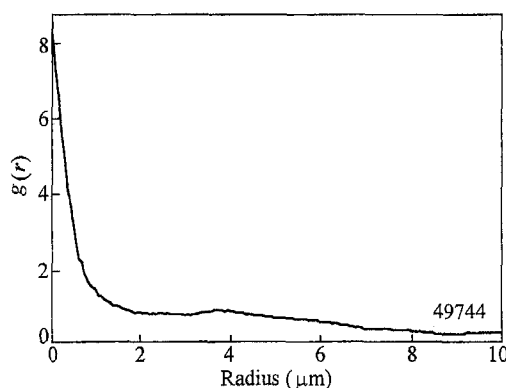


Fig. 11 The radius dependence of the correlation function $g(r)$

Another means of obtaining the correlation function is to take the Fourier transform of the binary image, multiply it by its complex conjugate and inverse transform the image ($(\text{FFT} \times \text{FFT}^*)^{-1}$). The resulting image can then be radially averaged to obtain the function $h(r) = g(r) - 1$. Finally, the Fourier transform of the domain image will yield the scattering function due to the domains.

In the case of PSOH M_w 950 surfactant, this process has been carried out for a film just after the nucleation point and a comparison was made with the profile of the “off specular” neutron reflectivity. This profile may be interpreted as a broad distribution peaking in the region of ca $10^{-4} \text{ \AA}^{-1}$ in Q_x , the horizontal momentum transfer. The Fourier transform of the height-height correlation function from the electron micrography is not inconsistent with this, an indication that for this system transferability of the film to the electron microscope grid and its subsequent treatment has not been destructive of the micron scale texture induced by the nucleation process.

CONCLUSIONS

The results presented show that durable nanoscale and micron scale structures may be produced at polymeric surfactant interfaces and that chemical control of the structures formed and of their persistence may be possible. The ability of reflectivity measurements to measure these processes in real time and at the air-liquid interface has been sketched, as has the complementarity of reflectivity studies and electron microscopy.

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