Polymer Confinement in Surfactant Bilayers of a Lyotropic Lamellar Phase

E. Z. Radlinska,[1,2] T. Gulik-Krzywicki,[3] F. Lafuma,[1] D. Langevin,[4] W. Urbach,[4] C. E. Williams,[2] and R. Ober[5]

[1]*Laboratoire de Physico-Chimie Macromoléculaire, Université Paris VI, CNRS URA 278,*
Ecole Supérieure de Physique et de Chimie Industrielles de la Ville de Paris-10, rue Vauquelin, 75231 Paris Cédex, France
[2]*Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Centre Universitaire Paris-Sud, 91405 Orsay Cédex, France*
[3]*Centre de Génétique Moléculaire, CNRS, 91190 Gif-sur-Yvette, France*
[4]*Laboratoire de Physique Statistique, Ecole Normale Supérieure-24, rue Lhomond, 75231 Paris Cédex, France*
[5]*Laboratoire de Physique de la Matière Condensée, Collège de France, 75231 Paris Cédex, France*

We report on small-angle x-ray scattering and free-fracture electron microscopy studies of a nonionic surfactant/water/polyelectrolyte system in the lamellar phase region. The surface tension data show that the polymer-surfactant interaction strongly depends on the polymer charge content. We demonstrate that regardless of the charge content the polymer molecules are confined inside the bilayers. The chains are collapsed into individual coils which are randomly spread in the bilayers. The polymer molecules cause both local deformation and softening of the bilayer.

The behavior of mixtures of surfactants and polymers in water has been studied for a long time [1]. These systems have important applications in materials science, cosmetics, pharmacology, medicine, and biology. In binary solutions the surfactant molecules aggregate into a wide variety of microstructures with different topology of the interface between the hydrophobic and hydrophilic regions. It has been postulated theoretically [2–4] and shown experimentally that addition of even a relatively small amount of polymer affects both the microstructure and elastic properties of the interface via the specific polymer-surfactant interactions. In particular, the polymer-induced vesicle to micelle [5], rod micelle to spherical micelle [6], and microemulsion to gel [7,8] transitions have been recently reported.

In this work we describe a ternary lamellar system of surfactant, water, and polyelectrolyte of a particular property: The polymer molecules are fully incorporated into the surfactant bilayers. This is demonstrated using freeze-fracture electron microscopy and small-angle x-ray scattering (SAXS). Various structural models have been previously proposed for polymers solubilized into a surfactant lamellar phase: the polymer molecules were thought either to be confined in the water regions [9,10], or to cross between those regions through the bilayer [11], or to remain on the surface of the bilayer [12]. We are not aware, however, of any previous experimental evidence for polymer confinement inside the bilayers in the form of isolated chains.

The ternary mixtures studied by us are based on a binary system of a nonionic surfactant, n-dodecyl pentaoxyethylene glycol ether ($C_{12}E_5$), mixed with water, which at room temperature has a large lamellar phase region. To this system we add up to several weight percent of a water-soluble polymer, poly(styrene-co-styrene sulfonate) with degrees of sulfonation ranging from 30% to 90%. Poly(styrene-co-Na sytrene sulfonate) (abbreviated as $PS_{1-x}NaPSS_x$, x being the degree of sulfonation or charge content) is a random copolymer of highly hydrophobic polystyrene units and hydrophilic polystyrene sulfonate ones. It was obtained by postsulfonation of a polystyrene with a molecular weight of 250 000 and a polydispersity (M_w/M_n) of 2 [13].

The behavior of poly(styrene-co-styrene sulfonate) in water is unusual for polyelectrolytes. It has been shown previously [13] that the structure of $PS_{1-x}NaPSS_x$ in semidilute water solutions exhibits stronger correlations than predicted by the classical correlation hole model [14], thus inferring that the hydrophobicity of the polymer backbone is significant compared to the long-range Coulomb interactions. Unlike other water-soluble polymers, $PS_{1-x}NaPSS_x$ at a low degree of sulfonation has high affinity for nonionic surfactants, as shown by the surface tension data. Indeed, the value of surface tension depends on the number of free surfactant molecules in the mixed system, which in turn depends on the interplay between the processes of self-assembly and surfactant-to-polymer binding both in the solution and at the surface. There is a clear indication of a surfactant-polymer interaction for $x = 0.45$ over the concentration range $10^{-6}M$ to $10^{-2}M$ of $C_{12}E_5$ (Fig. 1). In particular, the surface tension curves for 0.1% and 0.3% of polymer content suggest that the addition of polymer depletes the surface of surfactant molecules which bind to the polymer in the solution. There is no evidence, however, for the binding of the surfactant to the polymer with the charge content of 90% at any polymer concentration (Fig. 1).

$C_{12}E_5$ in water self-assembles into a rich variety of phases [15]. In particular, a liquid crystalline lamellar mesophase L_α consisting of surfactant bilayers with quasi-long-range smectic order is formed over a wide range of composition and temperature. The experimental data for
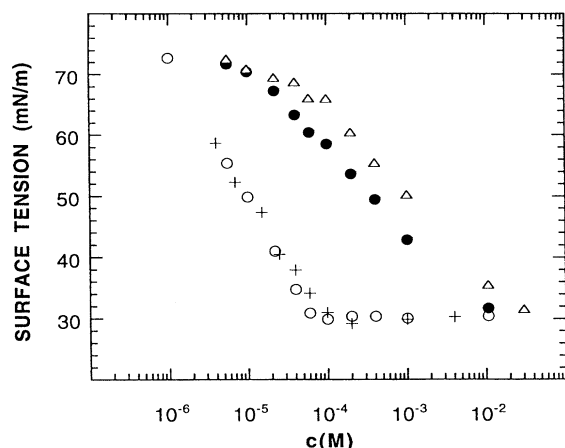
FIG. 1. Surface tension of the $C_{12}E_5$/water/$PS_{1-x}NaPSS_x$ ($x = 0.45$ and $x = 0.90$) system measured using the Wilhelmy plate method at room temperature; c is the surfactant concentration. Data for the binary $C_{12}E_5$/water system are shown with empty circles; full circles and triangles correspond to 0.1 wt% and 0.3 wt% of polymer of the sulfonation degree $x = 0.45$, respectively, and crosses correspond to 0.3 wt% of polymer of the sulfonation degree $x = 0.90$.
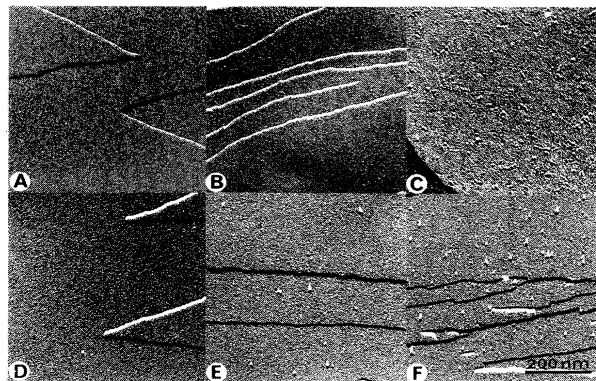

FIG. 2. Freeze-fracture electron microscopy images for samples of surfactant-to-water ratio equal to 3.39 with and without polymer. (a) Binary $C_{12}E_5$/water system, 77.2 wt% of surfactant. (b),(c) Sulfonation degree of polymer $x = 0.30$, concentration of polymer 0.2 wt%, and 2.3 wt%, respectively. (d),(e),(f) Sulfonation degree of polymer $x = 0.90$, concentration of polymer 0.3 wt%, 0.9 wt%, and 2.2 wt%, respectively.

the concentrated ternary mixtures reported here have been acquired in the region of high surfactant content where the L_α phase exists at room temperature. In particular, we report data for samples with the surfactant-to-water ratio 3.39, which corresponds to 77.2 wt% of surfactant and 22.8 wt% of water in the binary system. The samples were organized into series that always had a constant surfactant-to-water ratio and progressively increased concentration of the polymer. The measurements were repeated at several points of time from one week to three months after the samples have been prepared, and no differences were observed.

Freeze-fracture electron microscopy (EM) images (Fig. 2), obtained using the method described in Ref. [16], demonstrate a well defined lamellar structure, and the interlayer distances are in very good agreement with the SAXS-determined values. The surfaces exposed by cleavage (and visible on the images) are midsections through the hydrophobic center of the bilayer [17]. These surfaces appear smooth for the binary $C_{12}E_5$/water mixture. For the ternary $C_{12}E_5$/water/polymer systems additional objects are clearly seen. These objects have a wormlike appearance (length about 300 to 1000 Å) for the low polymer charge content [Fig. 2(c)]. Upon increased degree of sulfonation they become granular [diameter about 150 Å, Figs. 2(d)–2(f)]. Because of the cleavage properties of the freeze-fractured bilayers the objects seen cannot be attached to the hydrophilic surfaces of the lamellae but have to be enclosed inside the bilayers [18]. The thickness of the unperturbed bilayer is 22 ± 1 Å and of the water layer 18 ± 1 Å, so

these objects must cause strong local deformation of the lamellar structure. The concentration of these objects, calculated from the EM images of the replicas (Fig. 2 and other data), is in good agreement with the concentration number of polymer molecules added to the samples. The change of form upon increased charge content from extended to granular observed for some of the objects is as expected for $PS_{1-x}NaPSS_x$ in an organic solvent: The strongly hydrophobic backbone of polymer should be extended inside the bilayer at the low charge content and assume a much more compact form at high charge content. We conclude that the objects we observe are the images of molecules of $PS_{1-x}NaPSS_x$, all of them confined inside the bilayers.

The similarity of the confinement of polymer molecules in the concentrated liquid crystalline phase, independent of their charge content, provides strong argument that the total free energy of the system is dominated by the major components. This happens despite the fact that in dilute solutions the specific interactions between the surfactant and polymer molecules strongly vary, depending on the polymer degree of sulfonation (Fig. 1).

The confinement of polymer molecules inside the surfactant membranes causes an increase of the average bilayer thickness, spatially modulates the surfactant-water interface, and may affect the system's elasticity. These effects are clearly reflected in the SAXS data (Fig. 3). The Bragg peak shifts in a manner consistent with the increase of the lamellar period by 1% to 4%. Because the ratio of surfactant-to-water molecules in the samples is constant, swelling of the bilayer is entirely caused by incorporation of the polymer molecules into the structure. Figure 4 shows the shape of the first harmonic of the structure factor. For the moderate charge content
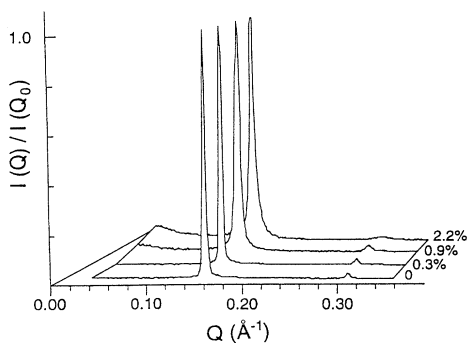
FIG. 3. SAXS spectra for the $C_{12}E_5$/water/PS_{1-x}NaPSS$_x$ system for the polymer sulfonation $x = 0.90$ at 25 °C. Data for four different polymer concentrations are shown: 0 (binary $C_{12}E_5$/water system), 0.3, 0.9, and 2.2 wt%.

(e.g., $x = 0.45$) the Bragg peak only slightly broadens with increased polymer concentration. For the highest degree of sulfonation ($x = 0.90$) the broadening is very pronounced.

Theoretical fits shown in Fig. 4 correspond to the predictions of Caillé theory for the structure factor of thermally undulating lamellae [19,20]. We have used the line shape formula derived by Nallet, Laversanne, and Roux [21] which results from the convolution of the thermally broadened line shape for a finite-size lamellar domain with a Gaussian component (of width σ), which in Ref. [21] represents the experimental resolution function. Data presented in this work were acquired with the experimental resolution of 1.5×10^{-3} Å^{-1}, and for the polymer charge content 45% the experimental data in the entire polymer concentration range could be fitted using this value. For the 90% charge content, however, reasonable fits could only be obtained assuming an effective resolution that systematically increases with the polymer concentration (Fig. 5). It was not possible to obtain good fits by varying the domain size L only, and it was kept constant at 2500 Å. We interpret the concentration dependent Gaussian component as caused by an additional line broadening due to the deformation of individual lamellae caused by the presence of large, globular polymer molecules inside the bilayers. The random distribution of strains is expected to result in a Gaussian line shape, which is to be convoluted with the instrumental line shape. This effect is analogous to the lattice strain broadening discussed by Warren and Averbach [22]. As convolution of two Gaussians is a Gaussian, the superposition of the finite instrumental resolution and the strain broadening would lead to a Gaussian line shape, in accordance with our analysis. For lower charge contents the polymer molecules assume a more extended shape [Fig. 2(c)], and the strain broadening cannot be detected in SAXS spectra (Fig. 5).

The fitted values of the Landau-Peierls exponent $\eta \sim 1/\sqrt{KB}$ (where K and B are the bulk moduli for cur-
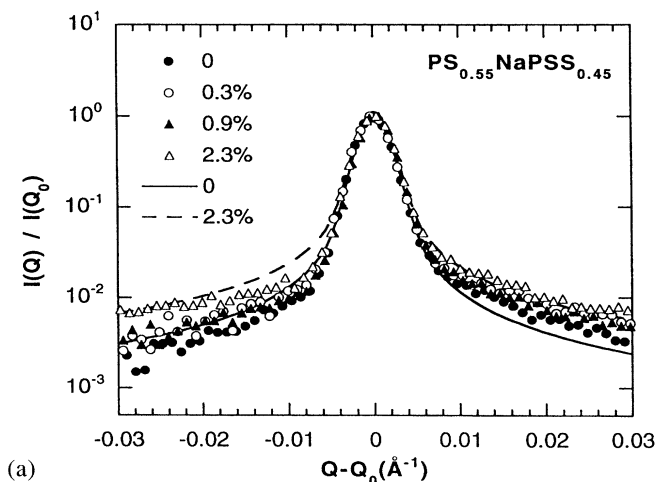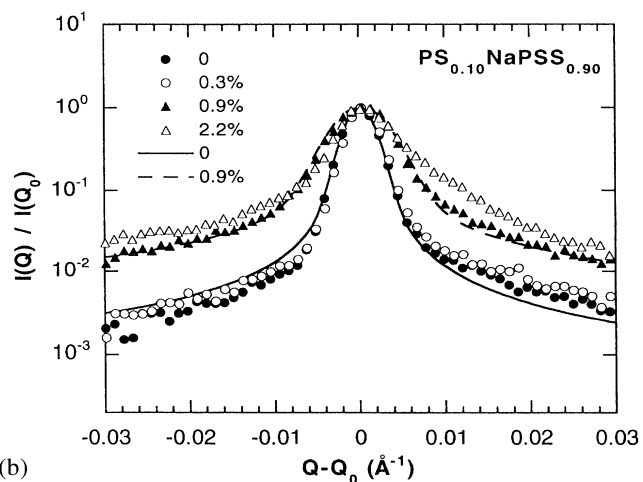
FIG. 4. Line shape of the first harmonic for various $C_{12}E_5$/water/polymer systems. Each set of data was normalized to the peak intensity equal to unity and peak position $Q - Q_0 = 0$. The polymer sulfonations are (a) $x = 0.45$ and (b) $x = 0.90$. For all the samples surfactant-to-water weight ratio is constant and corresponds to 77.2 wt% of surfactant in water. Each set of experimental points corresponds to different polymer concentration: 0 (binary C12E5/water system), 0.3, 0.9, and 2.3 wt% (a) and 0, 0.3, 0.9, and 2.2 wt% (b). The solid and dashed lines are examples of fits obtained using the results of Nallet theory [21].

vature elasticity and compressibility of the membranes, respectively [21]) systematically increase with increasing polymer concentration (Fig. 5). We also observe an excess scattering in the small-Q region, particularly pronounced for the samples with larger concentrations of highly charged polymer (Fig. 3). This may be due to the spatial fluctuations of the interlayer distances or alternatively to softening of the interactions between the bilayers, these two possibilities being eventually related.

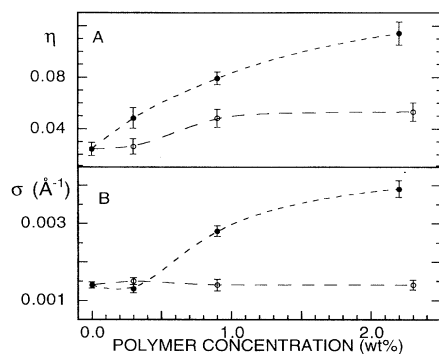In conclusion, we have presented experimental evidence showing that in the lamellar phase region of

FIG. 5. Variation of the Landau-Peierls exponent η (a) and the Gaussian width σ (b) versus polymer concentration for the first harmonic of the SAXS spectra. Empty circles correspond to 45% of the polymer sulfonation and full circles to 90% of the polymer sulfonation. The lines are guides for the eye only.

the $C_{12}E_5$/water/poly(styrene-co-styrene sulfonate) system upon addition of the polymer a pronounced deformation and softening of the structure occurs (SAXS data). Freeze-fracture electron microscopy results unequivocally demonstrate that the polymer molecules enter the bilayers and remain incorporated as isolated entities inside them for all charge contents between 30% and 90%. The polymer molecules appear extended inside the bilayers at low charge content and become globular as the charge content increases.

[1] E. D. Goddard, in *Interactions of Surfactants with Polymers and Proteins,* edited by E. D. Goddard and K. P. Ananthapadmanabhan (CRC Press, Inc., Boca Raton, 1993).

[2] P. G. de Gennes, J. Phys. Chem. **94**, 8407 (1990).

[3] J. T. Brooks and M. E. Cates, J. Phys. Chem. **99**, 5467 (1993).

[4] K. M. Palmer, M. Goulian, and P. Pincus, J. Phys. II (France) **4**, 805 (1994).

[5] K. Seki and D. A. Tirrell, Macromolecules **17**, 1692 (1984).

[6] J. C. Brackman and J. B. F. N. Engberts, Langmuir **7**, 46 (1991).

[7] C. Petit, Th. Zemb, and M. P. Pileni, Langmuir **7**, 223 (1991).

[8] C. Quellet, H. F. Eicke, and W. Sager, J. Phys. Chem. **95**, 5642 (1991).

[9] C. Ligoure, G. Bouglet, and G. Porte, Phys. Rev. Lett. **71**, 3600 (1993).

[10] M. Singh, R. Ober, and M. Kleman, J. Phys. Chem. **97**, 11 108 (1993).

[11] P. Kekicheff, B. Cabane, and M. Rawiso, J. Colloid Interface Sci. **102**, 51 (1984).

[12] I. Iliopoulos and U. Olsson, J. Phys. Chem. **98**, 1500 (1994).

[13] W. Essafi, F. Lafuma, and C. E. Williams, Am. Chem. Soc. ACS Symp. Ser. **548**, 278 (1994).

[14] P. G. de Gennes, P. Pincus, R. M. Velasco, and F. Brochard, J. Phys. (Paris) **37**, 1461 (1976).

[15] R. Strey, R. Schomäcker, D. Roux, F. Nallet, and U. Olsson, J. Chem. Soc. Faraday Trans. **86**, 2253 (1990).

[16] P. Hervé, D. Roux, A.-M. Bellocq, F. Nallet, and T. Gulik-Krzywicki, J. Phys. II (France) **3**, 1255 (1993).

[17] J. P. Sergrest, T. Gulik-Krzywicki, and C. Sardet, Proc. Natl. Acad. Sci. U.S.A. **71**, 3294 (1974).

[18] T. Gulik-Krzywicki, Biochim. Biophys. Acta **415**, 1 (1975).

[19] A. Caillé, C. R. Acad. Sci. Ser. B **274**, 891 (1972).

[20] C. R. Safinya, D. Roux, G. S. Smith, S. K. Sinha, P. Dimon, N. A. Clark, and A. M. Bellocq, Phys. Rev. Lett. **21**, 2718 (1968).

[21] F. Nallet, R. Laversanne, and D. Roux, J. Phys. II (France) **3**, 487 (1993).

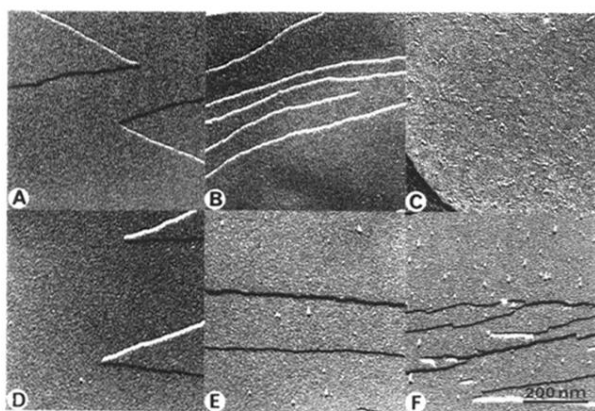[22] B. E. Warren and B. L. Averbach, J. Appl. Phys. **21**, 595 (1950).

FIG. 2. Freeze-fracture electron microscopy images for samples of surfactant-to-water ratio equal to 3.39 with and without polymer. (a) Binary $C_{12}E_5$/water system, 77.2 wt% of surfactant. (b),(c) Sulfonation degree of polymer $x = 0.30$, concentration of polymer 0.2 wt%, and 2.3 wt%, respectively. (d),(e),(f) Sulfonation degree of polymer $x = 0.90$, concentration of polymer 0.3 wt%, 0.9 wt%, and 2.2 wt%, respectively.