Renormalization of Helfrich's Interactions between Fluid Membranes in a Lyotropic Lamellar Phase by Addition of Amphiphilic Copolymers

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We study the effect of an amphiphilic block copolymer on the thermodynamic properties of a lyotropic lamellar phase into which it is incorporated. A quantitative analysis of the small angle neutron scattering spectra of these samples shows that the polymer strongly enhances the stabilizing Helfrich's interactions between membranes, by increasing the effective bilayer thickness. The smectic compressibility of the lamellar phase becomes insensitive to the addition of salt, as soon as the Debye length is smaller than the thickness of the layer of copolymer adsorbed onto the membrane. This effect is similar to the "steric repulsion" of anchored polymer layers in colloidal dispersions. [S0031-9007(98)08129-0]

The simplest liquid crystalline phase of membranes is the lamellar phase L_α: It has the symmetry of a smectic-A lyotropic liquid crystal and consists of a one-dimensional stack of bilayers of one or more amphiphilic components separated by solvent layers. The wealth of information collected over the past two decades on the L_α phase designates it as convenient tools to investigate interactions between membranes and other components. In particular, an increasing interest is directed today towards ternary lamellar phases consisting of surfactants, water, and polymers [1–12]. Previous studies have shown that the macromolecules (guest component of the lamellar phase) can occupy *various locations* in such systems. It has been shown experimentally [13] that for charged bilayers (ionic amphiphiles), in pure water, the smectic order is stabilized by long-range electrostatic interactions, whereas in high salt brine (few 10^{-1} mol/l) the electrostatic interaction is screened beyond distances shorter than the smectic periodicity so that the stability of the phase arises from the much weaker so-called Helfrich's interaction between membranes [14]:

$$V_{\text{Helf}} = \frac{3\pi^2 (kT)^2}{128\kappa} \frac{1}{(d - \delta)^2},$$ (1)

where d is the smectic period, δ is the bilayer thickness, and κ is the bending modulus of a single bilayer.

X-ray and neutron scattering technics have been accepted as very powerful techniques to study the organization as well as the fluctuations of various self-assembled systems. Quantitative treatments of the neutron (or x-ray) scattering patterns of a smectic phase allow one to measure the dimensionless Caillé parameter η [15], characterizing the power-law singularities at the Bragg peaks. η is defined in terms of the smectic elastic constants by

$$\eta = \frac{q_0^2 kT}{8\pi \sqrt{K\overline{B}}},$$ (2)

where K is the smectic curvature modulus (related to the bilayer bending modulus κ and to the smectic periodicity d according to $K = \kappa/d$, $\overline{B}$ is the smectic compression modulus related to the bilayers-bilayers interactions and q_0 is the position of the first Bragg singularity, $q_0 = 2\pi/d$. Interestingly, when the interlamellar forces are dominated by entropic undulations, we expect η to follow the simple purely geometrical expression [13],

$$\eta = \frac{4}{3}\left[1 - \frac{\delta}{d}\right]^2.$$ (3)

Addition of polymer in a lamellar phase creates new effective polymer-mediated interlamellar forces which strongly depend both on the architecture of the polymer and on the polymer/bilayer interactions. Addition of amphiphilic copolymers in a lamellar phase strongly enhances the repulsive interlamellar forces as revealed by stiffening of the Bragg singularities of the scattering spectra of the L_α phase [10]. However, the origin of these extra long-range repulsive interactions in flexible L_α phases with anchored amphiphilic copolymers is presently not elucidated.

In this Letter we describe a pseudoternary lamellar system of cationic surfactant, cosurfactant, brine, and amphiphilic triblock copolymer. The central hydrophobic block adsorbs onto or inserts inside the fluid bilayers, while the two hydrophilic tails remain in the intermembrane aqueous regions, decorating the bilayers. We have explored the polymer-induced interactions between the fluid membranes by small-angle neutron scattering (SANS) experiments, in the domain of the phase diagram where the lamellar structure is conserved upon the addition of copolymer. The powder intensity spectra have been fitted with the line shape formula derived by Nallet, Laversanne, and Roux [16]. This fitting procedure has been successfully used for several lamellar systems [3,16,17], and allows one to measure the Caillé parameter

η. We proceed in two steps. First, we incorporate increasing amounts of polymer in the undulation stabilized phase (solvent: brine with 0.2 mol/l NaCl concentration) at a fixed membrane volume fraction. Second, we fix both the bilayer and the polymer concentration at suitable values and only vary the salt concentration in the range 0 mol/l (pure water) to 0.2 mol/l. Doing so, we monitor the strength of the electrostatic interlayer interactions. In these two series of experiments, the measurements of the Caillé parameter η are in agreement with the picture where the two grafted polymer layers on both sides of each bilayer modify the Helfrich's interaction by simply renormalizing the membrane thickness. It means that in Eqs. (1) and (2) the bare membrane thickness δ_0 should be simply replaced by an effective membrane thickness δ_{eff},

$$\delta_{\mathrm{eff}} \equiv \delta_0 + 2h, \qquad (4)$$

where h is the effective thickness of the polymer layer attached on each side of a bilayer membrane.

The L_α phases are obtained from the system CPCL (cetylpyridinium chloride, a cationic surfactant)/octanol/ brine. The salinity of the solvent is fixed at 0.2 mol/l for the first series of experiments and is varied in the range 0 mol/l (pure water) to 0.2 mol/l for the second series. The alcohol to surfactant ratio is fixed: $M_{\mathrm{oct}}/M_{\mathrm{CPCL}} = 0.95$ in light water and $M_{\mathrm{oct}}/M_{\mathrm{CPCL}} = 0.91$ in heavy water, so that the lamellar structure is preserved at all salinities. The bilayer thickness has been measured by scattering according to the classical swelling law: $\delta = 26.4 \pm 0.5$ Å. The polymer is a triblock amphiphilic copolymer with trade name pluronics F68, a commercial product used as received. It consists of two identical polyoxyethylene (PEO) blocks of 76 monomers each, symmetrically bounded to a central shorter hydrophobic polyoxypropylene (PPO) block of 29 monomers. The PPO block adsorbs onto or inserts inside the membrane, whereas the two PEO tails remain in the aqueous solvent and decorate the membrane. The radius of gyration of one PEO tail is $R_G \approx 19$ Å [18]. Depending on the polymer to membrane weight ratio $\alpha = M_{\mathrm{F}_{68}}/(M_{\mathrm{oct}} + M_{\mathrm{CPCL}})$, one expects two regimes for the polymer grafted layers: at low α, a mushroomlike structure, and a brushlike structure in the opposite case. The smooth crossover α^* between these two regimes can be crudely estimated, $\alpha^* \approx 0.5$: It corresponds to the overlap limit of PEO mushrooms of area $\Sigma = \pi R_G^2$. The fact that we used a triblock copolymer with a central hydrophobic block rather than a diblock copolymer is not crucial: Indeed, we have performed some experiments with an end-functionalized PEO of 112 monomers with a short aliphatic sticker, and have obtained very similar behaviors. Figure 1 shows how the phase diagram of the initial CPCL/octanol/brine 0.2 mol/l NaCl at 20 °C L_α phase is modified by the addition of F68. Here we focus only on the salient features. First of all, there
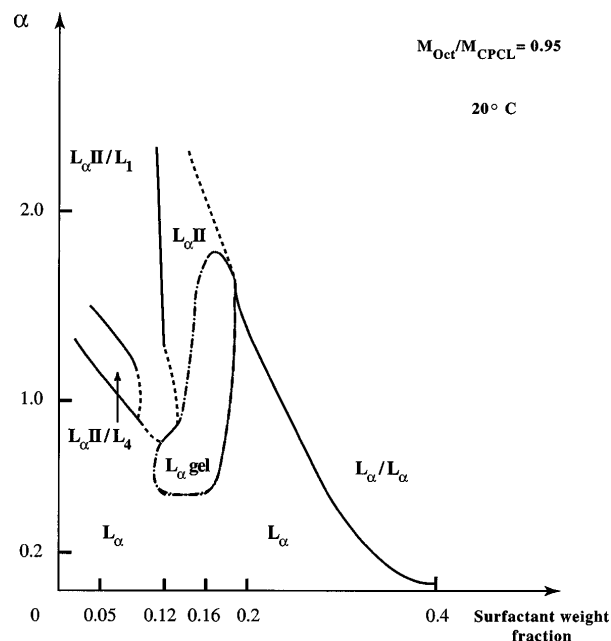

FIG. 1. Phase diagram of the system CPCL/octanol/F68/Brine at 20 °C. Fixed weight ratio $M_{\mathrm{Oct}}/M_{\mathrm{CPCL}} = 0.95$; salinity: [NaCl] = 0.2 mol/l; x-axis weight fraction of octanol + CPCL; y-axis: weight ratio $\alpha = $ polymer/octanol + CPCL.

is a large domain where the L_α structure is preserved upon the addition of copolymer. However, note the existence of a closed region in which the mechanical properties of the lamellar phase are those of a gel. This "phase" called $L_{\alpha,\mathrm{gel}}$ is identical, we think, to the new lamellar gel discovered by Warriner et al. [10]. Interestingly, we note that as in Ref. [10] this gelation is uncorrelated to changes in lamellar structure and smectic elasticity. Finally, at low membrane concentration, we observe a classical sequence of lyotropic phases by increasing the copolymer concentration, i.e., L_α, L_αII (coexisting lamellar crystallites and multilayer vesicles), L_4 (unilamellar vesicles), L_1 (micelles). This sequence is reminiscent of the spontaneous formation of vesicles in lyotropic lamellar phases induced by the addition of amphiphilic copolymers [19,20].

Small angle neutron scattering data were collected on the beam line D11 at ILL in Grenoble and on the beam line PACE at LLB in Saclay. For contrast reasons H$_2$O was replaced by D$_2$O. Density corrections have been made to compare heavy and light water samples. The data were put on absolute scale, and all treatments are standard. Figure 2 shows a series of SANS powder scans corresponding to the peaks of a lamellar structure along a line of increasing polymer to amphiphile weight ratio α at constant weight fraction of membrane $M_s = 20\%$. The observed behavior (as first noticed by Warriner et al. on another system [10]), where the addition of amphipilic copolymer correlates with the stiffening of the first Bragg peak and the emergence of higher harmonics in the scattering profile, suggests that
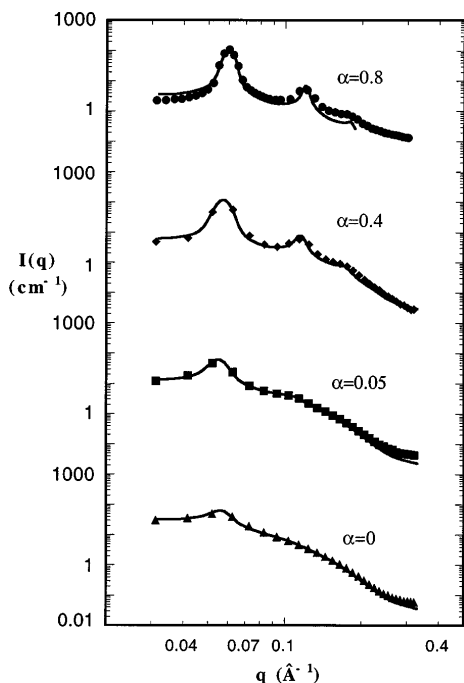
FIG. 2. SANS patterns of a series of lamellar phases of constant surfactant weight ratio 20% for four different polymer to surfactant weight ratio α (salinity $= 0.2$ mol/l; and $M_{oct}/M_{CPC1} = 0.95$), and corresponding fits (full lines of these patterns obtained from the Nallet $et\ al.$ model [16]).

PEO coated membranes in a flexible multilayer system experience an enhanced repulsive interaction as a function of increasing polymer to amphiphile ratio α. Another interesting feature (to be discussed in more detail in a future publication): In the brush regime ($\alpha > \alpha^*$), the Bragg peaks of the lamellar phase progressively shifts to higher q values, as the polymer concentration at constant surfactant volume fraction increases. This result can be quantitatively explained by a thinning down of the bilayer, due to competing stretching of the polymer brush (in the z direction) and lateral stretching of the membrane (in the x-y plane) [9].

In order to study quantitatively the polymer-mediated repulsive interaction, we have fitted the SANS patterns at constant membrane volume fraction and various polymer contents using the Nallet $et\ al.$ model [16], as detailed in Ref. [3]. Examples of fits are given in Fig. 2. Doing so, we have obtained the variation of the Caillé parameter η as a function of the polymer to membrane weight ratio α, as shown in Fig. 3. In this case, the membrane volume fraction is fixed $\phi_s = 23\%$. The Caillé parameter η decreases sharply as α increases, until it reaches a plateau for $\alpha \approx \alpha^* \approx 0.5$ (crossover to the brush regime). For $\alpha = 0$, the fitted value of η is $\eta_{exp} \approx 0.78 \pm 0.02$. This value agrees with the expected theoretical value for an undulation interaction, $\eta_{theo} \approx 0.78$, and is obtained by inserting the measured bare bilayer thickness $\delta = 26.4 \pm 0.5$ Å and the measured smectic periodicity $d = 114.2$ Å

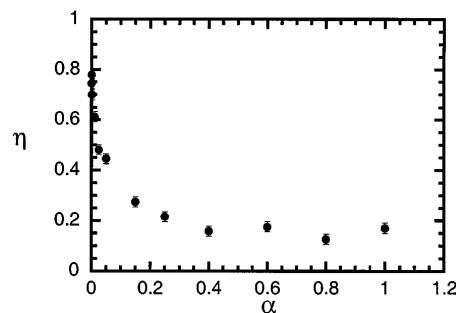

FIG. 3. Caillé parameter η versus polymer to surfactant weight ratio α (surfactant weight ratio 20% in D_2O; NaCl $= 0.2$ mol/l).

of the lamellar phase without polymer in Eq. (3). In the plateau regime ($\alpha \gtrsim 0.5$), the fitted value η is $\eta_{exp} \approx 0.15 \pm 0.02$, whereas the expected theoretical value is $\eta_{theo} \approx 0.18$. Again, this theoretical value is obtained from Eq. (3), where the bare membrane thickness is replaced by the effective bilayer thickness $\delta_{eff} \approx \delta_0 + 2R_G$ ($R_G \approx 19$ Å). Two interesting features should be noticed. First, the effective polymer thickness h seems to reach a maximum value $h \approx R_G$, as soon as the mushrooms begin to overlap and form a continuous brush layer on both sides of the membranes. This saturation effect is related, we think, to the lateral stretching of the membrane which opposes the perpendicular stretching of polymer tails in the brush regime; it is in agreement with the predictions of Hristova and Needham [9]. Second, the strong decrease of η at very low α values indicates that each polymer mushroom induces a local renormalization of the bilayer thickness on an area much larger than the natural area of the mushroom, $\Sigma^* = \pi R_G^2$. This effect arises from the bending rigidity of the bilayer which induces in plane (x, y)-correlations in the z position of one given bilayer; therefore a mushroom not only prevents interbilayer contact at the (x, y) position where it stands, but also at all distances below the corresponding in plane correlation length ξ_{xy}. A theoretical model for this effect is under current progress.

Then we have investigated seven series of samples at fixed amphiphile concentration ($\phi_s = 23\%$); in each series the polymer to membrane weight ratio α is kept constant (in the range 0 to 0.8 from one series to the other) as a function of the mean salinity. Figure 4 shows the variations of the Caillé parameter, η, as function of the mean salinity for each series of samples. For $\alpha = 0$ (no polymer), it appears that η increases monotonically with salinity, in agreement with the relative strength of electrostatic versus Helfrich's interactions. As some polymer is added, the situation is different: η still increases with ionic strength of the solvent, until it reaches a plateau. Both the plateau value and the threshold salinity at which this plateau appears are smaller at higher α. The interpretation is simple. For a charged lamellar phase, decorated
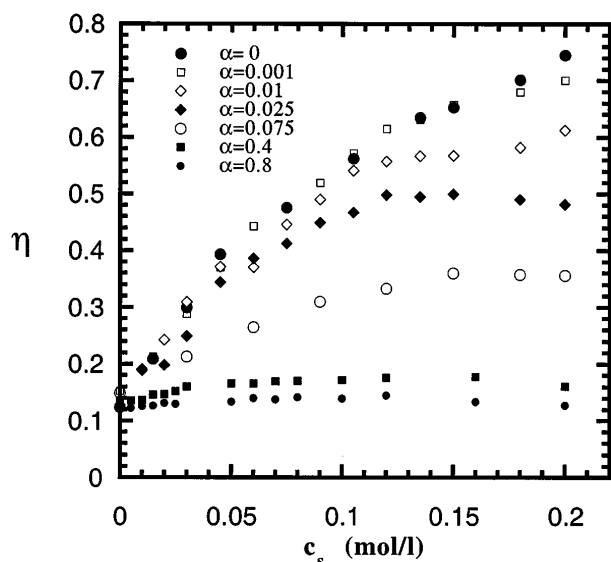
FIG. 4. Plot of the Caillé parameter η as a function of the mean salinity of the lamellar solvent at different polymer/surfactant weight ratio α. In all experiments the weight fraction of surfactant is fixed $M_s = 20\%$ ($\phi_s = 23\%$).

by grafted polymer layers in brine, there are two characteristic length scales. The first one is the electrostatic Debye screening length λ_D, which roughly corresponds to the thickness of the counterions layer on both sides of a charged membrane. The second characteristic length is the thickness of the effective polymer layer h grafted on each side of the membrane, which depends on α. Then, the system becomes insensitive to the further addition of salt, as soon as λ_D becomes smaller than h. This type of behavior is similar to what is observed in a suspension of polymer-coated colloidal particles in a solvent at high ionic strength. In this latter case, the grafted polymer layers induce a steric repulsion between neighboring particles which prevents the suspension against flocculation. However, for lyotropic lamellar phases, this steric repulsion is long range, and of Helfrich's type, since membranes are *fluctuating* colloidal objects.

In conclusion, we have achieved an experimental realization of an amphiphilic copolymer grafted onto the fluid membranes of a lyotropic smectic. The comparison with the polymer-free reference series clearly reveals the polymer specific contribution to the effective repulsion between bilayers. We have shown, by an analysis of the SANS spectra of these mixed lamellar phases, that this effective interaction is a steric repulsion. Since the fluid membranes of a lyotropic lamellar phase are *fluctuating* objects, this steric repulsion can be viewed like a *long-range renormalized Helfrich's interaction* between membranes: the thickness of each bilayer is increased by an amount equal to twice the thickness of a grafted polymer

layer surrounding it. In spite of its simplicity, this picture accounts almost quantitatively for both the strong stiffening of the Bragg peaks and the gradual insensitiveness to added salt of charged bilayers decorated by increasing amounts of amphiphilic copolymers. An important feature remains to be understood: How the effective copolymer layer thickness is related to the grafting area density of copolymers. Such a more quantitative investigation is in current progress.

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