Bending moduli of a nonadsorbing-polymer-containing lyotropic lamellar phase: An experimental study

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We investigate the effect of the incorporation of a neutral water-soluble nonadsorbing polymer polyvinylpyr-rolidone (PVP) on the bilayer bending moduli κ and $\bar{\kappa}$ of the lamellar phase L_α composed of cetylpiridinium-chloride (CPCL)/hexanol/H$_2$O. The mean bending modulus κ is obtained from the measurement of quadrupolar splittings of perdeuterated hexanol by deuterium solid state NMR. It is found that κ is insensitive to the amount of polymer in the lamellar phase, in agreement with the theoretical predictions. Observations with the polarizing microscope of topological defects in the lamellar phase allow a qualitative study of the Gaussian bending modulus $\bar{\kappa}$. Addition of a small amount of polymer in the lamellar phase induces a large proliferation of focal conic domains of second species (positive Gaussian curvature). Cryo-TEM confirms that the polymer drastically modify the texture of the lamellar phase. These results indicate clearly that the presence of the nonadsorbing polymer strongly decreases $\bar{\kappa}$, in contradiction with theoretical predictions. [S1063-651X(98)06901-3]

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I. INTRODUCTION

An increasing interest is directed today towards *three-components* lyotropic L_α lamellar phases [1]: they consist of surfactant *bilayers* (often involving surfactant and cosurfactant) periodically stacked in space, separated by a solvent (that is an effective two-components smectic-A phase), into which a *guest component* (protein [2], colloidal particles [3] or polymers [4–13]) is incorporated. Previous studies on macromolecules solubilized into a surfactant lamellar phase have shown that the polymer molecules can occupy a variety of locations in such systems. They can be confined in the interlayer solvent [5,6,12,13] and do not adsorb onto or incorporate into the surfactant bilayers, entirely localized in the membrane [7], localized both in the bilayers and in the solvent [9–11] or adsorb onto the bilayers [8]. The experimental system we have studied consists of the L_α phase obtained from the system CPCL (cetyl pyridinium chloride)/hexanol/water (for which we have the most extensive set of structural data [14]) in which we incorporate a large water-soluble polymer PVP (polyvinylpyrrolidone). In the absence of added salt, the smectic order is stabilized by strong long-range electrostatic interactions (CPCL is a cationic surfactant), and we have several experimental evidences that the polymer is effectively located in between the bilayers, does not penetrate through the bilayers, and shows no specific affinity with the membrane, so that the confinement is effective and the adsorption regime is avoided [5,12].

The elastic properties of a lyotropic lamellar phase L_α can be characterized by three fundamental smectic elastic constants: the layer compression modulus $\bar{B}$ related to the bilayer-bilayer interactions, and the two smectic curvature moduli K and $\bar{K}$ related to the smectic periodicity d and respectively to the bilayer mean bending modulus κ and to the bilayer Gaussian bending modulus $\bar{\kappa}$ according to $K = \kappa/d$ and $\bar{K} = \bar{\kappa}/d$. An important issue in surfactant physics is the monitoring of the elastic smectic moduli. In a previous paper [12], some of us have calculated the nonadsorbing-polymer contribution to the layer compression modulus $\bar{B}$: they have shown that this contribution depends both on the smectic periodicity d and on the polymer concentration in the solvent $\bar{\Phi}$, reflecting the four different regimes of polymer confinement within infinite slits. In all cases this contribution is negative, meaning that the polymer-mediated interaction tends to destabilize the smectic order. These predictions allowed a quantitative interpretation of several L_α/L_α critical polymer induced phase separations, which were observed in two different surfactant systems [12,13].

The shift in the bending moduli of a surfactant bilayer upon addition of adsorbing homopolymer to the external phase has been theoretically considered by several authors [15–18]. The effect of *nonadsorbing* polymer on the elastic moduli of a bilayer has been addressed by Brooks [17] using the same formalism as in [16]. A simple functional approach was adopted and provided the following results: depletion of the polymer, like adsorption, leads to a reduction in κ and an increase in $\bar{\kappa}$. In mixed polymer-surfactant systems, the reduction in κ would increase the flexibility of the bilayers, whereas the increase in $\bar{\kappa}$ would tend to favor the formation of more handles. Both mean field theory and scaling theory were used and predicted the following contributions $\Delta\kappa$ and $\Delta\bar{\kappa}$ on the elastic moduli of a bilayer due to nonadsorbing polymer [17]:

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$$\frac{\Delta\kappa}{k_BT} \simeq -0.55\,\frac{\phi_b\xi_E}{6a}, \quad \frac{\Delta\bar{\kappa}}{k_BT} \simeq +0.86\,\frac{\phi_b\xi_E}{6a} \quad \text{(mean field)},$$

$$\tag{1}$$

with ϕ_b the bulk polymer volume fraction, a the Kuhn length of the polymer, and ξ_E the Edwards correlation length of the bulk solution:

$$\frac{\Delta\kappa}{k_BT} \simeq -0.042, \quad \frac{\Delta\bar{\kappa}}{k_BT} \simeq +0.067 \quad \text{(scaling).} \tag{2}$$

The important result is that these contributions, whatever the theoretical approach (mean field or scaling theory) are *very small in comparison with thermal energies, and consequently should be experimentally difficult to measure.*

The aim of this paper is to check this theoretical prediction on the experimental system we have studied: the measurement of the bilayer mean bending modulus κ was performed using a recent NMR technique [19]; it resides in the measurement of quadrupolar splittings by deuterium solid state NMR of a deuterium-labeled molecule embedded in the membrane. The measurement of the Gaussian bending modulus $\bar{\kappa}$ is much more difficult. To our knowledge, the only way to get an *estimate* of $\bar{\kappa}$, is to study the texture of the lamellar phase, by observation with the polarizing microscope of defects in this phase, as proposed by Kléman *et al.* [20,21]. The observation of focal conic domains of positive Gaussian curvature, like spherulites, leads to an estimate of the ratio $\bar{\kappa}/\kappa$ [21].

The outline of the paper is as follows. In Sec. II we present the polymer-surfactant system we have studied and emphasize the experimental evidences that allow us to assert that the polymer does not show any specific affinity with the surfactant, is effectively located in between the bilayers, and does not penetrate through the bilayers, so that the confinement is effective and the adsorption regime is avoided. In Sec. III we present experimental data for the mean bending modulus of the membrane obtained from the measurement of quadrupolar splitting by deuterium solid state NMR [19]. The cosurfactant (hexanol) was replaced by perdeurated hexanol with the same cosurfactant-surfactant molecular ratio. We first measure κ along a dilution path for the lamellar system *without* polymer. Second, we study the variation of κ as a function of polymer concentration for the different lamellar spacings. In Sec. IV we report the effect of polymer addition on the nature and density of the topological defects of the L_α phase, observed by polarizing light microscopy, which allows an estimate of $\kappa/\bar{\kappa}$ [20,21]. Cryo-TEM confirm the change of the lamellar texture, induced by polymer incorporation.

II. EXPERIMENTAL SYSTEM

The experimental system was presented elsewhere [5,12]. We incorporated a large water-soluble polymer into a L_α phase made of charged bilayers. The L_α phases are obtained from the system CPCL (cetylpyridinium chloride)/hexanol/water, at room temperature, for which we have the most extensive set of structural data [14]. In all samples the alcohol to surfactant weight ratio is fixed: $m_{\text{hex}}/m_{\text{CPCL}} = 0.9$, and corresponds to an alcohol rich domain of the lamellar phase
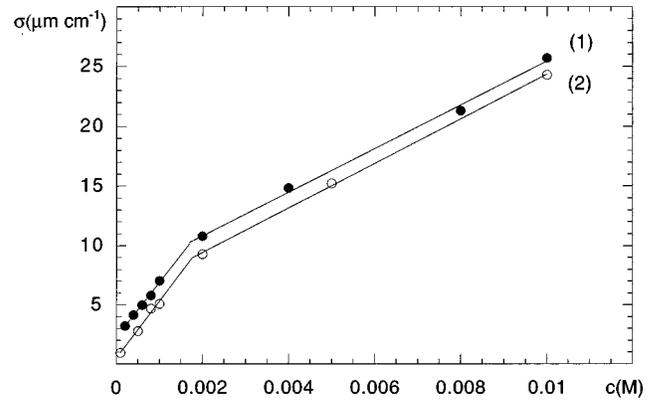

FIG. 1. Conductivity ($\mu\text{m cm}^{-1}$) vs molar concentration of hexanol/CPCL in water. The weight ratio $m_{\text{hex}}/m_{\text{CPCL}} = 0.2$ is fixed. (1): no PVP; (2): 2.5% PVP in weight. The slope's breaks correspond to the cmc.

with an oily streak texture [20]. Polyvinylpyrrolidone (PVP) was used as the polymer. This a commercial product received from Aldrich and used without further purification. Water is a good solvent for PVP [22]. The reported number average molecular weight is $M_N = 360\,000$ g/mole; we measured its weight average molecular weight by light scattering: $M_w = 750\,000 \pm 10\%$ g/mole, so the polydispersity index is about 2. The radius of gyration as determined by light scattering is about 60 nm in water and the overlapping weight concentration ϕ^* is found close to 0.15%. We have also investigated the texture of some lamellar samples, into which PVP with much smaller molecular weight $M_N = 10\,000$ g/mole was incorporated.

One crucial point was to check that PVP is a *nonadsorbing* polymer for the fluid membranes we consider. It is well known that nonionic polymers (such as PVP) do not interact (or very weakly) with *cationic* surfactants (such as CPCL) in micellar solution [23]. However, the bilayers of the present system are made from a mixture of CPCL and hexanol. So, to be sure that PVP does not show any specific interaction with either CPCL or hexanol, we have performed conductivity measurements to study the effect of PVP on the critical micellar concentration (CMC) of a solution of hexanol and CPCL in water with a fixed weight ratio $m_{\text{hex}}/m_{\text{CPCL}} = 0.2$ (located in the L_1 domain of the hexanol/CPCL/water phase diagram). In Fig. 1, the conductivity of a CPCL/hexanol solution with the above weight ratio is plotted along a dilution path in two different solvents: the first one is simply water, and the second one is a semidilute solution of PVP in water (with a weight concentration $\bar{\Phi} = 2.5\%$). There is a small difference between the two corresponding critical micellar concentrations: $c^* = 181 \pm 0.1 \times 10^{-3}$ mol l^{-1} without polymer, and $c^* = 193 \pm 0.1 \times 10^{-3}$ mol l^{-1} with polymer. Note that we have made the same measurements without hexanol and we have obtained a similar shift in the critical micellar concentration, i.e., $c^* = 123 \pm 0.1 \times 10^{-3}$ mol l^{-1} without polymer and $c^* = 1.34 \pm 0.1 \times 10^{-3}$ mol l^{-1} with polymer. These shifts of the cmc are very small and do not seem to be sensitive to the presence of hexanol: we believe that they are not significant.

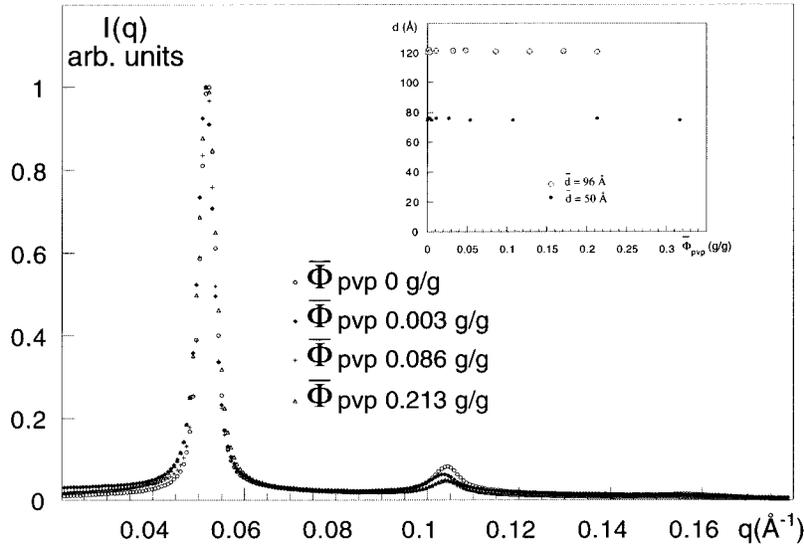We have also investigated two series of lamellar phases

FIG. 2. Intensity vs $q(\text{Å}^{-1})$ for a series of samples of constant membrane volume fraction $\psi=0.212$, but with several concentrations of polymer in pure water $\overline{\Phi}$. Inset: lamellar periodicity vs polymer volume fraction in pure water, for two series of lamellar phases with the same membrane volume fraction: open circles: $\psi=0.212$; solid circles: $\psi=0.323$. The lamellar periodicities remain unchanged whatever is the polymer concentration.

$(m_{\text{hex}}/m_{\text{CPCL}}=0.9)$ of constant volume fraction ψ ($\psi=0.328$ for the first series and $\psi=0.212$ for the second series) in an aqueous solution of PVP. The volume fraction of polymer *in the solvent* has been varied from 0 to 0.44. All samples remained monophasic, transparent, and birefringent. Figure 2 shows the x-ray scattering patterns for the second series ($\psi=0.212$), at several polymer concentrations. All samples exhibit the first and second order harmonics of the structure factor of a lamellar phase. The first Bragg peak position q_0 remains remarkably constant whatever the polymer concentration as inferred from the inset of Fig. 2 where the lamellar periodicity $d=2\pi/q_0$ is plotted as a function of polymer concentration in the solvent, for two different membrane concentrations. We interpret quantitatively q_0 in terms of the dry thickness of the bilayers δ: $q_0=2\pi\psi/\delta$. The first Bragg peak position q_0 is in agreement with the picture where the polymer is distributed into water only and leaves the bilayer dry thickness constant ($\delta=2.60\pm0.05$ nm [12]).

In conclusion, we have obtained several experimental evidences that PVP does not show any specific affinity with self-assemblies of CPCL/hexanol mixtures in water: the polymer is effectively located in between the bilayers of the lamellar phase, does not penetrate through the bilayers, and shows no specific affinity with the membrane so that the adsorption regime is avoided. Our experimental system therefore pictures a nonadsorbing polymer confined into infinite soft slits made of fluid membranes.

III. POLYMER CONTRIBUTION TO THE BILAYERS' MEAN BENDING MODULUS

A. Theoretical background

A recent technique has been reported for the measurement of the bilayer bending modulus κ in the lamellar phase of a lyotropic system [19]. It resides in the measurement of quadrupolar splitting of a deuterated molecule embedded in the membrane by deuterium solid state NMR. By separating the different motional contributions accounting for the reorientation of the C-D bonds with respect to the magnetic field, Auguste *et al.* [19] have calculated within a simple Gaussian theory the effect of thermal fluctuations of the film upon the recorded quadrupolar splitting $\Delta\nu_Q$:

$$\Delta\nu_Q=\alpha\left(\frac{3}{1+(k_BT/8\pi\kappa)\ln(1+\kappa(\pi/a)^4d/\overline{B})}-1\right),\quad(3)$$

where α is a constant that depends strongly on the internal properties of the film, i.e., bilayer thickness, the area per polar head, and microscopic cutoff a (which is a molecular size parallel to the film of a few angstroms), and d is the smectic period.

Thus, $\Delta\nu_Q$ is directly related to the bending modulus of the membrane κ but also to the intermembranous interactions via the smectic compression modulus $\overline{B}$. Note, however, that this $\overline{B}$ dependence of $\Delta\nu_Q$ appears only as a logarithmic correction of the κ dependence.

B. Experiment

We have made two series of lamellar samples. The first one corresponds to a dilution line of the ternary system hexanol/CPCL/water; i.e., we have measured the quadrupolar splitting as a function of the layer spacing d, in order to obtain the value of the bending modulus κ of the membrane without polymer. In the second series of samples the membrane volume fraction was kept constant (corresponding to a lamellar periodicity $d=8.6$ nm) but the polymer concentration in the solvent $\overline{\Phi}$ varied from 0 to 20%. We have measured the quadrupolar splitting as a function of $\overline{\Phi}$.

All samples were prepared with 50 mg of perdeuterated hexanol mixed with the appropriate quantity of protonated hexanol and other components: in all cases, the *molecular*
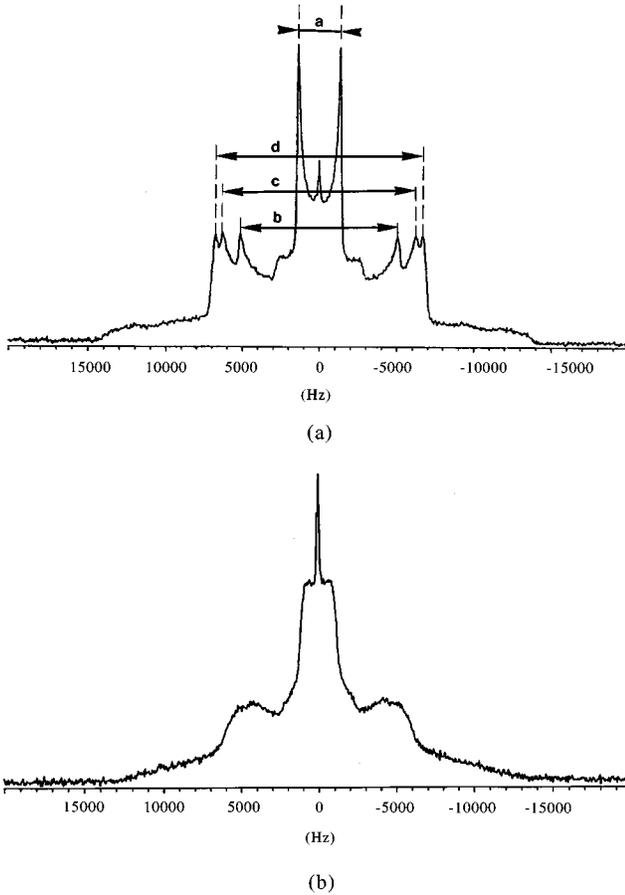
(a)

(b)

FIG. 3. NMR spectra of perdeuterated hexanol in the water-hexanol/CPCL lamellar system for two dilutions (a) $\overline{d}=2.5$ nm, (b): $\overline{d}=9.5$ nm. For the more concentrated sample [Fig. 3(a)], one can distinguish four different quadrupolar splittings corresponding to the four nonequivalent C-D bounds in the hexanol molecule.

ratio hexanol/CPCL is constant and corresponds to the *weight* ratio $m_{\text{hex}}/m_{\text{CPCL}}=0.9$ of the nondeuterated lamellar phases. Each sample (total weight of about 1 g of lamellar phase) is sealed in order to prevent solvent or alcohol evaporation and centrifuged. Measurements were performed after three weeks at rest for the samples at a temperature of 333 K. Experiments were carried out on a Bruker MSL 200 spectrometer, operating at 30.7 MHz for deuterium. The temperature was regulated to 298 ± 1 K. NMR signals were recorded with either a quadrupole echo technique [24] ($\pi/2$ pulse width of 6 μs, pulse spacing 25 μs) or a composite quadrupolar echo pulse sequence [25]. The experimental resolution is about ±50 Hz. Data treatment was accomplished on a VAX/VMS 4000 computer (DEC, USA).

C. Results

1. Dilution line of the lamellar phase without polymer

Figure 3 shows the experimental NMR spectra of perdeuterated hexanol in the water-hexanol-CPCL lamellar system, for the two extreme dilutions ($\overline{d}=1.5$ and 9.5 nm). For the more concentrated sample [Fig. 3(a)] one can distinguish up to four different quadrupolar splittings. The most intense $\Delta\nu_{Qa}$ is that of the terminal CD$_3$ bound in hexanol, which
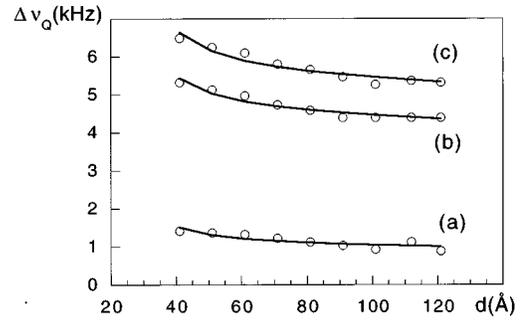

FIG. 4. Plot of the three different quadrupolar splittings $\Delta\nu_{Qa}$, $\Delta\nu_{Qb}$, $\Delta\nu_{Qc}$ of the lamellar system hexanol/CPCL/water as a function of the smectic period $d(\text{Å})$. The open circles correspond to the experimental points. The plain lines are the best fits obtained from Eqs. (3) and (4). The corresponding mean bending modulus of the bilayer is $\kappa=1.7\pm0.5k_BT$.

has the maximum freedom. The three other splittings $\Delta\nu_{Qb-d}$ can be associated to the CD$_2$ groups of the hexanol molecule. The central isotropic peak is related to the natural abundance of deuterium in the aqueous solvent. It should be noticed that the traces of these spectra are typical of randomly oriented samples (powder spectrum) [26]. In Fig. 4, measurements of the $\Delta\nu_{Qa}$, $\Delta\nu_{Qb}$, and $\Delta\nu_{Qc}$ quadrupolar splittings are plotted versus the repeat distance d of the stack of lamellae (which was independently measured by x-ray diffraction).

For these samples, the smectic order is stabilized by long-range electrostatic interaction in pure water, and the corresponding smectic compression modulus is [27]

$$\overline{B}_{\text{elec}}=\frac{\pi k_BT}{2l_B}\frac{d}{(d-\delta)^3},\qquad(4)$$

where $l_B=e^2/(4\pi\epsilon k_BT)\approx0.72$ nm is the Bjeerum length at room temperature and $\delta=2.6$ nm is the bilayer thickness.

Putting the expression of $\overline{B}$ given by Eq. (4) in Eq. (3), we have fitted the experimental results of Fig. 3. One finds $\kappa=1.7\pm0.5k_BT$. This indicates that the naked membrane is very flexible. This result is in good agreement with previous ones on the same system, obtained with a different experimental technique [28].

2. Addition of polymer

For the second series of samples, the variation of the quadrupolar splittings $\Delta\nu_{Qa-c}$ versus the polymer weight concentration in water ($0<\overline{\Phi}<0.2$) for a lamellar phase of smectic periodicity $d=8.6$ nm is plotted in Fig. 4. The quadrupolar splitting remains remarkably constant whatever is the polymer concentration. In these samples, the layer compression modulus $\overline{B}$ is the sum of two terms [12]: the first one is the electrostatic contribution, given by Eq. (3); it is constant for all samples of this series, since the smectic periodicity is fixed. The second term is the polymer contribution to $\overline{B}$, which varies as $\overline{\Phi}$ and is always negative [12]. For all polymer concentrations we have investigated (except for the less concentrated one $\overline{\Phi}=0.1\%$) the polymer is in the three-dimensional semidilute regime of confinement and its contribution to $\overline{B}$ reads [12]
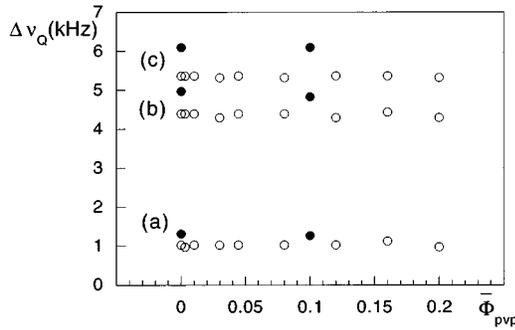
FIG. 5. Plot of the quadrupolar splitting $\Delta \nu_{Qa-c}$ of the lamellar phase of the system hexanol/CPCL/water/PVP as a function of the polymer weight fraction in water $\bar{\Phi}$. Open circles: smectic periodicity $d=112$ Å; solid circles: $d=61$ Å.

$$\bar{B}_{pol} \simeq -1.57 k_B T \frac{d}{b(d-\delta)^3} \bar{\Phi}^{3/4}, \tag{5}$$

where $b \approx 0.3$ nm is the monomer length of the polymer. Note that this contribution is always smaller than the electrostatic contribution. The effective layer compression modulus is then $\bar{B} = \bar{B}_{elec} + \bar{B}_{pol}$. Using the set of experimental values, it is easy to check that the variation of the logarithmic term in Eq. (3) as a function of polymer concentration is negligible in the entire range of polymer concentration we have studied. This means that the expected variations of $\Delta \nu_Q$ with respect to the polymer concentration due to $\bar{B}$ are less than the experimental resolution (50 Hz) and consequently cannot be observed. As a result, the hypothetical variations of $\Delta \nu_Q$ as a function of polymer concentration, would only result from the polymer contribution to the bending modulus of the bilayers.

However, no variation of the quadrupolar splitting versus the polymer concentration is observed (see Fig. 5): it shows evidence that, the contribution of a nonadsorbing polymer to the mean bending modulus of a bilayer is completely negligible (much less than the thermal energy), in agreement with Brooks predictions [17] [see Eqs. (1) and (2)].

IV. POLYMER CONTRIBUTION TO THE GAUSSIAN BENDING MODULUS

A. Theoretical background

The Gaussian bilayer bending modulus $\bar{\kappa}$ is responsible for the changes of layer topology. When $\bar{\kappa}$ is sufficiently negative, the bilayers form many disconnected aggregates such as vesicles; conversely when $\bar{\kappa}$ is positive, the layers form a bicontinuous phase like the sponge phase. It has been found, in several surfactant-cosurfactant-brine systems, that the L_α phase can be divided into two distinguishable regions, where the bilayers have different textures. In these mixtures the change in bilayer organization is governed by the alcohol-surfactant ratio. Observations by optical polarizing microscopy have revealed two types of focal conic domains: at low alcohol to surfactant ratio i.e., in the vicinity of the L_1 phase, Maltese crosses [focal conic domains of second species (FCD-II)] corresponding to large multilamellar vesicles with a positive Gaussian curvature referred to as spherulites

are found; these spherulites are dispersed in a lamellar matrix. At high alcohol to surfactant ratio, i.e., in the vicinity of the L_3 phase, only few defects, referred to as oily streaks [focal conic domains of first species (FCD-I)] are observed often dispersed in a so-called marbled texture. FCD-I and FCD-II differ by the nature of their singularities, and consequently by the sign of their Gaussian curvature G. $G<0$ for FCD-I and $G>0$ for FCD-II. Their different stabilities are related to $\bar{\kappa}$ differing in magnitude and also in sign. $\bar{\kappa}>0$ for FCD-I, whereas $\bar{\kappa}<0$ for FCD-II, so that the Gaussian bending energy $\bar{\kappa}G$ is negative. For a spherulite of radius R, the bending energy reads

$$W_b = \int_0^R \left(\frac{1}{2} \frac{4K}{r^2} + \frac{\bar{K}}{r^2} \right) 4\pi r^2 dr = 4\pi(2\kappa + \bar{\kappa}) \frac{R}{d}. \tag{6}$$

From Eq. (6), it is clear that spherulites are energetically favored with respect to a flat texture as soon as $\bar{\kappa}<-2\kappa$. Boltenhagen et al. [29] have given a simple model for the formation of a thermodynamically stable set of spherulites; in particular, they have shown that the bending energy W_b is the single relevant term in the case where the density of spherulites is high, i.e., when $R \leq l \leq R^2/\lambda$, where l is the mean distance between spherulites and $\lambda = \sqrt{K/\bar{B}}$.

B. Experiment

We have investigated the L_α phase of the mixed system CPCL/hexanol/water/PVP. The membrane volume fraction was kept constant (21%) for all the samples corresponding to a smectic periodicity of about 12.6 nm. In all samples the alcohol to surfactant weight ratio is fixed: $m_{hex}/m_{CPCL} = 0.9$. This value corresponds to alcohol-rich side of the lamellar phase. The volume fraction of polymer in the solvent has been varied from 0 to 0.20. PVP with two different number average molecular weight, $M_N = 360\,000$ g/mole and $M_N = 10\,000$ g/mole, was used. The samples were introduced by capillarity in flat cells (20 mm$\times$20 mm). The glass slides were separated by Mylar bands resulting to a controlled thickness of 75 μm. The cells were immediately sealed with an UV polymerizable resin. The samples were kept two weeks at rest at room temperature (≈ 20 °C). Observations were conducted by polarizing microscopy, at room temperature. Two different lamellar samples were also checked by cryotransmission electron microscopy: one is polymer free, with a membrane volume fraction of 0.212, and the other one has the same membrane volume fraction, but the solvent consists now of an aqueous solution of PVP (polymer volume fraction in the solvent $\bar{\Phi}=1\%$, molecular weight: 360 000). The samples were prepared in two different ways, which gave exactly the same results on all the different preparations: either it was blotted face-on (which is known to be more direct and cause less gradient than the side blotting usually used for negative staining samples), or the specimen was deposited as a very thin layer and vitrified as fast as possible after deposition. We cannot assure that there is no gradient at all, but as the two methods gave the same results, we are quite confident that it has been limited as much as possible. The grids were mounted on a gatan cold stage (-184 °C) and observed on a Philips CM12Q operat-
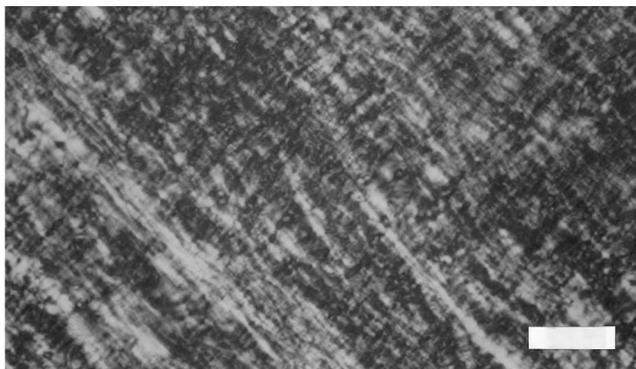
FIG. 6. Polarization micrograph of the lamellar phase in the ternary system hexanol/CPCL/water ($m_{hex}/m_{CPCL}=0.9$). Membrane volume fraction $\psi=21\%$. The micrograph was taken between crossed polarizers at room temperature. Bar: 100 μm. Note the typical marbled texture for this sample *without polymer*.

ing at 120 kV. The electron micrographs were recorded at low magnification in order to see the macroscopic organization of the samples.

C. Results

In Fig. 6, a typical marbled birefringent texture is observed for the sample *without* polymer. Note that no FCD-II is observed. The corresponding TEM micrograph is shown in Fig. 7: it is also a typical image of a lamellar phase. The gradual change of grey indicates the staking of bilayers in the lamellar phase: the darker the grey color is, the larger the number of stacked bilayers; the small white circles are holes in the membrane. As soon as some polymer is added, the texture of the samples is strongly modified, even at very low polymer concentration (Figs. 8 and 9). In all cases, one observes a dense and polydisperse distribution of circular mal-
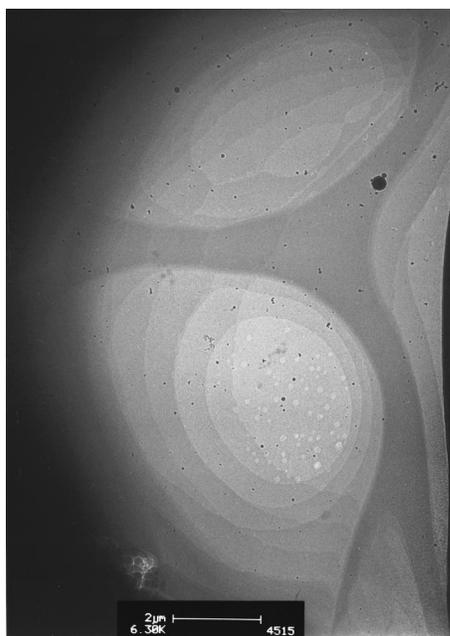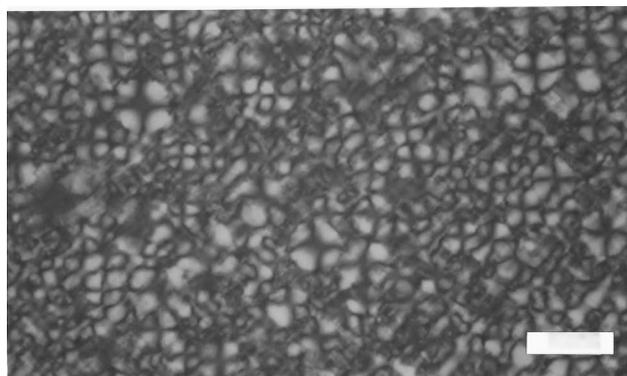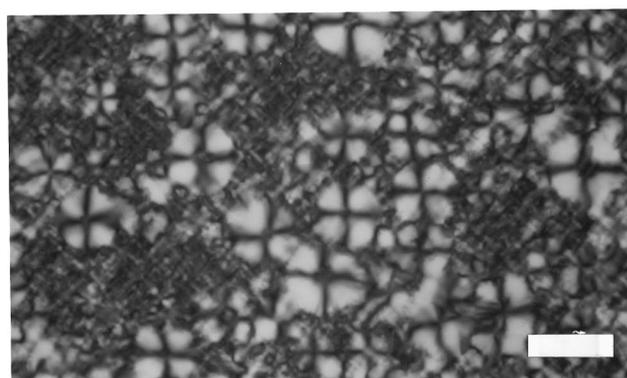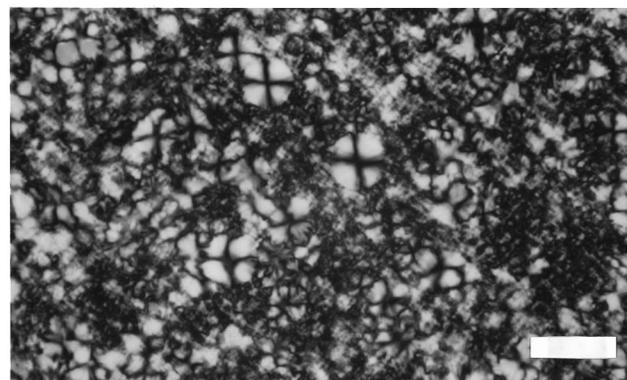

FIG. 7. TEM micrograph of the lamellar phase of the ternary system hexanol/CPCL/water. Membrane volume fraction ψ $=0.212$.

(a)

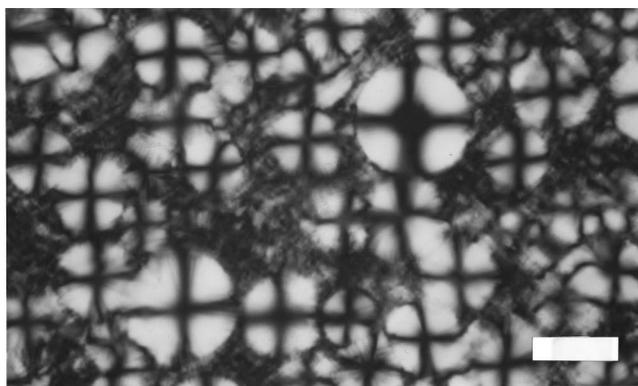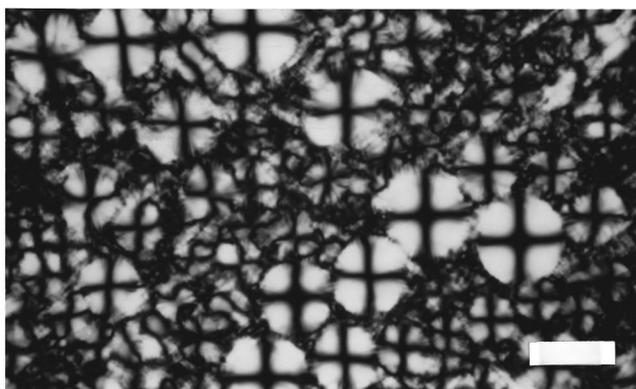**(b)**

(c)

FIG. 8. Polarization micrograph of the lamellar phase in the quaternary system hexanol/CPCL/water/PVP ($m_{hex}/m_{CPCL}=0.9$). Membrane volume fraction $\psi=21\%$. Number average molecular weight of the polymer: $M_N=360\,000$. $\bar{\Phi}$: weight fraction of polymer in water: (a) $\bar{\Phi}=0.1\%$; (b) $\bar{\Phi}=1\%$; (c) $\bar{\Phi}=8\%$. The micrograph were taken between crossed polarizers at room temperature. bar: 100 μm.

tese crosses located at different levels of the sample thickness, surrounded by a birefringent matrix. The corresponding TEM micrograph is shown in Fig. 10: the change of grey reveals the stacked bilayer structure as in the absence of polymer; however, the white closed lines delineate polydisperse ovoid objects embedded in the lamellar matrix. The egg-shaped spherulites could correspond to spherical objects having been stretched during the deposition; the lapse of

(a)

(b)
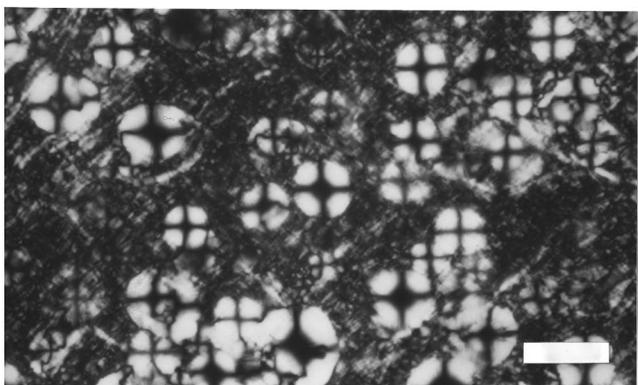
(c)

FIG. 9. Polarization micrograph of the lamellar phase in the quaternary system hexanol/CPCL/water/PVP ($m_{\mathrm{hex}}/m_{\mathrm{CPCL}}=0.9$). Membrane volume fraction $\psi=21\%$. Number average molecular weight of the polymer: $M_N=10\,000$. $\bar{\Phi}$: weight fraction of polymer in water: (a) $\bar{\Phi}=1\%$; (b) $\bar{\Phi}=8\%$; (c) $\bar{\Phi}=20\%$. The micrographs were taken between crossed polarizers at room temperature. Bar: 100 μm.

time between deposition and freezing is too short to allow the relaxation of the deformation constraint. The main optical observations are as follows:

(i) Addition of polymer in the solvent leads to the formation of a dense polydisperse distribution of large spherulites whatever the polymer concentration ($0.1\%<\Phi<20\%$) and polymer molecular weight ($10\,000$ or $360\,000$). Note, how-
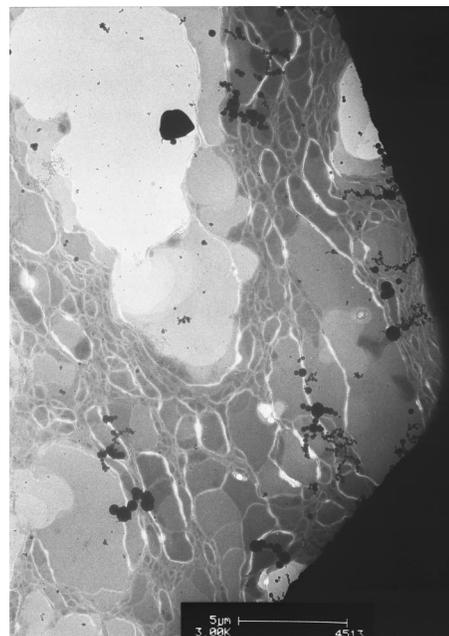

FIG. 10. TEM micrograph of the lamellar phase of the mixed system CPCL/hexanol/PVP/water. Volume fraction of membrane $\psi=0.212$. Volume fraction of polymer in the solvent: $\bar{\Phi}=0.01$.

ever, that the volume fraction of spherulites seems to decrease at very high polymer concentration. Note also that TEM reveals the existence of very small spherulites.

(ii) The mean radius R of the FCD-II (corresponding to the radius of the spherulites) seems to depend on the polymer molecular weight, at low polymer concentration. This is particularly evident for the lower polymer molecular weight (Fig. 9) below the overlap concentration. $R\sim 50$ μm for $10M$ PVP and $R\sim 20$ μm for $360M$ PVP.

Recall that all lamellar samples we have studied are made at fixed membrane composition, i.e., $m_{\mathrm{hex}}/m_{\mathrm{CPCL}}=0.9$. For the sample without polymer, this composition corresponds to a domain of the lamellar phase very close to the sponge phase in the case where water is replaced by brine as solvent. As shown in Refs. [28, 20] the increase of $m_{\mathrm{hex}}/m_{\mathrm{CPCL}}$ leads to the increase of $\bar{\kappa}$ from negative values up to positive ones. Boltenhagen *et al.* [20] have given an experimental estimation of the ratio $\bar{\kappa}/\kappa$ for a lamellar phase made from a mixture of hexanol, CPCL, and brine (1% by weight of NaCl) as solvent and close to the $L_\alpha-L_3$ phase boundary. They found $+6\lesssim\bar{\kappa}/\kappa\lesssim+10$, depending on the cosurfactant to surfactant weight ratio. Assuming this value for the ratio $\bar{\kappa}/\kappa$ in the salt free system and using the value of κ measured in the preceding section ($\kappa=1.7k_BT$) one obtains a rough estimation of the Gaussian bending modulus of our membrane without polymer: $\bar{\kappa}\sim+14\pm3k_BT$. Note the positive sign, which implies that FCD-II (with positive Gaussian curvature) are not expected and indeed are not observed (see Fig. 6). The effect on the phase behavior upon addition of water soluble nonadsorbing polymer to the external solvent of the lamellar phase is to fill this phase with FCD-II. From Eq. (6) and Ref. [29], we can conclude that $\bar{\kappa}\lesssim-2\kappa$. On the other hand we have demonstrated in the previous section that κ is not changed upon addition of polymer. It can be inferred that in our system the shift in the Gaussian bending modulus of a

surfactant bilayer upon addition of *nonadsorbing polymer is strongly negative*. We estimate this shift to be at least $\Delta \bar{\kappa} \sim -15 k_B T$. This experimental result *disagrees qualitatively and quantitatively* with the theoretical work of Brooks [17]. The shift we observe seems to be negative rather than positive as predicted, and its value (several $k_B T$ units) is about two orders of magnitude larger than predicted [see Eqs. (1) and (2)]. This surprising result raises the question of whether some experimental artifact is not responsible for this discrepancy. We have anticipated the following possibilities:

(i) The spherulites might be not stable: However, the FCD-II we observe are spherical ones and should correspond to thermodynamically stable domains [21]. Moreover, we never succeeded in obtaining oriented samples for the polymer-containing lamellar phases contrarily to the lamellar phases without polymer. We believe then that the spherulite texture is thermodynamically stable.

(ii) It is well known that the Gaussian bending modulus of a bilayer is very sensitive to the alcohol-surfactant ratio of the membrane [28,21]. One can imagine that PVP interact with hexanol, leading to a decrease of alcohol in the membrane and therefore to the formation of spherulites. However, all experimental results reported in Sec. I show that PVP has no specific interaction with hexanol. Furthermore, in Fig. 8 it appears clearly that the density of FCD-II decreases at high polymer concentration ($\Phi > 12\%$). This result is inconsistent with a hypothetical interaction between the alcohol and the polymer. In this case, one should observe an increase of the spherulite density by increasing the polymer concentration in the surrounding solvent, and even finally the disappearance of the bilayer topology, which should be replaced by a micellar structure. This is not the case: the smectic order is preserved at all polymer concentration, provided that no salt is added.

This polymer effect on the Gaussian bending modulus of the bilayer seems to be quite general. It has been also observed [30] for the same polymer but with another membrane (Triton$\times$100/Triton$\times$35/decane) [13].

V. CONCLUSION

The aim of this paper was to provide experimental results for the effects of the mean and Gaussian bending moduli of a surfactant bilayer due to nonadsorbing homopolymer. Recent theoretical works predict that the polymer contribution to the mean bending modulus is always negative and the polymer contribution to the Gaussian bending modulus is always positive, whatever is the polymer-surfactant interaction (depletion or adsorption). For the case of nonadsorbing polymer, the polymeric shifts in the elastic moduli are expected to be very small (much smaller than $k_B T$) in comparison to the bare surfactant bending moduli, and therefore nonmeasurable. Our results indicate that the polymer contribution to the mean bending modulus is very weak, in agreement with theoretical predictions. The experimental results concerning the polymeric shift to the Gaussian bending modulus are much more surprising. We have reported clear experimental evidence that the polymer shift in the Gaussian bending modulus of the surfactant membrane is strongly negative. This experimental fact disagrees qualitatively and quantitatively with theoretical predictions.

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