Structure and Elastic Properties of 10–12 Pentacosadiyonic Acid Langmuir Films

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Received December 26, 2000. In Final Form: June 27, 2001

Monolayers of the polymerizable 10–12 pentacosadiyonic acid amphiphile spread on a basic buffer are studied both before and after polymerization. We have established the phase diagram of the unpolymerized Langmuir film by isotherm measurements, Brewster angle microscopy, and grazing incidence X-ray diffraction experiments. Diffuse scattering experiments performed at the European Synchrotron Radiation Facility allowed us to investigate the structure and elastic properties of the different monomer phases and the modifications induced by polymerization.

I. Introduction

Amphiphilic molecules form Langmuir monolayers at air/water interfaces and such films have attracted much attention not only from a fundamental point of view but also with regard to their potential applications after they have been transferred to a solid substrate. These Langmuir–Blodgett films have been employed in fields as different as molecular electronics,7 integrated optics,8 and biology.9 For such applications, good mechanical and thermal stabilities of the systems are required. Those properties can be improved by cross-linking the molecules of the monolayer. The use of diacetylene groups in this context was demonstrated first by Wegner.5 In our study, we worked with 10–12 pentacosadiyonic acid (PCA), which can form either red- or blue-colored linear polymers under UV radiation due to the diacetylene rod that separates the C₁₀ and C₁₂ segments of the hydrophobic tail. Films formed by PCA at the air/water interface have already been studied.⁵–⁷ It has been shown that in order to be polymerized, the diacylenic films have to be at an appropriate density⁵,¹⁰,¹¹ and the change of color has been related to the molecular density of the film after the polymerization has taken place. A number of UV–visible spectroscopic studies have been performed with the aim of optimizing the irradiation time in order to maximize the extent of polymerization without damaging the film or of explaining the change of color.⁵,⁹,¹¹,¹² From a structural point of view, comparisons between the molecular organization before and after polymerization have been obtained by X-ray reflectivity,¹³ electron diffraction,¹³,¹⁴ and optical microscopy.¹⁴ By controlling the pH of the subphase and the surface pressure, Goettgens et al.¹⁵ tried to optimize the stability and the homogeneity of the PCA monolayers.

Despite all these studies, the 2D phase diagram of PCA is still not well-known. We have therefore undertaken an investigation of the relation between the 2D molecular structure of a PCA monolayer and its elastic behavior before and after polymerization. The article is organized as follows: after the Experimental Section (II) and important details on the film preparation in section III, isotherm studies of PCA spread on a basic buffer are presented in section IV. The effects of the polymerization on the structure and on the elastic properties of PCA films are discussed in sections V and VI. Major conclusions are summarized in section VII.

II. Experimental Section

A. Imaging of the Film: Brewster Angle Microscopy. At the Brewster angle, the reflection coefficient for parallel polarization of light is extremely sensitive to the presence of a film

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Figure 1. Geometry of (a) reflectivity experiments and (b) diffuse scattering experiments.

The reflectivity experiment (Figure 1a) consists of measuring the reflection coefficient of an interface as a function of the out-of-plane wave-vector transfer \( q_z \). The detected beam is equal to zero, i.e., with \( \theta_i = \theta_d \). An increase of the incident angle \( \theta_i \) results in a deeper incident wave penetration and therefore an increase in scattering from the subphase. The detected signal also integrates a diffusely scattered component due to finite-size resolution effects. Since the separation into a specular and a nonspecular part is, in general, not possible, the latter contribution must also carefully be taken into account in order to obtain a correct analysis of the measured reflectivity curves.

The off-specular (or diffuse) surface scattering experiment performed here and illustrated in Figure 1b consists of the measurement of the intensity scattered in the plane of incidence as a function of the wave-vector transfer. In contrast to the reflectivity experiment, the angle of incidence \( \theta_i \) is kept fixed at a value \( \theta_i < \theta_c \), the critical angle for total external reflection. In such an experiment, the normal \( q_n \) dependence of the scattered intensity is coupled with the \((q_x, q_y)\) (in-plane modulus of the fluctuation mode) dependence and can be described by the convolution model:

\[
I(q) \propto \int dx \, dy \left( e^{i q_n (y-y_0)} - 1 \right) e^{i (q_x x + q_y y)} R(x,y)
\]  

where \( R(x,y) \) is the Fourier transform into real space of the angular resolution function. Consequently, the analysis of the nonspecularly diffuse beam should allow not only the determination of the normal structures (it will be interesting to compare the accuracy obtained with both techniques) but also the investigation of the statistical mechanics of out-of-plane fluctuations of amphiphilic interfaces.

Both the interface roughness, characterized in particular by the rms roughness \( z \), and the height–height correlation function \( c(r) \) can be obtained from the diffuse scattering. The fluctuation spectrum for a fluid interface including the effects of gravity, surface tension \( \gamma \), and bending rigidity \( K \) can be obtained by Fourier transforming the free energy27,28 and applying the equipartition theorem. It is expected to be given by

\[
\langle z(-q)z(q) \rangle = \frac{k_B T}{\Delta \rho \gamma + \gamma(q)q^2 + K(q)q^4}
\]

where the three terms in the denominator respectively describe the limitation of out-of-plane fluctuations by gravity at large scales, by capillarity, and by the bending rigidity modulus at short length scales. Although the validity of eq 3 is still to be demonstrated29 from an experimental point of view, it has been used in this work to assess the importance of bending effects.


at the D24 beamline at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE), and the geometry is shown in Figure 2. The incident angle \( \theta_i \) was also fixed at 85% of the critical angle for total external reflection, and the horizontal wave vector transfer \( q_h = (4\pi/\lambda) \sin \psi \) was sampled by changing the horizontal scattering angle \( \psi \).

III. Film Preparation and Isotherm Measurements

The isotherm measurements were performed either in a large homemade Langmuir trough (700 cm²) adapted to grazing angle X-ray experiments or in a smaller Riegler & Kirstein trough (140 cm²) that could easily be inserted in a Brewster angle X-ray experiments or in a smaller Riegler & Kirstein trough.

Figure 2. Geometry of diffraction experiments: (a) front view; (b) side view.

Fourier transformation of the fluctuation spectrum given by eq 3 yields the correlation function to be inserted in eq 2:

\[
\langle z(0)z(x,y) \rangle = \frac{k_B T}{2\pi^2} [K_0(r\sqrt{\Delta p\rho r}) - K_0(r\sqrt{\rho/K})] \tag{4}
\]

where \( r^2 = x^2 + y^2 \) and \( K_0 \) is the modified Bessel function of second type of order zero. The X-ray reflectivity experiments were performed with the laboratory reflectometer described in ref. 29. But, because of the relative complexity of the molecules studied and the limitations of the reflectivity technique, these experiments have only allowed a rough characterization of the vertical structure of the films. The X-ray diffuse scattering experiments were performed at the CRG-IF (BM32) beamline of the European Synchrotron Radiation Facility (ESRF). The desired radiation (\( \lambda = 0.0688 \text{ nm} \)) was selected by use of the (111) reflections of two silicon monochromator crystals and the angle of incidence on the liquid surface was fixed after reflection by a flat mirror at \( \theta_i = 0.85\theta_c \). We took great care to limit the background, as described in ref. 26. The beam footprint on the trough was controlled by a primary slit of typical size 0.13 x 1 mm², and the resolution was controlled by a pair of slits of typical size 2 x 2 mm² and 0.25 x 4 mm² positioned, respectively, after the sample (210 mm from the center of the trough) and in front of the detector (720 mm from the center of the trough). We checked on a bare surface of pure water that resolution effects were correctly described by eq. 2.

The in-plane structure of the PCA monolayers was determined by grazing angle X-ray diffraction experiments (GXRD) performed at the D24 beamline at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE), and the geometry is shown in Figure 2. The incident angle \( \theta_i \) was also fixed at 85% of the critical angle for total external reflection, and the horizontal wave vector transfer \( q_h = (4\pi/\lambda) \sin \psi \) was sampled by changing the horizontal scattering angle \( \psi \).

organic solvents. It was therefore evident that the PCA, purchased from Lancaster, was always partially polymerized and could not be used as received. To remove the polymer, solutions of PCA were filtered several times before preparation of the spreading solutions. Because of the high reactivity of PCA, the solutions were then stored in the dark at 5 °C.

The quality of the films depends significantly on the spreading solvent and the concentration of the spreading solutions. At concentrations higher than 1 mg/mL, nuclei of the bulk phase can be formed during film deposition. On the other hand, the amphiphile can dissolve partially into the subphase at very low concentrations. An ideal spreading solvent must fulfill the following requirements: it has to dissolve the amphiphile, spread it homogeneously over the whole surface, be insoluble in the subphase, be volatile, and be chemically inert. To test solvents with regard to these criteria, isotherm measurements were performed at fixed compression velocity and temperature (4.8 x 10⁻³ nm² molecule⁻¹ s⁻¹, 19 °C) for various spreading solvents: 1,1,2-trichloroethane, chloroform, toluene, and a 1:9 ethanol-hexane mixture. (A solution with pure 1,1,1-trichloroethane, without stabilizing agents, was also tested but did not spread on water.) The results are shown in Figure 3.

Small shifts (±0.02 nm/molecule) of the molecular area at which the increase in surface pressure occurs can be noticed. They can be attributed either to small concentration errors (defined as ±0.01 mg/mL in the volume spread or to real physical differences (see below). More interesting is the change in the surface pressure of the low-molecular-area "plateau" of the isotherms, i.e., the collapse pressure at which the film undergoes a transition from a monolayer to a multilayer or a bulk phase. As can be seen in Figure 3, the pressure at which collapse occurs depends on the solvent. For solutions in 1,1,2-trichloroethane and toluene, the collapse pressure of the film is significantly lower than that observed with chloroform or the ethanol-hexane mixture. This may be the result of the poor spreading properties of these two solvents on water. We therefore preferred to use chloroform or a mixture of ethanol and hexane, which spread well. Nevertheless, with chloroform there is a possibility that highly reactive radicals could be formed with a risk of breaking the diacetylene rods and introducing defects into the monolayer. The ethanol-hexane mixture is less reactive, but ethanol is soluble in water, and if care is not taken, a partial solubilization of the amphiphile may occur. The loss of material depends on the solvent used, and the overall collapse pressure is lower when ethanol is used.
the chain length of the amphiphile and on the volumes of the deposited droplets. By using the smallest (10%) fraction of ethanol that allowed a total solubilization of the PCA into the ethanol–hexane mixture, we optimized the spreading technique by carefully creating tiny droplets (1 μL) and letting them gently touch the subphase. When this procedure was followed, no loss was observed in the isotherms (compare Figure 3 panels a and c). Note that with this procedure there is a bump in the isotherm at high pressure, which is indicative of a nucleation barrier. It is much less pronounced with the other solvents, indicating that nuclei are either already present or much easier to nucleate with trichloroethane, toluene, or chloroform. All further experiments presented in this work have then been performed with the 1:9 ethanol–hexane spreading solvent.

Another important parameter is the nature of the subphase. For PCA, we have observed that on pure water the monolayer is unstable and collapses. It has been observed\(^{(15)}\) that the monolayer can be stabilized with respect to collapse to bilayers or multilayers by spreading on a basic subphase. The PCA headgroups ionize at high pH, and a repulsive force appears between them consistent with the fact that sheets in the multilayer stack would repel each other. This phenomenon is illustrated in the isotherms shown in Figure 4, which are consistent with those reported by Goettgens et al.\(^{(15)}\) Although the collapse pressure increases with increasing pH, it also becomes more difficult to reach the smaller molecular areas necessary for polymerization. For this reason, we chose to carry out our experiments on a subphase maintained at pH 7.5 by a sodium tetraborate buffer.

**IV. Isotherm Studies**

Isotherms of PCA spread on a sodium tetraborate buffer at pH 7.5 at temperatures ranging between 17 and 30 °C are shown in Figure 5. The form of the isotherms is reminiscent of that of simple fatty acids or phospholipids on pure water.\(^{(34,35)}\) The transition plateau reveals the presence of at least two distinct phases. An evaluation of the compressibilities of these phases can be obtained by the relation

\[
\chi_T = \frac{1}{A} \frac{\partial A}{\partial \Pi} \tag{5}
\]

One has to note that if the monolayer is inhomogeneous (we will see from the BAM studies that this is indeed the case), eq 5 will only give a rough approximation of the real compressibility.\(^{(36)}\) Starting from \(\Pi = 0\) mN/m at large molecular areas, there is a slow increase of the surface pressure that is the signature of a very compressible phase (40 mN/m), with molecular area \(A \approx 0.7\) nm\(^2\); we will call this the expanded phase. There is then a plateau characteristic of a first-order transition from the expanded phase to a denser phase (condensed phase). After the transition is completed, the compression of the condensed phase gives rise to a steep increase in pressure. The compressibility of this phase (2.4 mN/m) is about 16 times smaller than that of the expanded phase. The monolayer undergoes collapse at 33 ± 1 mN/m (0.215 ± 0.015 nm\(^2\)).

The PCA film was exposed to UV radiation both in the expanded phase and in the condensed phase, with the help of a commercial Hg vapor lamp (\(\lambda = 254\) nm), under argon atmosphere to protect the film from ozone oxidation. The UV irradiation was stopped after a few minutes to avoid any alteration of the polymerized layer, easily revealed by an increase in surface pressure. Powdered sulfur was deposited on the film to visualize its flow under a gentle stream of air. After the irradiation, no motion of the condensed phase could be observed; the film appears to be rigid. In addition, the appearance of a pale pink color of the layer after irradiation is typical of the polymerized PCA.\(^{(6,9,11)}\) In contrast, there was no evidence of any long-range polymerization after irradiation of the expanded phase. The layer remained as fluid as before exposure, and no pink color could be observed. This suggests that the polymerization of PCA films is a selective process with respect to the structure of the monolayer, in agreement with the often quoted topochemical nature of the polymerization reaction.\(^{(15,17,29)}\) If the surface pressure of the condensed phase is kept constant during irradiation, the molecular area of the film is reduced by about 10%. Similarly, if the average molecular area is kept fixed during the polymerization, there is a decrease in surface pressure. Both observations suggest a rearrangement of the molecules within the film. The often proposed (but rarely checked) explanation is the contraction of the two-dimensional molecular network\(^{(7,14)}\) during polymerization. We note finally that the polymerized film can be com-

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pressed to a much higher pressure than the unpolymerized film (>40 mN/m) without collapsing.

V. Structural Study

A. Expanded Phase. The expanded phase could not be detected with our Brewster angle microscope. In addition, at 22 °C and for a molecular area equal to 0.5 nm², no molecular structure could be observed by GIXD experiments. Both results confirm that, as expected from the isotherm measurements and UV irradiation, the expanded phase is not organized. To characterize the vertical structure of the molecules in the expanded phase, X-ray reflectivity experiments were carried out with the laboratory reflectometer (Figure 6a), and X-ray grazing incidence diffuse scattering experiments (Figure 6b) were performed at the ESRF.

We first discuss the shape of these curves. In the normalized reflectivity data curve (Figure 6a), beyond $q_z \cdot 10^9 \text{m}^{-1}$, the signal coming from the monolayer, about $10^7$ times less intense than the incident beam, is no longer perceptible. This is not the case for the diffuse scattering data (Figure 6b), which allow the detection of a weaker signal ($10^-8$ times the incident beam intensity). This extension of the measurements toward larger wave vectors ($q_z = 6 \times 10^9 \text{m}^{-1}$) provides a better accuracy on the determination of the structural parameters. This new and more efficient method of investigation of the normal structure of a film is, in our opinion, one important result of this work. Moreover, the grazing angle of incidence need not be changed during an experiment, which is a great advantage when synchrotron radiation is used. The experiment is then much easier to carry out since the angle of incidence can be fixed with a simple mirror instead of a complicated beam deflector.

It is interesting to note that synchrotron reflectivity experiments did not give much better results than those performed in the laboratory with a sealed tube source. In fact, the better results obtained in the X-ray diffuse scattering geometry are mainly due to the effect of the limitation of the bulk scattering thanks to an incident angle fixed below the critical angle of total external reflection. Even though systematic reflectivity experiments were performed on the laboratory reflectometer, emphasis will be put on the diffuse scattering data obtained on the BM32 beamline. In Figure 6b, $I/I_0$ has been multiplied by $q_z$ in order to reduce the ordinate scale to 2 orders of magnitude instead of the 8 orders obtained experimentally, which allows a better view of details.

The experimental data were fit with a four-box model (Figure 7a): one for the upper alkyl chain (thickness $l_{\text{alky}}$...
electron density $\rho_{\text{alk2}}$, one for the diacetylene rod (thickness $l_{\text{diac}}$, electron density $\rho_{\text{diac}}$), one for the lower alkyl section (thickness $l_{\text{alk1}}$, electron density $\rho_{\text{alk1}}$), and one for the COOH headgroup (thickness $l_h$, electron density $\rho_h$). According to the fit, the overall thickness of the monolayer is about 1.86 nm, with $l_{\text{alk}} = 0.86$ nm, $l_{\text{diac}} = 0.25$ nm, $l_{\text{alk1}} = 0.50$ nm, and $l_h = 0.25$ nm. The lengths obtained from this kind of experiment are projections over an axis normal to the interface. Thus, since the total thickness we measure is small compared to the thickness of the fully stretched molecule (3.1 nm), it implies that the chains must be highly tilted and/or disordered in the expanded phase. For the electron densities, the parameters of the fit are $\rho_{\text{alk}}/\rho_{\text{water}} = 0.85$, $\rho_{\text{diac}}/\rho_{\text{water}} = 0.93$, $\rho_{\text{alk1}}/\rho_{\text{water}} = 1.04$, and $\rho_h/\rho_{\text{water}} = 1.10$. This progressive decrease of the densities, from the acid head on the subphase to the upper alkyl chains, is again indicative of a disordered expanded phase. The role of the diacetylene rods will be examined in section V(D). Let us finally mention that the surface tension given by the model is consistent with the value directly obtained from the Wilhemy balance measurement.

**B. Condensed Phase.**

A. Texture. As previously mentioned, coexistence between the expanded phase and a condensed phase takes place upon compression. In contrast to the expanded phase, the nucleation (Figure 8a) and growth (Figure 8b,e,f) of the condensed phase could be observed with BAM. By carefully controlling the pH and the temperature, a condensed phase with very long-range ramified structures (> 1 mm) was systematically observed (Figure 8e,f). These domains are highly ordered. This texture could be the one leading to the well-ordered polymer of ref 15. Upon further compression, the condensed domains come into contact. Nevertheless no deformation could be observed at the 10 μm scale, which is the resolution of our BAM. If the stress becomes too great, the film collapses, and three-dimensional bright...
nm$^2$, 0.22 nm$^2$. From the near constancy of these areas and the molecular area layer by layer from the simple expression

$$A = \text{molecular area layer by layer from the simple expression}$$

we can estimate the subphase, as it was for the expanded phase. From the fit to the carboxyl group including the degree of the distance from the best fit corresponded to the carboxyl group including the height of the headgroup obtained from the fit parameters (Table 1), we can perform the same calculation of the molecular areas as for the unpolimerized film. We obtain $A(\text{alk}_2) = 0.22$ nm$^2$, $A(\text{diac}) = 0.23$ nm$^2$, $A(\text{alk}_1) = 0.26$ nm$^2$, and $A(h) = 0.22$ nm$^2$. From the near constancy of these areas and the marked profile in the electron density, it is evident that the condensed phase is structured.

Table 1. Fit Parameters of X-ray Diffuse Scattering Experiments Recorded on the Condensed Phase and on the Polymerized Monolayer

<table>
<thead>
<tr>
<th></th>
<th>condensed phase</th>
<th>polymerized monolayer</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$ (mN/m)</td>
<td>63</td>
<td>63</td>
</tr>
<tr>
<td>$\rho_{\text{alk}_2/\text{water}}$</td>
<td>0.93 ± 0.01</td>
<td>0.92 ± 0.01</td>
</tr>
<tr>
<td>$\rho_{\text{alk}_1/\text{water}}$</td>
<td>1.08 ± 0.02</td>
<td>1.26 ± 0.03</td>
</tr>
<tr>
<td>$\rho_{\text{diac}/\text{water}}$</td>
<td>0.96 ± 0.02</td>
<td>0.96 ± 0.02</td>
</tr>
<tr>
<td>$\rho_{h/\text{water}}$</td>
<td>1.27 ± 0.02</td>
<td>1.24 ± 0.02</td>
</tr>
<tr>
<td>$l_{\text{alk}_2}$ (nm)</td>
<td>1.27 ± 0.02</td>
<td>1.29 ± 0.03</td>
</tr>
<tr>
<td>$l_{\text{diac}}$ (nm)</td>
<td>0.28 ± 0.02</td>
<td>0.18 ± 0.02</td>
</tr>
<tr>
<td>$l_{\text{alk}_1}$ (nm)</td>
<td>0.73 ± 0.02</td>
<td>0.96 ± 0.03</td>
</tr>
<tr>
<td>$I_0$ (nm)</td>
<td>0.32 ± 0.02</td>
<td>0.30 ± 0.03</td>
</tr>
<tr>
<td>$K (k_B T)$</td>
<td>250 ± 100</td>
<td>500 ± 100</td>
</tr>
</tbody>
</table>

* Buffer pH was 7.5.

**c. In-Plane Structure.** To explore the two-dimensional crystallinity of the condensed phase, we have performed GIXD experiments (LURE – DCI). Figure 10a shows the diffraction pattern of a monolayer compressed at a surface pressure $\pi = 10$ mN/m, at 22 °C. Upon polymerization, the film thickness increases from 2.60 to 2.73 nm whereas the thickness of the diacetylene rods decreases (Table 1). The latter observation is explained by the fact that the polymerization imposes a horizontal order, and the inhomogeneities are reminiscent of those of a solid.

**b. Vertical Plane Structure.** Once again, to study the vertical structure of the condensed phase, reflectivity and diffuse scattering experiments were performed. As previously explained, better results are obtained with the diffuse scattering experiments. Figure 9 (b) shows the measured diffuse spectrum of the film at 22 °C and compressed to $\Pi = 10$ mN/m, $A = 0.29$ nm$^2$ obtained with this technique. As in the case of the expanded phase, the data were fitted with a four-box model. In this case, however, the height of the headgroup obtained from the best fit corresponded to the carboxyl group including the first methylene rather than the COOH group alone (Figure 7b). One can note that the electron density is no longer a decreasing function of the distance from the subphase, as it was for the expanded phase. From the fit parameters given in Table 1, we can estimate the molecular area layer by layer from the simple expression $A = N_s \rho$, where $s$ is the thickness of the layer and $\rho$ is its electron density, and where the number of electrons is taken equal to $N_s (\text{alk}_2) = 89$, $N_s (\text{diac}) = 24$, $N_s (\text{alk}_1) = 64$ and $N_s (h) = 31$. The molecular areas are $A(\text{alk}_2) = 0.22$ nm$^2$, $A(\text{diac}) = 0.23$ nm$^2$, $A(\text{alk}_1) = 0.26$ nm$^2$, and $A(h) = 0.22$ nm$^2$. From the near constancy of these areas and the marked profile in the electron density, it is evident that the condensed phase is structured.

**C. Polymerized Film. a. Vertical Plane Structure.** Figure 9 allows the comparison of the diffuse scattering curves of the same PCA film before (●) and after (○) polymerization at a pressure $\Pi = 10$ mN/m. Upon polymerization, the film thickness increases from 2.60 to 2.73 nm whereas the thickness of the diacetylene rods decreases (Table 1). The latter observation is explained by the fact that the polymerization imposes a horizontal average position to the diacetylene rods, as illustrated in Figure 12. The increase of the film thickness suggests a decrease of the molecular area and of the in-plane lattice constant. The $\pi - I$ curve (Figure 12) is shown and the ordinate axis for the condensed phase transition is reversible. The condensed phase transition is reversible. The film thickness suggests a decrease of the molecular area and of the in-plane lattice constant. The latter observation is explained by the fact that the polymerization imposes a horizontal order, and the inhomogeneities are reminiscent of those of a solid.
gives rise to two peaks at 1.473 ± 0.010 and 1.545 ± 0.010 Å⁻¹ (Figure 13a) plus one much weaker Bragg singularity at 2.55 ± 0.02 Å⁻¹ (not shown in the figure). Thanks to this last singularity, the three peaks could be indexed with confidence as $q_{10}$ for the first one, $q_{01}$ and $q_{-11}$ for the second degenerated one, and $q_{11} (q_{11}^2 = q_{01}^2 + q_{10}^2 - 2q_{01}q_{10} \cos 2\alpha)$ for the last one. The dimensions of the associated oblique unit cell (Figure 13b) are $a_{10} = 5.05$ Å, $a_{01} = 4.81$ Å, and $\alpha = 58^\circ$ (Figure 13b), and its area of 0.205 nm² is consistent with the value deduced from diffuse scattering experiments. From these results, it is interesting to note that during polymerization, the lattice area shrinks by about 10% (the molecular area was around 0.23 nm² before polymerization). This contraction not only explains the decrease of pressure observed when the average molecular area is kept constant during UV irradiation but also is fully consistent with the decrease in the average molecular area recorded on isotherm measurements when the polymerization is done at constant pressure. A possible scheme of polymerization of the PCA monolayer is proposed in Figure 11.

Göbel et al. examined the changes upon polymerization of the vertical structure in monolayers of a two-tailed diacetylenic lipid [dimethylbis(2-hexacosanoic-10,12-dinoyl)oxaethylammonium bromide, “Bronco”] by X-ray reflectivity and determined the in-plane structure by GIXD. They also observed an increase in the thickness of the film upon polymerization and attributed it to a decrease in the tilt angle. (In their analysis they imposed the constraint that the electron densities in the two alkane segments be the same and that the lengths of the chains be proportional to the number of methylenes, which rules out the possibility of different extent of disorder in the two segments.) They carried out GIXD measurements, and electron diffraction studies only on polymerized films.

**D. Influence of the Diacetylenic Rod.** The thicknesses of PCA monolayers in the expanded phase and in the condensed phase are small compared with those of fatty acids of comparable molecular weight such as behenic and melissic acid. This suggests that the chains are either disordered or tilted in PCA films. The reason is probably partly due to the diacetylene rods, which introduce an asymmetry in the molecule and divide the alkyl chains into two relatively short segments ($C_{10}$ and $C_{12}$). The van der Waals attractions between each of these segments...
contributes to the stability of the PCA films but probably not enough to compensate for the entropic effects (amplified by the possibility of the diacetylene rod to rotate round the axis of the alkyl chains). Moreover, it is interesting to note that the difference between the thicknesses of the expanded and condensed phases is more important than that between the two phases in fatty acid monolayers. The thickness of PCA films is very sensitive to external conditions and particularly to the surface pressure. Once again, the asymmetry introduced by diacetylene rods in the molecule is probably responsible for this effect. It provides the upper and lower alkyl chains the flexibility needed to change the monolayer structure upon compression. To finish with the role of the diacetylene rod, we recall that the condensed phase of PCA was found to be more stable than that between the two phases in fatty acid monolayers. The difference between the thicknesses of the expanded and condensed phases is more interesting to note that the difference between the flexible PCA chains in the expanded phase allows such a rearrangement.

A. Bending Rigidity.

The scattering by the expanded monolayer at the air/water interface was unambiguously interpreted as being associated with the intensity scattered in the plane of incidence (x, z) by the expanded monolayer. The sensitivity of the experiment is approximately $\gamma/\gamma_{\text{max}}^2$, where $\gamma_{\text{max}}$ is the position of the last interference maximum. Despite the care taken to limit the background, the effective wave-vector range where $K$ has a limiting effect on the fluctuation spectrum remains quite restricted. This is due to the small value of $\sqrt{K/\gamma}$ for films spread at the air/water interface. Nevertheless, a high value of the bending rigidity modulus $K = (250 \pm 100)k_B T$ was unambiguously necessary to fit the condensed-phase spectrum, whereas the curve recorded for the expanded phase could be fitted with a much lower bending rigidity (a few times $k_B T$). This expected increase in $K$ when the compressibility of the film decreases has recently been observed with the same technique for an arachidic acid monolayer spread on a pure water subphase.

In the case of the polymerized PCA film, the covalent bonds between the molecules stiffen the monolayer, as revealed by the larger value of the bending rigidity modulus $K = (500 \pm 100)k_B T$ required to fit its fluctuation spectrum (Figure 9, O).

B. Buckling of the Polymerized Monolayer.

Finally, the intensity scattered in the plane of incidence (x, z) by a highly compressed polymerized monolayer is presented in Figure 14b as a function of the longitudinal wave vector transfer $q_x$ at $q_z = 0.5$ nm$^{-1}$. In this experiment, performed with the laboratory diffractometer, both $\theta_1$ and $\theta_2$ change in order to keep $q_z$ constant (Figure 14a). The central peak at $q_x = 0$ corresponds to the specular condition. More interesting are the broad peaks observed at $q_x = \pm (3 \times 10^{-3})$ nm$^{-1}$, which are absent in all of the scattering curves of unpolymerized PCA film before it collapses. These singularities reveal a well-defined wavelength in the polymerized system ($\lambda = 2\pi/q_x \approx 2$ μm) that can be attributed either to height fluctuations or to density inhomogeneities within the film. The latter possibility is not consistent with the fact that this excess scattering is not observed with the unpolymerized film, which is as inhomogeneous as the polymerized one. Moreover, the bending rigidity of the polymerized film is larger and it can be compressed without collapsing to a much larger pressure than the unpolymerized film (>40 mN/m). We interpret this excess scattering as being associated with a buckling of the overcompressed polymerized film in the vertical direction. This process is the only one that would allow a relaxation of the stresses as other mechanisms of collapse are not possible because of the covalent bonds.

Buckling of a polymerized octadecyltrichlorosilane monolayer at the air/water interface and of a solid phospholipid phase on a formamide subphase have already been observed in the same range of in-plane vector transfer. Recently, diffuse scattering techniques have been suc-

VI. Elastic Properties

A. Bending Rigidity.

The scattering by the expanded and condenced PCA films was fitted to the fluctuation spectrum of eq 3 including a $k_\perp^4$ term. The sensitivity of the experiment is approximately $\gamma/\gamma_{\text{max}}^2$, where $\gamma_{\text{max}}$ is the position of the last interference maximum. Despite the care taken to limit the background, the effective wave-vector range where $K$ has a limiting effect on the fluctuation spectrum remains quite restricted. This is due to the small value of $\sqrt{K/\gamma}$ for films spread at the air/water interface. Nevertheless, a high value of the bending rigidity modulus $K = (250 \pm 100)k_B T$ was unambiguously necessary to fit the condensed-phase spectrum, whereas the curve recorded for the expanded phase could be fitted with a much lower bending rigidity (a few times $k_B T$).

B. Buckling of the Polymerized Monolayer.

Finally, the intensity scattered in the plane of incidence (x, z) by a highly compressed polymerized monolayer is presented in Figure 14b as a function of the longitudinal wave vector transfer $q_x$ at $q_z = 0.5$ nm$^{-1}$. In this experiment, performed with the laboratory diffractometer, both $\theta_1$ and $\theta_2$ change in order to keep $q_z$ constant (Figure 14a). The central peak at $q_x = 0$ corresponds to the specular condition. More interesting are the broad peaks observed at $q_x = \pm (3 \times 10^{-3})$ nm$^{-1}$, which are absent in all of the scattering curves of unpolymerized PCA film before it collapses. These singularities reveal a well-defined wavelength in the polymerized system ($\lambda = 2\pi/q_x \approx 2$ μm) that can be attributed either to height fluctuations or to density inhomogeneities within the film. The latter possibility is not consistent with the fact that this excess scattering is not observed with the unpolymerized film, which is as inhomogeneous as the polymerized one. Moreover, the bending rigidity of the polymerized film is larger and it can be compressed without collapsing to a much larger pressure than the unpolymerized film (>40 mN/m). We interpret this excess scattering as being associated with a buckling of the overcompressed polymerized film in the vertical direction. This process is the only one that would allow a relaxation of the stresses as other mechanisms of collapse are not possible because of the covalent bonds.

Buckling of a polymerized octadecyltrichlorosilane monolayer at the air/water interface and of a solid phospholipid phase on a formamide subphase have already been observed in the same range of in-plane vector transfer. Recently, diffuse scattering techniques have been suc-


cessfully applied to study the buckling induced by the adsorption of charged copolymers at the air/water interface,\textsuperscript{40} and we can conclude that it would be very interesting to perform such experiments on overcompressed polymerized PCA films.

\section*{VII. Conclusion}

In conclusion, the study of the structure and elastic properties of 2D PCA films, spread on a basic buffer, before and after polymerization by UV irradiation, has been exposed in this article. The expanded phase was found to be a very compressible, non ordered and non polymerizable 2D phase. Thanks to the Brewster angle imaging technique, the nucleation and the growth of the condensed phase have been observed in situ. By carefully controlling the temperature and the pH, very long range inhomogeneous but highly ordered domains were observed. Exposed to UV light, the condensed phase gives rise to a polymerized monolayer. X-ray scattering experiments performed either on the laboratory reflectometer, on the BM32 beamline at ESRF, or on the D24 beamline at LURE have allowed the investigation of the vertical structure and of the in-plane crystalline structure of the monolayer before and after polymerization. An important result of the work is the demonstration that the normal structure of monolayer films can be determined efficiently and precisely from the diffuse scattering. The contraction of the 2D molecular network during polymerization has been proved and a polymerization process has been suggested. The high bending rigidity necessary to fit the X-ray diffuse scattering experiments performed on the polymerized monolayer gives evidence of the stiffening of the layer due to the covalent bonds formed between the molecules of PCA during the polymerization. Finally, when it is highly compressed, the polymerized film has been found to buckle in the third dimension.

\textbf{Acknowledgment.} This study has benefited from financial support from the NATO organization. We thank C. Blot and D. Luzet for indefectible support.


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\textbf{Figure 14.} (a) X-ray diffuse scattering experimental configuration in which the intensity is scattering in the incidence plane (x, z) while $q_z = 0.5 \text{ nm}^{-1}$ remains constant. (b) X-ray diffuse scattering curve observed on a highly compressed polymerized monolayer. The arrows indicate the position of the diffusion due to the buckling of the film.