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On the stability of Langmuir films of pyramidic mesogens

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Pyramidic mesogens forming thermotropic liquid crystal bulk phases were spread in an air–water interface. Pressure surface measurements and polarizing microscopy on the Langmuir films were used to characterize the various states of these pyramidic-like molecules. For two compounds bearing short lateral aliphatic chains, the surface pressure isotherms exhibit a large plateau region corresponding to a metastable monolayer in which the molecules may adopt an 'edge-on' arrangement. The coexistence of multilayered, anisotropic, slowly growing domains with the monolayer in the plateau region has been observed at long time scale. The film area relaxation kinetics at constant surface pressure show the existence of two nucleation mechanisms for the formation of these domains.

1. Introduction

The ability of classical amphiphilic molecules to form monolayers at an air–water interface is a well known phenomenon [1]. Recently, molecules forming thermotropic liquid crystalline bulk phases were investigated at the air–water interface. Calamitic molecules forming nematic mesophases in the bulk were spread at the air–water interface [2–5]. It appears that many of these compounds may undergo multilayer formation above certain compression rates. This singular feature may be a consequence of the existence of strong liquid crystal mean field ordering and weak polar interactions between the mesogenic molecules and the water molecules [5]. Some discotic mesogens have been also spread at the air–water interface [4–11].

From surface pressure measurements, we have shown previously that some pyramidic mesogens may be spread in monolayers at the air–water interface [12]. A multilayer arrangement of the molecules was also suggested to explain the large observed plateau in the π–A isotherms and the low molecular areas for further increase in the film surface pressure. An optical polarizing microscope set on a Langmuir trough allowed observation of the formation of anisotropic domains at a pressure corresponding to the plateau transition [13].

In this work, we were interested in a study of the stability of Langmuir films of these pyramidic mesogens. The study of the decrease in area of the films at constant surface pressure enabled us to enhance the metastability of these monolayers and to obtain kinetic results on the nucleation and growth mechanisms of the 3-dimensional phase from the monolayer of these pyramidic compounds.

2. Experimental

2.1. *Materials*

Two types of compound were used for the films' preparations. They were synthesitized and purified by Zimmermann. The molecules have a pyramidic-like

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central core to which six long side chains are bound at the pyramid base. These molecules have, on average, a three-fold symmetry axis (see figure 1). In the bulk state, these compounds exhibit mesophases [14, 15] which are stable at room temperature. Optical microscopy [15] and X-ray patterns [16] showed that these mesophases are columnar.

The compounds studied differ in the nature of the function that links the alkyl chain to the pyramid base, which is a tribenzocyclononene (TBCN) system, or in the length of the alkyl chains:

Hexanonanoyloxy-TBCN (ester I): the long chains are nonanoyloxy ($CH_3(CH_2)_7COO$–). In the bulk it exhibits a biaxial mesomorphic (P_D) phase stable in the 23·9–152·6°C range.

Hexanonyloxy-TBCN (ether): the long chains are nonyloxy ($CH_3(CH_2)_8O$–). This compound exhibits a uniaxial mesomorphic (P_A) 3D phase stable between 18·7°C and 66·1°C.

Pentadecanoyloxy-TBCN (ester II): for this compound, the long aliphatic chains are pentadecanoyloxy ($CH_3(CH_2)_{13}COO$–). It exhibits in the bulk a columnar P_C mesophase in the 80·5°C–134·6°C temperature range [15].

The high purity of these materials has been checked by TLC, NMR (270 MHz) and combustion analysis [15].

2.2. *Thermodynamical methods*

The ester and ether compounds were spread from $2{\cdot}5 \times 10^{-4}$ M solutions in Normapur chloroform from Prolabo. The water was purified in a milliQ system from Millipore.

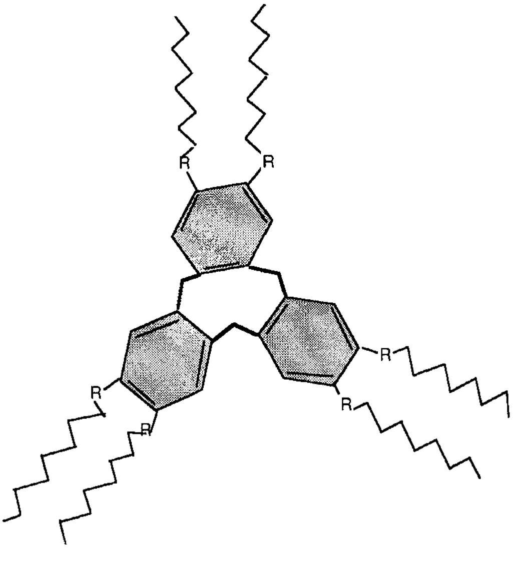

Figure 1. Structures of the pyramidic compounds. Hexanonanoyloxy-TBCN (ester I): the long chains are nonanoyl ($R = CH_3(CH_2)_7COO$–). Hexanonyloxy-TBCN (ether): the long chains are nonyloxy ($R = CH_3(CH_2)_8O$–). Pentadecanoyloxy-TBCN (ester II): the long aliphatic chains are pentadecanoyloxy ($R = CH_3(CH_2)_{13}COO$–).

The diagrams of the surface pressure (π) versus the area per molecule (A) have been obtained by using two different commercial Langmuir balances using two different techniques for the surface pressure measurement. The first apparatus (FBI Krüss film balance) gives the film surface pressure by measuring the displacement of a movable barrier against which the film is compressed (Langmuir method). The second apparatus (CEA-LB 105 film balance) measures the surface pressure by means of the Wilhelmy plate method. A thin piece of filter paper, which is perfectly wet by water, is suspended on a vertical displacement detector, partially immersed in and normal to the subphase. This balance is equipped with a pressure servo-electronic system, that could maintain the surface pressure constant. This system was used to study the film area relaxation at constant surface pressures.

For all the surface pressure (π)–molecular area (A) diagrams, the film was compressed with a speed equal to $30\,\text{Å}^2\,\text{molecule}^{-1}\,\text{min}^{-1}$ and at a temperature equal to 20°C.

2.3. *Polarizing microscopy*

Optical observations were made on the films by means of a Polyvar–Met microscope (Reichert–Jung), set on a home-built Langmuir trough. A Hamamatsu video camera with an image intensifier enabled us to visualize the film and record images on a video tape. The film was observed without the use of any fluorescent probe, and only by reflection of linearly polarized light. The reflected light was received after passing through a rectilinear analyser. The light intensities of the recorded images were then measured from the video tape at the end of the compression (about $140\,\text{Å}^2\,\text{molecule}^{-1}$).

3. Results and discussion

Figure 2 presents the π–A isothermal diagrams for the pyramidic compounds spread from chloroform solution and obtained by the Langmuir method. For both ester I and ether pyramidic compounds, the surface pressure remains equal to zero, within the accuracy of our measurements, for molecular areas greater than $305\,\text{Å}^2$.

For ester I, a first break in the pressure increase occurs at $232\,\text{Å}^2$ with a hump which indicates that the film is not in an equilibrium state during its compression. The molecular area range 305–$232\,\text{Å}^2$ corresponds to a liquid-expanded phase (LE). Indeed, the corresponding part of the π–A isotherm extrapolates to zero pressure at a molecular area about $300\,\text{Å}^2$. This molecular area leads to an area about $50\,\text{Å}^2$ per nonyl chain. This value is in agreement with the molecular area occupied by a single chain of fatty acids in a liquid-expanded monolayer [17]. In this phase, the base of the pyramids are 'flat', lying at the air–water interface—side-on arrangement. A large plateau occurs at a pressure of about $9{\cdot}5\,\text{mN}\,\text{m}^{-1}$ and corresponds to an LE–condensed phase transition. The molecular areas in the condensed phase are found to be about $A = 66\,\text{Å}^2$. On compressing the film further, the π–A isotherm of ester I exhibits a second plateau which may correspond to the formation of a second layer.

For the ether, the film also shows a transition from an LE phase to a condensed phase, for which the molecular area is about $300\,\text{Å}^2$. The LE–condensed phase transition is reached without any hump at $\pi = 4{\cdot}5\,\text{mN}\,\text{m}^{-1}$ and $A = 264\,\text{Å}^2$.

The classical liquid expanded–liquid condensed phase transition, usually observed for fatty acid films and which involves solely an ordering of the aliphatic chains, could not explain the low molecular areas of the observed condensed phase.

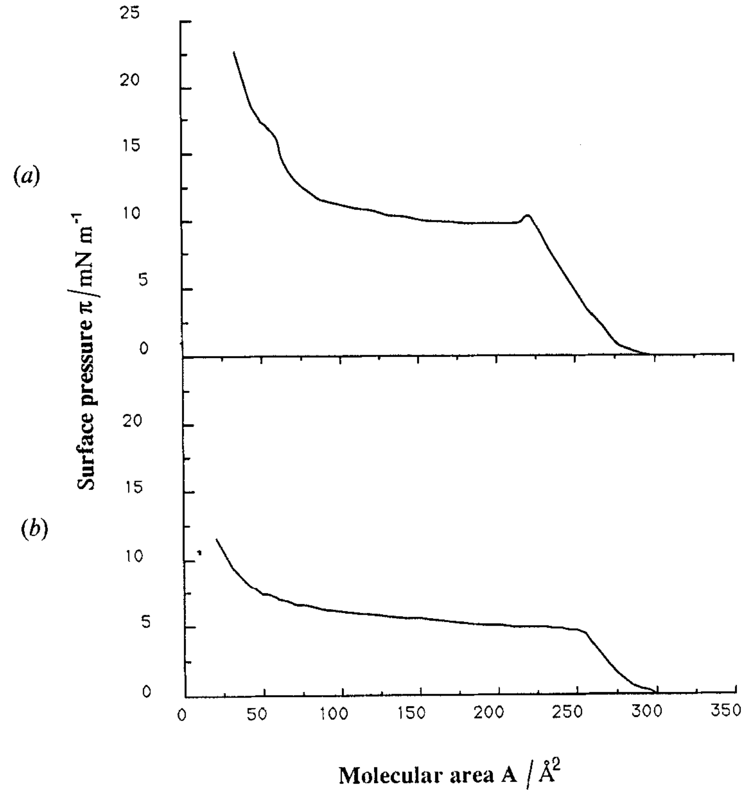

Figure 2. Surface pressure (π) versus molecular area (*A*) isotherms; subphase: purified water (pH = 5·7), temperature: 20°C, barrier speed: 30 Å^2 molecule^{-1} min^{-1}. (*a*): Ester I; (*b*): ether.

One should consider, for both compounds, a side on–edge on phase transition [8–11] which involves the whole molecule and not only its chains. In the edge-on molecular arrangement, the base of the pyramidic core is perpendicular to the air–water interface, three of the aliphatic chains of the molecules are in the water subphase and the three others are in the air. This arrangement is in agreement with the observed molecular area of the condensed phase. Indeed, if one assumes that the monolayer is in a liquid-condensed state, this molecular area would be in agreement with the 22 Å^2 that a fatty acid molecule occupies in such a state [1].

The π–*A* isothermal diagrams of films of the ester I and ether compounds, obtained by the Wilhelmy method, are very similar to those obtained by the Langmuir method, except in two points:

the surface pressures measured by the Wilhelmy method are lower by about 2 mN m^{-1}.

the occurrence of a second break appears in the ether π–*A* isotherm at a molecular area about 66 Å^2, and a surface pressure slightly higher than the plateau pressure. This molecular area is the same as that corresponding to the formation of the second layer. This shows that during compression, a similar process occurs for both compounds.

The difference between the surface pressure values obtained by the Wilhelmy method and the Langmuir method could be related to the difference reported by Rondelez and Koppel [6] for monolayers of discotics molecules and by Rettig *et al.* [17] for monolayers of polymeric mesogens which possess high viscosities. This difference could originate from a non-normal orientation of the Wilhelmy plate induced by the film viscosities during compression.

It is necessary to note that if one stops compressing the films from their condensed phase, a relaxation of the surface pressure to that of the plateau transition is observed. This shows that the condensed phase is metastable and hence should lead to a collapse. However, after a cycle of one compression and one decompression, a second compression shows identical π–A isotherms for the first and the second compressions of the film. We conclude that this surface pressure relaxation is due to a reversible collapse.

The effect of the aliphatic chain length is shown by the results obtained on the ester II—pentadecanoyloxy-TBCN. The π–A isotherm of this compound also exhibits a large plateau corresponding to an LE–condensed phase transition. In this case, the molecular areas are in agreement with those of a side-on arrangement for both phases (see figure 3).

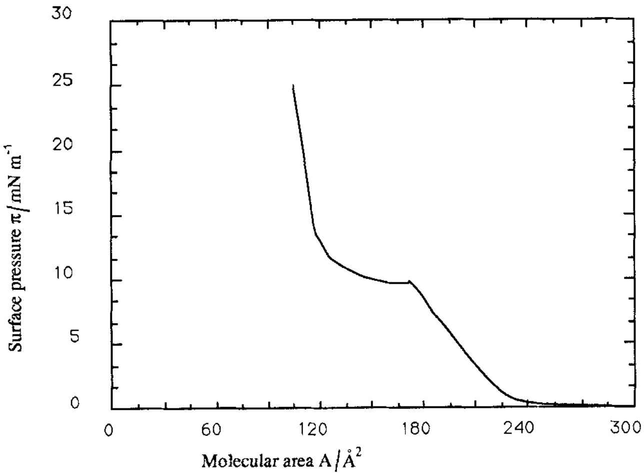

Figure 3. π–A isotherms of pentadecanoyloxy-TBCN (ester II); subphase: purified water (pH = 5·7), temperature: 20°C, barrier speed: 30 Å^2 molecule^{-1} min^{-1}.

3.3. *Polarizing microscopy*

We observe, when the film was compressed to the plateau region, the coexistence of the monolayer with small anisotropic domains. For ester I, they are narrow elongated stripes of a few hundred micrometers length and a few micrometers width. For the ether, we observe disc-like islands with a diameter of a few tens of micrometers. When decompressing the monolayer, these domains disappear for pressures lower than the plateau pressure. To explain the optical anisotropy, in the plane of the air–water interface, an edge-on arrangement of the molecules in the domains must be assumed.

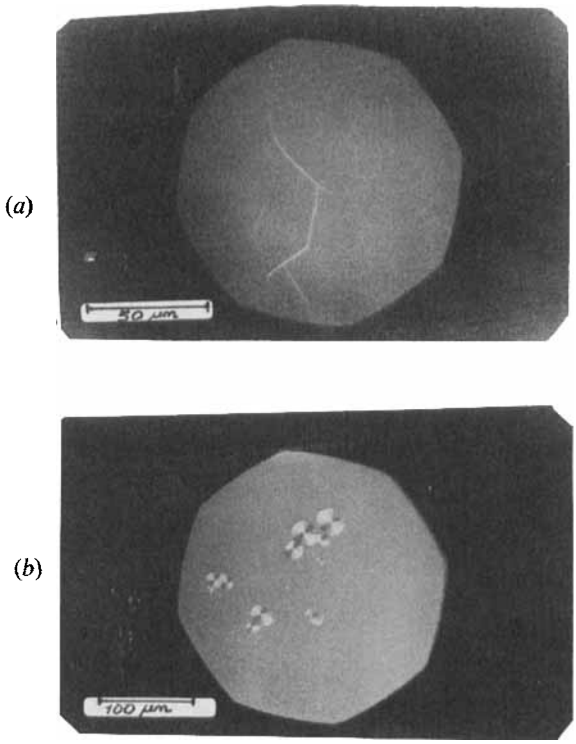

Figure 4. Anisotropic domains observed in the ester I and the ether Langmuir films, between polarizer and analyser; molecular area: 140 Å^2, temperature: 20°C, subphase: purified water. (*a*) Ester I domains between crossed polarizers; (*b*) ether domains; the analyser makes a 5° angle with the polarizer.

The domains, and especially those for ester I, were observed to move slowly in the microscope field. The slow motion of the domains show that the viscosities of the monolayers are quite important, as suspected above.

The brighter domains of ester I have their long axes oriented at ±45° with respect to the electric field of the incident polarized light (see figure 4(*a*)). The domains whose long axes are parallel or perpendicular to the polarizing axis are not seen. This shows that the neutral lines are parallel and perpendicular to the long axes of the domains.

For the ether the typical domains display bright quadrants which are all visible when the polarizer and the analyser are crossed (see figure 4(*b*)). These quadrants are separated by sharp dark lines which are parallel and perpendicular to the polarizer. The neutral lines of the observed domains are radial and orthoradial.

From light reflectivity measurements on these domains, we developed a new technique to determine their thicknesses and their optical anisotropy [13]. We applied these optical results and found that in the observed domains, the molecules are stacked in rectilinear columns for ester I and in spiral columns for the ether, in the same way as for the bulk mesomorphic states of these compounds. We also found that domain thickness varies with time, approximately from 60 Å to 300 Å (from a few minutes to several hours).

Microscopic observations under polarized light, made on pentadecanoyloxy-TBCN (ester II), show the formation of round-shaped domains, optically isotropic in the plane of the air–water interface. This isotropic feature of these domains may be due to a stacking of the molecules in columns, in the normal direction to the interface. The important length of the hydrophobic chains may forbid an edge-on arrangement.

3.4. *Molecular area relaxation at constant surface pressure*

This section presents preliminary results of a study on the collapse mechanism for transforming the monolayer molecular arrangement into the multilayered anisotropic domains observed at the metastable isotherm plateau region.

Figure 5 shows, for the ester I film, the experimentally determined change of the film area versus time at a surface pressure equal to 7 mN m^{-1} (measured by the Wilhelmy method). This pressure is reached just before the hump of the π–A isotherm. The kinetics of the collapse mechanism can be determined by plotting different functions of time. The best correlation between the experimental data and

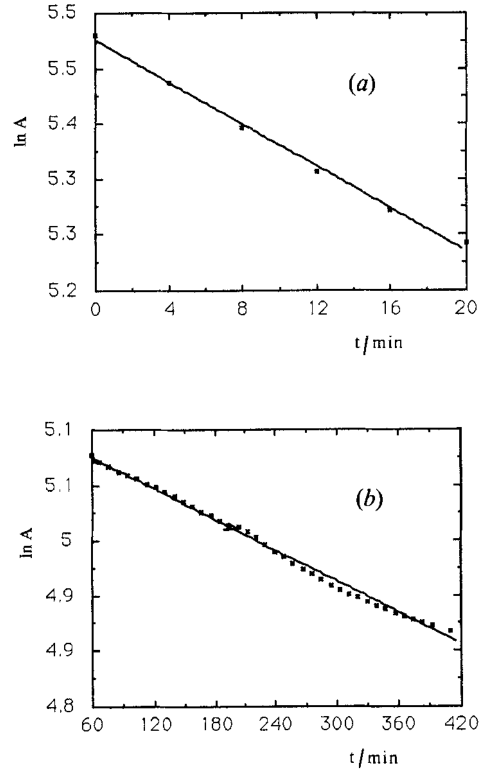

Figure 5. Plot of the logarithm of the film area versus time, at a constant surface pressure (7 mN m^{-1}) corresponding to the end of the liquid-expanded state for the ester I film. Two time stages (*a*) and (*b*) are described by relaxation times of about 80 min and 1600 min, respectively.

the various functions is obtained by considering the process to occur in two distinct time stages (0–20 min and above 60 min), each described by a suitable exponential law. The corresponding relaxation times are about 80 min and 1600 min, respectively. The first stage can describe a bidimensional nucleation and growth from the monolayer state. The second stage may correspond to the growth of a 3D phase nucleated at the first stage.

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