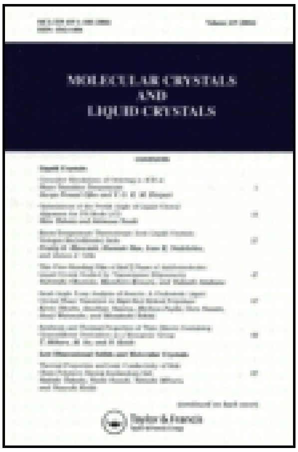

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Dynamic Behavior of Pyramidic Liquid Crystal Film at the Air-Water Interface

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DYNAMIC BEHAVIOR OF PYRAMIDIC LIQUID CRYSTAL FILM AT THE AIR-WATER INTERFACE

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Abstract Molecular organization of the different phases of a pyramidic liquid crystal film spread at the air-water interface has been investigated using Langmuir balance and current displacement techniques simultaneously. The mesogenic compound exhibits a main transition from an expanded phase to a metastable condensed phase. The results are in agreement with previous polarized and fluorescence light microscopy measurements and grazing incidence X-ray reflectometry. The study shows that the molecules are oriented edge-on in the condensed phase and side-on in the liquid expanded phase. The value of the dipole moment of the pyramidic molecules is given in the liquid expanded phase. Two kinds of displacement current curves were obtained depending on the kinetic of compression.

INTRODUCTION

The molecular organization of amphiphilic molecules spread at the air-water interface has been studied recently with much interest in relation with the development of new structural tools.[1,2] For example, molecules forming thermotropic liquid crystalline bulk phases were investigated[3,4] by means of isotherm measurements, polarized optical microscopy and grazing incidence X-ray diffraction.

From surface pressure measurements, we have shown previously that pyramidic mesogens may be spread in monolayers at the air-water interface.[5,6,7] The pressure-area isotherm exhibits a wide plateau corresponding to the coexistence of an expanded phase and a condensed metastable phase. The formation of long multilayered slowly growing domains was observed from the condensed metastable phase. By means of polarized light microscopy, it was possible to measure the anisotropy and the thickness of these domains. Molecular interactions lead to the formation of columns which depend on the shape of the molecule and the distribution of hydrophobic and hydrophilic parts.

By means of grazing incidence X-ray diffraction the thickness and the lattice parameters of the three dimensional domains[7] have been studied. Results were consistent with an edge-on conformation where the base of the pyramidal core is normal to the air water interface.

In the present paper, we have studied the kinetic behavior of pyramidic liquid crystal films spread at the air-water interface using a displacement current measuring technique in order to detect an electrical change in the film originated from the motion of molecules during the film compression. At the same time we have recorded the isotherm diagrams of the surface pressure versus the molecular areas. Besides the kinetic results, these electrical measurements confirm previous hypothesis about molecular reorientation from horizontal to vertical position. We are also giving an estimated value of the dipole moment.

EXPERIMENTAL

Materials

The pyramidic mesogen was synthetized and purified by Zimmermann et al..[8] The molecules present a pyramidic-like central core to which six hydrophobic side chains are bound by hydrophilic ester groups (Figure 1). The pyramidic height is about 1.51 nm. In the bulk, this compound exhibits mesophases which are stable at room temperature. Optical microscopy[8] and X ray diffraction[9] showed that these bulk mesophases are columnar.

The pyramidic base is a tribenzocyclononene (TBCN) system. The alkyl chains are nonanoyloxy ($CH_3(CH_2)_7COO$-). In the bulk it exhibits a biaxial mesomorphic (P_D) phase. The length of all-trans C9 chains is 1.17 nm yielding a maximum width of 9-TBCN of about 3.4 nm. The high purity of these materials has been checked by TCL, NMR (270 Mhz) and combustion analysis.

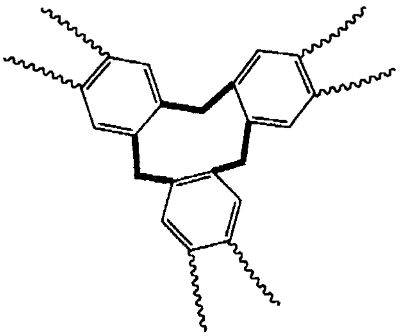

FIGURE 1 Schematic representation of the structure of the 9-TBCN pyramidic compound. The six lateral chains are nonanoyl.

Isotherm measurements

The pyramidic liquid crystal compounds were spread from a $C = 2.5 \times 10^{-4}$ M chloroform solution (Normapur, Prolabo). The deionized water was purified using a UHQ II Elga system. The isotherm diagrams of surface film pressure π versus molecular area A were obtained with a Langmuir type balance (Lauda Film-waage or FB1 Krüss), at 21° C and pH = 5.7. The Lauda trough which is used for the displacement current technique has a maximum area of $S_0 = 910$ cm^2 (15 cm wide). The trough temperature was controlled by using RM6 Lauda thermostat. The surface pressure was measured with an accuracy of about 0.1 mN.

Displacement current technique

In order to investigate the electrical properties of the films we used a current measuring technique[10,11] monitored together with the Langmuir type balance.

Figure 2 shows the experimental set-up. In this technique, two stainless steel electrodes, of rectangular shape, were placed to be parallel to the air-water interface. Electrode 1 was suspended in air and electrode 2 was immersed in water. The area of electrode 1 was $S_e = 80$ cm^2. It was electrically shielded by a surrounding metallic box. For all our experiments, we adjusted the distance between electrode 1 and air-water interface to $d_e = 2$ mm by using a micrometer screw.

The sample solution of concentration $C = 1.73\ 10^{-4}$ M was spread on pure water in the Lauda trough and maintained at a constant temperature. During compression, an induced charge is generated on upper electrode when either orientation of polar molecules on the interface or the number of molecules under the electrode 1 is changed.

The displacement current I was measured by an electrometer (Keithley 617) connected to a computer. Simultaneously the surface pressure-molecular area isotherm were recorded. The accuracy of the current measurements was about 0.01 pA.

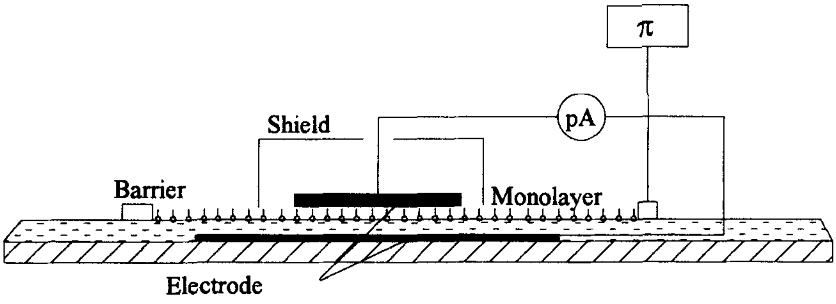

FIGURE 2 Schematic representation of the displacement current measurement device.

RESULTS AND DISCUSSION

Figure 3 presents the whole surface pressure-area isotherm obtained with the Krüss balance. The compression rate was 0.3 nm^2/(molecule.mn); the corresponding time for an isotherm plot was about 11 mn. The surface pressure remained equal to zero for molecular areas greater than 3.05 nm^2, within the accuracy of our measurements. These molecular areas correspond to a gas-liquid phase transition. During compression of the ester film and for molecular areas between 3.05 and 2.32 nm^2, the π-A isotherm agrees with a liquid expanded (LE) phase. At these large molecular areas, the monolayer is stable and formed of flat laying molecules with their pyramidal base on the air-water interface (side-on arrangement). A first break in the pressure occurs at 2.32 nm^2 followed by a hump.

A large plateau takes place at $\pi = 9.5$ mN/m which was found equal to the spreading pressure of the mesogen. Using polarizing and fluorescence microscopy[5] we have observed the coexistence of the monolayer in an expanded phase and a metastable condensed phase, at this plateau pressure. Long slowly growing anisotropic domains were observed to form from the condensed phase. By grazing incidence X-ray reflectometry, we have shown that the condensed phase is an edge-on phase (EO) and that the three dimensional thickness domains, growing from this phase, is between 9.6 and 24 nm and corresponding to 4 and 10 layers.[7]

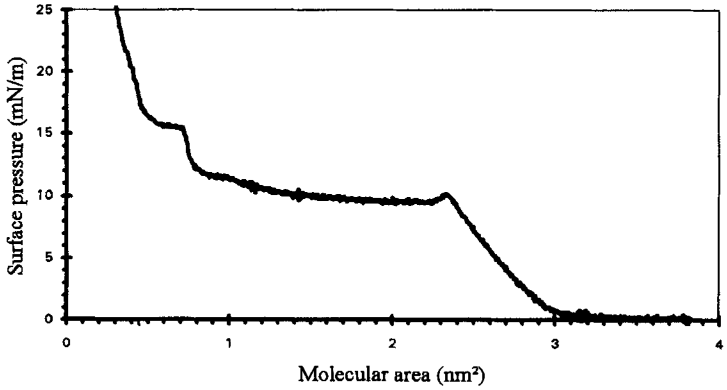

FIGURE 3 π-A isotherm diagram of the 9-TBCN pyramidic compound. Temperature: 21°C, subphase: purified water, barrier speed: 0.3 nm^2/(molecule.mn), pH = 5.7.

The displacement currents generated during the film compression are illustrated on I-A curves shown in Figure 4 and 5. The increase in current is related to changes in the number N of spread molecules under the electrode 1 and in the perpendicular component μ_Z of the mean molecular dipole moment.

According to Iwamoto and Majima[10,11] the changes in N and μ_Z values induce charges Q on the upper electrode :

$$Q = -\sum_{i=1}^{N} \frac{(\mu_z)_i}{d_e} - \frac{\varepsilon_0 s_e \phi_s}{d_e} = -\frac{N\mu_z}{d_e} - \frac{\varepsilon_0 s_e \phi_s}{d_e}$$

where $(\mu_z)_i$ is the perpendicular component of the dipole moment of a molecule i.

During the film compression, a displacement current I is generated. If we assume that the surface potential ϕ_S of the water does not change during compression the current I is given by :

$$I = \frac{\mu_z}{d_e}\frac{dN}{dt} + \frac{N}{d_e}\frac{d\mu_z}{dt}$$

The polarity of the induced current is positive, i. e. the current flow from the electrode 1 towards the electrode 2.

Figure 4 shows a I-A diagram obtained for a film which was compressed from a molecular area of about 3.1 nm^2 until 1.5 nm^2. The spread volume was equal to 200 μl, the barrier speed was v = 0.52 mm/s. The measured value of the displacement current in these experimental conditions for a molecular area of 3 nm^2 was I = + 0.02 pA.

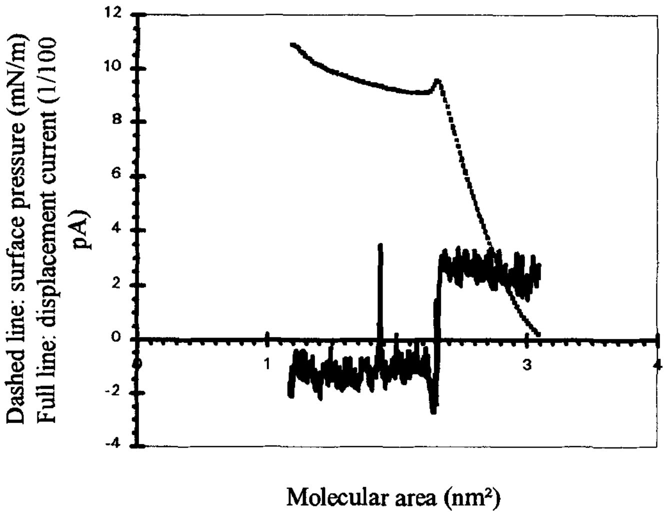

FIGURE 4 π-A (dashed line) and I-A (full line) diagrams of 9-TBCN film spread at the air-water interface and compressed from the liquid expanded phase. Barrier speed : 0.52 mm/s; pH = 5.7; T = 21°C; electrode height d_e = 2 mm.

As in the LE phase, where the dipole moment orientation remains constant, the induced current is given by :

$$I = \frac{\mu_z}{d_e}\frac{dN}{dt} = \frac{\mu_z}{d_e}\frac{S_e L v}{N_0 A^2} \qquad (1)$$

where L, v and N_o represent respectively the width of the through, the barrier speed and the total number of the spread molecules. From the above measured value of the current, at A = 3 nm^2, we can deduce a value of μ_z equal to 4.0 D.

This total dipole moment μ_z results from two contributions: i) the hydrophilic part (-COO-) to which is associated a dipole moment noted μ_1, and ii) the terminal C-H bond of the aliphatic chains to which is associated a dipole moment noted μ_2. According to the study of the Langmuir film of ethyl palmitate spread at the air-water interface[12], the value of the vertical component μ_{z1} of μ_1 is about 0.5 D, in the expanded phase. As the vertical component μ_{z2} of μ_2 has been measured by Iwamoto et al.[10,11] for the stearic acid film. For this compound, the resulting dipole moment, μ_{z2} = 0.2 D, is mainly due to the terminal C-H bond of the aliphatic chain. Since both μ_{z1} and μ_{z2} are directed in the same way, from water to air, a resulting value of μ_z for our pyramidic molecule is $\mu_z = 6(\mu_{z1} + \mu_{z2}) \approx 4.2$ D. This value is in good agreement with the value of μ_z deduced from the above measured displacement current.

It is interesting to note the existence of a break in the current increase during compression of the LE phase, at a molecular area about 2.6 nm^2. This break has also been reported by Iwamoto et al..[10,11] It has been explained by a decrease of μ_z, due to a change in the configuration and in the moment bonds of the hydrophilic carboxylic head group. Therefore, in our study a similar re-arrangement may occur within the hydrophilic part of the pyramidic molecule, which is the ester function that links the aliphatic chains to the pyramidal core.

At the beginning of the Liquid-Expanded/Edge-On (LE-EO) transition, we have observed an abrupt jump of the current I from +0.02 pA to -0.01 pA. This jump to a negative value is a direct proof for the already stated LE-EO transition. Indeed, since a horizontally oriented dipole induces no charges on the upper electrode, the transition of the molecular dipole moment from a vertical to a horizontal direction leads to a decrease of the electrode charge. However, during the LE-EO transition two phases coexist.[6,7] This means that all the dipoles do not rotate to the horizontal direction at the same time. Consequently, the induced displacement current I at a given molecular area A, results from two currents. The first one, which is of a positive polarity, is due to the increase of the number N of the still vertically oriented dipoles (LE phase) at the given molecular area A. The second one, which is of a negative polarity, is due to the decrease of N following the molecular reorientation. Thus it is necessary in this case to calculate the net variation dN/dt.

According to the lever rule, the number N of the vertical dipoles under the upper electrode, at the molecular area A, is given by :

$$N = \frac{S_e}{A}\frac{(A - A_{EO})}{(A_{LE} - A_{EO})}$$

where A_{LE} is the molecular area in the LE phase and A_{EO} the molecular area in the EO phase. From the π-A isotherm, we can deduce $A_{LE} = 3\ \mathrm{nm}^2$ and $A_{EO} = 0.66\ \mathrm{nm}^2$ by extrapolating to zero π pressure. The net variation of N is :

$$\frac{dN}{dt} = -\frac{A_{EO}S_e v}{(A_{LE} - A_{EO})N_0A^2}$$

Hence we can deduce the expression of the displacement curent I' during the LE-EO transition:

$$I' = -\frac{\mu_z}{d_e}\frac{A_{EO}S_e v}{(A_{LE} - A_{EO})N_0A^2} \qquad (2)$$

If we apply equation (2) to calculate I' at a molecular area equal to 2 nm^2 and in the experimental conditions used in figure 4, we find $I'_{calc} = -0.014$ pA which is of the same order as the measured displacement current $I' = -0.01$ pA for a molecular area $A = 2\ \mathrm{nm}^2$.

We have noticed a different behavior of the measured displacement current at the Gas-LE plateau transition, in the zero pressure area. If we begin compression from molecular areas larger than those of the LE phase, an intense displacement current of about 30 pA is obtained. Figure 5 shows one of the I-A diagram recorded during film compression from a molecular area of about 4 nm^2 to 1.5 nm^2. The barrier speed was equal to v = 0.87 mm/s. We have observed many and intense fluctuations of the displacement current values. This behavior may be explained, since in the gas phase where the molecular area is large, the aliphatic chains lay probably parallel to the air-water interface. So, the contribution of the dipole moment of the terminal C-H bond of the aliphatic chains vanishes. The induced displacement current results from two contributions: first, the increase of the total number of molecules located under the upper electrode and second the increase of the mean value $<\mu_z>$ of the vertical component of the molecular dipole moment.

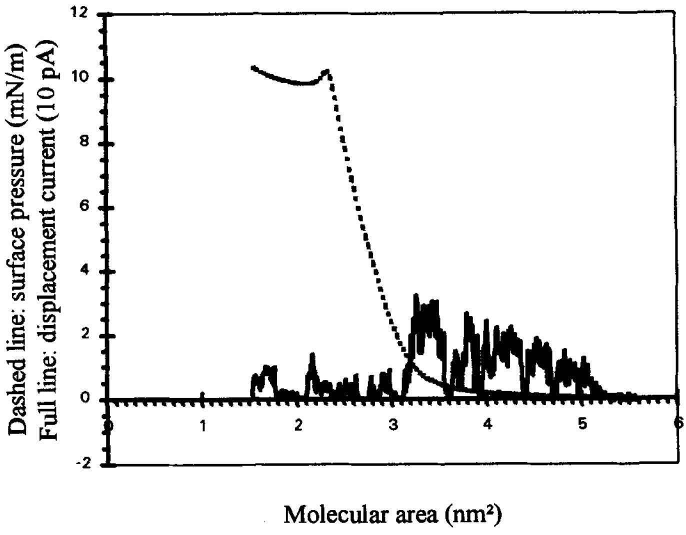

FIGURE 5 π-A (dashed line) and I-A (full line) diagrams of 9-TBCN film spread at the air-water interface and compressed from the π = 0 area. pH = 5.7; T = 21°C; barrier speed = 0.87 mm/s.

The sharp fluctuations of I can be easily understood if we take into account the coexistence of the gaz and the LE phases. The study of the film by fluorescence microscopy allowed us to show that the two phases can coexist either as bubbles[5] or as alternating stripes of the gas phase and the LE phase (Figure 6). Hence during compression, heterogeneous domains for which the molecular density and the vertical component of the dipole moments are very different flow under the electrode. Moreover, we also observed, that many fluctuations in the current value still remain in the LE expanded phase and in the LE-EO transition, for this compression speed. This means that the film is heterogeneous during compression at the indicated barrier speed. Hence, in these conditions, we can conclude that the film is not in an equilibrium state.

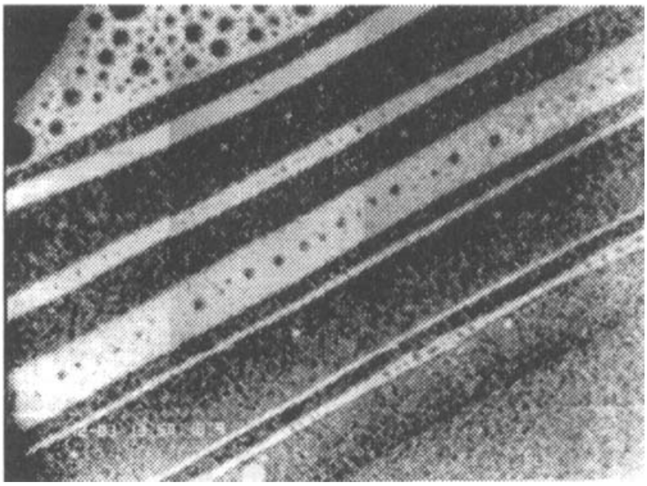

FIGURE 6 Structure of the 9-TBCN film observed by fluorescence microscopy, at the gas-liquid expanded transition. A fluorescent probe was added to the spreading solution. The bright and dark parts correspond respectively to the liquid expanded phase and gas phase.

In this work, we have shown by means of the displacement current technique that a monolayer of a pyramidic liquid crystal spread at the air-water interface exihibits a gas phase in which the pyramidal core of the molecules lay flat on the water surface. In this phase the mean direction of the aliphatic chains of the molecules is parallel to the interface. Then the film shows a liquid-expanded phase in which the molecular organization is similar to the gas phase except that the aliphatic chains are tilted. The dipole moment of the molecules was found to be about 4 Debyes. At further compression rate, a transition to an edge-on phase occurs where the dipole moment is shown to be oriented parallel to the air water interface. We have also explained the shape of the current displacement versus molecular areas.

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