

Formation of Liquid Crystalline Phases from a Langmuir Monolayer

K. A. Suresh* and A. Bhattacharyya

Raman Research Institute, Bangalore 560 080, India

Received June 10, 1996. In Final Form: November 22, 1996[®]

We report the transformation of a two-dimensional monolayer at the air–water interface into three-dimensional liquid crystalline phases on continuous tuning of the surface molecular density. On compressing a 4'-*n*-octyl-4-cyanobiphenyl monolayer, at room temperature, we obtain multilayer domains whose thicknesses range from a few layers to hundreds of layers. Above 28 °C, these domains undergo a phase transition and change to much thicker lenslike domains. On expansion, these domains revert to the monolayer. Although these domains originate from a monolayer, we find that they exhibit features typical of liquid crystals.

Introduction

It is known that some compounds which exhibit thermotropic liquid crystalline (LCr) phases in bulk can also form stable two-dimensional (2D) Langmuir monolayers.^{1–3} It is interesting to find out whether the molecules that form 2D monolayers can also organize themselves into a three-dimensional (3D) liquid crystalline phase at the air–water interface. Surprisingly, in spite of many reports^{4–7} on monolayer transforming into multilayers, there have been no studies to characterize the phase of these 3D multilayer domains. We have characterized the phase of the multilayer domains obtained on compressing a Langmuir monolayer employing the techniques of reflection and polarizing microscopy. We find that, at room temperature, the multilayer domains, which have thicknesses of the order of a fraction of a micrometer, exhibit features of a smectic A phase. With an increase of temperature, these multilayer domains undergo a phase transition resulting in very thick (1–40 μm) lenslike domains. Our studies show that in the temperature range 28–36 °C, these lenslike domains exhibit a nematic phase, and above 36 °C they exhibit an isotropic phase. Further, on decreasing the surface molecular density, we recover the monolayer. Apart from demonstrating a transformation of a monolayer into a liquid crystal or vice versa, this study is of importance in understanding the forces that result in liquid crystals⁸ and those that stabilize monolayers.^{9,10}

Experimental Section

Our studies were carried out on a 4'-*n*-octyl-4-cyanobiphenyl (8CB) monolayer. The material was obtained from BDH and used as received. In bulk, 8CB exhibits the sequence of transitions: crystal 20.5 °C smectic A 33.3 °C nematic 41.5 °C isotropic. The monolayer was formed by depositing 50 μL of dilute (millimolar) 8CB solution (in chloroform) using a microsyringe on Millipore Milli-Q filtered water contained in a Teflon

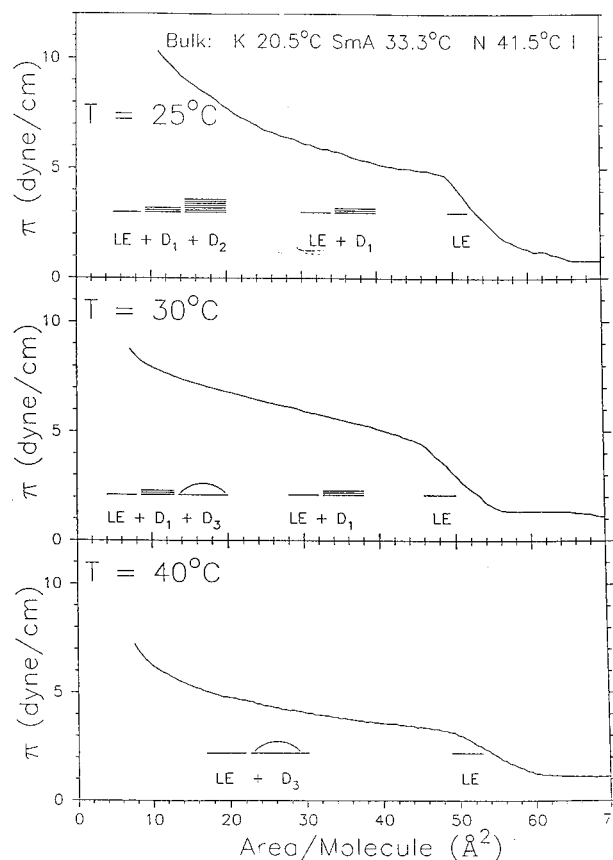


Figure 1. Surface pressure (π)–area per molecule isotherms at different temperatures (T) for the 8CB monolayer. The compression rate was 0.05 ($\text{\AA}^2/\text{molecule}$)/s. The different structures observed are shown schematically. Here D_1 represents the “three-layer” phase, D_2 the optically flat domains, and D_3 the lens-shaped domains. Transition temperatures of 8CB are also shown. Key: crystal (K); smectic A (SmA); nematic (N); isotropic (I).

trough (size 35 cm \times 10 cm). In every experiment, the trough was first cleaned thoroughly with a detergent solution. Then it was filled with fresh chromic acid and left overnight. After the chromic acid was removed, the trough was rinsed repeatedly with Millipore water until all traces of the acid and other contaminants were eliminated. The trough was considered “properly clean” when Millipore water completely dewetted the surface on emptying. The cleanliness was further confirmed by reproducibility of the pressure area isotherms. The monolayer was compressed at different rates using a Teflon barrier driven by a computer-controlled motor. We used surface manometry to locate the phase transition points. The surface pressure was measured by Wilhelmy plate method¹¹ using a platinum blade.

[®] Abstract published in *Advance ACS Abstracts*, January 15, 1997.

(1) Dorfler, H. D.; Kerscher, W.; Sackmann, H. *Z. Phys. Chem.* **1972**, *251*, 314.

(2) Suresh, K. A.; Blumstein, A.; Rondelez, F. *J. Physique* **1985**, *46*, 453.

(3) Ulman, A. *An Introduction to Ultrathin Organic Films*; Academic Press: San Diego, CA, 1991.

(4) Xue, J.; Jung, C. S.; Kim, M. W. *Phys. Rev. Lett.* **1992**, *69*, 474.

(5) Friedenber, M. C.; Fuller, G. G.; Frank, C. W.; Robertson, C. R. *Langmuir* **1994**, *10*, 1251.

(6) de Mul, M. N. G.; Mann, J. A., Jr. *Langmuir* **1994**, *10*, 2311.

(7) Schmitz, P.; Gruler H. *Europhys. Lett.* **1995**, *29*, 451.

(8) Swanson, B. D.; Sorensen, L. B. *Phys. Rev. Lett.* **1995**, *75*, 3293.

(9) Li, M.; Acero, A. A.; Huang, Z.; Rice, S. A. *Nature* **1994**, *367*, 151.

(10) Bak, P. *Rep. Prog. Phys.* **1982**, *45*, 587.

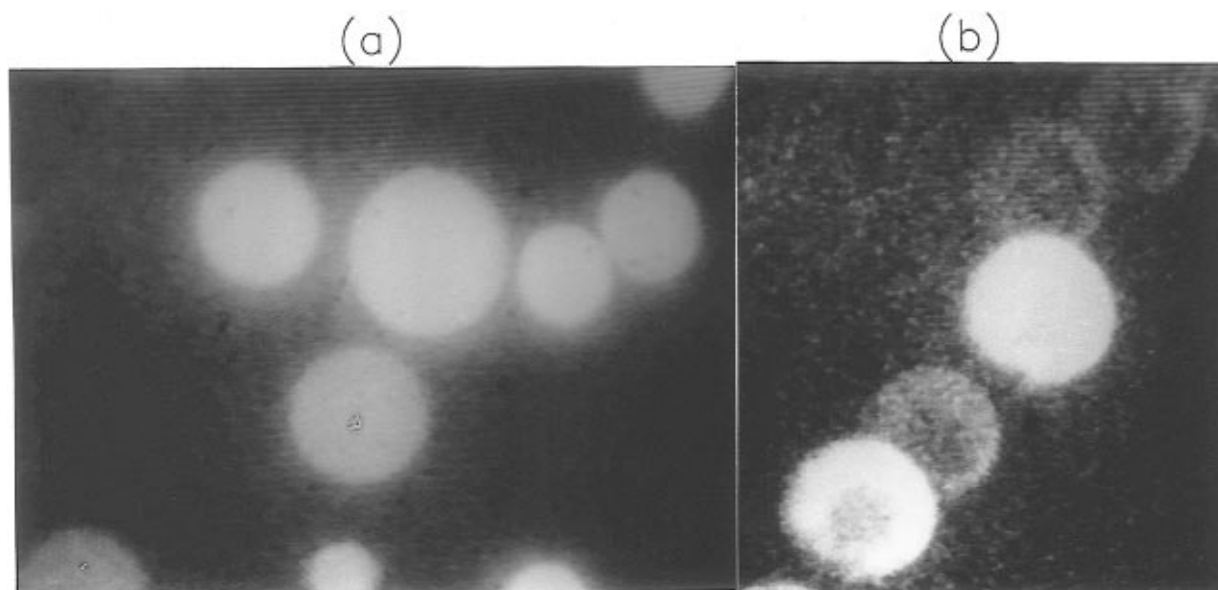


Figure 2. Images of 8CB monolayer under a fluorescence microscope at about $10 \text{ \AA}^2/\text{A/M}$. (a) D_2 domains at $25 \text{ }^\circ\text{C}$. The different intensity levels indicate different thicknesses (fraction of a micrometer). Scale of the image: $1450 \text{ }\mu\text{m} \times 1100 \text{ }\mu\text{m}$. (b) D_3 domains at $30 \text{ }^\circ\text{C}$. Here some domains are in focus while others are out of focus. Scale of the image: $550 \text{ }\mu\text{m} \times 600 \text{ }\mu\text{m}$. In these pictures, the dark background (which appeared gray under the microscope) represents a D_1 domain.

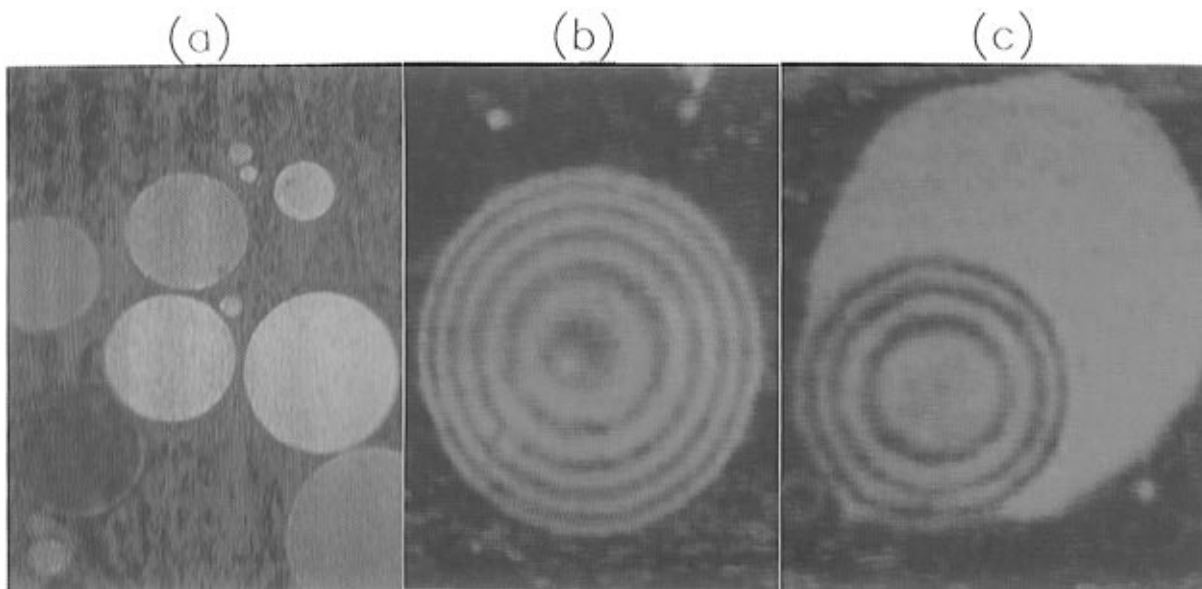


Figure 3. Images of 8CB domains at about $10 \text{ \AA}^2/\text{A/M}$ under a reflection microscope. (a) D_2 domains at $25 \text{ }^\circ\text{C}$. The different colors indicate different thicknesses. The uniform color of each domain indicates its optical flatness. Scale of the image: $810 \text{ }\mu\text{m} \times 1100 \text{ }\mu\text{m}$. (b) A lens-shaped D_3 domain at $30 \text{ }^\circ\text{C}$. Scale of the image: $200 \text{ }\mu\text{m} \times 300 \text{ }\mu\text{m}$. (c) The domain shown in (b) on cooling to $28 \text{ }^\circ\text{C}$. An optically flat D_2 domain growing out of the lens-shaped D_3 domain. Scale of the image: $240 \text{ }\mu\text{m} \times 300 \text{ }\mu\text{m}$.

To characterize the 3D phases, we used epifluorescence,¹² reflection and polarizing microscopy. For fluorescence, a dye 4-(hexadecylamino)-7-nitrobenz-2-oxa-1,3-diazole (obtained from Molecular Probes, USA) was added to get a molar concentration of 0.5% in 8CB. The monolayer was directly observed under the microscope (Leitz, Metallux 3). The images were obtained using a photon-intensified CCD camera (Model P 46036A/V22, EEV, England) and viewed on a Sony color monitor. For reflection studies, the same Leitz microscope was used with a reflection mode adapter. In a polarizing microscopic (Leitz, orthoplan) study, the monolayer was formed by depositing an appropriate amount of 8CB solution, to get required area per molecule (A/M), on Millipore water contained in a circular glass trough (diameter 10 cm). The glass trough facilitated the transmission study of

the domain textures in a parallel beam of light between crossed polaroids. In reflection and polarizing microscopy, images were obtained using a color CCD camera (Sony) and viewed on a color monitor.

Results and Discussions

The surface pressure (π)–area (A) isotherms at different temperatures are shown in Figure 1. The plateau at A/M greater than 60 \AA^2 represents the gas and liquid expanded (LE) two-phase region. The region with steeply increasing π ($A/M \approx 48\text{--}55 \text{ \AA}^2$) is the LE phase. The region below $A/M \approx 48 \text{ \AA}^2$ corresponds to the coexisting LE and 3D domains. We found that below $28 \text{ }^\circ\text{C}$, the slope of the isotherm between 20 \AA^2 and $48 \text{ \AA}^2/\text{A/M}$ was sensitive to the compression rate. Incidentally, only for fast compressions ($0.1(\text{ \AA}^2/\text{molecule})/\text{s}$), this region was nearly a plateau, as observed by Xue *et al.*⁴

(11) Adamson, A. W. *Physical Chemistry of Surfaces*, 5th ed.; John Wiley Sons: New York, 1990.

(12) Knobler, C. M. *Adv. Chem. Phys.* **1990**, *77*, 397.

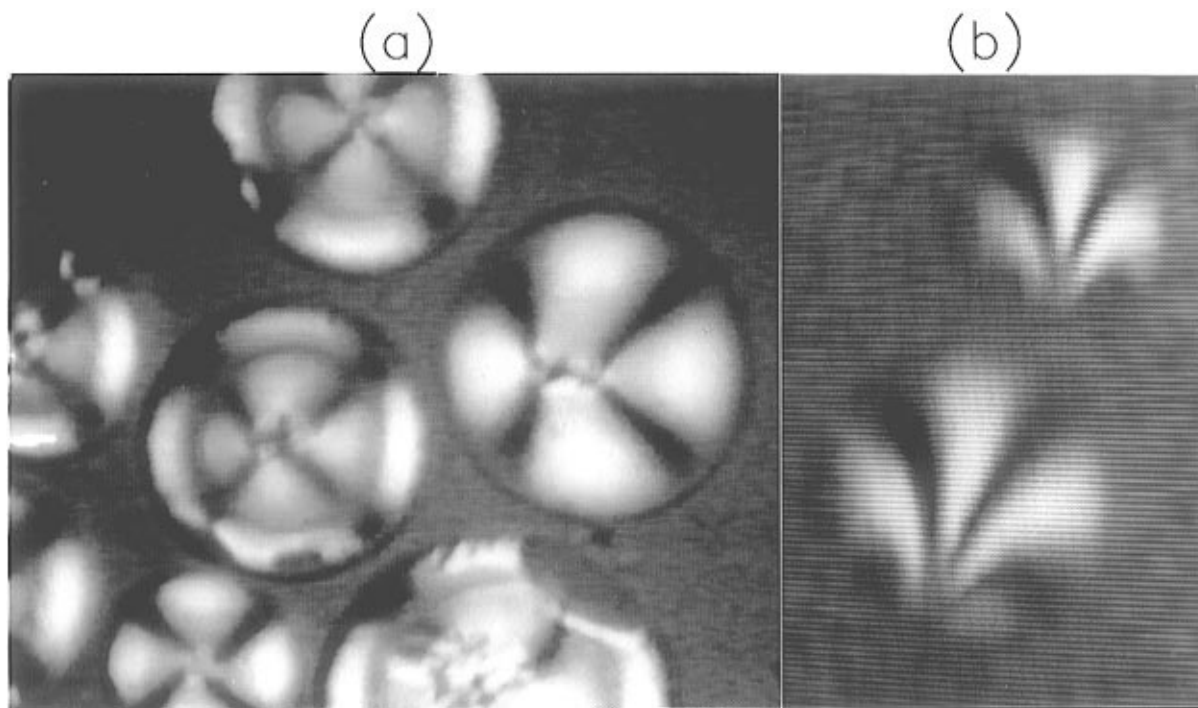


Figure 4. Images of 8CB domains at 30 °C around $10 \text{ \AA}^2 \text{ A/M}$ under a polarizing microscope. (a) Schlieren textures. The extreme right domain shows a pair of $1/2$ strength defects, and the one at the bottom left shows a $+1$ defect. Scale of the image: $300 \mu\text{m} \times 260 \mu\text{m}$. (b) Two boojum defects. Scale of the image: $105 \mu\text{m} \times 160 \mu\text{m}$.

To characterize the phases indicated by π - A studies, we first employed epifluorescence microscopy. Under the microscope, in the gas and LE coexistence region, the LE phase appeared bright compared to the gas phase, which appeared dark. In general, the intensity contrast has been attributed¹³ to differences in the solubility of the dye in different phases. However, in the case of the gas and LE phases, the contrast has also been attributed¹² to the differences in density and the quenching of the dye in the gas phase. On compression of the monolayer in the coexistence region, the whole monolayer became uniformly bright ($A/M \approx 55 \text{ \AA}^2$), indicating the onset of the LE phase. At temperatures below 28 °C, circular domains (D_1) brighter than the background LE phase appeared on compressing to $48 \text{ \AA}^2 \text{ A/M}$. In view of earlier studies⁴⁻⁷ on 8CB, we expect D_1 domains to correspond to a “three-layer” structure. On further compression, even before this structure occupied the entire surface, we observed, around $20 \text{ \AA}^2 \text{ A/M}$, the formation of new and still brighter domains (D_2) with different intensity levels (Figure 2a). Under similar conditions, Brewster angle microscopic studies⁶ on 8CB indicate the occurrence of domains of different thicknesses. On this basis, we suggest that the different intensities of the D_2 domains are due to their different thicknesses. Very interestingly, the D_2 and D_1 domains coexisted along with the LE phase. Also they were seen in focus in the same plane. In our microscope, with vertical traveling facility, defocusing due to a height difference of $1 \mu\text{m}$ or more could be detected. Hence, we inferred the thicknesses of the D_2 domains to be less than a micrometer. Between 28 and 36 °C, on compression, D_1 domains appeared in the LE phase around $45 \text{ \AA}^2 \text{ A/M}$ and coexisted with the LE phase. Further, around $20 \text{ \AA}^2 \text{ A/M}$, instead of the large D_2 domains, we observed smaller domains (D_3) of much higher brightness and thickness. Also they were of different thicknesses as they were seen in focus at different focal planes (Figure 2b). This effect was made use of to determine the thicknesses of these

domains. The thicknesses were in the range 1–40 μm . Above 36 °C, on compression, D_3 domains appeared in the LE phase around $45 \text{ \AA}^2 \text{ A/M}$, and coexisted with the LE phase. On expansion, these domains disappeared slowly giving rise to the LE phase. However, we found hysteresis in the actual π - A isotherm.

We undertook reflection microscopy to study the surface topography of D_2 and D_3 domains. In reflection, the LE phase and the D_1 domains were not visible. When the monolayer was compressed below $20 \text{ \AA}^2 \text{ A/M}$, either D_2 or D_3 domains were seen depending on temperature. Below 28 °C, the D_2 domains exhibited different but uniform colors (Figure 3a). The uniformity of color in a domain indicated its optical flatness. The interference colors indicated the domain thicknesses to be at least $\lambda/2n$ (λ = wavelength of light and n = effective refractive index of the domain). From this result and our epifluorescence observations, we estimated the thicknesses of the D_2 domains to be of the order of a fraction of a micrometer. Above 28 °C, the D_2 domains changed to D_3 and developed interference rings (Figure 3b). The rings were due to the interference between light reflected from the air–domain interface and the domain–water interface. The ring structure indicated varying thickness. On heating, each such domain decreased in size (area) while the number of rings increased. This indicated growth of the domain in the third dimension. These features were seen even up to 40 °C. On cooling, around 28 °C, the rings slowly disappeared giving rise to a uniformly colored region of much larger area (Figure 3c). This indicated a transition from D_3 to D_2 domains. The results of fluorescence and reflection studies did not depend upon whether the LE phase was first heated and then compressed to $20 \text{ \AA}^2 \text{ A/M}$ or first compressed and then heated.

To identify the phases in the domains, we studied the monolayer in transmission. In this study, the domains were visible only for A/M less than 20 \AA^2 . Below 28 °C, we saw large transparent D_2 domains. At temperatures above 28 °C, these transformed into D_3 domains with

(13) Qiu, X.; Ruiz-Garcia, J.; Stine, K. J.; Knobler, C. M.; Selinger, J. V. *Phys. Rev. Lett.* **1991**, *67*, 703.

schlieren textures¹⁴ typical of a nematic phase with defects of strength ± 1 and $\pm 1/2$ (Figure 4a). Interestingly, we also observed in some domains a boojum-like texture^{15,16} which corresponds to a point singularity on the domain surface. Some of the boojums were stable (Figure 4b) while others changed over to schlieren textures. Such changes in textures demonstrated that the director field gets easily deformed as in normal nematics. Above 36 °C, the textures in D₃ domains disappeared. These transparent D₃ domains cast shadows which indicated a convex lens shape. On cooling, the schlieren textures reappeared in these domains around 36 °C. On further cooling, below 28 °C, the D₃ domains changed to D₂ in which the textures disappeared over most of the area except for a few defects at the periphery of the domains.

An attempt to clearly distinguish the D₃ domains that occur above 36 °C from the D₂ domains through conoscopy was not very successful. However, in convergent light, between crossed polaroids, the D₂ domains exhibited colors of nonuniform intensity, while the D₃ domains above 36 °C were colorless. This indicated that the D₂ domains were birefringent, while above 36 °C the D₃ domains were isotropic. These observations and the optical flatness as seen in reflection suggest that the D₂ domains were most likely in the smectic A phase.

From these different observations, we infer that the 3D domains found for A/M less than 20 Å² exhibit different phases depending on temperature. Below 28 °C, these domains are flat and have a smectic A order. In the range 28–36 °C they become lens shaped with a nematic order, and above 36 °C the domains possess isotropic order. These transition temperatures are lower compared to those exhibited by pure 8CB in bulk. These temperatures are reproducible and do not depend on the thickness of the subphase (water) below the monolayer. The shift in the transition temperatures is very likely to be due to the presence of water in the bilayers constituting the LCr domains. The presence of water in the films has been suggested by Xue *et al.*⁴ based on their experiments. de Mul and Mann⁶ have also considered factors like water content of the bilayers.

(14) Demus, D.; Richter, L. *Textures of Liquid Crystals*; Verlag Chemie: Weinheim and New York, 1978.

(15) Riviere, S.; Meunier, J. *Phys. Rev. Lett.* **1995**, *74*, 2495.

(16) Galatola, P.; Fournier, J. B. *Phys. Rev. Lett.* **1995**, *75*, 3297.

Interestingly, at any temperature, on increasing the area per molecule these domains smoothly transform to the LE phase. It appears that the transition between the monolayer state and the 3D islands results from the competition between the energy of adsorption on the air–water interface and the cohesive intermolecular forces of bulk phases. Our experiments indicate that the mechanical compression of the Langmuir monolayer allows the variation of energy of adsorption continuously. The formation of a stable 8CB monolayer in the LE phase can be attributed to the strong attractive interaction between the polar group of the molecules and water. The mechanisms involved in the formation of the 3D liquid crystalline phase are more complicated. At high surface molecular density, the energy of adsorption becomes weaker as the molecules change their orientation with respect to the interface.¹⁷ This can favor the formation of 3D islands. However, more studies are required to understand the different mechanisms involved in the process.

Conclusion

Our studies show that the 8CB monolayer evolves continuously into an LCr phase on compression. This transformation from the monolayer to the LCr phase on compression and the reverse transformation to monolayer on expansion indicates that the molecular organization can be continuously tuned by the surface molecular density. This is the first demonstration of the formation of a 3D liquid crystalline phase at the air–water interface starting from a monolayer. Our results may be interpreted to indicate that at high area per molecule, the intermolecular forces that stabilize the monolayer dominate, resulting in adhesion of molecules to the subphase, while at low area per molecule, the intermolecular forces that result in liquid crystals dominate leading to a 3D cohesion of molecules.

Acknowledgment. We thank G. S. Ranganath for helpful discussions.

LA960574A

(17) Thanks are due to a reviewer for helpful views on this point.