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L. Komitov^a, B. Stebler^a, G. Gabrielli^b, M. Puggelli^b, A. Sparavigna^c & A. Strigazzi^c

^a Physics Department, Chalmers University of Technology, S-41296, Göteborg, Sweden

^b Chemistry Department, University of Florence, 1-50121, Firenze, Italy

^c Physics Department, Polytechnic of Turin, 1-10129, Torino, Italy

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Amphiphilic Langmuir-Blodgett Films as a New Tool for Inducing Alignment Transition in Nematics

L. KOMITOV and B. STEBLER

Physics Department, Chalmers University of Technology, S-41296 Göteborg, Sweden

and

G. GABRIELLI and M. PUGGELLI

Chemistry Department, University of Florence, I-50121 Firenze, Italy

and

A. SPARAVIGNA and A. STRIGAZZI

Physics Department, Polytechnic of Turin, I-10129 Torino, Italy

Mono- or multilayers of egg lecithin, distearoylphosphatidylcholine lecithin (DSPC-L), dimiristoylphosphatidylcholine lecithin (DMPC-L) and stearic acid (SA) deposited by Langmuir-Blodgett technique were used as aligning films in a nematic liquid crystal cell for obtaining a uniform homeotropic orientation and a temperature driven surface transition close to the clearing point. An excellent homeotropic alignment of the liquid crystal was obtained when a monolayer of DMPC-L, DSPC-L or SA was used. In these cases, a sharp and reversible transition from the homeotropic orientation to a set of circular domains, where the liquid crystal molecules have a degenerate quasi-planar alignment, was observed a few tenths of a degree below the nematic-isotropic phase transition.

Keywords: Langmuir-Blodgett films, surface transition, nematics

INTRODUCTION

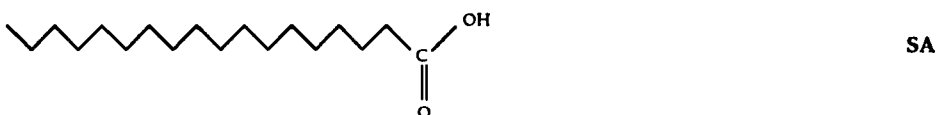
The alignment and the anchoring strength of liquid crystal molecules at the confining surfaces are playing a vital role for the functioning of liquid crystal displays. Therefore, a lot of attention was given to these topics during the last decade. Among the various techniques used so far for achieving a high degree of uniformity in the alignment of liquid crystal molecules, only the Langmuir-Blodgett technique is capable of ensuring a deposition of organic aligning films with controlled molecular order and thickness, in addition to a very high reproducibility. Mono- and multilayers of amphiphiles, such as lecithin, are known to produce an excellent homeotropic alignment of the molecules in liquid crystal layers.^{1–3} Recently, a surface

induced transition from homeotropic to planar orientation was observed in a nematic liquid crystal layer when a thin lecithin film was used for alignment purposes.^{4,5} The transition was found to take place above a critical temperature T_c , in most cases several degrees below the clearing point T_{N-I} of the liquid crystal. The transition was reversible without or with hysteresis, depending on the initial alignment conditions. However, the technique used in these cases, by dipping the glass substrates into diluted solution of lecithin in chloroform, was not capable of assuring a controlled thickness or molecular order of the lecithin films. Therefore, for a more detailed study of the alignment transition, we utilized amphiphilic films, deposited by Langmuir-Blodgett technique, as aligning layers.

In this paper, we present the results of our investigations on the alignment transition, when mono or multilayers of several different amphiphilic materials were used.

EXPERIMENTAL

The cells used in our experiments were of the conventional sandwich type consisting of two parallel glass or quartz substrates kept by Mylar spacers at a distance of about 12 μm . On the inner surfaces of the substrates identical mono- or multi-amphiphilic layers were deposited as aligning films, i.e., the experimental cells possessed symmetric boundary conditions. The liquid crystal material used in our study was ZLI 2585 (Merck) with a nematic phase in the temperature interval from -20°C to 70°C . It was introduced into the cells by the capillar forces. Egg lecithin, distearoylphosphatidylcholine lecithin (DSPC-L), dimiristoylphosphatidylcholine lecithin (DMPC-L) and stearic acid (SA) were chosen as materials for the aligning films, deposited by Langmuir-Blodgett technique. As known, egg lecithin is a mixture of several different phosphatidylcholines possessing a hydrophilic group (polar head), soluble in water, and hydrophobic alkyl chains of different lengths and structures, unsoluble in water. DSPC-L, DMPC-L and SA were chosen because of their well defined steric structures (Figure 1). DSPC-L has two rigid aliphatic chains with 18 carbon atoms, as long as the one of SA, whereas DMPC-L has two shorter and more flexible aliphatic chains with 14 carbon atoms each, like the myristic acid (MA). Both substances have the same phosphatidylcholine polar head.⁶ SA was chosen because of the simple structure, with a carboxylic polar (hydrophilic) head and one aliphatic chain with 18 carbon atoms. All these substances are capable of forming stable spreading monolayers at the water-air interface, where the amphiphilic molecules are lying with their polar groups into the water and with the hydrocarbon chains upright toward the air. Especially, SA forms a very condensed monolayer at the water-air interface which could easily be transferred onto a solid support with hydrocarbon chains almost perpendicular to the solid surface. In order to cover the surface of solid substrate with mono- or multilayers, Langmuir's sequence must be performed. The first step is, to prepare in a condensed phase a monolayer of the chosen substance, spread all over the water-air interface. Next, the monolayer is transferred from the liquid support onto the solid substrate by means of extraction or immersion of the substrate at a controlled



	DSPC-L	DMPC-L	SA
A_o (\AA^2)	25	35	20
$1/C_S$ (mN/m)	90	36	80

FIGURE 1 Structural formulae of DSPC-L, DMPC-L and SA, along with table of the limiting area A_0 (\AA^2), corresponding to the in-plane cross section of one aliphatic chain, and the modulus of surface compressibility $1/C_s$ (mN/m), characterizing the Langmuir-Blodgett monolayer onto the liquid support.

speed, keeping the surface pressure constant. Repeating these procedures, it is possible to overlap several monolayers in a multilayer structure with a desired order. The monolayers of the four substances listed above were obtained by spreading their chloroform solutions on a liquid support which in our experiments was bidistilled water with 10^{-2} mol NaCl. The surface pressure as a function of the area per molecule was measured by the Wilhelmy method, using a discontinuous compression in order to achieve a surface equilibrium. A compression rate of 40

cm^2/min was chosen in order to obtain the surface equilibrium for each value of the pressure and of the effective area per molecule. The spreading isotherms were taken at room temperature (20°C). Since the surfaces of the substrates used, like glass (covered or not with SiO_x) and quartz, were hydrophilic, the deposition of the first monolayer by Langmuir-Blodgett technique was done by extraction of the solid substrate immersed in the water support through the water-air interface, where the monolayer was spread. Therefore, during the transferring procedure, the molecules of amphiphilic substances will start to attach themselves to the solid substrate with their polar head groups, whereas their hydrocarbon chains will point towards the air, being almost perpendicular to the substrate surface. The transfer of the monolayer was performed by a Joyce-Loebl Model 4 instrument⁷ using an extraction speed of $1 \text{ cm}/\text{min}$. On Figure 1 are shown the limiting area A_0 corresponding to the in-plane effective cross section of one aliphatic chain, obtained by extrapolation of the linear part of the spreading isotherms⁸ at high pressure and the modulus of surface compressibility C_s^{-1} , an important characteristic of the actual surface phase.⁹

In the case of egg lecithin, the monolayer spread onto water support exhibited several surface phases which were more stable the more they were condensed. The transferring pressure in this case was chosen in the most condensed zone of the isotherm. In the case of SA, the limiting area A_0 corresponds almost to the cross section of the aliphatic chain (20 \AA^2), indicating an average vertical orientation of the chains with respect to the water-air interface and thus a presence of a condensed phase, which was confirmed by the ellipsometric investigations.¹⁰ In the case of DSPC-L, the obtained value of 25 \AA^2 for the limiting area A_0 is somewhat higher than the one corresponding to the vertical orientation of the hydrophobic chains, which indicates a small tilt of both chains. On the other hand, in the case of DMPC-L, the value of the limiting area of about 35 \AA^2 per chain indicates a less rigid orientation of the chains, i.e., a chain's orientation is more tilted with respect to the water-air interface⁶ and consequently indicates the presence of a more expanded monolayer. The compressibility coefficients show the existence of a more condensed phase in the case of DSPC-L and a more expanded one in the case of DMPC-L, as one could expect from the difference in the length of their hydrophobic chains. Therefore, a surface pressure of $13.5 \text{ mN}/\text{m}$ was used for transferring mono- or multi-layers of SA and DSPC-L, whereas a pressure of $11.5 \text{ mN}/\text{m}$ was used in the case of DMPC-L.

MONOLAYERS OF EGG LECITHIN

Monolayers of egg lecithin were deposited on two different types of substrate-quartz and glass. The surface of the glass substrates was covered with a 150 \AA thick layer of SiO_x obliquely evaporated at 60° with respect to the substrate normal. The liquid crystal material was introduced into the cells in the nematic phase by the capillary forces. The liquid crystal flow during filling the cell was coinciding with the pulling direction of the monolayer. The initial alignment of the liquid crystal molecules in the quartz cell was predominantly reversely pretilted quasi-planar, i.e., in this case, a splay deformation was present.^{11,12} A set of micro-sized spots,

about 1 μm , was found to cover the whole area of the virgin quartz cell (before undergoing the nematic-isotropic transition) (Figure 2). The spots had a color different from those of the surrounding, an indication of difference in the molecular tilt. It was found that the molecular tilt had a preferred direction coinciding with the pulling direction of the monolayer. On heating, a continuous change of color in both, spots and surrounding area, took place, thus indicating a gradual change in the birefringence and in the molecular tilt as well (Figure 3).

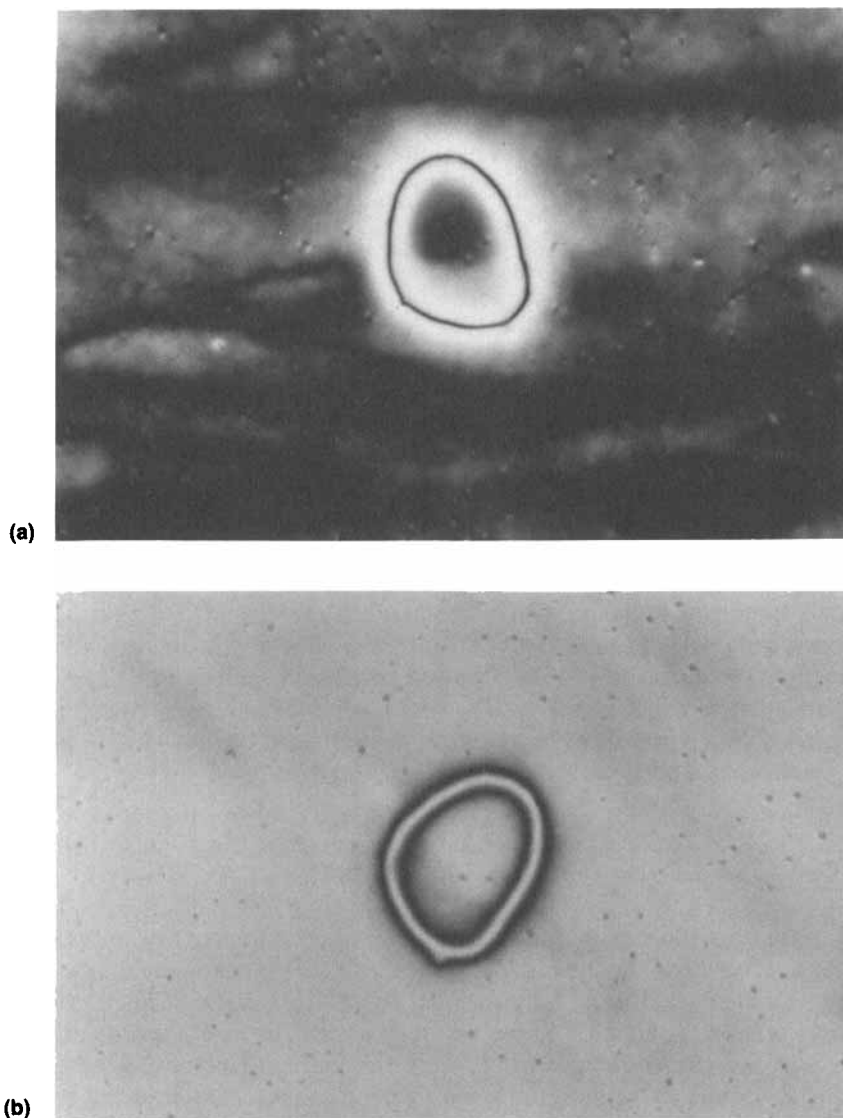


FIGURE 2 Nematic liquid crystal cell with egg lecithin monolayer as an aligning film, placed between crossed polarizers, in a position (a) with the preferred direction of orientation parallel to the transmission direction of the polarizer and (b) rotated at 45 degrees. In the spots, the molecular tilt angle with respect to the substrate surface is larger than in the surrounding area. See Color Plate I.

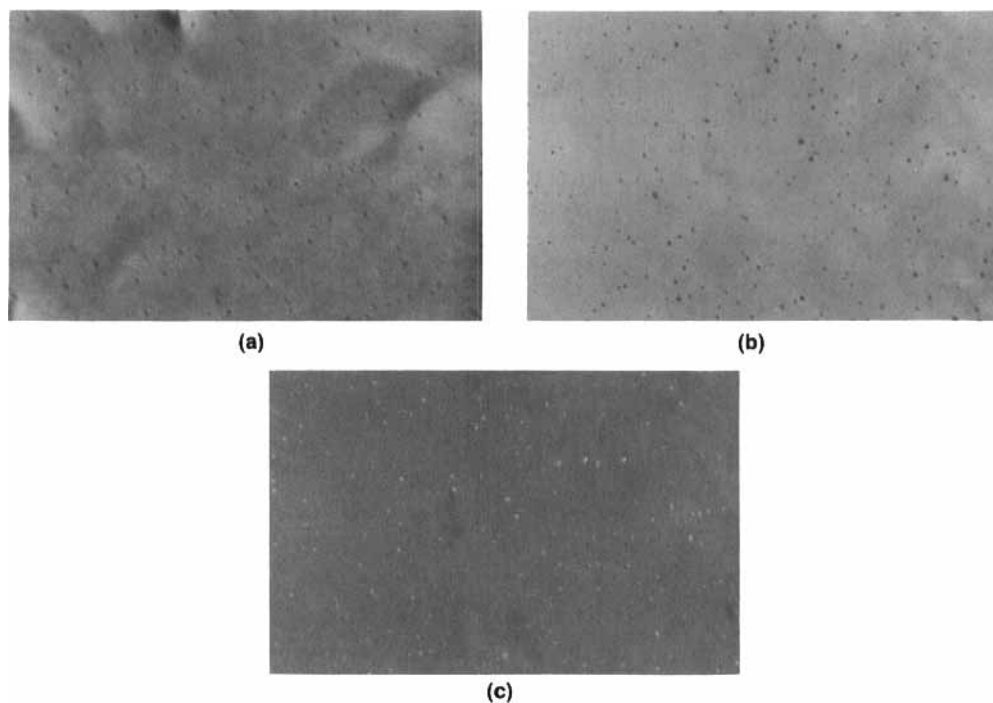


FIGURE 3 The cell from Figure 2 at different temperatures (a) 22°C, (b) 58°C and (c) 67°C. The interference colors of both spots and surrounding area are changing due to the diminishing of the birefringence Δn and the molecular tilt with increasing temperature. The molecular tilt angle in the spots remains larger than in the surrounding area. See Color Plate II.

Poor homeotropic alignment was observed in the cell with glass substrates the inner surfaces of which were covered with a thin SiO_x layer. In this cell, a continuous alignment transition from homeotropic to planar took place on heating and was found to be reversible. Moreover, the initial homeotropic alignment in the cell disappeared after a couple of months and was replaced by poor quasi-planar alignment, indicating a partial dilution of the lecithin into the liquid crystal.

MONOLAYERS OF DSPC-L, DMPC-L AND SA

Monolayers of DSPC-L, DMPC-L and SA were deposited onto ordinary soda glass substrates after carefully cleaning their surfaces. The character of the observed alignment transition in the cells with the monolayers of DSPC-L, DMPC-L and SA, respectively, as aligning films, was quite different from the one taking place in the above mentioned cases. First of all, the initial alignment in these cells was found to be perfectly homeotropic, with a complete extinction of the transmitted light on cell rotation between crossed polarizers. Secondly, on heating, a sharp transition from the low temperature homeotropic alignment to a set of bright circular domains was observed to take place in all these three cases in a very narrow temperature range, just below the clearing point. The transition resembled a first

order one, like the nematic-isotropic phase transition, and it was reversible and reproducible, with a small temperature hysteresis (about 0.9°C). The alignment transition in the cell, placed between crossed polarizers, with a DMPC-L monolayer as an alignment film, is illustrated in Figure 4. At low temperatures the initial alignment in the cell, as mentioned above, was homeotropic and thus optically

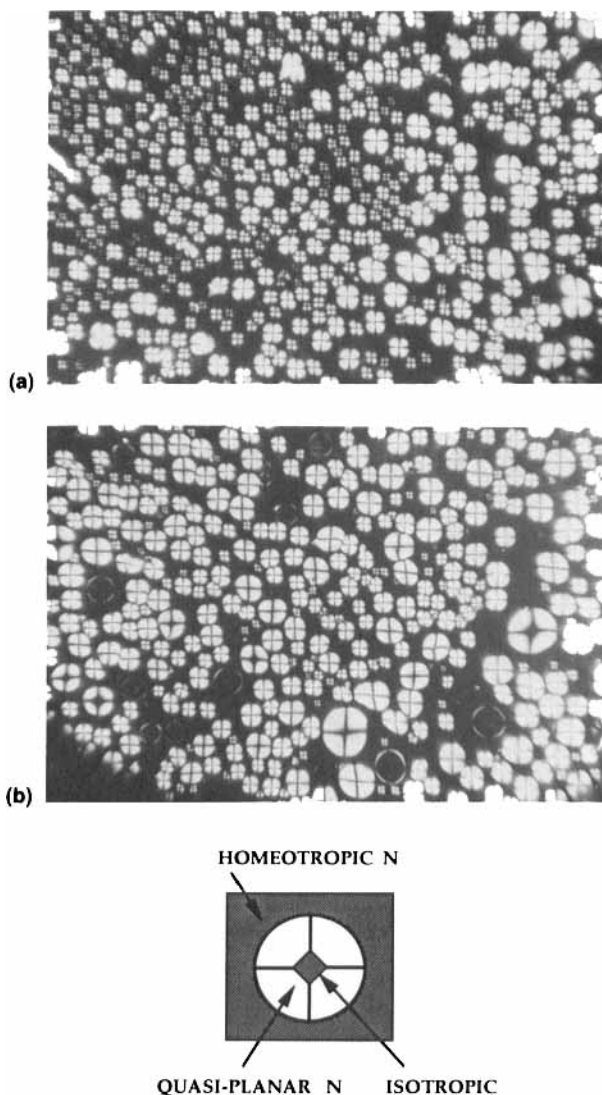


FIGURE 4 Nematic liquid crystal cell with DMPC-L monolayer as an aligning film, placed between crossed polarizers, on heating. (a) The temperature driven alignment transition of the liquid crystal molecules from a homeotropic orientation to a set of circular domains with a quasi-planar degenerated alignment takes place near the clearing point T_{N-I} . The domains are surrounded by the nematic phase with homeotropic orientation (the dark area). (b) Appearance of the isotropic phase inside the domains. Some domains are coalesced, thus forming larger sized ones. The temperature increases from (a) to (b). See Color Plate III.

dark. On heating, just 0.5°C below the nematic-isotropic transition, a set of bright circular domains with dark crosses covered the cell area. If the temperature was held constant for a while, then some of the domains coalesced, thus forming larger domains. Increasing the temperature further, the transition to the isotropic phase took place, first inside the domains, as shown in Figure 4. On cooling from the isotropic phase, the nematic phase appeared in the form of the same set of bright

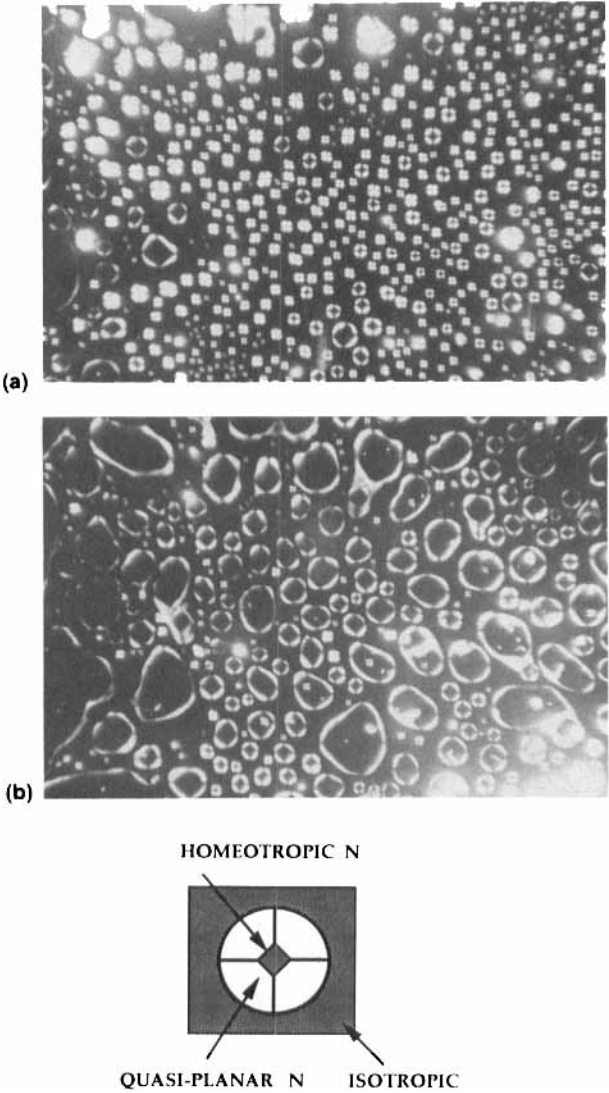


FIGURE 5 Alignment transition in the cell from Figure 4 under cooling. (a) The beginning of the nematic-isotropic phase transition. The nematic phase appears as a set of circular domains with a quasi-planar degenerated alignment of the molecules. The domains are surrounded by the isotropic phase and the alignment transition from quasi-planar to homeotropic takes place inside the domains. (b) With the coalescence of the domains the area with homeotropic orientation of the nematic phase increases. The temperature decreases from (a) to (b). See Color Plate IV.

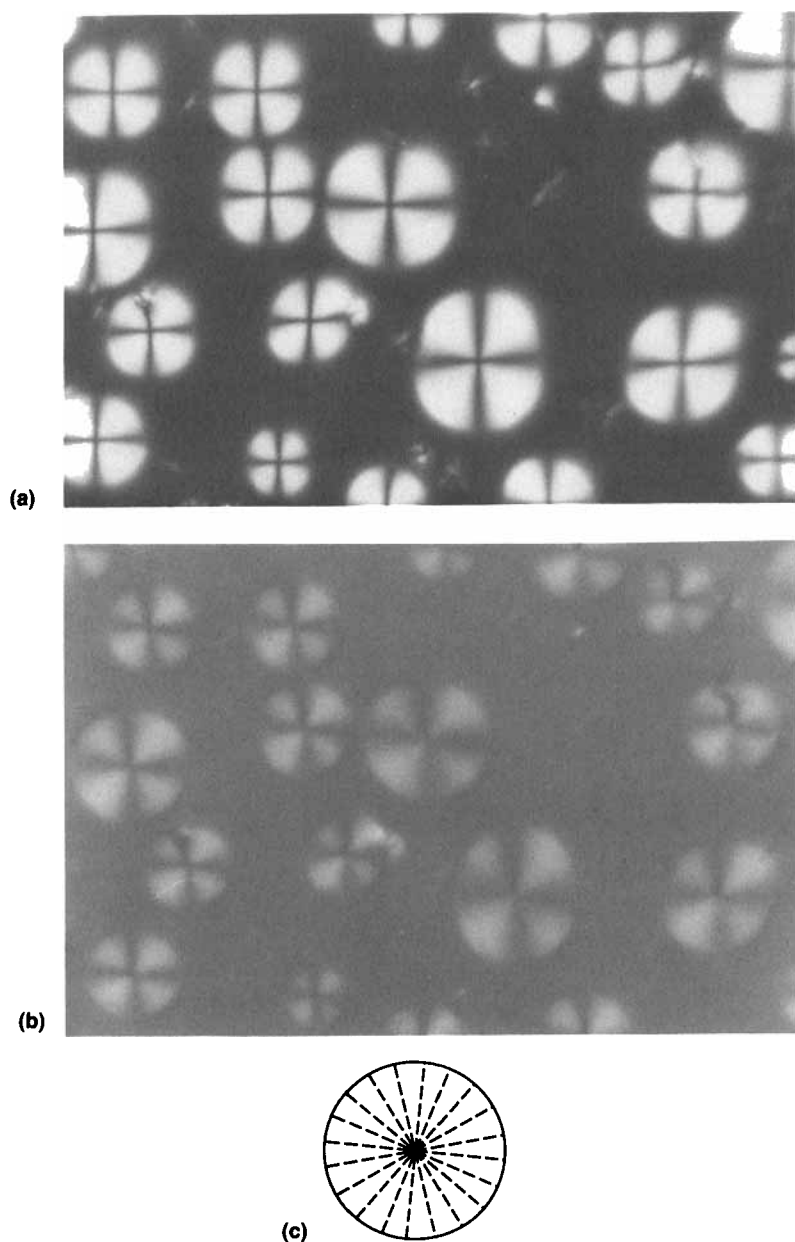


FIGURE 6 Alignment transition to the cell from Figure 4 between crossed polarizers, on heating. (a) Without and (b) with $\frac{1}{4}$ wave plate. (c) The director field inside the domains (star configuration). See Color Plate V.

circular domains like the one on heating. However, now, the domains were surrounded by isotropic phase. A tendency to domain coalescence with time was observed also in this case. Decreasing the temperature further, an alignment transition to homeotropic orientation took place inside the domains, spreading quickly

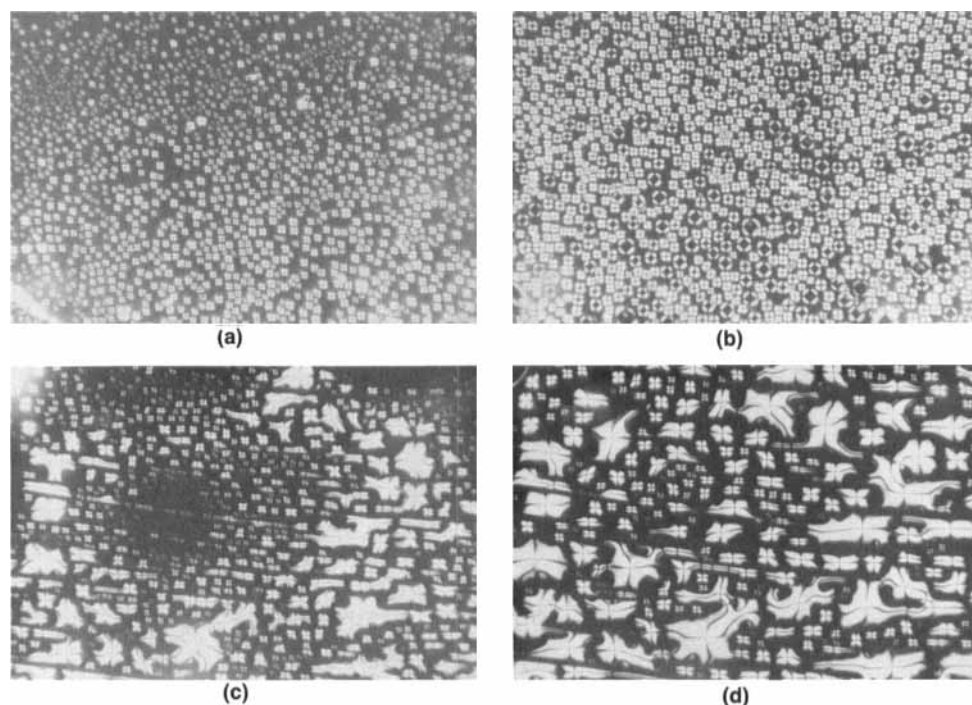


FIGURE 7 Alignment transition in the nematic liquid crystal cell with SA monolayer as an aligning film, placed between crossed polarizers, on heating. (a) The beginning of the transition. The size of the domains with quasi-planar degenerated alignment of the liquid crystal molecules is smaller than the corresponding ones in the cells with DSPC-L or DMPC-L aligning monolayers. (b) Coalescence of the domains with germs of isotropic phase inside them. On cooling from the isotropic phase (c) the domains with nematic phase, possessing a quasi-planar degenerated alignment of liquid crystal molecules, mostly have an elongated shape along the pulling direction of the substrates and they form a set of regular arrays. (d) Coalescence of the domains with decreasing temperature. See Color Plate VI.

in the whole of their volume (Figure 5). We investigated the character of the liquid crystal alignment in the bright domains by means of a $\frac{1}{4}$ wave plate (Figure 6). It was found that the molecules there possessed a degenerate quasi-planar alignment with a local preferred direction along the radius of the domain. Here, we would like to underline that besides the similarities, there are several important differences in the alignment transitions taking place in these three cases. First, the domains with the smallest initial size were found in the case of SA monolayer (Figure 7) while the largest domains were found in the case of DSPC-L monolayer (Figure 8). Second, while the alignment transition in those three cases on heating appeared in the form of a set of bright circular domains, during cooling the domains in the case of SA monolayer had more or less elongated form but with the same type of degenerate alignment of the liquid crystal molecules like the one in the circular domains depicted in Figure 6. Moreover, the domains in the cell with SA aligning layer appeared more or less regularly ordered with a preferred direction along the one of drawing the substrate as one can see on Figure 7. However, the character of the alignment transition changed with time, less in the case of DSPC-L and DMPC-L monolayers and more in the case of SA monolayers. After a couple of

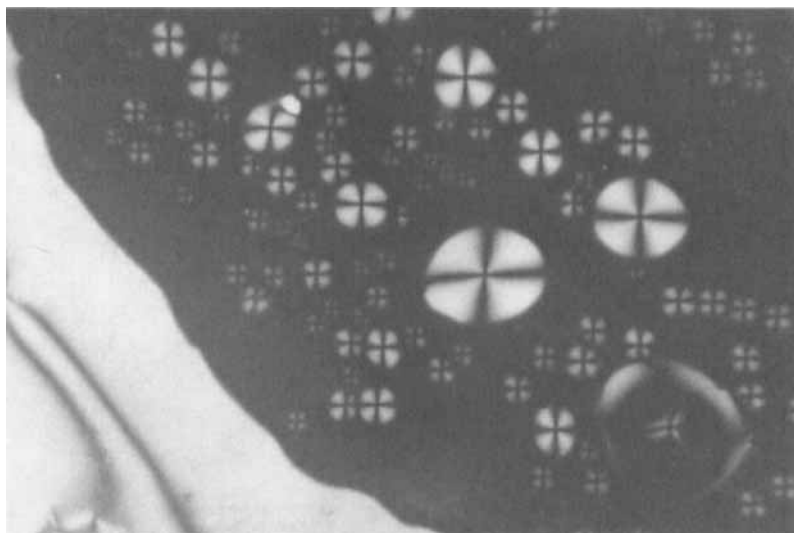


FIGURE 8 Alignment transition in the nematic liquid crystal cell with DSPC-L monolayer as an aligning film, placed between crossed polarizers, on heating. Note the presence of large circular domains with a quasi-planar degenerated alignment of the liquid crystal molecules. See Color Plate VII.

months, the form of the domains, appearing during the alignment transition in the cell with DSPC-L monolayer, became more elongated but without any change in the degenerate character of the alignment of the liquid crystal molecules inside the domains. In the other two cases a certain change of this alignment, especially marked in the cell with SA monolayer, took place. In the cell with DMPC-L monolayer the alignment transition changed partially its character only on cooling, when some of the circular domains appeared with a molecular alignment the director of which was along the domain meridians. However, instead of a set of bright domains appearing, a continuous type of alignment transition was found to take place on heating the cell with SA aligning monolayer. The nematic phase appeared in the form of circular domains but now with a degenerate quasi-planar molecular alignment possessing a local preferred direction following the meridians of the domains, only on cooling, as illustrated in Figure 9.

MULTILAYERS OF SA

The alignment transition taking place in a cell with aligning film built up of five layers of SA, deposited on both substrate surfaces by Langmuir-Blodgett technique, was found to be similar to the one observed in the cell with only one SA aligning monolayer (Figure 10). The only difference was that the transition in this case did not change its character significantly with time.

DISCUSSION

Although the inner surfaces of the quartz cell were covered with an egg lecithin monolayer, no homeotropic alignment of the liquid crystal molecules was observed

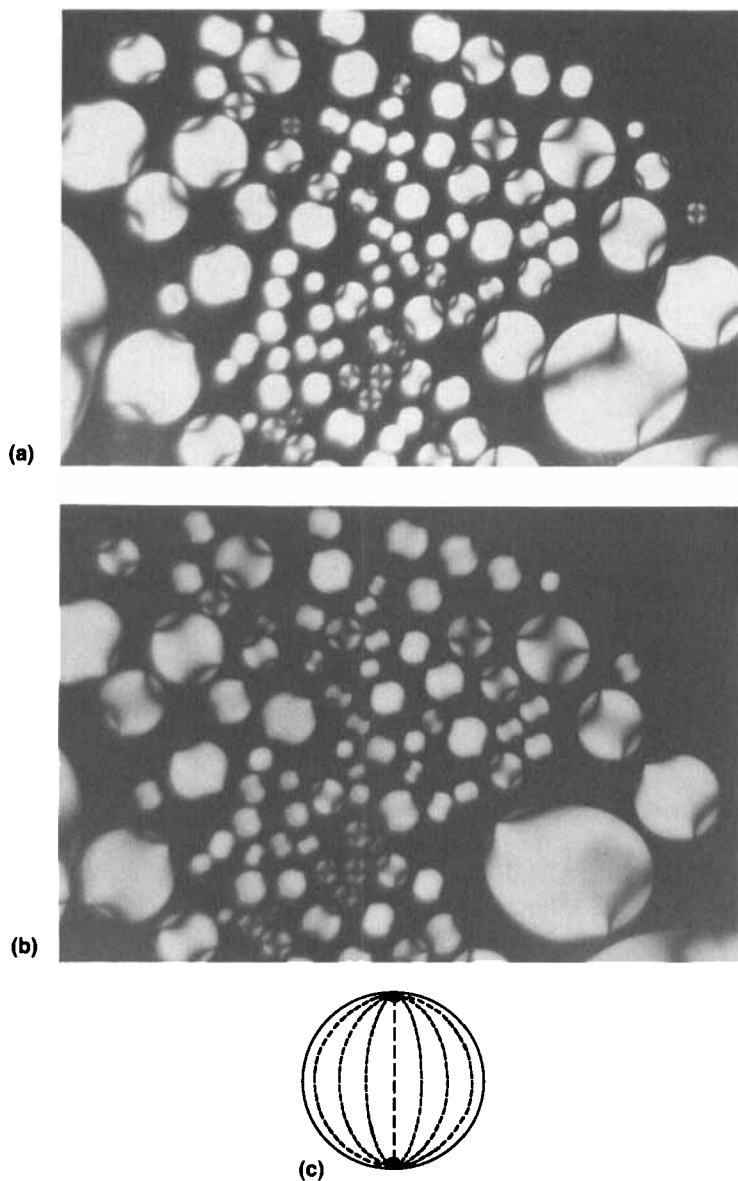


FIGURE 9 The cell from Figure 7 after a couple of months. On cooling from the isotropic phase (a) without and (b) with $\frac{1}{2}$ wave plate. (c) The director field inside the domains (bipolar configuration). See Color Plate VIII.

in this case. However, quite intense thermal fluctuations of the liquid crystal molecules were found in a large temperature interval, an indication of their weak anchoring to the solid surfaces. It is quite possible that, due to the low adhesion to the quartz material, a percentage of the lecithin molecules is solved in the liquid crystal, and thus the concentration of anchored lecithin molecules might not suffice to produce a homeotropic alignment. The optical investigations of the quartz cell

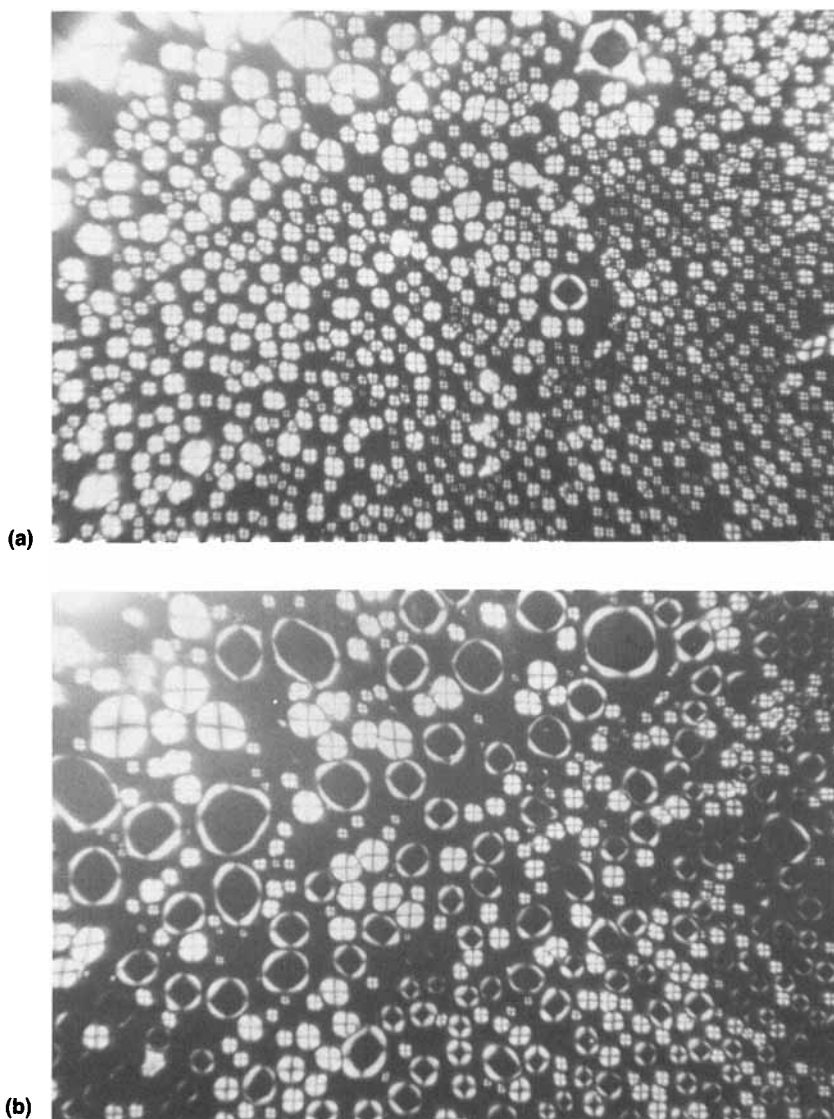


FIGURE 10 Alignment transition in the nematic liquid crystal cell with pentalayers of SA as an aligning film, placed between crossed polarizers, on heating. The character of the transition is the same as in the case of SA monolayer aligning film but it is more stable with time. The temperature is increasing from (a) to (b). See Color Plate IX.

between crossed polarizers showed that, due to the liquid crystal flow during the filling, the tails of the lecithin molecules were tilted in the opposite sense, thus creating an initially deformed alignment. In the virgin cell the tilt was very large and an initial splay deformation of the liquid crystal layer (a quasi-planar alignment), confirmed by conoscopy, took place (Figure 11). Due to the birefringence of the liquid crystal material, all the irregularities in the aligning monolayer were visualized. The color of the microsized spots observed in the quartz cell was found

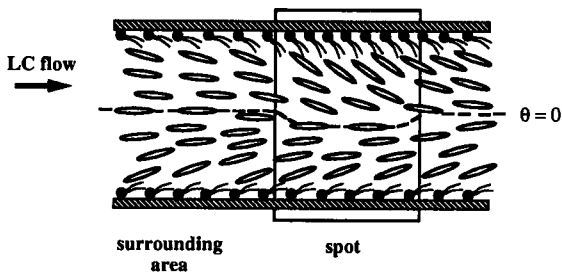


FIGURE 11 Schematic view of the nematic liquid crystal cell with egg lecithin monolayer as an aligning film. The local variation of the molecular tilt θ is a possible reason for the appearance of the spots. As a result, they have different interference colors indicating a lower effective birefringence Δn_{eff} , and higher net tilt, of the molecules inside the spots, than in the surrounding area.

to be of lower order than the one of the surrounding, which meant that the spots possessed a lower effective birefringence Δn_{eff} and thus a larger molecular tilt with respect to the substrate (Figure 11). In fact, the effective birefringence Δn_{eff} is given by

$$\Delta n_{\text{eff}} = \frac{\Delta n}{d} \int_0^d \cos^2 \theta \, dz$$

where $\theta(z)$ denotes the local tilt angle vs. the coordinate z normal to the cell plates, $\Delta n = n_e - n_o$ is the birefringence, n_e and n_o being extraordinary and ordinary refractive indices of refraction. The above relation is valid if $\Delta n \ll n_o$, as is true for the nematic material ZLI 2585. As easily seen from a M. Levy color chart,¹³ Δn_{eff} and thus the average $\langle \cos^2 \theta \rangle$ is lower in the spots than in the surrounding area, meaning that the average tilt angle $\langle \theta \rangle$ is greater in the micro-sized spots (see Figure 3). One possible reason for the existence of the spots could be that, before being transferred from the liquid support onto the solid substrate, some of the lecithins probably form small aggregates (islands) in the monolayer, thus creating a different molecular tilt in the liquid crystal layer later on. The other possible reason might be the existence of holes in the lecithin aligning monolayer. But, as reported in Reference 14, the size of the holes observed in the monolayer of lecithin was smaller than 100 Å. Therefore, they seem to be a less probable reason for the existence of the spots in the cell, the size of which was found to be about 1 μm diameter.

In the cell with substrates covered with SiO_x , due to the roughness of the SiO_x film, the effective contact surface is larger than the one of the flat quartz substrates. Therefore, one may assume that the amount of lecithin molecules per unit substrate area was higher in the cell with SiO_x aligning layer. Indeed, a poor homeotropic alignment was observed in the cell at the beginning. Later on, with time, this alignment disappeared probably for the same reason as in the previous case.

In conclusion, the monolayer of egg lecithin is not useful for obtaining a stable and uniform homeotropic alignment of the liquid crystal molecules. The reason may not simply be found in the dissolution process but it is quite possible also that the egg lecithin, being a mixture having different adhesion forces of the various

lecithin components, reacts in a complex manner during the process of transfer of the monolayer from the liquid to the solid support. It seems that the same problem of partial dissolution of the aligning monolayer in the liquid crystal material with time was also present in the other three cases, although it was not quite as pronounced there, no matter that the carboxylic polar head of SA is less polar than the phosphatidylcholine head of DSPC-L and DMPC-L. Only the properties of the aligning film consisting of five layers of SA was not affected that much by the dissolution process.

The observed difference in the equilibrium size of the bright circular domains in the cells with DSPC-L, DMPC-L or SA monolayers, respectively, might be related to the structural and packaging differences between these compounds. In fact, the most interesting question is—why the alignment transition in these cases appears in the form of circular domains, possessing a degenerated quasi-planar alignment.

Let us take the simplest case of SA aligning monolayer. As known, the packaging of the molecules in this monolayer is so dense that their tails, all of them being in the extended form (trans-conformation) at room temperature, are almost in a vertical position with respect to the surface of the liquid support. The molecules still keep their order after transferring the monolayer onto a solid substrate with hydrophilic surface. Applying the one dimensional model of Safran *et al.*¹⁵ to the case of SA aligning monolayer and using as parameters the tail length $l \approx 24 \text{ \AA}$, the head effective diameter $d_0 \approx 5.0 \text{ \AA}$ and the equilibrium distance between the centers of neighboring tails $s \sim 5.0 \text{ \AA}$, the equilibrium value of the reduced nearest-neighbor distance ϵ was calculated to be $\epsilon = 0$. This means, according to Safran *et al.*, that at room temperature the ground state of SA monolayer must be with non-uniform tilt, i.e., the ground state contains soliton-antisoliton pairs with at most one soliton in excess, due to topological reasons. Soliton and antisoliton states resemble micellar clusters with the tails splaying outwards or bunched up closer than the heads, respectively (Figure 12). Bringing the SA monolayer in a direct contact with a nematic liquid crystal material, as was done in our experiment, the location of soliton-antisoliton pairs could be visualized due to the liquid crystal birefringence. The expected pattern is a set of circular domains. Indeed, such a pattern was found experimentally to appear close to the nematic-isotropic phase transition but never far below it. The reason could be that the interaction between the liquid crystal and the surfactant monolayer somehow is suppressing the occur-

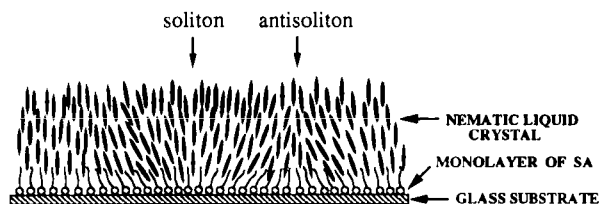


FIGURE 12 Schematic view of soliton-antisoliton pairs in a nematic cell with substrates covered by SA monolayer as aligning film. Clusters of soliton-antisoliton pairs are randomly distributed over the whole substrate area, giving a homeotropic alignment of the liquid crystal in the bulk and being the germs of the circular domains in the alignment transition.

rence of the set of soliton-antisoliton clusters at room temperature. This reason seems quite obvious. As a matter of fact, the liquid crystal–surfactant interactions lead to a homeotropic alignment of the liquid crystal as a result of complete or partial penetration of liquid crystal molecules between the molecules of the aligning surfactant monolayer. Being in such a contact with the liquid crystal, the tails of surfactant molecules could not freely adopt a tilt, as in the case air–monolayer interface, i.e., they are in a way locked to their vertical position due to the nematic matrix. The formation of such clusters becomes possible just when the order parameter of the liquid crystal is approaching zero and the tails of surfactant molecules can easily change their position from vertical to tilted, exactly as has been observed experimentally. Obviously, to explain the alignment transition in the case of thin aligning films of surfactants, in particular aligning monolayers, one needs a more general model than the one proposed by Safran *et al.*, in which the interactions between the liquid crystal material and the aligning monolayer are taken into account as well. Moreover, additional experiments giving more detailed information about the mechanism of the alignment transition in nematics, when a monolayer of surfactant is used as an aligning film, are necessary for a better understanding of this transition. Some of these experiments are under way.

CONCLUSION

The temperature driven surface transition from homeotropic to planar alignment in nematic cells has been investigated. The Langmuir-Blodgett procedure for mono- and multi-layer deposition of surfactants on solid supports was employed in order to achieve well defined and reproducible surface conditions in the cells. Several different surfactants like egg lecithin, distearoylphosphatidylcholine lecithin (DSPC-L), dimiristoylphosphatidylcholine lecithin (DMPC-L), and stearic acid (SA) were used in such a surface pretreatment. The egg lecithin monolayer was found to be less useful for achieving a homeotropic alignment, probably due to its mixed nature. Only a quasi-planar orientation of the nematic molecules at room temperature, with a preferred alignment along the filling direction, was found with such an aligning monolayer. Moreover, the cell area was covered with microsized spots, where the molecules had a larger tilt angle than those in the surrounding area. A self aggregation of similar lecithins in the form of small islands, before transferring the monolayer onto the solid substrate, was supposed to be the reason of the existence of spots. Instead, the other surfactants were found to give a perfect homeotropic alignment of the nematic molecules. Moreover, a sharp and reversible transition from homeotropic alignment to a set of circular domains with in-plane degenerated quasi-planar alignment was found a few tenths of a degree below the liquid crystal clearing point. The transition is reminiscent of a first order change like the nematic-isotropic transition. The only difference obtained in those three cases was that the domains appearing in cells with substrates treated with DSPC-L or DMPC-L, were of larger size and showed more random distribution than the ones which were found in the cell treated with SA during the homeotropic-planar alignment transition. A possible reason could be that the Langmuir-Blodgett mono-

layers of two-tailed lecithins are less condensed than the stearic acid, thus ensuring a more efficient interdigitation between the nematic molecules and the tails, which turn out to be almost uniformly inclined and at the same time being in a symmetrical position with respect to the substrate normal. Note that such an effect is more pronounced in the case of DMPC-L, which has shorter alkyl chains, thus being more inclined. Instead, at the critical point of the alignment transition, the stearic acid exhibits a more regular and a more dense two-dimensional set of smaller sized domains, suggesting the presence of soliton-antisoliton couples formed by the chains (cones up and down), which allows small germs of surface transition, again due to the interdigitation. Moreover, the Langmuir-Blodgett pentalayer of SA was found to behave in the same way as the monolayer of the same surfactant, only that its properties remained more stable with time, whereas those of the monolayer were less stable, probably due to the partial dissolution of surfactant molecules in the nematic sea.

In conclusion, the Langmuir-Blodgett aligning layers of mono-compound surfactants are demonstrated to be a powerful tool for achieving a uniform homeotropic alignment of nematic liquid crystal molecules and for obtaining a temperature driven surface transition near the liquid crystal clearing point. Although the origin of the alignment transition in the nematic layer mediated by the confining surfaces is still not fully understood, the steps presented in this paper toward perfection of orientation and transition control seem promising for the future application of this phenomenon.

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