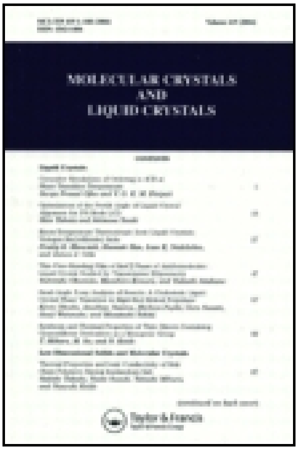

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Droplets Nucleation in Smectic-C* Free-Standing Films

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Droplets Nucleation in Smectic-C* Free-Standing Films

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The behavior of freely suspended smectic-C* (SmC*) films at the bulk Smectic-C*- cholesteric (N*) phase transition has been investigated. According to our experimental observations, the heating of the SmC*free-standing film above the bulk SmC*-N* phase transition can give rise to conventional layer thinning transitions or to nucleation of N* droplets trapped inside the film.
The optical texture observations show that a N* droplets confined in the SmC* host phase are accompanied by topological defects. Due to the boundary condition fixed by the anisotropic host phase elastic interactions between droplet-defect pairs appear.
These interactions drive the self-organization of the droplet-defect pairs in chain-like structures. In this paper, we present the experimental conditions acting on the droplet nucleation process and on the droplet chaining.

Keywords: Free-standing film; Droplet nucleation; Interactions

INTRODUCTION

In the Liquid Crystal (LC) field, the surface phenomena have a strong influence. For conventional solids, it is well known that the surface melts below the temperature of the phase transition in the bulk. Unlike conventional solids, numerous experiments on free-standing films have already demonstrate that the smectic order remains near the LC-air interfaces well above the bulk Smectic-Isotropic phase transition [1-4]. In freely suspended films the stacks of molecular layers are parallel to the interfaces and the number of layers can range from thousand to only two layers.

Films are ideally suitable to investigate the surface phenomena induced by the LC-air interface as a function of the film thickness. Stable free-standing films exist only with phases exhibiting smectic order (SmA, SmC, SmC*...). Thus, all the phase transitions between layer structure to non-layer structure should give rise to critical phenomena. One of the most interesting phenomenon is the layer thinning transition that occurs above the bulk transition temperature. The experiment of Stoebe *et al* in 1994 [4] reported the surprising behavior of films at the SmA-Isotropic phase transition. They found that thin SmA films neither melt nor rupture when they are heated above the bulk SmA-I transition, the films remain stable owing to a series of layer thinning transitions. The layer thinning transition starts just above the bulk SmA-I transition temperature for thick films. After successive thinning a 2-layer film ruptures approximately 30K above the bulk temperature. The thinning transitions were also observed for SmA-Nematic [5; 6] and SmA*-I transitions [7]. This scenario widely described in the literature also occurs in our compound.

The second interesting scenario is the nucleation of droplets in the film just above the layer structure to non-layer structure phase transition. The existence of such inclusions demonstrates that the LC-air interface stabilize the phase with positional order. Thus, the isotropic or nematic inclusions are trapped inside the film. Although the nucleation of isotropic or nematic droplets in smectic free-standing film has already been observed respectively at the SmA-I and SmA-nematic phase transitions [5-7] a collective behavior of the particles has never been mentioned.

In this paper, we report an inclusion nucleation process at the SmC*-cholesteric (N*) phase transition. Due to the in plane anisotropy of the SmC* phase the N* droplets interact and quickly selves-organize in chain like structures. The understanding of the interactions in a 2-dimensions system lies on an analysis of the topological defects.

Topological defects are a consequence of broken continuous symmetry induced by the droplet nucleation. We will discuss the experimental conditions acting on the appearance of droplets and on the main parameters to obtain stable droplets chains.

EXPERIMENTAL

Materials

Experiment were carried out on free-standing films of the n=11 member of a series (S-4-alkoxybiphenylyl (S)-4-(1-methylhepthyloxy)benzoates) ranging from seven to twelve. According to DSC and optical microscopy, the n=11 compound (11BSMHOB) exhibits the following phase sequence: Crystal (56.5°C) SmC* (106.1) N* (123.9°C) Isotropic. As the other compounds of the series, the 11BSMHOB material presents interesting properties for free-standing films studies due to the first order phase transition between a layer structure (the SmC* phase) and a non-layer structure (the N* phase). On increasing temperature, the helical pitch varies from 0.45 μm to 0.73 μm in the SmC* temperature range and from 0.82 to 0.6 μm in the N* one. The spontaneous polarization ranges from 30 nC/cm^2 to 40 nC/cm^2 in the ferroelectric temperature range. As for the polarization, the tilt angle is quasi temperature independent and displays a value of 45° at the SmC*-N* phase transition. The detailed physical properties of this series have been published elsewhere [8].

Experimental setup

Free standing films are built up using a wiper and an aperture in a metal slide. The hole diameter is 5 mm. The experimental setup enables simultaneous reflectivity measurements and optical observations via reflected light microscopy. From the reflectivity spectrum we determine the number of layers in the film [9]. The number of layers of the studied films can range from thousand to a few layers. The film texture is observed between crossed polarizers with an optical microscope (Olympus BX 60 or Leitz) either in reflection or transmission mode. When the film thickness is small in comparison with the helical pitch in the SmC* phase, the c-director field can be mapped from the texture observations. The c-director is the projection of the molecules onto the xy plane (the layer plane). According to the c-director position with respect to the polarizers, the texture can varies from dark to bright. The pictures presented in this paper have been made using a camera or a video camera.

RESULTS AND DISCUSSION

Thermal droplet nucleation process

The used thermal droplet nucleation process is always the same. The film is stretched at 100°C in the SmC* phase. Few minutes are necessary to obtain a uniform c-director orientation, then the film is heated at a rate of 2°C/min using a Mettler hot stage. As soon as N* inclusions nucleate in the film (see figure 1a), the temperature is stabilized. Note that the heating rate has a clear influence on the droplets density trapped inside the film. Higher is the rate, higher is the droplets density.

On the other hand, the temperature of appearance of these droplets depends on the film thickness. In any case, the droplets nucleate at higher temperature than the bulk SmC*-N* phase transition. This temperature shift increases with decreasing film thickness. The classical layer by layer thinning transition takes place in thinner films, approximately less than 25 layers.

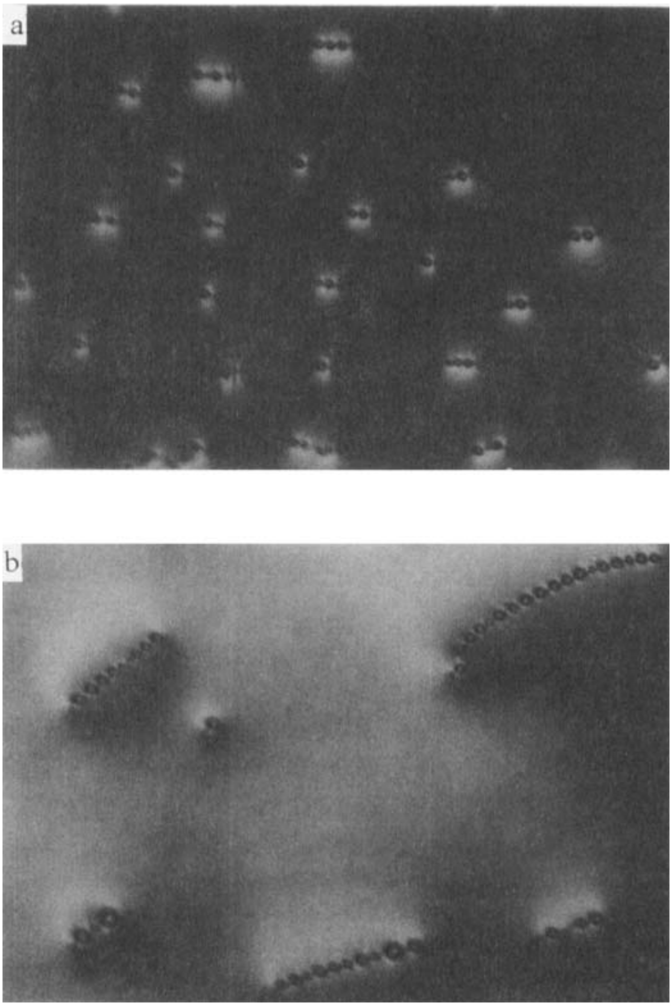

FIGURE 1 (a) Optical micrograph takes a few seconds after the droplets nucleation in the film.

(b) One minute later, the organization of the droplets in chain-like structures is well achieved (in reflection mode, between crossed polars, with a quater wave plate, 1 millimeter correspond to 4.5 microns).

See Color Plate XIX at the back of this issue.

Molecular organization inside the droplets

First, on heating, the temperature shifts between the nucleation of droplets and the bulk SmC*-N* phase transition strongly suggest that the local order in the droplets is cholesteric.

On the other hand, in appropriate conditions large size droplets can be obtained and a texture observation inside a droplet becomes possible. In this case, by cooling the film just below the bulk SmC*-N* phase transition we can observe a clear change of texture in the droplet. This change of texture can be attributed to the phase transition towards the SmC* phase. In fact, after this transition the droplet slowly "deflates" in the film and gives rise to a smectic island thicker than the film. Note, that the island thickness may be non uniform (see figure 2). Most of the islands exhibit stepped structure characteristic of smectic layering. The thickness steps of the islands are visible as concentric circle of different color on figure 2. Each color corresponds to a different thickness.

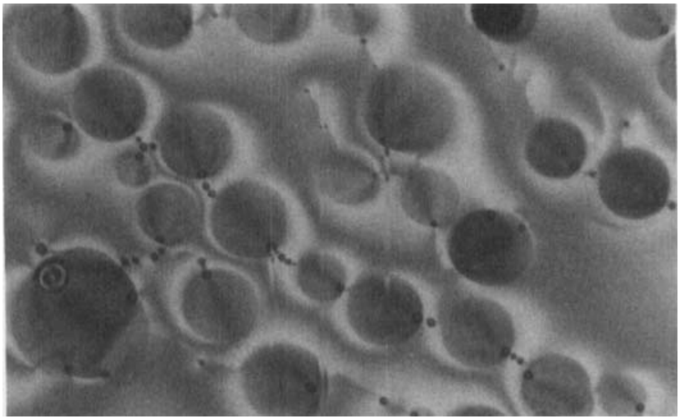

FIGURE 2 Optical micrograph showing on cooling the transformation of the droplets in concentric islands of decreasing thickness. The concentric circle of different color in the island correspond to thickness steps (in reflection mode, between decrossed polars, 1 millimeter corresponds to 4.5 microns width).

See Color Plate XX at the back of this issue.

Why can cholesteric droplets nucleate in the film?

There are different theories concerning the stability of free standing film above the smectic phase [4-5;10-13]. All these theories concern the conventional layer thinning transition, because up to now it was the classical way for free standing films to recover stability. The temperature dependence predicted by the different theoretical models are rather close to each other. Thus, unfortunately a good fitting of the experimental temperature dependence of the thinning transition has generally not been able to discriminate between models. According to our experimental observations, there is at least two different scenarios for free standing films to recover its stability. These two scenarios can be summarized as follows. The first one corresponds to the conventional layer thinning transition in which the thickness can decrease of several block of layers, or layer by layer. The layer by layer thinning transition has been studied for the n=7 member of this series and this layer by layer transition occurs only for relatively thin films, less than 25 layers [14]. For thicker films the layer transition induce the disappearance of several layers. The material corresponding to those layers is expelled towards the meniscus [15]. In the second scenario, there is nucleation of N* droplets trapped inside the film. This nucleation is an other way to induce a layer thinning transition. In fact, the material is not expelled towards the meniscus, but gathered inside droplets. Such thinning transition takes place without observation of a thinning front that usually accompanies a conventional thinning transition. These two scenarios can be understood using the simple model [4, 5] based on the assumption that the smectic order occurring on the boundary of the film is characterized by a penetration length ξ at a given temperature. If the film thickness t is less than twice the penetration length the film is stable over the bulk cholesteric temperature range. When 2ξ become smaller than t the film is no more stable and undergoes the conventional thinning transition or a thinning transition accompanied by droplets nucleation. The heating rate seems to be an important parameter, to induce either conventional layer thinning (low heating rate) or droplets nucleation (high heating rate).

Interactions between droplets

Observation of such inclusions have already been reported respectively at the SmA-I or SmA-N* [6, 7]. In these cases, the inclusions remain randomly located in the film. In our case the situation is completely different, when the droplets appear they are randomly located, but then they self organized in chain like structures. The figure 1 shows the droplets few seconds after their formation. The phenomenon of organization is quite fast; this is the reason why, in the figure 1a some droplets are already two or three in a line. The figure 1b shows the part of the free standing film one minute later. The organization of the droplets in chain-like structures is now well achieved. This self organization of the droplet is obviously induced by a long range attractive force and also a short range repulsive force to prevent close contact of the droplets and then coalescence.

The understanding of the interactions between droplets arises from an analysis in term of topological defects [16]. In our free standing film before the nucleation of the droplets the orientation of the c-director is continuous and quite uniform. The observation of the texture between crossed polarizers (see figure 3a) reveals that the boundary condition of the c-director around the droplets is radial. Thus, the particle plays the role of a topological defect known as radial hedgehog (see figure 3b). Moreover, close to the particle there is an associated defect constituted of a distorted four-armed star of alternating dark and bright regions. The four dark branches are connected to the N* inclusion. This associated defect is known as an hyperbolic hedgehog (see figure 3c) [17].

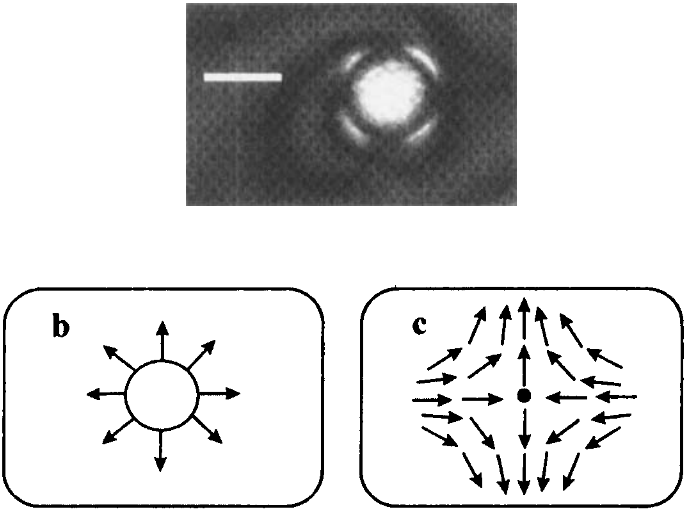

FIGURE 3 (a) Microscope picture of a droplet with its associated four armed star of alternating dark and bright regions (in transmission between crossed polarizers, white bar :10 microns).

(b) Schematic configuration of the c-director around the droplet. The droplet with the normal boundary condition is topologicaly equivalent to a radial hedgehog defect (Topological charge = +1).

(c) Schematic configuration of the c-director around the associated defect. This defect is called "hyperbolic hedgehog defect" due to the c-director configuration around the point defect (Topological charge = -1).

The association of a hyperbolic hedgehog with the droplet allows the c-director to be homogeneously aligned far from the droplet-defect pair assembly as shown by figure 4.

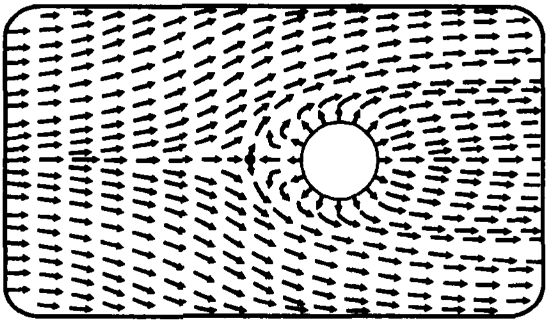

FIGURE 4 Introduction of a particle with normal boundary conditions in the homogeneous orientation of the c-director field induces the formation of a hyperbolic hedgehog.

In summary, the appearance of a droplet breaks the continuous orientation of the c-director field and induce the nucleation of a topological defect near the droplet to allow the connection at long distance with the c-director field. This problem is analogous with a charge conducting sphere in a uniform external electric field. If the charge on the conducting sphere is large enough, there is a point close to the sphere at which the electric field vanishes. The electric field configuration around this point is identical to the c-director field configuration in the vicinity of the hyperbolic hedgehog defect [16].
Hyperbolic and radial hedgehog exhibiting respectively a -1 and +1 topological charges (corresponding to the number of time the unit circle is wrapped), the droplet-defect pairing allows the net topological charge of the film to be conserved and equal to zero.
Such association of a hyperbolic defect with a droplet has already been observed for nematic emulsions (water droplet dispersed in nematic host fluid). For these three dimensions systems [18], the droplet defect pairs exhibit a dipolar symmetry. According to recent theoretical predictions from D. Pettey, T.C. Lubensky and D. Link [19] relative to thicker islands in free standing films the elastic interactions resultant from distortions of the c-director are also expected to exhibit a dipolar character. We observe N* droplets instead of thicker islands, but the two experimental systems are topologicaly equivalent. The experimental observations clearly confirmed the dipolar character of the droplet-defect pair. Indeed, the droplet-defect pairs attract each other at long

range and organize themselves in chain-like structures. As illustrated by figure 1b, few minutes after their nucleation no free isolated droplet-pairs are observed. The attracting force between the droplets acts at very long range; several times the droplet size. The velocity of approach of the defect-pairs is now under investigation in order to know if the force between the particles scales as D^{-4} (where D is the distance between two isolated droplet-defect pairs) as obtained for 3-dimensions systems. The droplet chains exhibit a good stability versus time; this organized structure made from droplet-defect pairs can remain stable several tens of minutes. Such stability need a sufficient short range repulsive force.
As shown by figure 5, the presence of the hyperbolic defect between droplets provides the repulsive barrier between droplets and prevents coalescence. The sequence in the droplets chains is always the same: a droplet, a hyperbolic defect, a droplet and so on; consequently such chains exhibit the same number of defect as droplets that insures the neutrality of the topological charge of the film.

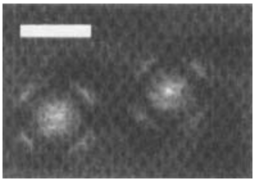

FIGURE 5 Microphotograph of two droplet separated by the hyperbolic defect. The hyperbolic defect acts as a repulsive barrier between droplet and prevents the coalescence (in transmission between crossed polarizers, white bar : 10 microns).

The figure 6 shows more complicated chain-like structures with junction with two branches. Such behavior occurs either when the droplets density is very high or when the c-director boundary condition is not uniform at long distance. In any case, these complicated structures are difficult to understand. Moreover, due to the coalescence process the time stability of the droplets chains is rather short.

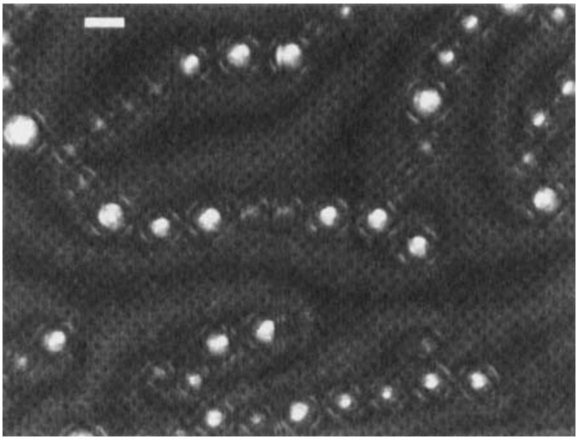

FIGURE 6 Microphotograph of droplet chain with more complicated structure (in transmission between crossed polarizers ; white bar : 20 microns).

CONCLUSION AND PROSPECTS

The investigation of various thickness free-standing films above the bulk SmC*-N* phase transition shows that two different scenarios can occur. Either the film recovers its stability by the conventional layer thinning transition in which the material corresponding to the suppressed layer(s) is expelled towards the meniscus, or by the nucleation of N* droplets trapped inside the film. In the second scenario, instead to be expelled towards the meniscus, the material gathers in N* inclusions, and also gives rise to a layer thinning transition. A slow heating rate seems to favor the classical layer thinning transition while a fast heating rate (>1°C/min) induces the N* droplets nucleation. The most interesting phenomenon is the self-organization of the droplets in chain-like structures. The used compound exhibits all the required physical properties to obtained N* droplets nucleation and especially strong interactions between droplets. The particularly long range attractive interaction between the droplets is probably induced by the strong anisotropy in the layer plane. The balance of the short range repulsion provided by the hyperbolic defect between the droplets and the long range attraction is crucial to obtained stable droplets chains.

Indeed, even if all the compounds of the series exhibits similar physical properties (tilt angle, spontaneous polarisation, and pitch values) the stability of the chain-like structure changes with the chain length. We are now investigating other similar chiral and non-chiral materials in order to understand the role of chirality, anisotropy and spontaneous polarisation in such phenomena.

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