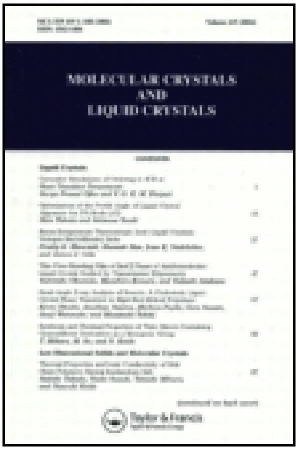


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Boundary Dependence of the Formation of New Phase at the Isotropic-Nematic Transition

H. Yokoyama [a], S. Kobayashi [a] & H. Kamei [a]

[a] Electrotechnical Laboratory, 1-1-4 Umezono, Sakura-mura, Niihari-gun, Ibaraki, 305, Japan

Version of record first published: 17 Oct 2011.

To cite this article: H. Yokoyama, S. Kobayashi & H. Kamei (1983): Boundary Dependence of the Formation of New Phase at the Isotropic-Nematic Transition, Molecular Crystals and Liquid Crystals, 99:1, 39-52

To link to this article: http://dx.doi.org/10.1080/00268948308072027

Mol. Cryst. Liq. Cryst., 1983, Vol. 99, pp. 39–52
0026-8941/83/9904–039/$18.50/0

Printed in the United States of America

Boundary Dependence of the Formation of New Phase at the Isotropic-Nematic Transition

H. YOKOYAMA, S. KOBAYASHI, and H. KAMEI

Electrotechnical Laboratory, 1-1-4 Umezono, Sakura-mura, Niihari-gun, Ibaraki, 305, Japan

(Received January 28, 1983)

The phase separation of a mesogen-nonmesogen mixture was studied with particular emphasis on the effects of boundary conditions imposed at container walls such as rubbed polyvinylalcohol (PVA) film, obliquely evaporated SiO film, free surface, etc. Microscopic observations revealed that the equilibrium shapes of a nematic or isotropic liquid formed on a substrate in the temperature range of isotropic-nematic coexistence varies greatly depending on the nature of the substrate. Typically the contact angle of a nematic liquid formed at the isotropic-substrate interface is 0° on a rubbed PVA film and at the free surface, and is nearly 180° on an SiO film. The connection between the substrate induced ordering and the contact angle is discussed.

INTRODUCTION

Properties of a liquid crystal (LC)-solid substrate interface have attracted a great deal of interest with respect to the substrate induced alignment of LCs.[1] Recently great progress has been made in the quantitative evaluations of LC-substrate interactions by the introduction of the wall-induced pretransitional birefringence.[2–5] It was shown that the surface order parameter in the isotropic phase of a LC on various substrates varies seriously according to the nature of the substrate, even though the substrate induced alignments are apparently indistinguishable in the nematic phase.[2–4] However, the connection of the surface order parameter with thermodynamic quantities such as the interfacial tensions, which are of central importance in discussing the substrate induced alignment, has not been clarified so far.

In a previous paper,[6] we showed that in the isotropic-nematic coexistence region of a mesogen-nonmesogen mixture, the nematic phase forms a uniform surface layer adjacent to the substrate on cooling from the isotropic phase if the substrate strongly orients the LC molecules, while on a substrate with negligible orienting effect the nematic phase appears in the form of spherules.

The purpose of this paper is to present the results of more detailed microscopic observations of the shapes that a "new phase" takes not only on cooling from the isotropic phase but also on heating from the nematic phase on various substrates, and to show that these shapes can be consistently understood as determined by the interfacial tensions among the substrate, the nematic phase and the isotropic phase. Here "new phase" stands for nematic phase for cooling and isotropic phase for heating. Finally the relation between the formation of new phase and the substrate induced ordering is discussed.

EXPERIMENTAL

The material used is a mixture of 4-cyano-4′-*n*-pentylbiphenyl (5CB) and a nonmesogen, hexamethylbenzene, $C_6(CH_3)_6$. Figure 1 shows the visually determined phase diagram for this mixture. The boundary conditions tried are listed in Table I. Sandwich type cells were constructed using 36-μm-thick polyester film spacer. The cells were filled with the mixture by the method of Kondo, *et al.*[7] A free film of pure 5CB was suspended over a circular hole (2 mm in diameter) made through a 30-μm-thick Teflon film. All the experiments were done with 2.9 mol% mixture except for the

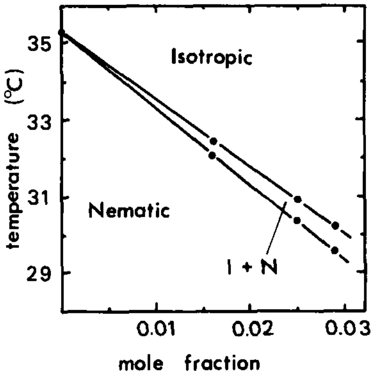


FIGURE 1 Phase diagram for $C_6(CH_3)_6$/5CB.

TABLE I

Boundary conditions, their methods of preparation and induced alignments.

Boundary condition	Method of preparation	Alignment
Rubbed PVA	Glass slides were spin-coated with an aqueous solution (1%) of polyvinylalcohol (PVA), 1400 molecular weight, and dried, and then rubbed with lens cleaning paper.	Homogeneous
Bare PVA	Glass slides were spin-coated with an aqueous solution (1%) of PVA and dried.	Random parallel
SiO film (60°)	SiO was evaporated onto a glass substrate at 60° from the normal of the substrate at the rate of 7 Å/s for 90 s in the vacuum of 10^{-6} Torr.	Homogeneous
SiO film (0°)	SiO was evaporated onto a glass substrate from the normal at the rate of 14 Å/s for 90 s in the vacuum of 10^{-6} Torr.	Random parallel
Free surface	5CB was freely suspended over a hole (2 mm in diameter) made through a 30-μm-thick Teflon film. The thickness of the suspended film was about 30 μm.	Homeotropic
Cleaned glass	Glass slides were cleaned by a hot (90°C) detergent and rinsed with distilled water and dried.	Homeotropic
CTAB film	Glass slides were dipped into a chloroform solution (0.5%) of cetyltrimethylammonium bromide (CTAB). After dried, excess CTAB was wiped out with paper.	Homeotropic

case of freely suspended film for which pure 5CB was used in order to compare the results with the published data for the surface tension of 5CB.[8]

Formations of new phase on cooling and heating were observed with a millidegree-temperature-controlled polarizing microscope, the details of which are presented elsewhere.[9] The temperature was scanned in such a way that the isotropic-nematic coexistence region was passed in a period longer than one hour: more specifically, the scanning rate was slower than 0.6°C/h for the 2.9 mol% mixture and 0.02°C/h for pure 5CB which showed 0.02°C-wide isotropic-nematic coexistence region when purchased from BDH. Although the nucleation rate of new phase, as is naturally expected, increased with the temperature scanning rate, the shapes of new phase were rather insensitive to it.

RESULTS

Before presenting the results of microscopic observations, it may be of help for later purposes to consider briefly the equilibrium shapes of a new phase

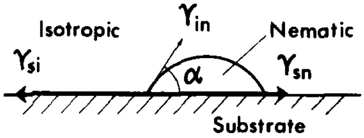


FIGURE 2 A nematic drop in contact with a substrate, formed in the isotropic liquid. γ's are interfacial tensions and α is the contact angle.

formed on a substrate in terms of relevant interfacial tensions of the system. As an example, we only consider the shape of nematic liquid formed on cooling from the isotropic phase, as shown in Figure 2 where the interfacial tensions and the contact angle of nematic phase are defined in an usual manner. The interfacial tensions and the contact angle satisfy the well known Young's equation,

$$\gamma_{si} - \gamma_{sn} = \gamma_{in} \cos \alpha, \tag{1}$$

which shows that the difference, $\gamma_{si} - \gamma_{sn}$, can be directly deduced from the knowledge of the contact angle and the isotropic-nematic interfacial tension. In Table II, shapes of new phase are qualitatively classified according to the contact angle of the new phase. In Type 1, the new phase does not wet the substrate at all ($\alpha = 180°$). Type 3 is the case in which the contact angle, α, is 90°. In Type 5, the new phase completely wets the substrate ($\alpha = 0°$). Type 2 and Type 4 represent the intermediate situations.

Table III shows the features of new phase formation for the boundary conditions listed in Table I on cooling ($I \rightarrow N$) and on heating ($N \rightarrow I$) together with the surface order parameter in the isotropic phase. A few typical observations are explained in some detail below.

On a substrate coated with polyvinylalcohol and rubbed unidirectionally with paper (rubbed PVA), as the temperature is lowered from the isotropic phase, the field of view is gradually brightened and the nematic phase appears in the form of uniform surface layer except for the vicinity of some surface defects (see Figure 3a). On further cooling, the surface layer grows normal to the surface and clear birefringence color appears between crossed polarizers.

Figure 3b shows the formation of isotropic phase on heating from the nematic phase. As the temperature is increased, the isotropic phase appears as small spherules which grow rather rapidly. The central part of a spherule becomes dark between crossed polarizers, when the diameter of the spherule almost reaches the cell thickness (~40 μm) in a few minutes from its formation.

TABLE II

Qualitative classification of the shapes of new phase formed on a substrate

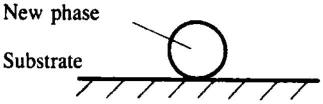
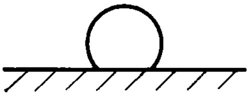
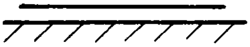
Type of formation	Shape of new phase	Contact angle
1		$\alpha = 180°$
2		$180° > \alpha > 90°$
3		$\alpha = 90°$
4		$90° > \alpha > 0°$
5		$\alpha = 0°$

TABLE III

Types of new phase formation on cooling (I → N) and on heating (N → I) for various boundary conditions

Boundary condition	Type of formation 1	2	3	4	5	Surface order parameter
Rubbed PVA	N → I				I → N	0.27[a], 0.17[b]
Bare PVA			N → I I → N			—
SiO film (60°)		I → N		N → I		0[a,c,d]
SiO film (0°)		I → N		N → I		—
Free surface	N → I				I → N	>0[e]
Cleaned glass		I → N		N → I		0[d]
CTAB film		N → I		I → N		0.32[d], 0.20[d]

[a] Results for 5CB with 2.5 mol % $C_6(CH_3)_6$, Ref. 6.
[b] Result for pure 5CB, Ref. 4.
[c] Result for pure 5CB, Ref. 2.
[d] Results for pure 5CB, Ref. 3.
[e] Suggested from the temperature dependence of the surface tension, Ref. 8.

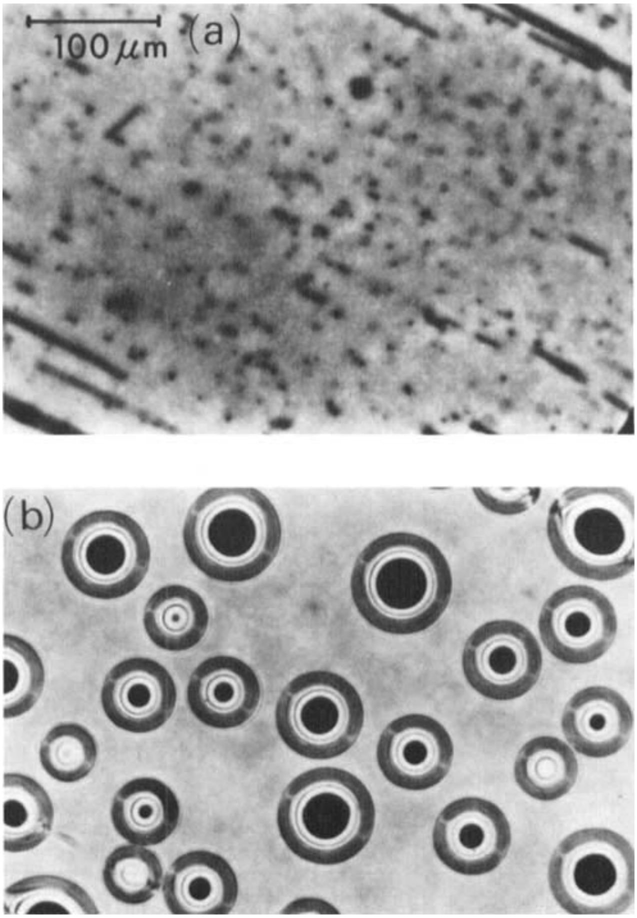


FIGURE 3 New phase formation on rubbed PVA. (a) Nematic surface layer formed at the isotropic-substrate interface on cooling. (b) Spherules of isotropic liquid in homogeneously aligned nematic phase. Regions filled with the isotropic liquid from the lower through the upper substrates can be seen dark between crossed polarizers. Cell thickness ~40 μm.

In order to see the effect of unidirectional rubbing imposed on PVA films, isotropic-nematic transitions on a bare PVA film were observed. In the nematic phase the director of the LC showed no particular direction over the substrate. Figure 4 shows the formation of new phase on a bare PVA film. As the temperature is lowered from the isotropic phase, the nematic phase appears as circular domains. When the diameter of the domain becomes nearly twice as large as the cell thickness, the texture of the domain changes abruptly to the one that is typical to a nematic film sand-

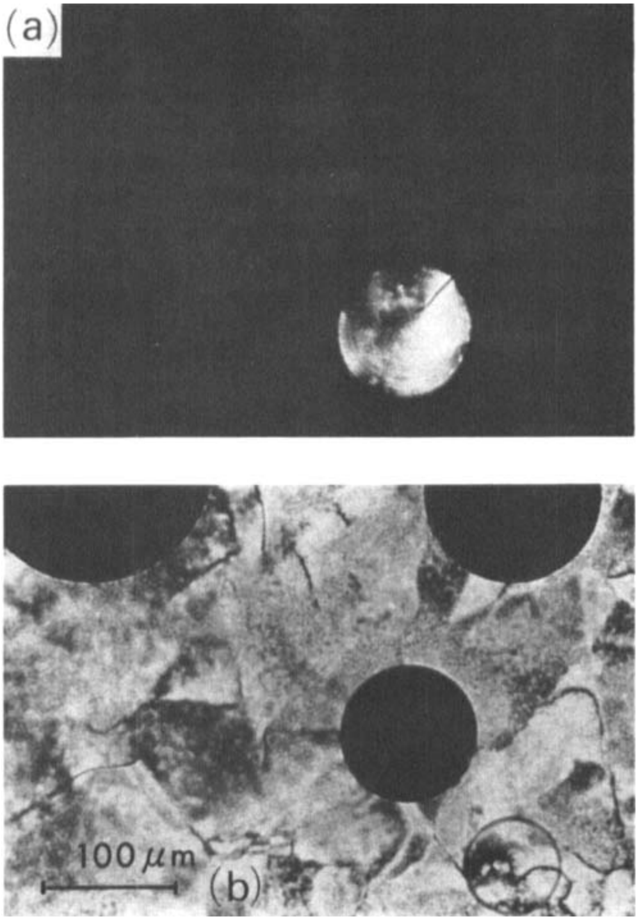


FIGURE 4 New phase formation on bare PVA. (a) A nematic domain formed in the isotropic liquid on cooling, just gaining the texture typical to a nematic film sandwiched between bare PVA films. (b) Isotropic domains formed in randomly oriented nematic phase on heating. Two types of domains can be seen; dark and clear (bottom right). The clear one is an isotropic domain in contact with either substrate. Cell thickness ~40 μm.

wiched between bare PVA films (Figure 4a). It should also be noticed that the boundary of the domain is rather clear-cut. These observations show that the nematic liquid formed on a bare PVA film takes a quasi-hemispherical shape (Type 3). The features of the isotropic phase formation are very similar to those of nematic phase formation, provided the roles of the isotropic and nematic phases are exchanged.

Figure 5 shows the features of new phase formation on an SiO film evaporated at 60° from the normal of the substrate. As the LC is cooled

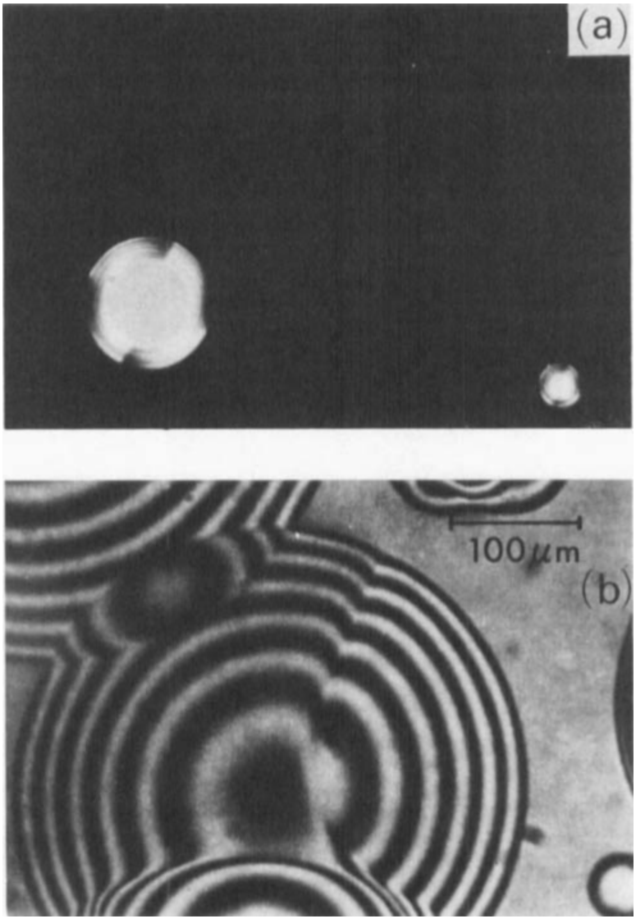


FIGURE 5 New phase formation on SiO film (60°). (a) Nematic domains formed in the isotropic phase on cooling. The larger domain is homogeneously aligned in its central region. (b) Circular isotropic domains on heating observed with monochromatic light (wavelength = 560 nm). Concentric birefringence rings are due to the thickness change of the isotropic domain. Domains in contact with either upper or lower substrate are overlapping each other. Cell thickness ~40 μm.

down from the isotropic phase, small spherules of nematic phase appear and grow rather rapidly. The diameter of these spherules reaches the cell thickness in a few minutes to change their texture to a homogeneous one. This situation bears a close resemblance to the formation of isotropic phase on rubbed PVA, although the new phase is the nematic phase at present. The formation of isotropic phase on an SiO film, however, is a little different from the nematic phase formation on rubbed PVA. On SiO film

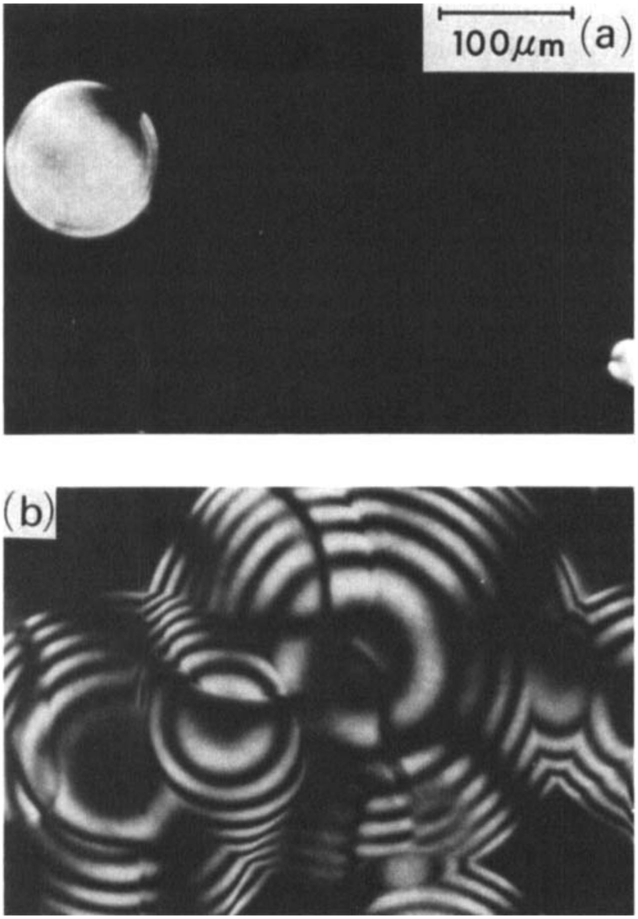


FIGURE 6 New phase formation on SiO film (0°). (a) Nematic domains formed in the isotropic phase on cooling. (b), Circular isotropic domains formed in randomly oriented nematic phase on heating, observed with monochromatic light (wavelength = 560 nm). Concentric birefringence regions are due to the thickness change of the isotropic domain. Domains in contact with either upper or lower substrate are overlapping each other. Cell thickness ~40 μm.

(60°), the isotropic phase does not form a completely uniform surface layer, but a flat circular domain adjacent to the substrate: the contact angle of the isotropic phase is small but finite.

We have also observed the formation of new phase on an SiO film evaporated from the normal of the substrate. When the LC was injected into the cell in the isotropic phase and cooled down to the nematic phase, the LC orientation showed no particular direction over the substrate. Figure 6 shows the textures observed in the coexistence region. On lowering the temperature, small spherules of nematic phase appear and grow to recover the initial orientational profile in the nematic phase. On heating from the nematic phase, flat circular domains of isotropic phase appear. Therefore, the features of new phase formation for SiO film (0°) are essentially similar to those for SiO film (60°). However, the contact angle of isotropic phase on SiO film (0°) is somewhat larger than that on SiO film (60°).

In the case of a freely suspended film, the LC molecules were aligned perpendicular to the surface. On cooling from the isotropic phase, a nematic surface layer with schlieren texture appears (Figure 7a). The schlieren texture may be due to the point disclinations at the isotropic-nematic interface, which appear as a result of perpendicular orientation at the free surface and the nearly tangential orientation imposed at the isotropic-nematic interface.[10] On further cooling, the number of disclination points decreases and the birefringence color appears. When the temperature is increased from the nematic phase, spherules of isotropic phase are formed with radial dark brushes between crossed polarizers (Figure 7b).

DISCUSSIONS

For any boundary condition, the textures in the isotropic-nematic coexistence region could be maintained at fixed temperatures for 10 h or more, unless the temperature was very near the boundaries of the coexistence region where a certain degree of super-heating or -cooling always exists. In addition, the domains of new phase took an almost circular shape, except for the case of Type 5 formation, and even when two neighboring domains fused together, the circular shape was regained in a few minutes. These experimental facts might show that the observed shapes are, in effect, the ones in thermal equilibrium conditions. In an equilibrium, Young's equation, Eq. (1), states that the sum of the contact angles of the isotropic and nematic phases equals 180°, which leads to a consistency condition for the Types of new phase formation that the Types for cooling and heating must be located symmetrically about Type 3. The results shown in Table III satisfy this condition at least qualitatively.

To the authors' knowledge, there is no such measurement of LC-solid substrate interfacial tensions as to be of help in interpreting the present observations. In the case of LC-vapor interface, however, Gannon and Faber[8] performed a precise measurement of surface tension for 5CB. They showed that the surface tension of 5CB increases with the temperature in

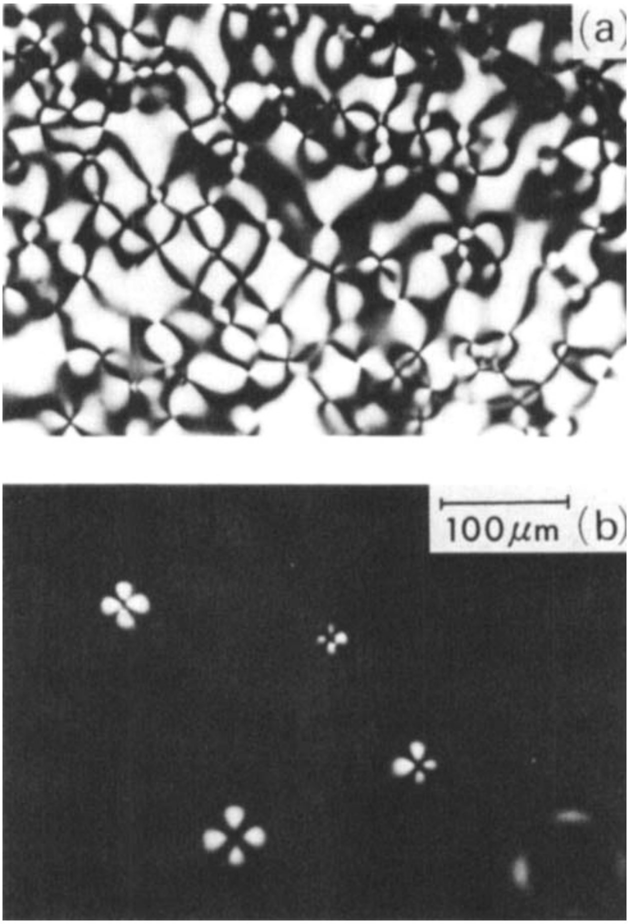


FIGURE 7 New phase formation for freely suspended film. (a) Surface nematic layer with schlieren texture observed on cooling. (b) Spherules of isotropic phase in homeotropically aligned nematic phase (heating).

the neighborhood of the isotropic-nematic transition point where it shows a discontinuous rise of 0.34 erg/cm^2. As for the isotropic-nematic interfacial tension, γ_{in}, the Landau-de Gennes theory[11] gives 1.1×10^{-2} erg/cm^2 if the parameters for 5CB obtained by Coles[12] and the correlation length of 200 Å are assumed. Therefore, neglecting the energy associating the elastic deformations due to the boundary conditions, we obtain from Eq. (1) the contact angle of 0° for a nematic liquid at the free surface of 5CB. This is in agreement with the present microscopic observation of Type 5 formation on cooling (see Figure 7a).

Next we discuss the relation between the formation of new phase and the substrate induced ordering, using a simple theoretical model. According to Navascués and Berry[13] we assume the solid substrate to be completely rigid and split the interfacial tensions in the following form:

$$\gamma_{sf} = \gamma_s + \gamma^*_{sf}, \qquad f = i \text{ or } n,$$

where γ_s comes from the solid-solid interaction and γ^*_{sf} represents the contributions of the solid-liquid and the liquid-liquid interactions. Using this form in Eq. (1) we obtain

$$\gamma^*_{si} - \gamma^*_{sn} = \gamma_{in} \cos \alpha \tag{2}$$

We also assume that the state of the liquid can be characterized by the usual order parameter, Q, right up to the surface. The dependence on the impurity concentration can be implicitly taken into account through the order parameter, since the correlation length of the concentration is expected to be much smaller than the correlation length of the order parameter.

Taking the quasi-thermodynamic approach, which has been applied to the free surface and the isotropic-nematic interface of LCs,[8,11,14] we express γ^*_{sf} as a functional of the order parameter field, $Q(z)$, where z-axis is taken along the outward normal of the substrate with the origin on the surface;

$$\gamma^*_{sf} = \gamma[Q(0)] + \int_0^\infty f(Q(z))\, dz \tag{3}$$

$\gamma[Q(0)]$ is the free energy due to the direct interaction between the substrate and the LC and is assumed to be a function of only the surface order parameter, $Q(0)$. $f[Q(z)]$ represents the local free energy density at z excess to the bulk free energy density (e.g., the Landau-de Gennes free energy) and is in general a function of $Q(z)$ and its derivatives. For the sake of stability of coexisting isotropic and nematic phases, $f(Q) = 0$ at $Q = 0, Q_b$ and $f(Q) > 0$ elsewhere: Q_b is the bulk order parameter for the nematic phase. Let $F(Q_0, Q_\infty)$ be the value of the integral, $\int_0^\infty f[Q(z)]\, dz$, minimized with respect to $Q(z)$ under the conditions that $Q(0) = Q_0$ and $Q \to Q_\infty$ as $z \to \infty$. Then we obtain

$$\begin{aligned} \gamma^*_{si} &= \gamma(Q_i) + F(Q_i, 0) \\ \gamma^*_{sn} &= \gamma(Q_n) + F(Q_n, Q_b) \end{aligned} \tag{4}$$

where Q_i and Q_n are the surface order parameters for the isotropic and the nematic phases, respectively. The isotropic-nematic interfacial tension is given by

$$\gamma_{in} = F(0, Q_b) \tag{5}$$

It is possible to draw a few general conclusions[14] from above expressions:

(i) $Q_i \leq Q_n$, in particular $Q_i = Q_n$ when $Q_i \geqq Q_b$,

(ii) $|\gamma^*_{si} - \gamma^*_{sn}| < \gamma_{in}$ when $0 \leq Q_i < Q_b$, $Q_n \neq 0$, (6)

$\gamma^*_{si} - \gamma^*_{sn} = \gamma_{in}$ when $Q_n = Q_i \geqq Q_b$, (7)

$\gamma^*_{sn} - \gamma^*_{si} = \gamma_{in}$ when $Q_n = Q_i = 0$. (8)

The first conclusion states an intuitively obvious fact that the surface order parameter in the isotropic phase never exceeds that in the nematic phase. The second is concerned with the connection between the surface induced ordering and the contact angle of the new phase. Equation (7) shows that the solid-isotropic interfacial tension is just the sum of the tensions of the solid-nematic and the isotropic-nematic interfaces, provided the surface order parameter in the isotropic phase is greater than the bulk order parameter of the nematic phase. This is similar to Antonow's rule[16] for three coexisting fluid phases and can, therefore, be understood on the basis of a simple physical picture that a macroscopic layer of nematic phase exists at the solid-isotropic interface. In other words, Type 5 formation on cooling is expected on a substrate which induce, in the isotropic phase, a surface order greater than the bulk nematic order. This is actually the case for rubbed PVA (see Figure 3a), for which the surface order parameter is in fact as large as the bulk order parameter (see Table III). In the context of the present model, $Q_i \geqq Q_b$ is possible only when $\gamma(Q)$ decreases with Q rather steeply, which implies that a rubbed PVA film exerts a strong anisotropic force on LC molecules along the rubbing direction. The observations for bare PVA also show that this force originates from the changes caused by the rubbing and is responsible for the homogeneous alignment on a rubbed PVA film.

Characteristics of new phase formation on SiO films are rather insensitive to the angle from which SiO is deposited onto the substrate (see Table III), though SiO film (60°) gives a homogeneous alignment of good quality and SiO film (0°) does not. This clearly indicates that the LC-solid substrate interaction which homogeneously aligns the LC molecules, and the interaction which gives the gap in the interfacial tension are of somewhat different nature. This is in contrast with the case of rubbed PVA mentioned above.

The grooved structure of an obliquely evaporated SiO film has been thought as a plausible mechanism for the homogeneous alignment of LCs.[1] If an ideal grating like structure is assumed for the surface, the elastic deformation energy due to the surface structure vanishes when the LC takes a homogeneous alignment with its axis parallel to the grooves.[17] Therefore, the ideal grooves, which result in a homogeneous alignment, do not contribute any elastic energy to the interfacial tensions. This is in complete agreement with the present observations. However, in a real LC-obliquely evaporated SiO system, the elastic energy does not vanish even if the LC assumes a homogeneous alignment. This is because the grooves are not necessarily smooth in the direction of alignment.[18] The residual elastic energy of this type may be present on SiO film (0°) as well and is approximately proportional to the square of the order parameter through the order parameter dependence of elastic constants. In this respect, the surface of an SiO film is expected to oppose the liquid crystalline order.

This antagonistic nature of SiO films to the LC ordering means that $\gamma(Q)$ is an increasing function of Q, if it is possible to cast the residual elastic energy into $\gamma(Q)$. Assuming, here, $\gamma(Q)$ to be an increasing function of Q, we obtain

$$Q_i = 0, \qquad Q_n < Q_b, \qquad \gamma^*_{si} < \gamma^*_{sn} \tag{9}$$

These results are in qualitative agreement with the experiment except for the case of Q_n which has not been measured so far. If we further take into account the fact that the contact angle of nematic phase on SiO film is close to 180°, which means $\gamma^*_{sn} - \gamma^*_{si} \sim \gamma_{in}$, we can show that Q_n is rather close to 0. Although this is a novel and interesting result, the derivation is based on several arbitrary assumptions. More elaborated experimental and theoretical investigations are required to elucidate this problem.

References

1. J. Cognard, *Mol. Cryst. Liq. Cryst. Suppl.*, **1**, 1 (1982).
2. K. Miyano, *Phys. Rev. Lett.*, **43**, 51 (1979).
3. K. Miyano, *J. Chem. Phys.*, **71**, 4108 (1979).
4. J. C. Tarczon and K. Miyano, *J. Chem. Phys.*, **73**, 1994 (1980).
5. D. W. Allender, G. L. Henderson and D. G. Johnson, *Phys. Rev.*, **A24**, 1086 (1981).
6. H. Yokoyama, S. Kobayashi and H. Kamei, *Appl. Phys. Lett.*, **41**, 438 (1982).
7. K. Kondo, F. Kobayashi, A. Fukuda and E. Kuze, *Jpn. J. Appl. Phys.*, **20**, 1773 (1981).
8. M. G. J. Gannon and T. E. Faber, *Philos. Mag.*, **A37**, 117 (1978).
9. H. Yokoyama, S. Kobayashi and H. Kamei, *Rev. Sci. Instrum.*, **54**, 611 (1983).
10. R. B. Meyer, *Mol. Cryst. Liq. Cryst.*, **16**, 355 (1972).
11. P. G. de Gennes, *Mol. Cryst. Liq. Cryst.*, **12**, 193 (1971).
12. H. J. Coles, *Mol. Cryst. Liq. Cryst. (Lett.)*, **49**, 67 (1978).
13. G. Navascués and M. V. Berry, *Mol. Phys.*, **34**, 649 (1977).
14. J. D. Parsons, *Mol. Cryst. Liq. Cryst.*, **31**, 79 (1975); *Phys. Rev. Lett.*, **41**, 877 (1978).
15. In deriving the results, use is made of the following: $F(Q,0) = F(Q,Q_b) + F(Q_b,0)$ when $Q \geqq Q_b$; $F(Q,0)$ is an increasing function of Q; $F(Q,Q_b)$ is a decreasing function of Q when $0 < Q < Q_b$.
16. A. W. Adamson, *Physical Chemistry of Surfaces*, John Wiley & Sons, New York (1976).
17. D. W. Berreman, *Mol. Cryst. Liq. Cryst.*, **23**, 215 (1973).
18. M. Kuwahara, H. Yayama, H. Onnagawa and K. Miyashita, *Oyo Buturi*, **50**, 1147 (1981) [in Japanese].