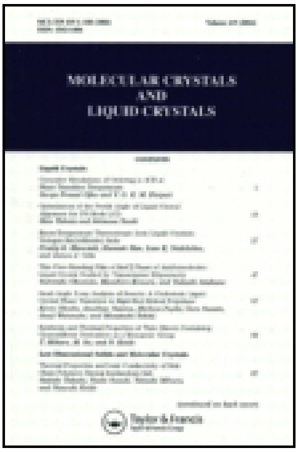

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Phase Transition Isotropic Liquid-Nematic in Films with Two Free Surfaces

P. Simova [a] & Y. Marinov [a]

[a] Institute of Solid State Physics of the Bulgarian Academy of Sciences, 1784 Sofia, Blvd., Lenin 72, Bulgaria

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Phase Transition Isotropic Liquid-Nematic in Films with Two Free Surfaces

P. SIMOVA and Y. MARINOV

Institute of Solid State Physics of the Bulgarian Academy of Sciences, 1784 Sofia, Blvd. Lenin 72, Bulgaria

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The nematic layer growing from the isotropic liquid of a free suspended film has been investigated. The selected substances possess different dielectric anisotropy, molecular orientation of the interfaces, latent heat of the N-I phase transition, a kind of phase under the nematic. It is found that the nematic layers of the two interfaces nematic-air arise and grow at very slow cooling independently if the thickness of the free film is ≥ 8 μm. After the upper nematic layer of some substances reaches ~ 5 μm thickness, the formation of drops begins under the layer on the interface nematic-isotropic liquid. For substances in which the molecules lie approximately in the interface N-I at the same experimental conditions the drops are not seen. It is found that the transition I-N does not depend on the kind of phase under the nematic if the nematic temperature region is not too small.

INTRODUCTION

The investigations of the free surface of drops from nematic liquid crystals have been carried out by numerous authors. Since 1930 Naggiar[1] had determined that the PAA molecules lie in the interface nematic-air. Later Bouchiat and Langevin-Cruchon[2] by measuring the polarized light reflectivity from the free nematic surface had confirmed the result of Naggiar for PAA establishing that its molecules lie in the interface nematic-air in the whole nematic region. For MBBA they found that the molecules conclude angle θ with the normal of the interface which depends on the temperature of the nematic phase. At clearing temperature T_c the molecules tend to perpendicular orientation to the interface, $\theta = 90°$, as at decreasing the temperature of the nematic phase the molecules tilt and at about ten degrees below T_c they remain in an almost constant tilt $\theta = 70°$. R. B. Meyer[3] investigated texturally the point disclinations of the free surface of drops from ethyl p-(p-methoxybenzylidene amino) zinnamate and gave a model of the directors field in the investigated nematic layer.

Parsons[14] considers theoretically the molecular orientation on the free boundary surface nematic-air in dependence of the molecular structure distinguishing quadrupolar and polar agreement. He found that at quadrupolar symmetry the equilibrium state of the interface nematic-air occurs when the molecules lie in the plane of the free surface. Besides, it follows from his theory that at the transition I-N the surface tension may fall down with a jump. The polar ordering always leads to straightening of the molecules perpendicular to the free surface. Due to the competition of the two effects, quadrupolar and polar ordering, the angle concluded by the molecular director with the normal to the interface may change between 0° and 90°.

As far as we know, Faetti and Fronzoni[5] are the first to investigate the orientation of the molecules of MBBA in a nematic film with two free surfaces. In dependence of the thickness of the nematic film, they get three kinds of nematic texture. When the thickness of the nematic layer is >70 μm, they observed under the polarizing microscope a bright texture with disclination lines. On the basis of a conoscopical investigation they concluded that the molecules are tilted inhomogeneously in the layer. Reducing the thickness, the film progressively grows dark as the conoscopic picture represents a black cross with circular isochromatic lines and the authors accepted homeotropic orientation but do not determine the transition thickness of the film between the first and the second case. At film thickness of about 10 μm the authors again observed tilting of the molecules of the interface. Later Faetti and Paleschi investigated the nematic-isotropic interface of fifth, sixth, seventh and eighth members of the homologous series of 4-cyano-4′-(n-alkyl) biphenyls. The polar angle θ_t, the anchoring energy W and the width of the interface I-N were determined.[6] Recently Belyaev, Malimenkov and Beresnev[7] investigated texturally the molecular orientation of the interface nematic-air connecting it with the direction of the averaged molecular dipole moment which, according to them, is directed toward the nematic phase.

The present communication gives the results from the textural investigation of the nematic layer growing from an isotropic phase into a freely suspended in-air film. Table I presents the investigated substances. The substances I, V, VI and VII expose only one meso-phase, the nematic, II and VIII, below the nematic-smectic

TABLE I

	Name	Temperature range of the mesophases (°C)	Dielectr. anisotropy
I	n-heptyloxycyanobiphenyle (70 CB)	Cr 53.5 N 75 I	$\Delta\varepsilon > 0$[8]
II	n-octyloxycyanobiphenyle (80 CB)	Cr 54.5 SmA 67.5 N 80 I	$\Delta\varepsilon > 0$[8]
III	4,n-octyloxybenzoic acid (OOBA)	Cr 100.3 SmC 107.9 N 147.7 I	$\Delta\varepsilon = 0.03$ at 140°C[9]
IV	4,n-decyloxybenzoic acid (DOBA)	Cr 96.5 SmC 124.6 N 142.6 I	$\Delta\varepsilon = 0.01$ at 140°C[9]
V	p-azoxyanizole (PAA)	Cr 117 N 135 I	$\Delta\varepsilon = -0.17$ at 125°C[10,11]
VI	p-ethoxybenzilidene-p-n-butylaniline (EBBA)	Cr 37 N 80 I[12]	$\Delta\varepsilon < 0$
VII	p-hexyloxyphenylester of p-butylbenzoic acid (HOPEBBA)	Cr 31 N 49.6 I	$\Delta\varepsilon = ?$
VIII	n-(p-ethoxybenzylidene)-p-aminoethylester of cinnamic acid (EOBAEECA)	Cr 81.4 SmB 119.3 SmA 157.3 N 160.2 I[12]	$\Delta\varepsilon = ?$

A phase and III and IV, below the nematic smectic C phase. The substances I and II possess a big positive dielectric anisotropy[13]; for the substances III and IV the dielectric anisotropy is very slightly positive and close to zero, the substances V and VI have a negative dielectric anisotropy. Unfortunately, we did not find literature data for the dielectric anisotropy of substances VII and VIII.

To obtain free films in air, aluminum foils have been used with thicknesses 50, 20 and 10 μm as a cylindrical hole was made in them of diameter ~1 mm. The cleaned foil with sizes 20 × 20 mm and the circular hole in the middle has been set in a thermostat on the microscopic table. At heating to temperature near to the transition into isotropic phase, a small quantity of the investigated substance is spread over the foil by the side of the hole and after melting it is smeared by means of a glass plate. Thus films are obtained in the cylindrical hole with a desired thickness. The conditions in the thermostat are such that two types of temperature gradients are obtained. First, as the aluminum foil is in contact with the metal substrate of the thermostat from below and with the air from above, in spite of its very small thickness, there is a very small vertical temperature gradient (of the order of hundredths of degree) in the film. Second, a radial gradient is created as the temperature of the film in contact with the aluminum foil is greater than that in the middle of the film. After stabilizing the temperature in the thermostat close to the clearing point T_c, it passed into isotropic phase, and at very slow cooling a growing of a nematic layer is observed in the isotropic liquid by means of a polarization microscope with crossed polarizers.

RESULTS

I. 70 CB

Films with thickness 16–8 μm have been investigated. At slow cooling of the isotropic liquid, the transition temperature in the nematic phase is reached first at the upper free surface. Then, a smeared grey "clover" (Figure 1a) appears on the dark field of the liquid ($P \perp A$) in the middle of the film, which takes shape gradually into a grey circle with four extinction shoulders not to be seen without polarizers. Reducing the temperature with hundredths of a degree the nematic layer grows, the circle gradually becomes bright yellow, its radius increases, concentric isochrome circles appear due to the double light reflection and in its center a black cross is observed on the white field (Figure 1b).

Following the transition isotropic liquid-nematic by focusing on the lower boundary surface, it is observed that when a nematic layer of certain thickness (as in Figure 1b but now out of focus) has been already obtained on the upper surface, on the lower interface a new cross is seen of short duration and immediately after that the two nematic layers—from the upper and lower interfaces—abruptly fuse in the center of the film (Figure 1c). At further temperature decreasing the radii of the nematic layers grow at both interfaces. It is seen in the mentioned photos that the boundary isotropic liquid-nematic is smeared, which shows the gradual thinning out of the nematic layer.

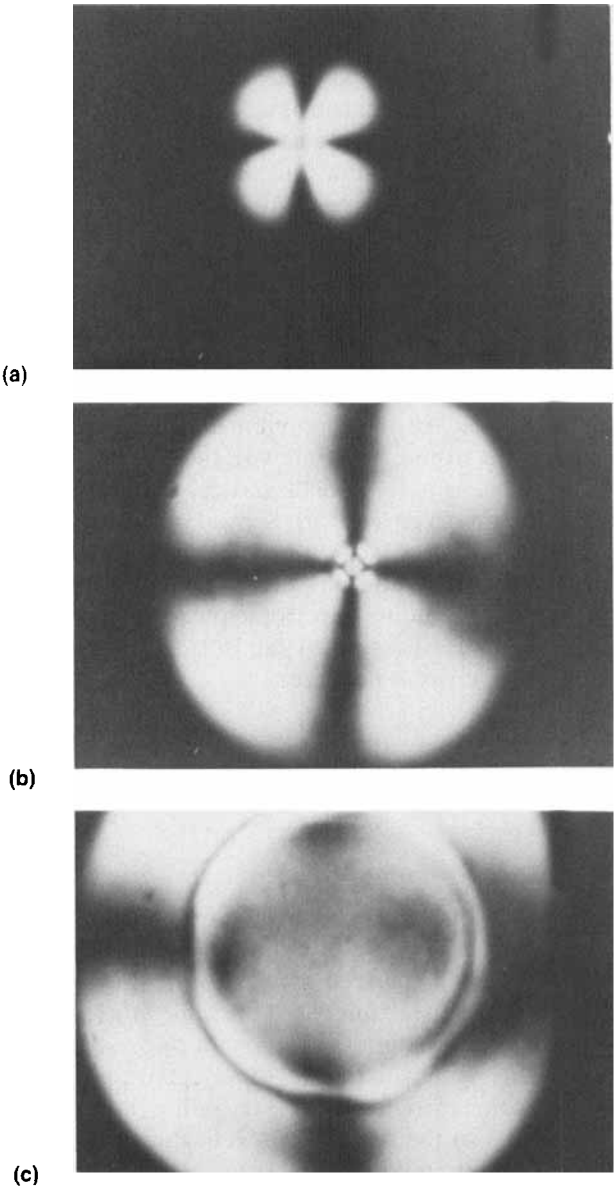

FIGURE 1 Microphotos of the 70 CB free film 14 μm thickness at the phase transition I-N $(P \perp A)$: a) appearance of the nematic layer of the upper free surface; b) growing of the same nematic layer; c) joined upper and lower nematic layers (the disclination circumference in focus).

As known, the molecule of 70 CB is asymmetric, possesses a strong dipole moment directed along the bond —CN, i.e., along the long axis of the molecule, which determines a great positive dielectric anisotropy of the nematic phase.[13] On every interface the molecules should be ordered in such a way to create maximum gradual transition or their energy of interaction should be maximal.[14] Then, according to References 4 and 7 as well, we may expect normal disposition of the molecules of 70 CB on the interface nematic-air.

If the molecules lie in the interface nematic-isotropic liquid point defects will be observed as nuclei with strength $m = \pm 1$. We accept in accordance with de Gennes[15] and Meyer[3] the following structure of the director's field in the nematic layers of 70 CB, in the process of cooling the free film from isotropic phase, presented in Figure 2. The microphotos in Figure 1 are in good agreement with Figure 2. The energy of singular point S contains a considerable part of the surface tension. For this reason the fusion of the upper and lower nematic layers in the film observed under microscope as "cracking" is most possible when points S touch. The experiment shows just that: the fusion occurs when the disclination points from above and from below are in one vertical line.

II. 80 CB

The transition I-N runs in the same way as in 70 CB. In Figure 3a the microphoto is presented of a film 80 CB with thickness 8 μm after joining the nematic layers of the upper and lower interfaces which is in full agreement with the director's field given in Figure 2c. Namely, in the middle, as a result of the homeotropic orientation of the molecules, light fading is observed, at that the picture does not change at rotation of the samples towards the polarizers. Figure 3b shows the film texture wholly passed in nematic phase at 75°C, which clearly expresses the homeotropic orientation of the molecules. The appearance of the interference slowly

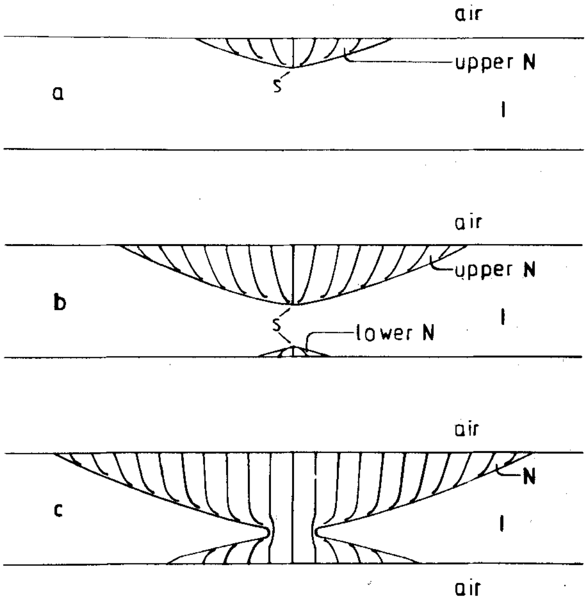

FIGURE 2 The structure of the director field of the nematic phase in the 70 CB free film: a) nematic layer of the upper free surface; b) independent nematic layers of the upper and of lower free surfaces; c) joined upper and lower nematic layers. The lines indicate the director n in the nematic phase.

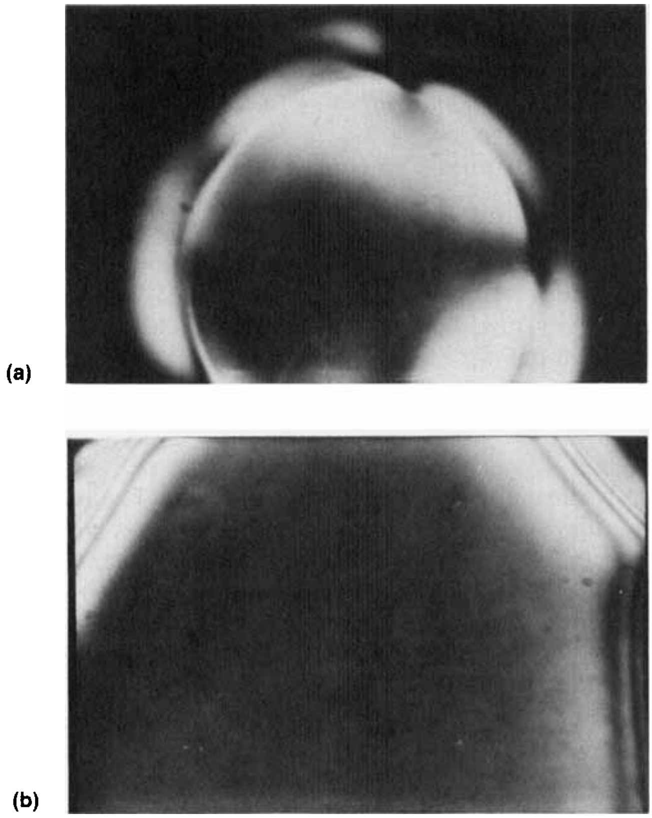

FIGURE 3 Microphotos of the 80 CB free film 8 μm thickness ($P \perp A$): a) joined upper and lower nematic layers; b) the totally passed in nematic phase film.

narrowing circles shows the film thickening to the wall of the aluminum cylinder and the molecular orientation perpendicular at the metal.

III. OOBA and IV. DOBA

Films have been investigated with thicknesses of 40 to 8 μm. On the upper interface isotropic liquid-air, in the process of cooling at the phase transition into nematic phase, consecutively in the black isotropic field one, two, three smeared grey spots are observed under microscope in the typical mode shown in Figure 4. Gradually the grey spot increases, takes the form of bright yellow circle and concentric isochromic circles appear (Figure 4b). In the process of cooling the thickness of the nematic layer reaches to the point when on the interface nematic-isotropic liquid spherical domains or drops begin to form observed even without polarizers (Figure 4c). Because of the incessant appearance of drops, it is not possible to notice the beginning of the nematic layer growth on the lower interface isotropic phase-air. However, the sharp fusion of the two nematic layers-upper and lower, by forming of dark circumference in the film, is fixed ascertaining that it is disclination line

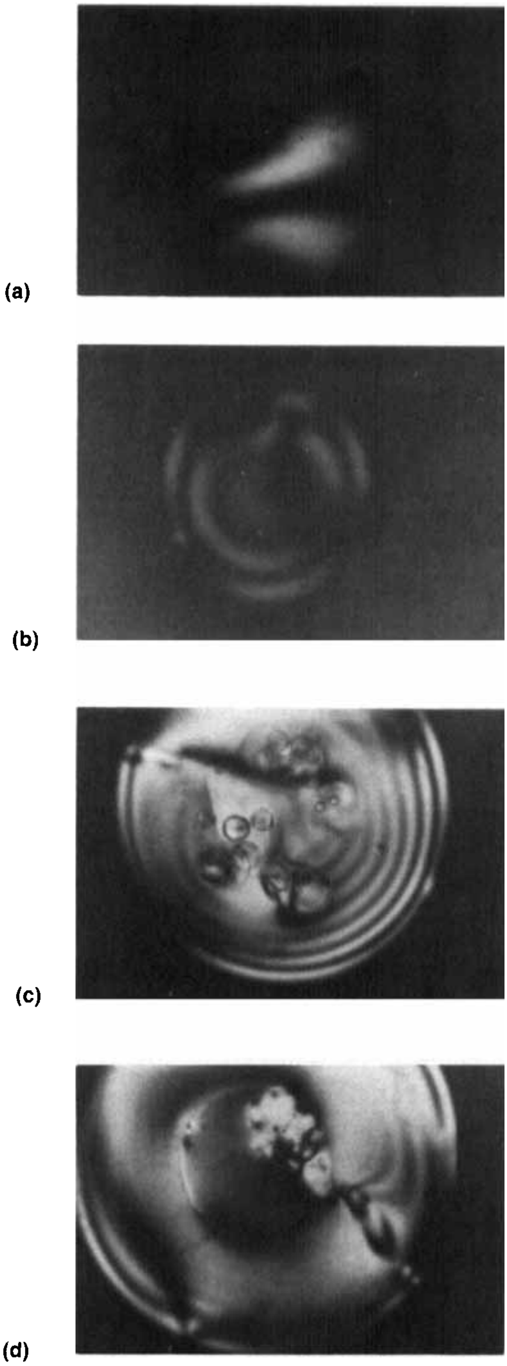

FIGURE 4 Microphotos of the OOBA free film 15 μm thickness at the phase transition I-N ($P \perp A$): a) appearance of the nematic layer of the upper free surface; b) growing of the upper nematic layer; c) the upper nematic layer ~5 μm thickness with drops on the I-N interface; d) joined nematic layers from upper and lower free surfaces.

(Figure 4d). When the whole film goes into a nematic phase, wide dark fields are observed in the texture on yellow background moving at random in the film.

The same results were obtained with DOBA films of thicknesses to 8 μm, while at OOBA under 15 μm the films broke. Besides, after the final transition in N the molecules in the film much more smoothly change their director and the wide dark fields are rather calm.

Plane orientation of the molecules in the nematic phase of the free film with thickness 40–8 μm is excluded because of the lack of shlieren texture. As the most probable one, we accept a tilt orientation of the OOBA (DOBA) molecules of the interface nematic-air at angle θ toward the normal to it with cone degeneration. The observed texture of the upper nematic layer (Figures 4b and 4c) does not give a possibility to answer the question how are the molecules of the interface N-I oriented. At orientation in the interface as well as in perpendicular and under an angle to it, on the smearing place of the two nematic layers—upper and lower, a disclination line will be obtained in the form of circumference (Figure 4d).

The comparison of the results obtained with 70 CB and 80 CB, OOBA and DOBA, shows an important difference: at reaching the upper nematic layer of OOBA or DOBA up to a certain thickness (determined approximately by microscope 5–6 μm) formation of drops (Figure 4c) begins on the interface with isotropic phase. It is known that the phase transition N-I is accepted as a slight first order transition. The latent heat of the transition N-I is 0.6 and 0.7 ccal/mol for OOBA and DOBA respectively.[16] On the interface N-I there is a molecular fluctuation and the molecular orientation may change. If we apply the conclusions of Parsons[4] referring to the interface N-air, for the interface N-I, and assume a description with two order parameters—quadrupolar Q and polar $\vec{p} = p\vec{n}$, ($\vec{n}$ is the molecular director), the surface tension is given by the expression

$$\gamma = \gamma_0 + \frac{1}{2}\gamma_Q\,(\vec{n}\cdot\vec{\kappa})^2 - \gamma_p\cdot\vec{n},\,\vec{\kappa}$$

where $\vec{k}$ is single vector along the normal to the interface N-I. The minimizing of γ toward $(\vec{n},\,\vec{\kappa}) = \cos\theta$ shows that θ can take different values from 0° to 90° depending on the ratio γ_p/γ_Q. Besides, according to Parsons $\gamma_p = \gamma_Q$ is critical point where the fluctuations in the angle θ tend to diverge. Turning back to the investigations of OOBA and DOBA, we can assume that at $T = T_c$ the values of γ_p and γ_Q are close and, therefore, great fluctuations are possible in the angle θ of the N-I interface leading to formation of drops. The observed texture of the 70 CB nematic layer is explained by accepting that the case is far from the critical point $\gamma_p = \gamma_Q$ while the molecule possesses a strong dipole moment and there is no diverging of fluctuations on the interface I-N. However, we cannot give an explanation for the present why in the free OOBA film the nematic layer reaches a certain thickness (5–6 μm) before beginning the drops formation.

V. PAA

A film with thickness 16 μm has been investigated. The nematic phase originates first on the upper free interface by a jump through a bubble around the center of the film. In the process of very slight cooling the diameter and the thickness of the nematic layer grow as the nematic is rather homogeneously yellow. Focusing the lower interface of the film by reaching the temperature of the phase transition I-N, there a bubble (Figure 5a) is also obtained by a sharp jump in its center. The obtained independent nematic layers of the two free boundary surfaces fuse after a certain growing. It is clearly seen in Figure 5b the obtained disclination circumference after this fusion. At further temperature decreasing the whole film goes into nematic phase.

As it was established, the PAA molecules lie in the plane of the interface nematic-air, $\theta = 90°$, as the director $\vec{n}$ may take an arbitrary direction in this plane.[1,2] In the case of PAA ($\theta = 90°$) the surface free energy and the surface tension entirely define by the quadrupolar order or

$$\gamma(Q) = \gamma_0 - \gamma_1 Q + \gamma_2 Q^2$$

where Q is the order parameter, γ_0 is the surface tension at $Q = 0$ and $\gamma_1 > 0$.[4]

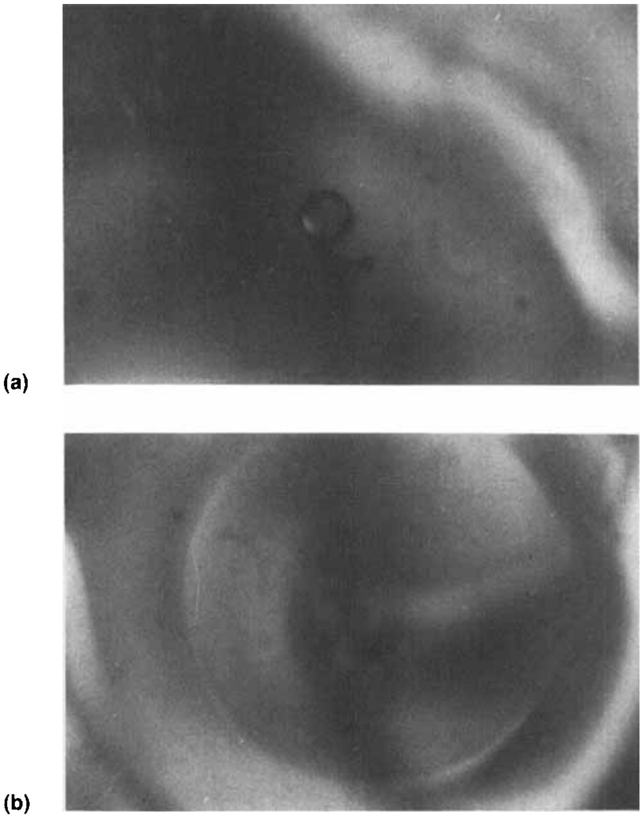

FIGURE 5 Microphotos of PAA free film 15 μm thickness ($P \perp A$): a) nematic layer of the upper free surface (out of focus) and appearance of the nematic of the lower free surface (in focus); b) joined upper and lower nematic layers at focusing the disclination circumference.

Therefore, when the film is cooled and passes the temperature of phase transition to nematic, the surface tension may fall down by a jump. It is a probable reason for the sharp origin of the nematic phase with the appearance of a drop in the middle of the film where the temperature is minimal. Moreover, the latent heat of the transition N-I is 0.15 ccal/mol[17] which is four times less than the latent heat of the same phase transition in OOBA and DOBA,[16] so that at PAA we have good reason to saying for a weak I order phase transition I-N. From the observed texture a conclusion can be drawn that the molecules lie in the interface N-I.

VI. EBBA

The growth of the nematic layer on the upper free surface of EBBA film of thicknesses 15–10 μm is the same as that one for 70 CB. The difference now is that the appearance of the nematic layer on the lower interface is much better observed. Figure 6 presents the microphoto of the grey spot with extinction cross appeared on the lower free surface. On the base of the observed textures, equal to those of 70 CB and 80 CB, a conclusion can be drawn that at T_c the molecules of EBBA are oriented in perpendicular to the interface nematic-air and lie in the interface nematic-isotropic liquid. This is in good agreement with the results from the investigation of MBBA.[2, 18–20]

VII. HOPEBBA

In the investigations of free films with thicknesses 16–14 μm the same textures are observed as for OOBA and DOBA. After a certain thickness of the upper nematic layer a formation of a few drops begins at depth of 5–6 μm of the interface with the isotropic liquid. In contrast to OOBA and DOBA the formation of drops is not so dramatic and for this reason the appearance of the grey spot can be fixed at growth of the nematic layer on the lower free surface of the film as well as the

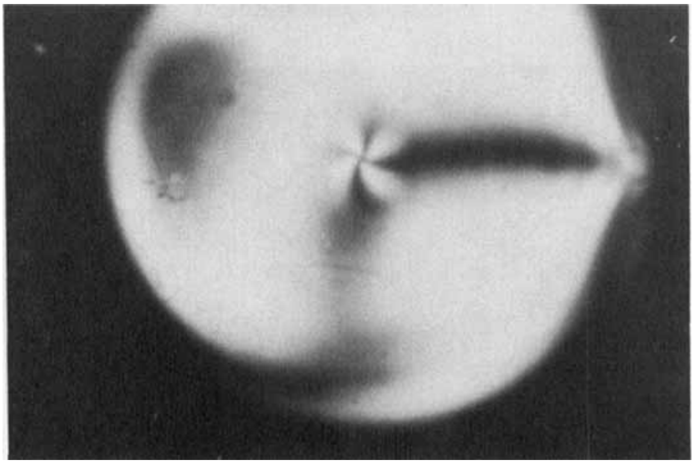

FIGURE 6 Microphoto of the EBBA free film 10 μm thickness ($P \perp A$). In focus the lower free surface at the growing of the nematic grey "four-leaved clover."

sharp fusion of the two independently grown nematic layers. Similar to OOBA and DOBA we accept as most probable the tilt molecular orientation of the interfaces.

VIII. EOBAEECA

This substance possesses a nematic phase with temperature interval only three degrees and exposes smectic A phase under N. At a free film with thickness 15 μm and with P⊥A, the Sm A phase (150°C) has a homogeneous dark grey texture. This means that the molecules are normally oriented to the free surface of the film and the smectic layers are in parallel to it. After transition in isotropic liquid and slow cooling from 164°C, reaching 158°C in the black isotropic phase (P⊥A) an oval is sharply formed of grey black colour in the middle of the film as a "cracking." The nematic phase has been formed in this oval and the texture shows with certainty a homeotropic orientation. At further cooling the sizes of this oval increase and gradually the whole film goes into nematic phase, and the dark nematic is enclosed with narrow yellow ring only at the edges. This yellow ring is easily explained: the molecules on the wall of the aluminum cylinder orient in perpendicular and lie approximately in parallel to the boundary surface. At some distance from the aluminum walls the molecules take normal orientation. At the opposite process of heating a gradual shrinkage is observed of the clearly outlined dark grey oval of the nematic layer surrounded by the black isotropic liquid and at 160°C a sharp transition takes place in I phase as the reduced oval of *N* in the middle of the film disappears.

CONCLUSION

For the first time gradual growing of a nematic layer is followed from an isotropic phase in a film with two free surfaces.

It is established that the two nematic layers at upper and lower free surfaces appear and grow with the temperature decrease independently one from another in free films with thicknesses ≥8 μm. At a certain depth in the film depending on its thickness and on the vertical temperature gradient the two nematic layers fuse. This fusion is observed under microscope as a sharp "cracking" after which a disclination circumference appears. The "cracking" can be explained according to us by the following way. If we note the curvature radius of the upper interface N-I by R_1 and the lower one by R_2, there will be difference in the pressure of the upper interface $\Delta P_1 = 2\gamma/R_1$, and $\Delta P_1 = 2\gamma/R_2$ of the lower one, where γ is the surface tension. As $R_2 < R_1$, it follows that $\Delta P_2 > \Delta P_1$. At touching of the two nematic layers and their fusion the differences ΔP_1 and ΔP_2 become equal. It also follows from deGennes[15] that the maximum approach of the two nematic layers from the upper and lower free surfaces before fusion should be 1–2 μm for the substances 70 CB, 80 CB, EBBA, and EBAPEEA where *S* points of disclination are obtained (Figure 3). Therefore, to observe two independent nematic layers, the minimum thickness of a suspended free in air film should be about 3 μm.

The equation of Landau for the free energy of a nematic is[15]:

$$F = F_0 + \frac{1}{2}A(T)Q^2 + \frac{1}{3}B(T)Q^3 + 0(Q^4),$$

where Q is the order parameter of the nematic phase, F_0 is the free energy at $Q = 0$. The presence of Q^3 means that the phase transition N-I is of first order. In many cases, however, it is emphasized that it is a weak first order transition, which means that the coefficient B is small. The results from the investigation carried out show that in some cases, e.g. at PAA and EOBAEECA this transition is more sharp than the transition of OOBA and DOBA. As pointed out, the latent temperature of the transition N-I of PAA is 4 times less than the one of OOBA and DOBA, from where it follows that the constant B too will be less for PAA than for OOBA and DOBA.

It was established that at the transition I-N in OOBA, DOBA, HOPEBBA spherical domains (drops) form on the interface N-I in free films with thickness ≥ 8 μm even at very slow cooling; no drops form in 70 CB, 80 CB, EBBA, PAA and EOBAEECA under the same conditions. The explanation offered in the paper about the formation of drops ($\theta \neq 90°$ and $\theta \neq 0°$ at I-N interface and $\gamma_p \approx \gamma_Q$ at T_c) cannot give an answer to the question why is it necessary for the nematic layer to reach thickness of several microns after which conditions create for formation of drops. Perhaps at nematic layers below this thickness the molecule fluctuations in the orientation of the interface with the isotropic phase are suppressed in the interface itself.

The investigation shows that the transition process I-N does not depend on the nature of the phase below the nematic one at cooling if the temperature interval of the nematic is not very small.

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