Orientational Structure Transformations Caused by the Electric-Field-Induced Ionic Modification of the Interface in Nematic Droplets

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The films of a polymer-dispersed nematic liquid crystal doped with an ionic surfactant were studied. The surface-anchoring modification effect caused by the local increase in the concentration of surface-active ions was observed at the polymer–liquid crystal interface under the action of an electric field. The modification of the boundary conditions leads to the transformation of the orientational structure of the nematic droplets and, as a result, to an appreciable change in their texture patterns and light-scattering efficiency at the interfaces. The monopolar director configurations (normal and curved) arising in the process of orientational structure transformations are considered and their typical textures are demonstrated. The possibility that the monopolar structure can be formed is theoretically substantiated by the computer simulation of the director field in a nematic droplet with the boundary conditions corresponding to the experiment.

INTRODUCTION

Impetuous development of nanotechnologies renders the study of surface phenomena increasingly topical. The effects occurring at the interface between the two media, of which one is liquid crystal (LC), are quite specific [1, 2]. The most spectacular feature is that the comparatively weak surface-anchoring forces not only can orient the near-surface LC molecules but also can affect the director configuration in a region offset by a few tens of microns from the interface. This property is basic to the functioning of all modern electrooptical LC devices, because it allows the desired orientational structure to be organized in an LC layer through the formation of appropriate boundary conditions. An external electric field reorients LC in its bulk but does not markedly change the interface structure. After switching off the field, the forces of surface interaction restore the initial director configuration in the bulk of LC.

This method of control is efficient only for LC objects of supramicron sizes, because the classical Freedericksz effect [3, 4] is characterized by the inverse proportional dependence of the threshold field strength on the LC layer thickness. Because of this, the threshold field in the LC objects of submicro- and nanosizes exceeds the electrical breakdown field, setting fundamental limits on the use of this effect in the control of thin LC layers or composites of the corresponding size.

A conceptually new approach was developed on the basis of the so-called local Freedericksz transitions [1, 5] consisting in the transformations of the director orientation in the bulk as a result of a change in the balance of the orienting actions of the different surface forces. A typical example is the reorientation of a nematic layer screened from a crystal substrate by a thin amorphous film (~10-nm thick) [6, 7]. The orienting actions of the film and substrate must be different, e.g., planar and homeotropic. The variation of the temperature [6] or film thickness [7] changes the balance of the orienting actions and, thus, initiates the reorientation of the LC layer.

In practice, the methods of modifying boundary conditions by an electric field are most essential. For this purpose, e.g., substrates coated with a ferroelectric LC polymer were used in [8]. After a change in the polarity of the applied voltage, the azimuthal director reorientation in the LC polymer induces the respective orientational transformation in the bulk of the nematic bordering such a substrate.

It is the purpose of this work to examine the possibility of modifying the surface anchoring at the polymer–LC interface through a local change in the concentration of the ionic surfactant in the near-surface layer under the action of an electric field.
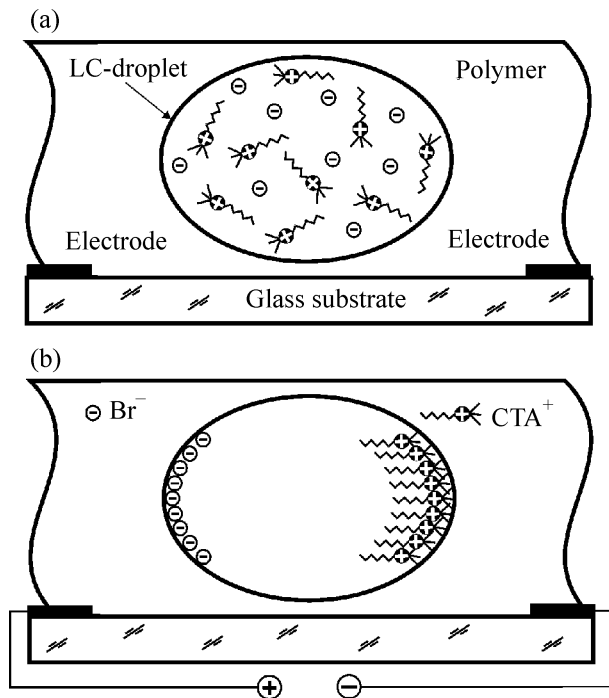
(a)

(b)

Fig. 1. Scheme of the experimental cell. (a) The electric field is switched off, ions are arranged chaotically; (b) the field is switched on, ions are localized near the respective electrodes.

EXPERIMENT

Films of a polymer-dispersed liquid crystal (PDLC) doped with an ionic surfactant were used as the objects of the investigation. The samples of PELS films were prepared by the solution technique [9, 10]. A mixture of LC, polymer, and ionic surfactant taken in a weight ratio of 1 : 1 : 0.01 was dissolved in ethanol. Familiar 4-*n*-pentyl-5-cyanobiphenyl (5CB) nematic with the clearing temperature $T_c = 34°C$ and refractive indices $n_{\parallel} = 1.725$ and $n_{\perp} = 1.534$ ($T = 22°C$) was chosen as an LC. Poly(vinyl butyral) (PVB, 1PP) was used as a polymeric component assuring the tangential (planar) anchoring to the 5CB molecules [11]. The PVB refractive index is $n_p = 1.492$.

Cetyltrimethylammonium bromide (CTAB) was used as an ion-forming surfactant providing normal (homeotropic) boundary conditions [11] at a certain concentration. When dissolved in LC, this compound dissociates into a negatively charged Br$^-$ ion and a positive CTA$^+$ ion. The surface-active properties of CTAB are due to the cations, which, when adsorbed at the interface, can form monomolecular layers in which the long alkyl chains $C_{16}H_{33}$ are oriented perpendicular to the surface.

To study the textural changes in nematic droplets, a cell (Fig. 1) with the electric field directed in the plane of the PDLC film was used. The separation between the electrode strips was 100 μm. Experiments were conducted with composite films subjected to uniaxial tension. The electrodes were fed with monopolar rectangular electrical pulses of 1-s pulse duration with an amplitude varying from 0 to 1000 V.

The texture patterns of the LC droplets were observed using a POLAM P-113 optical polarizing microscope equipped with a digital video camera in the geometry of crossed polarizers and with the analyzer turned off.

RESULTS AND DISCUSSION

The droplets of a 5CB nematic dispersed into a pure PVB matrix with the tangential anchoring are characterized by a bipolar director configuration [12]. The texture patterns of a nematic droplet and the corresponding director configurations typical of the studied composite film are demonstrated in Fig. 2. One can see that the orientational structure of the droplets is bipolar (Fig. 2a), evidencing the tangential anchoring for the chosen concentration of the CTAB surfactant.

In the geometry with the turned-off analyzer (Fig. 2a, left), two point boojum defects [13] are seen as dark spots at the end of the major axis of a prolate droplet. This became possible because of the large gradient of the refractive index in the vicinity of the defect and, hence, intense local light scattering. For the same reason, the pieces of the droplet boundary where the light polarization coincides with the local director orientation are also clearly seen. The gradient of the refractive index, $\Delta n = n_{\parallel} - n_p$, is maximal at these points. The boundary sections with the orthogonal arrangement of the director and light polarization are defined less sharply, because the gradient $\Delta n = n_{\perp} - n_p$ is minimal in this region.

In the geometry of crossed polarizers (Fig. 2a, center), two extinction bands originate from the defects situated at the poles of the droplet's major axis and expand gradually shading the central part of the droplet. The bipolar director configuration in the central section of the nematic droplet is schematically shown by the dashed lines at the right of Fig. 2a.

The droplet's photographs corresponding to the end of the pulse, when the electric vector is directed rightwards (see Fig. 1b), are shown in Fig. 2b. Analysis of the corresponding textures shows that the right boojum decomposes in this case and the director is almost uniformly aligned with the applied field at this half of the droplet. At the left half, the texture is little affected, suggesting that the initial director configuration is retained. The orientational structure corresponding to the new state of the droplet is shown in the right of Fig. 2b. Of the previously described structures, the field-free monopolar structure [12] of the lecithin-doped nematic droplets is the closest analog for this configuration.
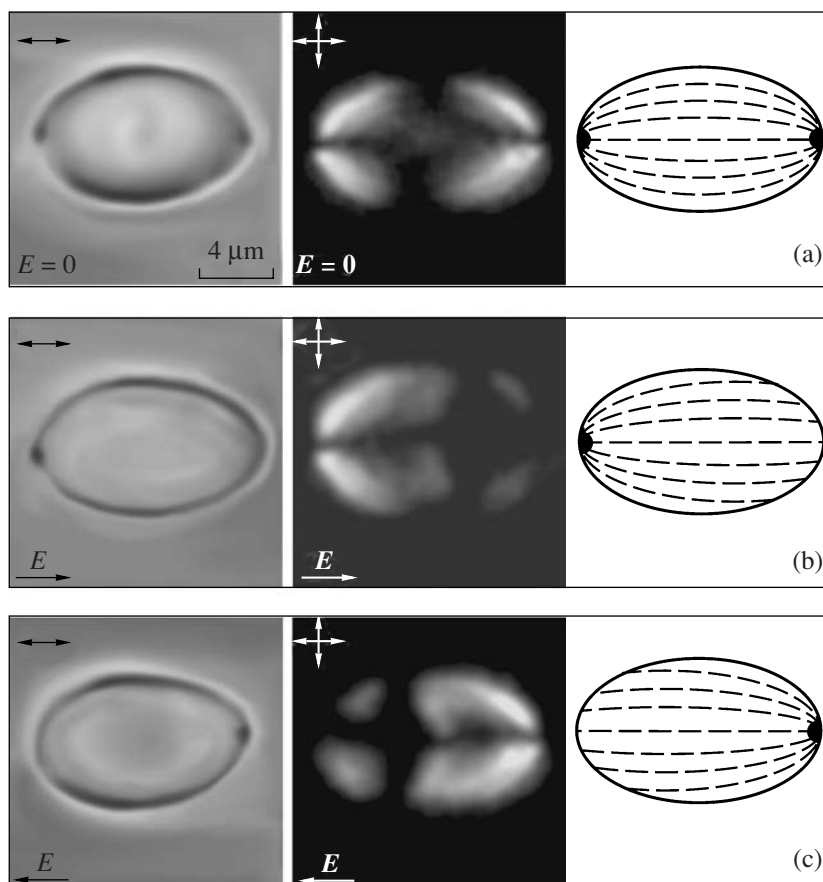
Fig. 2. (Left) Photographs of a nematic droplet with the turned-off analyzer; (center) photographs with the crossed polarizers; (right) the corresponding director configurations. The polarizer orientations are shown by the duplex arrows. The electric field $U = 280$ V is directed along the droplet major axis; (a) the field is switched off; (b) the electric vector **E** is directed to the right; (c) the vector **E** is directed to the left.

The reversal of the field direction (Fig. 2c) induces symmetric changes in the textures: the left defect decomposes, while the initial director distribution at the right half of the droplet is retained.

In this situation, the orienting action of the external field on the LC volume is not crucial. The concentration of the ionic impurity in the samples was such that the applied field was almost fully screened inside the droplet by the field of spatially separated ionic charges [14].

The observed transformation of the orientational structure in the LC droplet can convincingly be explained by the ion rearrangement. Under the action of the external field, the surface-active cations are concentrated near the droplet boundary facing the negative electrode to form here the CTA$^+$ monolayers with alkyl chains oriented mostly perpendicular to the interface. In the LC droplets studied, the fraction of CTAB was ~0.5 wt % or ~2.6×10^{-12} g for a spherical droplet with a radius of 5 μm. With regard to the molecular weight $M_{CTAB} = 6.04 \times 10^{-22}$ g, such a droplet contains ~4.3×10^9 CTAB molecules. The projection of a homeotropically arranged CTA$^+$ cation onto the interface is about

0.15×10^{-18} m^2 for the straightened *trans* conformation of the alkyl chain. With these parameters, four close-packed monolayers of the CTA$^+$ cations can form at the droplet surface facing the negative electrode. Clearly, the number of monolayers is maximal at the point closest to the cathode and it decreases with distance from this point. For comparison, the critical number of polar monolayers of stearic acid (whose molecules are similar in size and shape to the CTA$^+$ ions) in 5CB LC is two, while the number of nonpolar bilayers is ten [7]. In our case, the cation monolayers can also screen the orienting action of the PVB matrix and change the surface anchoring from tangential to homeotropic.

This modification occurs locally at the boundary area closest to the negative electrode. With distance from it, the concentration of the ionic surfactant decreases and the anchoring angle θ (between the LC director and the normal to the surface) changes gradually from 0 (in the region of the destroyed defect) to 90° in the boundary area adjacent to the minor axis of the ellipsoidal droplet. After the field reversal, the CTA$^+$ ions transfer to the left half of the droplet to form there
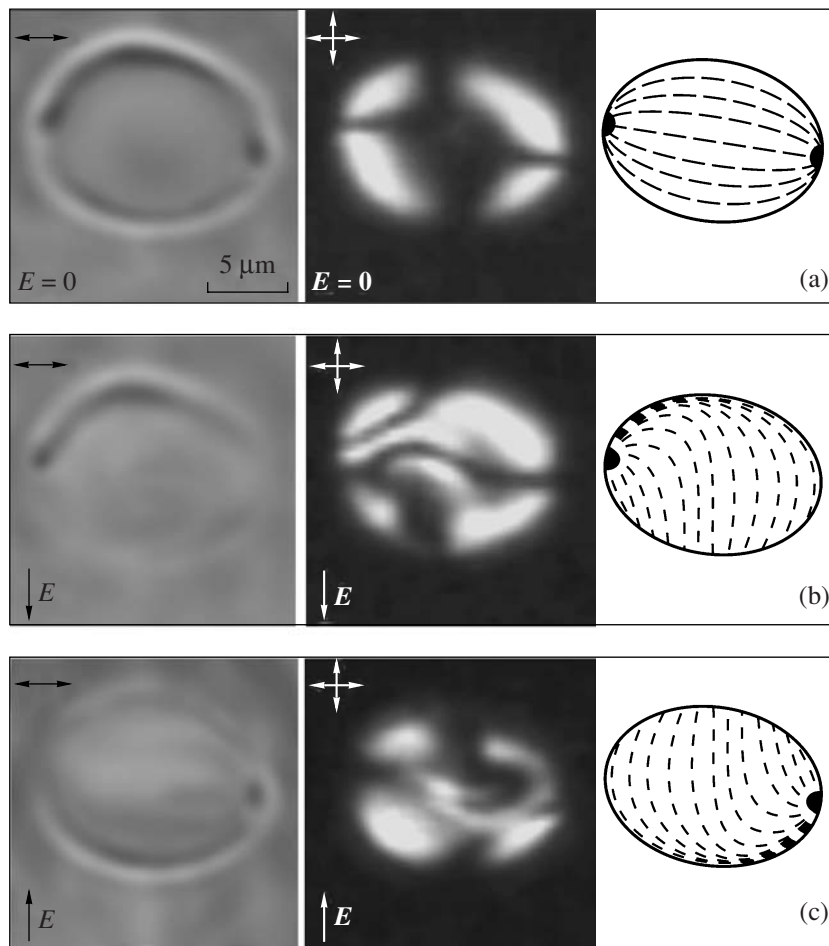
Fig. 3. The arrangement of images and notations are as in Fig. 2. The electric field $U = 950$ V is directed 81° to the droplet major axis; (a) the field is switched off; (b) the electric vector **E** is directed downwards in the figure plane; (c) the vector **E** is directed up.

a surface area with homeotropic anchoring. After the cation departure, the tangential boundary conditions and the surface boojum are restored at the right half of the droplet. As seen, the local increase in the concentration of the Br⁻ anion does not affect the surface anchoring.

The orientational structure transformations occurring in an LC droplet in the presence of a field perpendicular or nearly perpendicular to the bipolar axis of the droplet (Fig. 3) are explained in a similar way. In this case, the curved monopolar structure forms (Figs. 3b and 3c, right). One of the boojums is retained at the left half of the droplet in Fig. 3b and at the right half of the droplet in Fig. 3c. The other boojum decomposes, and the director lines deflect either downwards (Fig. 3b) or upwards (Fig. 3c) and crop out at the surface area saturated with the surface-active cations, where the boundary conditions become nearly homeotropic. At the opposite side of the droplet, where the Br⁻ anions are localized, the tangential anchoring is retained, as in the case shown in Figs. 2b and 2c.

Noteworthy is the fact that almost half of the visible droplet boundary is blurred when the field is perpendic-

ular to the bipolar axis (lower left in Fig. 3b or top left in Fig. 3c). This occurs because the refractive indices of the LC and polymer are equalized, as a result of which the scattering cross section for this light polarization becomes markedly smaller for such droplets than for the bipolar droplets. This inference is consistent with the results of our preliminary measurements of light transmittance, which showed that, in the presence of a constant electric field, the film transmittance increased two to three times, evidencing the promise of the use of this effect in electrooptical devices.

THEORY

The possibility that the monopolar structure can appear was analyzed theoretically by the computer simulation of director distribution in a nematic droplet. The LC free energy [15] was minimized in a single-constant approximation,

$$F = \frac{1}{2}\int K[(\nabla \cdot \mathbf{n})^2 + (\nabla \times \mathbf{n})^2]dV. \qquad (1)$$

Tangential anchoring
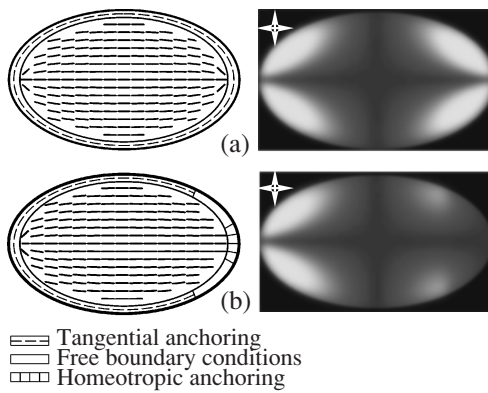Free boundary conditions
Homeotropic anchoring

Fig. 4. Numerical calculation of the director configuration and the texture in crossed polarizers for a nematic droplet with the size parameters and boundary conditions corresponding to the experiment (see Fig. 2). The boundary conditions (tangential, free, and homeotropic) are indicated in the droplet shells (left in the figure). (a) Bipolar orientational structure with the homogeneous tangential anchoring; (b) monopolar structure with the inhomogeneous boundary conditions.

Here, **n** is the unit vector along the director and K is the averaged elastic modulus. In [12], this approach was applied for the calculation of orientational structures in droplets with inhomogeneous boundary conditions. In this work, we used this method for the simulation of nematic droplets shaped as a prolate ellipsoid. As was discussed above, the field of spatially separated ions in the droplets compensates for the action of the external field. For this reason, the terms accounting for the LC energy in the electric field were omitted in Eq. (1). The values of the elastic modulus used for determining K were taken from [16]. The boundary conditions were chosen according to the experiment demonstrated in Fig. 2. Using the data obtained for the director configuration, the corresponding texture patterns for the crossed polarizer were calculated by the well-known theoretical method [17] (Fig. 4, right).

One can see (Fig. 4a) that this method properly describes the bipolar director configuration and the texture for the prolate nematic droplets. To simulate the monopolar structure shown in Figs. 2b and 2c, tangential anchoring was assumed for the greater part of the droplet surface (~0.7 of the visible boundary; see Fig. 4b, left). The homeotropic boundary conditions are introduced in a small portion (~0.1 of the boundary) on the right. The boundary conditions are free between these two regions. The resulting director configuration and the texture pattern (Fig. 4b) are, generally, consistent with the experiment (Figs. 2b, 2c), suggesting that the above analysis of the experimental data is correct.

CONCLUSIONS

Noteworthy are the distinctions between the observed effect and the phenomena initiated by ionic impurities in nematic LCs. Among these phenomena,

various types of electrohydrodynamic instability of nematics in an alternating electric field are well known [7, 18]. In such systems, the ionic vortex motion initiates corresponding flows in the LC. The initially homogeneous director orientation becomes destroyed and the LC volume breaks down into many light-scattering vortices.

Another type of phenomena was described in detail in [2] and is associated with the selective absorption of ions by the interface in the absence of an external field, as a result of which a double electrical layer forms near the surface. The electric field of the double layer can dominate other orientational actions of the substrate and govern the director orientaton at the LC surface.

The effect studied in this work is based on the combined action of two properties of the used dopants. The ion-forming ability of the impurity makes possible the electrically controlled transport of certain ions to the required place of the LC cell. The surface-active properties of the CTA^+ monolayers formed in this case allow the tangential orientational effect of the PVB matrix to be screened and the surface anchoring to be changed from tangential to homeotropic. A similar screening effect is described in [7] for Langmuir layers formed by molecules of stearic acid. However, the use of electrically neutral molecules cannot afford electrically controlled rearrangement of the surface anchoring.

The list of objects to which this effect can be applied is not restricted by the PDLC materials. These can be various LC structures in which the role of the substrate or matrix is played by solid media, polymers, liquids, etc. The results of our investigation are particularly topical for the design of new optoelectronic devices based on submicro- and nanostructured LC media.

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