Electrically Controlled Local Fréedericksz Transition in a Layer of a Nematic Liquid Crystal

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A local Fréedericksz transition caused by electrically controlled surface anchoring in a nematic liquid crystal has been implemented owing to the displacement of surface-active ions. In the initial case, the nematic is homeotropically aligned by monomolecular layers of cetyltrimethylammonium bromide cations adsorbed on the surface of substrates. One of the substrates in a static electric field becomes free of a cation layer and specifies planar boundary conditions; as a result, a homeoplanar orientation structure is formed. The features of the dynamics of the optical response of the cell under study that are characteristic of the effect under consideration are discussed.

INTRODUCTION

The local Fréedericksz transition is the reorientation of a liquid crystal under the action of external factors changing the surface anchoring of liquid-crystal molecules with a substrate [1]. The modification of boundary conditions is generally ensured by changing the balance of the orienting action of different surface forces. This modification can occur under the variation of the temperature [2] or thickness of the orienting layer [3], irradiation by light responsible for photoconformational transformations in surfactant molecules [4], and the action of an electric field changing the azimuthal direction of the easy orientation axis on the surface of a ferroelectric liquid crystal polymer [5]. For droplets of nematic liquid crystals that are doped with ionic surfactants and are dispersed in the polymer, the possibility of the electrically controlled switching of surface anchoring between the planar and homeotropic states in both the direct [6] and inverse [7] modes of the effect was shown. An attempt to implement an electrically controlled change in boundary conditions in the planar nematic layer with an ionic surfactant preliminarily deposited on substrates of the liquid crystal cell was made in [8]. However, a surface transition was not implemented in the pure form, because electrohydrodynamic instability is the dominant effect. The aim of this work is to implement the local Fréedericksz transition in a layer of a nematic liquid crystal caused by the modification of surface anchoring and to analyze the features of inherent orientational structure transformations.

SAMPLES AND INVESTIGATION METHODS

We study planar liquid crystal cells consisting of two glass substrates with transparent ITO electrodes on the inner sides and a layer of a nematic liquid crystal between them. The well-known 4-*n*-pentyl-4'-cyanobiphenyl (5CB) nematic with positive dielectric anisotropy ($\Delta\varepsilon > 0$), which was doped with cetyltrimethylammonium bromide (CTAB) as a cation surfactant, was used as the liquid crystal. The CTAB molecules in the liquid crystal dissociate into bromine anions and CTA$^+$ surface-active cations, which, being adsorbed on the substrate, can form a monomolecular layer specifying homeotropic surface anchoring [9].

Polymer films with a thickness of about 1.5 μm were preliminarily deposited on the electrodes. These films serve as an orienting coating and a protective layer preventing the contact of surfactant ions with the electrodes. Polymer films based on polyvinyl alcohol (PVA) and glycerin (Gl) solved in water were formed by the method of spin coating of the solution with subsequent drying. It is known that such films specify planar boundary conditions for the 5CB nematic [10]; i.e., molecules of the liquid crystal are oriented parallel to the interface. The easy orientation axis was formed by the mechanical rubbing of the polymer surface in a given direction. The cells were filled with the liquid crystal by the capillary method in the isotropic phase. The thickness of the liquid crystal layer in the samples under study was about 6 μm.

The optical textures of the planar nematic layer were studied by polarization optical microscopy with an Axio Imager A1 (Carl Zeiss) microscope equipped with an AxioCam MRc5 (Carl Zeiss) digital camera, which made it possible to perform the photo and video
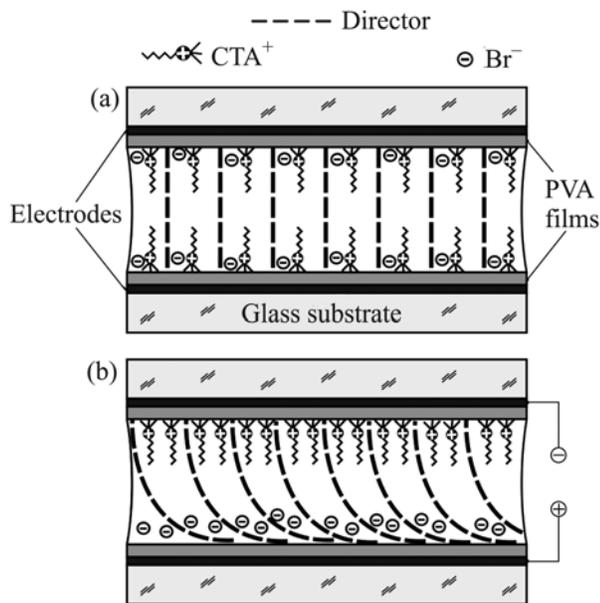
Fig. 1. Scheme for implementing the effect of the ion modification of the surface anchoring in the nematic layer. (a) Electric field is switched off; the number of CTA$^+$ ions adsorbed at the interface is sufficient for the formation of homeotropic anchoring on the upper and lower substrates. (b) Lower substrate in the static electric field becomes free of CTA$^+$ ions; the orienting polymer film on this substrate specifies the planar ordering of the liquid crystal.

Fig. 2. Microphotographs of the optical textures of the liquid crystal layer (a) in the initial state and (b, c) in the static electric field E with the strength $U = 3$ V directed (b) from the lower substrate to the upper one and (c) from the upper substrate to the lower one. The crossed polarizers are marked by double arrows. The lower substrate was rubbed in the direction R at an angle 45° to the polarizers. The upper substrate was not rubbed.

recording of proceeding processes. The observations were carried out in the crossed polarizer geometry. Rectangular monopolar pulses of the electric field from an AHP-3122 (AKTAKOM) generator were applied to the ITO electrodes.

To study the dynamics of the macroscopic optical response of the liquid crystal cell, we used a He−Ne laser (Linos) with a wavelength of $\lambda = 0.633$ μm. The laser radiation passed successively through the polarizer, liquid crystal cell, and analyzer and arrived at a photoreceiver. The diameter of the cross section of the laser beam was 1 mm. The measurements were performed in the crossed polarizer geometry. The angle between the direction of the rubbing of the substrates and the direction of polarizers was 45°. An electric signal was applied from the generator in parallel to the sample and a DISCO (Treid-M) USB oscilloscope to which a signal from the photoreceiver was applied. The oscilloscope was connected to a computer, which made it possible to store and process data.

RESULTS AND DISCUSSION

Figure 1 shows the scheme for implementing the effect of the electrically controlled modification of the surface anchoring. It is necessary to choose the concentration of CTAB in 5CB such that the nanolayer of CTA$^+$ cations adsorbed at the interface can screen the planar orienting action of the polymer film and specify

the homeotropic surface anchoring. In this case, the homogeneous ordering of the director oriented perpendicularly to the substrates appears in the entire nematic layer in the initial state (see Fig. 1a). When a static electric field is applied, surfactant ions move toward the corresponding electrodes and one of the substrates becomes free of the layer of CTA$^+$ surface-active cations. As a result, planar anchoring conditions characteristic of a polymer coating are formed on this substrate (Fig. 1b). Finally, the orientational transition from the homeotropic structure to the hybrid homeoplanar configuration of the director occurs in the liquid crystal cell.

The experimental conditions necessary for implementing the schemes described above can be ensured with the use of polymer coatings with the weight ratio of components PVA : Gl = 1 : 0.243 and 5CB nematic doped with the ionic surfactant in the ratio of 5CB : CTAB = 1 : 0.01. The photographs of the optical textures of the liquid crystal cell are shown in Fig. 2, where the electrically controlled switching of surface anchoring is demonstrated. One of the substrates was preliminarily rubbed, whereas the other substrate was used without rubbing. In the initial state, light does not pass through the optical system irrespective of its azimuthal rotation with respect to the crossed polarizers (see Fig. 2a). This indicates the homeotropic orientation of the director throughout the entire nematic layer. When the static electric field oriented from bot-
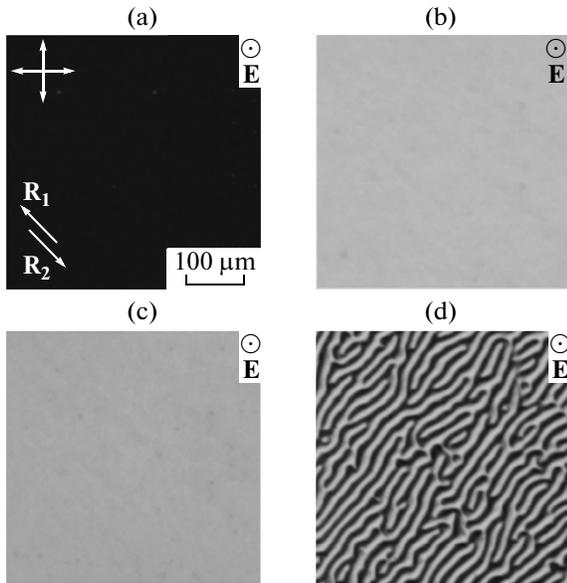
Fig. 3. Optical textures of the 5CB layer for the electric field strengths $U =$ (a) 2.7, (b) 3, (c) 3.3, and (d) 4 V. The notation is the same as in Fig. 2; $\mathbf{R}_1$ and $\mathbf{R}_2$ are the rubbing directions in the upper and lower substrates, respectively.

Fig. 4. Oscillogram of the optical response of the planar liquid crystal cell to the pulse of an electric field of 2.9 V. Numbers mark the boundaries of the characteristic time intervals. The time sweep scales are different in the left and right parts of the figure.

tom to top is applied (Fig. 2b), the homogeneous bleaching of the liquid crystal layer is observed in the steady-state regime. This means that the homogeneous planar ordering of the director oriented along the R direction over the entire area of the substrate is formed on the lower substrate. When the polarity of the electric signal is changed, the transmittance of the cell increases, but the optical pattern becomes sharply inhomogeneous (Fig. 2c). This is explained by the absence of an azimuthally separated direction on the unrubbed substrate with planar anchoring.

These changes in the transmittance of the liquid crystal cell cannot be attributed to the classical Frédericksz effect [11], because the 5CB nematic with $\Delta\varepsilon > 0$ was used in the experiment. In this case, the application of the external electric field perpendicular to the plane of the liquid crystal layer would lead to the stabilization of the initial homeotropic orientation of the director. Thus, these observations convincingly demonstrate the local Frédericksz transition in the planar nematic layer, which is due to the switching of surface anchoring from homeotropic to planar on the substrate with the anode electrode.

Figure 3 shows photographs demonstrating the optical textures of the liquid crystal layer for various control field strengths. In this case, both substrates were rubbed and put so that their rubbing directions were antiparallel. The reorientation process caused by the ionic-surfactant modification of surface anchoring is of a threshold character. For this liquid crystal cell, the reorientation process begins with the field strength $U = 2.8$ V. The threshold character is due to the exist-

ence of the critical density of the layer of adsorbed CTA^+ ions below which the orienting action of the polymer coating is no longer screened. When the static electric field is applied to the cell, surface active ions begin to leave one of the substrates. When the critical surface density is reached at a certain electric field strength, the modification of surface anchoring begins. The local Frédericksz transition is observed in the pure form in the range 2.8 V $< U <$ 3.5 V. At $U = 3.6$ V, the formation of the texture pattern of domains predominantly elongated perpendicular to the rubbing directions begins in the liquid crystal layer; these domains are clearly seen at $U = 4.0$ V (Fig. 3d). The formation of domains can be attributed to various surface phenomena [12], the analysis of which is beyond the scope of this work.

The texture patterns considered above correspond to the steady state of modified boundary conditions in the static electric field. However, the most interesting features of the effect under study are manifested in the response dynamics of the liquid crystal layer in the region of the leading and trailing edges of the rectangular electric pulse (Fig. 4). The pulse duration was 10 s. The transmittance was determined as $T = I_t/I_0$, where I_0 and I_t are the intensities of radiation after the first and second polarizers, respectively. The transmittance in the crossed-polarizer system at the homeotropic orientation of the liquid crystal is close to zero. The deviation of the director from the normal generally leads to the bleaching of the cell.

The complex picture of the optical response can be conditionally divided into a sequence of time intervals in each of which a certain physical effect dominates. First, a noticeable delay of the optical response with respect to the leading edge of the electric pulse is noteworthy ($\tau_{12} = 0.09$ s, where the subscript indicates two

points in Fig. 4 the interval between which is considered). This delay appears because ions cannot instantaneously block the action of switched-on external electric field $\mathbf{E}_0$ on the bulk of the liquid crystal. Therefore, in this interval, the classical Fréedericksz effect occurs and stabilizes the homeotropic orientation of the nematic with $\Delta\varepsilon > 0$ and the transmittance remains zero. The time of the separation of the ion cloud can be approximately taken as the time of the passage of ions through the liquid crystal layer [13],

$$\tau_T = \frac{l^2}{U_{LC} \cdot \mu}, \tag{1}$$

where l is the thickness of the liquid crystal layer, U_{LC} is the voltage on the liquid crystal layer, and μ is the mobility of ions. Using the values $\mu = 10^{-6}$ cm^2 s^{-1} V^{-1} [13], $U_{LC} = 1.44$ V (obtained taking into account the presence of polymer coatings), and $l = 6$ μm, we obtain the estimate $\tau_T = 0.25$ s, which is an upper limit for the possible action of the classical Fréedericksz effect. In reality, it is switched off earlier when the effective field $\mathbf{E}_{eff} = \mathbf{E}_0 + \mathbf{E}_i$ (where $\mathbf{E}_i$ is the electric field of the separated ions) decreases below the threshold value. Indeed, the delay time τ_{12} is noticeably shorter than the transit time τ_T.

At time instant 2, the external electric field $\mathbf{E}_0$ is mainly compensated by the field of ions $\mathbf{E}_i$. The layer of planar orienting coating free of CTA$^+$ cations on one of the substrates begins to rotate the director of the liquid crystal. This leads to an increase in transmittance. The T curve reaches a maximum of about 67%, then decreases to 33%, and is finally saturated. This behavior of transmittance can be predicted using the known relation [14] for an anisotropic plate in crossed polarizers. With the parameters of our experiment, it can be written in the simplified form

$$T = \sin^2 \pi \frac{\int \Delta n(l)dl}{\lambda}. \tag{2}$$

The numerator is the integral optical path difference for the ordinary and extraordinary beams on the thickness of the liquid crystal layer and λ is the wavelength of laser radiation. For the homeotropic nematic layer, the integral in Eq. (2) and, hence, the transmittance are zero. For the homeoplanar layer of the 5CB liquid crystal ($n_\parallel = 1.7057$, $n_\perp = 1.5281$ at $t = 25°C$ and $\lambda = 0.633$ μm [15]) with a thickness of $l = 6$ μm, this integral gives 0.511 μm in the approximation of a linear change in the slope of the director over the thickness of the layer. This means that, when the orientational structure of the liquid crystal varies smoothly from the homeotropic structure to the homeoplanar one, the transmittance increases to a maximum at an integral value of 0.317 μm and then decreases to $T = 32\%$, corresponding to an integral value of 0.511 μm. This behavior of transmittance is in good agreement with

the experiment. This agreement confirms the formation of the homeoplanar structure in the electric field.

The time of reaching the steady-state regime $\tau_{23} = 0.39$ s is in essence the time of the switching of surface anchoring plus the relaxation time of the homeotropic configuration of the bulk of the liquid crystal to the homeoplanar structure (Fig. 5a). The relaxation processes in the liquid crystal are described by the formula [13]

$$\tau_{rel} = \frac{\gamma l^2}{\pi^2 K}, \tag{3}$$

where γ is the rotational viscosity of the liquid crystal and K is the corresponding modulus of elasticity. Taking the average value $K = 6.3$ pN [16] and $\gamma = 0.09$ Pa s [17] for the 5CB liquid crystal, we obtain $\tau_{rel} = 0.05$ s. The τ_{23} value is larger than τ_{rel} by a factor of 8 apparently because of the total effect of two orientational processes indicated above.

The picture of a change in the transmittance after the switching-off of the controlling pulse is even more complicated. In this case, the liquid crystal layer at the beginning is subjected to the field of separated ions $E_i = E_0$. The classical Fréedericksz effect again occurs and is manifested in the reorientation of the majority of the bulk of the liquid crystal along the field except for a thin layer near the lower substrate (Fig. 5b). In the time $\tau_{45} = 0.01$ s, the transmittance undergoes the inverse evolution, first increasing to the same value of 67% and, then, decreasing to 11%. The complete quenching is impossible because of the presence of the aforementioned surface region, where a certain phase mismatching of the beams is collected. The switch-on time of the classical Fréedericksz effect is given by the formula [13]

$$\tau_{on} = \frac{\gamma l^2}{\varepsilon_0 \Delta\varepsilon E l^2 - \pi^2 K}, \tag{4}$$

where $\Delta\varepsilon$ is the anisotropy of the dielectric constant of the nematic and E is the electric field strength acting on the liquid crystal. Taking the above γ, l, and K values, as well as $\Delta\varepsilon = 11.2$ [18] and $E = 0.24 \times 10^6$ V/m, which were calculated taking into account the polymer coatings, we obtain $\tau_{on} = 0.02$ s. This estimate exceeds τ_{45} because the reorientation of the liquid crystal by the field of ions remains incomplete.

After the external field is switched off, two clouds of separated ions move toward each other. This leads both to a decrease in the liquid crystal layer between them, which is subjected to the field $\mathbf{E}_i$, and to a gradual decrease in the field to zero. At the same time, the nematic layer adjacent to the electrode from which bromide anions leave grows rapidly. The recovery of the homeoplanar structure begins here. This process becomes dominant at time instant 5 and lasts $\tau_{56} = 0.32$ s. This reorientation is in essence similar to a local transition in interval τ_{23}. For this reason, the indicated
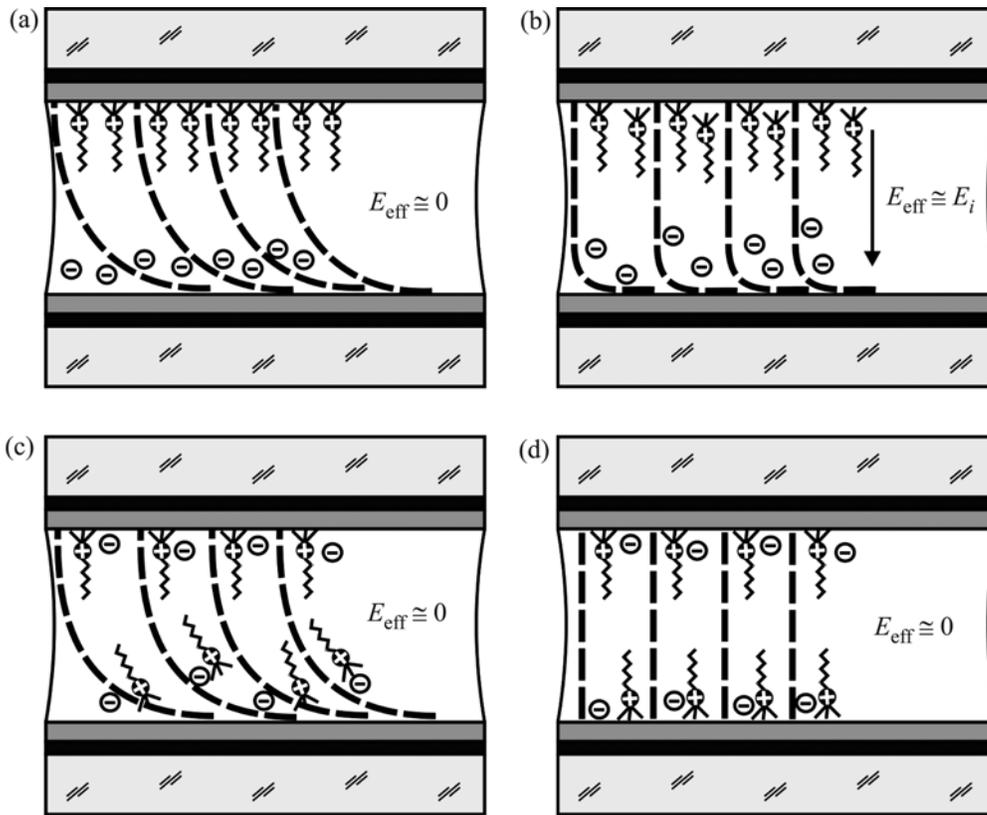
Fig. 5. Distributions of the director and surfactant ions in the liquid crystal layer at time instants marked by the following numbers in Fig. 4: (a) 4, (b) 5, (c) 6, and (d) 7.

time intervals are close to each other and the character of a change in the transmittance is identical.

The process begins to complete at time instant 6, when surface-active CTA^+ ions approach, owing to diffusion, the substrate with the planar orienting coating (Fig. 5c). They are adsorbed on this substrate and begin to form the homeotropically orienting layer, returning the orientational structure of the liquid crystal to the initial state (Fig. 5d). In this case, the character of a change in the transmittance becomes opposite. For this reason, the shape of the section of the oscillogram in the interval τ_{67} is an almost specular reflection of the interval τ_{56} at point 6, but is extended in time to the value $\tau_{67} = 1.08$ s.

CONCLUSIONS

The local Fréderickz transition under consideration is very sensitive to the concentration and composition of the components. The key role of the protective layer, which prevents the direct arrival of surfactant ions at the ITO electrodes, is particularly noteworthy. In the absence of this layer in our experiments, as well as in [8], electrohydrodynamic instability, which prevents the observation of the modification

of boundary conditions, dominated in the transformation of the orientational structure.

Compared to the classical Fréderickz effect, where oscillations of the optical response to the leading and trailing edges of the rectangular electric pulse coincide in the number of extrema [13], the local Fréderickz transition, which is caused by electrically controlled switching of boundary conditions, generally leads to a more complex dependence of transmittance. We have analyzed the oscillogram of the optical response of the cell under study with the known theoretical models describing the dynamics of ion and orientational processes in the liquid crystal. The dominant physical effects whose sequence accompanies the reorientation of the liquid crystal owing to the ion-surfactant modification of surface anchoring have been revealed.

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