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Multistability in Polymer-Dispersed Cholesteric Liquid Crystal Film Doped with Ionic Surfactant

A. P. Gardymova, V. Ya. Zyryanov*, and V. A. Loiko
Siberian Federal University, Institute of Engineering Physics and Radio Electronics, Krasnoyarsk, 660041 Russia
Kirensky Institute of Physics, Krasnoyarsk Scientific Center, Siberian Branch,
Russian Academy of Sciences, Krasnoyarsk, 660036 Russia
Reshetnev Siberian State Aerospace University, Krasnoyarsk, 660014 Russia
Stepanov Institute of Physics, National Academy of Sciences of Belarus, Minsk, 220072 Belarus
**e-mail: zyr@iph.krasn.ru*

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Abstract—A memory effect has been discovered in composite films based on a polymer containing dispersed cholesteric liquid crystal, which is related to the modification of the surface anchoring by an ionic surfactant under the action of an applied electric field. Parameters of electric signals are selected that ensure the switching of the composite film between some stable states with different levels of optical transmittance.

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In recent years, technologies aimed at reducing the energy consumed by liquid crystal (LC) displays have been developing extensively. The most effective solution to this problem can be based on the use of a bistability phenomenon that allows a preset optical state to be retained in the absence of an electric field. In this respect, much attention is devoted to cholesteric liquid crystals (ChLCs) in which bistable optical states of various types can be realized [1–7]. A most widely used effect that is already employed in display devices consists in switching a ChLC between stable states with a planar structure and a focal conic domain structure [1, 2, 7]. The cholesteric helix pitch P must be much smaller than the size D of a cavity filled with the LC. The planar structure of a ChLC selectively reflects the circularly polarized light component, while the domain structure intensively scatters radiation. If a ChLC is applied onto a light-absorbing substrate, the cell would reflect the light at a certain wavelength in one state and appear black in the other state. This effect is operative in both planar ChLC layers and ChLC droplets dispersed in a polymer film [1, 2]. The latter case is of special interest, since it enables the development of flexible bistable reflective displays [7], although the small pitch of the cholesteric helix makes necessary large control voltages. The memory effect is also characteristic of polymer-dispersed ChLC (PDChLC) films with a helicoid pitch comparable to the diameter of ChLC droplets ($P \cong D$) [8], but the retention of recorded information in this case requires a supporting voltage [9].

The aim of this study was to assess the alternative possibility of using PDChLC films in bistable optoelectronc devices and displays with nonvolatile data storage.

The samples of PDChLC films were prepared by the emulsification of a ChLC in an aqueous solution of polyvinyl alcohol (PVA) plasticized by glycerol (GL), followed by the evaporation of solvent [10, 11]. The ChLC represented a mixture of 4-*n*-pentyl-4'-cyanobiphenyl (5CB) with 1.5 wt % of cholesteryl acetate. The cationic surfactant (cetyltrimethylammonium bromide, CTAB) was dissolved in the ChLC mixture before the preparation of emulsion. The ratio of components in the obtained ChLC–PVA–GL–CTAB composition was 1 : 19 : 6 : 0.1 (w/w). As is known [11], LC molecules acquire a tangential orientation on the surface of PVA and that plasticized by glycerol. The surfactant (CTAB) in LCs decomposes into Br^- anions and cetyltrimethylammonium cations (CTA^+). At the indicated concentration, CTA^+ ions adsorbed on a polymer surface form a nanodimensional layer that changes the surface-anchoring character from tangential to homeotropic [12].

The morphology of composite films and the optical textures of ChLC droplets were studied using an Axio Imager A1m (Carl Zeiss) polarization microscope equipped with a digital video camera. The insets to Figs. 1–3 show photographs of the fragments of PDChLC films in various states as observed in crossed polarizers. The same geometry was used to measure the optical response of composite films to an applied electric field. For this purpose, a PDChLC film sample was confined between two glass plates with transparent ITO electrodes, this sandwich structure was arranged between crossed polarizers, and an alternating-sign electric signal of rectangular or sinusoidal

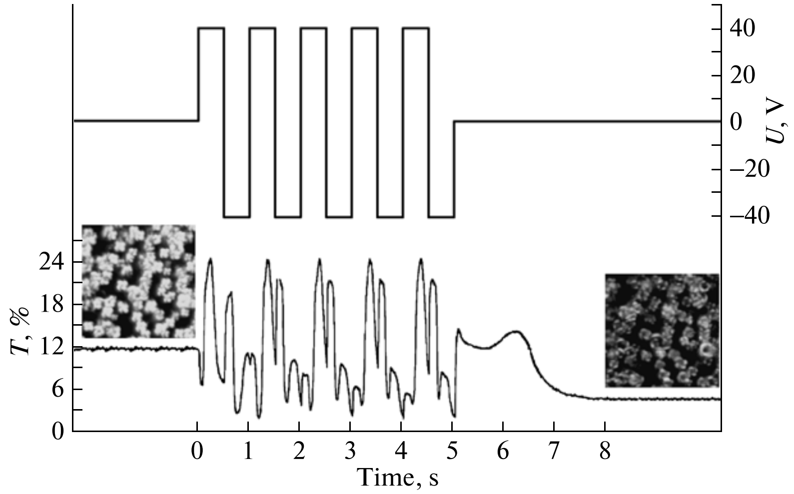

Fig. 1. Waveforms of (top) control electric voltage *U* and (bottom) optical transmittance of a PDChLC film switched from the initial state with a twisted radial structure into a stable intermediate state. Insets show photographs of film fragments in equilibrium states before and after electric field application (here and below, the photographs are obtained in crossed polarizers oriented parallel to graphical axes).

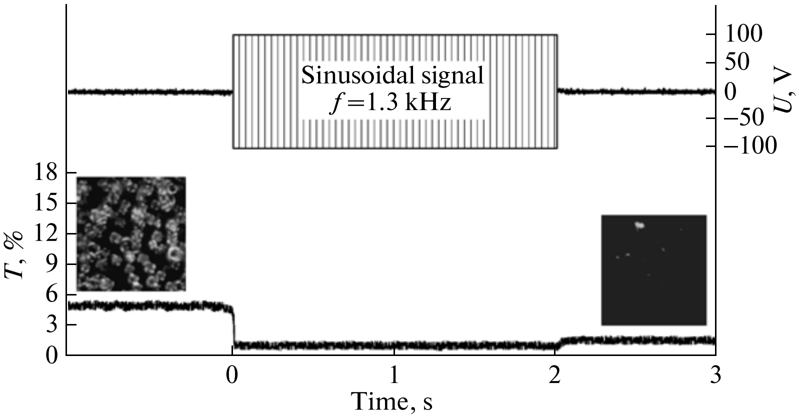

Fig. 2. Waveforms of the (top) control sinusoidal electric voltage *U* and (bottom) optical response of a PDChLC film switched from an intermediate state into a stable state with homogeneous LC director orientation in the droplets. Insets show photographs of film fragments in the corresponding states.

shape was applied to the electrode. The radiation of a semiconductor laser operating at $\lambda = 658$ nm was transmitted through the optical cell and detected by photodiode, the output signal of which was analyzed using a digital oscilloscope.

The PDChLC film thickness was 75 μm. The ChLC droplets in the film plane had round shapes with an average diameter of 9 μm. These droplets were arranged in the volume without overlap, which allowed the orientational structure of ChLC to be identified. In ChLC droplets without a surfactant, a twisted bipolar configuration of the LC director was formed that corresponded to a tangential anchoring. ChLC droplets containing about 10% CTAB exhibited a twisted radial structure characteristic of a homeotropic (perpendicular) orientation of LC molecules on the surface of the polymer matrix. The optical textures of these droplets in crossed polarizers resemble a bent Maltese cross (Fig. 1, left inset). Since the droplet transmits only a fraction of the incident light, while the optically isotropic polymer matrix does not transmit light in crossed polarizers, the total optical transmittance of a PDChLC film in the initial state amounts to only about 12% (Fig. 1).

Under the action of an applied electric field, the ChLC droplets can pass to either a stable state (with a homogeneous orientation of the director perpendicular to the film plane) or some intermediate stable structures. In the former case, the birefringence of the ChLC does not manifest and the light is not transmitted through these droplets (Fig. 2, right inset). Note that a small fraction of droplets (not exceeding 2% for the sample studied) does not pass to a homogeneous state, which accounts for a weak residual transmit-

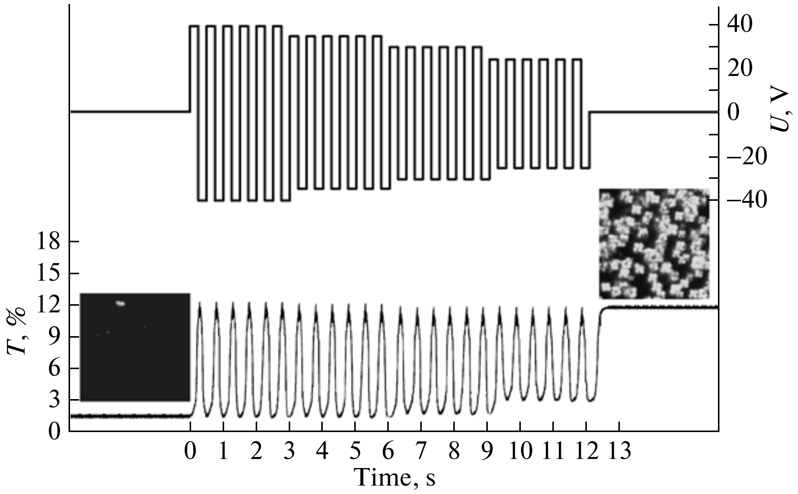

Fig. 3. Waveforms of (top) control electric voltage U and (bottom) optical response of a PDChLC film switched from a state with homogeneous LC director orientation into the initial state with a twist radial structure in the droplets. Insets show photographs of film fragments in the corresponding states.

tance (Fig. 2, right inset). In the intermediate states, the LC director in the central part is close to the normal to the film surface and is tilted in the equatorial region. For this reason, the light only passes through the side regions (adjacent to the visible boundaries) of droplets (Fig. 1, right inset). Thus, the optical transmittance of the PDChLC film in stable states varies within 1.5–12%.

Figures 1–3 present typical waveforms of the control electric signals (top) and the corresponding optical responses (bottom) observed upon the composite film switching to various equilibrium states. From the initial state with $T \sim 12\%$, the PDChLC film can be switched to stable intermediate states by applying rectangular voltage pulses at a frequency of 1 Hz (Fig. 1). Under the action of these pulses of both positive and negative polarity, ChLC droplets exhibit a complicated process of transformation of the orientational structure, which involves the contributions of various physical phenomena including the Freedericksz effect, modification of boundary conditions, and electrohydrodynamic instability related to the ion transport. The reorientation of the ChLC droplets manifests in the form of changes in the optical transmittance, which varies during the electric signal application within $T = 2.0$–24.5%. After switch-off of the field, the ChLC droplets relax within about 3 s to an equilibrium intermediate state. The resulting transmittance is determined by the control electric signal parameters and can be changed by varying the number, amplitude, and duration of pulses.

The minimum optical transmittance in a stable intermediate state achieved for the given samples controlled by rectangular pulses was about 4.5–5%. This value can be further reduced to 1.5%, but this requires applying a 1.3-kHz sinusoidal signal for 2 s after the rectangular pulses (Fig. 2). This additional action leads to a homogeneous orientation of the LC director in droplets and the resulting almost complete darkening of the optical picture (Fig. 2, right inset). After this transition to a homogeneous orientation, only a small fraction of droplets (about 1%) can relax with the time (for the first 100 h) to an intermediate structure, after which the system is completely stabilized.

Both intermediate and homogeneous structure of ChLC droplets can be returned to the initial state by applying rectangular voltage pulses with a frequency of 2 Hz, e.g., in order to return droplets into the initial state with a twisted radial configuration of the director and the corresponding optical transmittance, it is possible to use the sequence of signals shown in Fig. 3, with a gradually decreased (from 40 to 25 V) amplitude.

Thus, using ionic surfactants that modify the boundary conditions under the action of an applied electric field, it is possible to obtain a number of stable structural and optical states of a PDChLC film containing weakly twisted ChLC (i.e., with helicoid pitch comparable to the droplet size). This film material has good prospects for the development of electro-optical devices that do not require a fast response (electronic books, optical shutters, smart windows, etc.), but ensuring nonvolatile conservation of recorded information or a preset level of optical transmittance. Additional advantages of the proposed material are related to its flexibility, mechanical strength, and simple manufacturing technology. Subsequent investigations will be directed to optimization of the material composition and structure and the control signal parameters so as to improve the optical characteristics of potential opto-electronic devices, in particular to reduce the writing time and increase the contrast and optical transmittance level.

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