Liquid Crystal Materials with Ionic-Surfactant Operation

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Abstract—A conceptually new approach for developing methods of control of liquid crystals is discussed. The approach is based on modifying surface anchoring. A brief review of the authors' research on developing ionic-surfactant control of liquid crystalline materials is described. This approach is based on the effect of electrically induced modification of the boundary conditions by ions of surface-active compounds.

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INTRODUCTION

All of the known liquid crystalline devices [1] that are widely used in different fields of optoelectronics, especially in display technologies, are based on the classical Fréedericksz effect [2]. This is a reorientation of almost the whole volume of a liquid crystal (LC) under an external influence (an electric or magnetic field). It should be stressed that the LC layer closest to the surface maintains its initial orientation. After the field is switched off, the effect of the surface restores the initial director configuration in the bulk of the LC.

A conceptually new approach to controlling LC materials has been developed, based on anchoring transitions [3, 4] caused by changes in the summary orientating influence of different surface forces, resulting in a reorientation of the whole volume of the LC. An example is the reorientation of a nematic layer separated by an amorphous film about 10 nm in thickness from a crystalline substrate [4]. The orienting effects of the film and the substrate are different; in the considered case, they were planar and homeotropic, respectively. By varying the temperature or using optical irradiation, or a magnetic or electric field, we can change the balance of orienting forces and induce anchoring transitions. Ways of modifying the boundary conditions by electric field are most important for creating optoelectronic materials and devices. For example, it has been proposed that substrates covered with a ferroelectric LC polymer be used as electrically controlled orienting layers [5]. The azimuthal reorientation of the director (in the substrate plane) of the LC polymer caused by a change in the polarity of the applied voltage induces a corresponding change in orientation inside the bulk of the nematic in contact with the substrate.

In this work, we propose and realize a method of reorienting liquid crystals using the effect of modifying the surface anchoring via an electrically controlled change in the concentration of ionic surfactants at the surface.

RESULTS AND DISCUSSION

Orientation Structural Transitions in LC Droplets

Films of polymer-dispersed liquid crystal (PDLC films) made of nematic 4-n-pentyl-4-cyanobiphenyl (5CB) doped with cationic surfactant cetyltrimethylammonium bromide (CTAB), which in certain concentrations provides homeotropic boundary conditions, were studied. The orienting capability of the surfactant depends on the packing density of the surface active CTA⁺ ions, which is in turn defined by the CTAB concentration in the LC. The boundary conditions are defined mainly by the polymer matrix (tangential boundary conditions) at a low surfactant concentration and by the surfactant (homeotropic conditions) at higher concentrations. For the studied samples based on polyvinyl alcohol (PVA), tangential boundary conditions were observed up to a surfactant concentration of 0.8% in 5CB. Homeotropic conditions are observed at contents above 1.2%, and intermediate states exist in the range between these concentrations. A constant electric field can spatially redistribute the ions in an LC droplet, leading to a local change in the concentration of surface active CTA⁺ cations and thus to a change in the boundary conditions on part of the droplet's surface [6, 7] (Fig. 1).

Modification of surface anchoring transforms the orientation structure in the bulk of an LC droplet

(Fig. 1, bottom row) and consequently changes the optical properties of the composite. An inverse mode of the effect of electrically-controlled modification of interfaces by a nanolayer of ionic surfactant was observed and investigated in [8, 9]. This mode is achieved at higher CTAB concentrations, where part of the interface becomes free from CTA⁺, restoring the tangential boundary conditions in this region of the droplet that are defined by the polymer matrix. Dynamic characteristics of response of the PDLC films with ionic-surfactant control in the inverse mode were obtained in [10]. This method requires a weak controlling field (approximately one order of magnitude weaker than the one needed for reorientating LC droplets by the classical method).

Ionic-surfactant control of the orientation structure applied to droplets of a weakly twisted nematic (cholesteric) showed we can achieve the effect of structural and optical bistability caused by modifying boundary conditions [11]. The orientation structure of cholesteric droplets can in this case be switched between stable radial (Fig. 2a) and axial (Fig. 2c) configurations through metastable intermediate states (Fig. 2b) by varying the amplitude and shape of the electric signal.

Orientation Structural Transitions in an LC Layer

Electrically induced ionic modification of surface anchoring for controlling orientation structure can be used for a nematic layer. An LC cell with the nematic doped with CTAB is used in this case. In the initial state, the surfactant is distributed equally over both substrates and induces homeotropic anchoring, provided that its concentration is sufficiently high. As a result, the LC in the cell is oriented homeotropically (Fig. 3a). The concentration of surface active CTA^+ ions decreases on one of the substrates due to the electric field, changing the boundary conditions on the substrate and forming tangential anchoring conditions. The change in the boundary conditions results in reorientation of the director throughout the cell's volume (Fig. 3b) and the formation of a hybrid homeoplanar structure [12]. This orientational transition is of a threshold character, and in a certain range of controlling voltages occurs without the initiation of electrohydrodynamic instability. Analysis of the electrooptical response of an LC cell showed that the switching processes are of a complex nature and depend on the joint influence of different orienting factors: changes in the boundary conditions, the orienting influence of moving ions, and the effect of the uncompensated electric field on the LC bulk.

Three characteristic times of the optical response can be distinguished when considering the homeotropic—homeoplanar transition in an LC cell [13]: the delay time, switching time, and relaxation time. The delay time, defined as the time between the moment of



Fig. 1. (a) Effect of the electrically-controlled ionic modification of boundary conditions and corresponding changes in texture of a nematic droplet: (1) polymer matrix, (2) LC droplet, (3) glass substrate, (4) electrode, (5) Br⁻ ions, (6) CTA⁺ ions, (7) director field lines. Microphotographs of LC droplets made (b) without an analyzer and (c) between crossed polarizers. Upper row: the electric field is off; bottom row: the field is on. Directions of the polarizers are shown by double arrows; the direction of the field is shown by a single arrow.

applying the electric field and the onset of the optical response, is reduced quickly as the voltage increases. The switching time (between the moment of applying the electric field and achieving the saturation level of transparency) shows a nonmonotonous dependence on the controlling voltage. The relaxation (switching



Fig. 3. Effect of the electrically-controlled ionic modification of anchoring for an LC layer. (a) Electric field is off; CTA^+ cations absorbed on the surface induce a homeotropic orientation of the LC. (b) Electric field is on; polymer film on the bottom substrate provides planar anchoring. (1) Glass substrates with ITO electrodes; (2) orienting films; (3) CTA^+ ions; (4) molecules of the LC; (5) Br^- ions.

off) time is the period between the field switching-off and transparency level's return to its initial value; it increases quickly as the voltage increases, but reaches saturation at larger voltages. The characteristic times of switching in the considered transition are relatively long (subsecond). To reduce the response time, we designed a fast LC cell with an original orientational transition between the homeoplanar and twisted director configurations [14, 15]. This orientation structural transition allowed us to reduce the cell's optical response time to tens of milliseconds.

CONCLUSIONS

Ionic-surfactant operation can be used for both composite materials (dispersed droplets of an LC in a polymer film) and LC layers. Note that the proposed method is inferior to the known approaches based on the Fréedericksz effect with respect to the response time. However, it has such advantages as low controlling voltage, low power consumption (when using multistable structures), and no limitations on the













Fig. 2. Microphotographs of a droplet of a twisted nematic (cholesteric) doped with CTAB: (a) before switching on the electric field; (b) after exposure to dc electric field directed to the right; (c) after subsequent exposure to dc electric field directed to the left. Double arrows indicate the polarizer directions. Crossed arrows are shown in the photos taken with crossed polarizers of the indicated orientation. A single arrow is shown in the photos taken when the analyzer was switched off.

choice of LC media related to the sign and value of the dielectric anisotropy. Considering all these features, we conclude that the ionic-surfactant controlling technique is promising for practical use. Development of this approach could lead to the creation of new LC materials and devices that could widen the functional possibilities of modern optoelectronic techniques.

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REFERENCES

- 1. Blinov, L.M. and Chigrinov, V.G., *Electrooptic Effects in Liquid Crystal Materials*, New York: Springer, 1994.
- Freedericksz, V.K. and Zolina, V., *Trans. Faraday Soc.*, 1933, vol. 29, p. 919.
- 3. Dubois-Violette, E. and De Gennes, P.G., J. Phys., Lett., 1975, vol. 36, no. 10, p. 255.
- 4. Ryschenkow, G. and Kleman, M., J. Chem. Phys., 1976, vol. 64, no. 1, p. 404.

- 5. Komitov, L., Helgee, B., Felix, J., and Matharu, A., *Appl. Phys. Lett.*, 2005, vol. 86, p. 023502.
- Zyryanov, V.Ya., Krakhalev, M.N., Prishchepa, O.O., and Shabanov, A.V., *JETP Lett.*, 2007, vol. 86, no. 6, p. 383.
- Zyryanov, V.Ya., Krakhalev, M.N., and Prishchepa, O.O., Mol. Cryst. Liq. Cryst., 2008, vol. 489, p. 273.
- Zyryanov, V.Ya., Krakhalev, M.N., Prishchepa, O.O., and Shabanov, A.V., *JETP Lett.*, 2008, vol. 88, no. 9, p. 597.
- 9. Krakhalev, M.N., Prishchepa, O.O., and Zyryanov, V.Ya., *Mol. Cryst. Liq. Cryst.*, 2009, vol. 512, p. 152.
- Krakhalev, M.N., Loiko, V.A., and Zyryanov, V.Ya., *Tech. Phys. Lett.*, 2011, vol. 37, no. 1, p. 34.
- 11. Gardymova, A.P., Zyryanov, V.Ya., and Loiko, V.A., *Tech. Phys. Lett.*, 2011, vol. 37, p. 805.
- Sutormin, V.S., Krakhalev, M.N., Prishchepa, O.O., and Zyryanov, V.Ya., *JETP Lett.*, 2012, vol. 96, no. 8, p. 511.
- 13. Sutormin, V.S., Krakhalev, M.N., and Zyryanov, V.Ya., *Tech. Phys. Lett.*, 2013, vol. 39, no. 7, p. 583.
- Sutormin, V.S., Krakhalev, M.N., Prishchepa, O.O., Lee, W., and Zyryanov, V.Y., *Opt. Mater. Express*, 2014, vol. 4, no. 4, p. 810.
- 15. Timofeev, I.V., Gunyakov, V.A., Sutormin, V.S., Myslivets, S.A., Arkhipkin, V.G., Vetrov, S.Ya., Lee, W., and Zyryanov, V.Ya., *Phys. Rev. E*, 2015, vol. 92, p. 052504.

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