2010

Electric Field Induced Biaxiality and the Electro-Optic Effect in a Bent-Core Nematic Liquid Crystal

Mamatha Nagaraj
Trinity College Dublin, Ireland

Yuri Panarin
Technological University Dublin, yuri.panarin@tudublin.ie

U. Manna
Trinity College Dublin, Ireland

See next page for additional authors

Recommended Citation

Keith, C. et al. (2010). Electric field induced biaxiality and the electro-optic effect in a bent-core nematic liquid crystal. *Applied Physics Letters* vol. 96, pp. 1-3. doi:10.1063/1.3280817

Electric field induced biaxiality and the electro-optic effect in a bent-core nematic liquid crystal

Mamatha Nagaraj,[1] Y. P. Panarin,[1,2] U. Manna,[1] J. K. Vij,[1,a)] C. Keith,[3] and C. Tschierske[3]
[1]*Department of Electronic and Electrical Engineering, Trinity College Dublin, Dublin 2, Ireland*
[2]*School of Electronic and Communication Engineering, Dublin Institute of Technology, Dublin 8, Ireland*
[3]*Institute of Organic Chemistry, Martin Luther University Halle-Wittenberg, D06120 Halle, Germany*

(Received 10 September 2009; accepted 30 November 2009; published online 7 January 2010)

We report the observation of a biaxial nematic phase in a bent-core molecular system using polarizing microscopy, electro-optics, and dielectric spectroscopy, where we find that the biaxiality exists on a microscopic scale. An application of electric field induces a macroscopic biaxiality and in consequence gives rise to electro-optic switching. This electro-optic effect shows significant potential in applications for displays due to its fast high-contrast response. The observed electro-optic switching is explained in terms of the interaction of the ferroelectric clusters with the electric field. © *2010 American Institute of Physics*. [doi:10.1063/1.3280817]

Based on the generalized Maier–Saupe theory, Freiser[1] predicted that a reduction in the molecular symmetry could lead to the formation of a biaxial nematic (N_b) phase in liquid crystals (LCs) in addition to the observed uniaxial nematic phase. The biaxial nematic phase has a secondary director **m** perpendicular to the primary director **n**; the latter is always prevalent in the nematic phase. From a practical point of view, the switching of the secondary director is at least a factor of 100 faster than the primary one. Therefore such biaxial nematics with improved response offer significant advantages over the conventional nematics in applications for fast displays and photonic devices. The potential for faster devices has led to a significantly increased interest in theoretical, experimental, and computational studies on the biaxial nematic phase. The experimental proof for the existence of the N_b phase in a lyotropic LC system was reported in 1980.[2] The thermotropic biaxial nematic phase was discovered in 2004 in liquid crystalline polymers,[3] organosiloxane tetrapodes,[4,5] and in low molar mass bent-core systems.[6–8] The possibility for the existence of a biaxial nematic phase in biaxial parallelepiped (or bricklike) shaped molecules[9–11] and in bent-core systems[12–14] has been supported by numerous theoretical studies.

Experimental studies on a part of the temperature range of nematic phase of the bent-core LCs suggest the appearance of "cybotactic" (smecticlike) clusters.[15–21] In such molecules, two rodlike mesogenic groups linked together through a central unit exhibit a near-C_{2v} symmetry. The presence of biaxial clusters was considered a long time ago by De Vries.[22] In bent-core systems, a deviation from the calamitic shape and an existence of a large transverse dipole moment gives rise to unusually strong intermolecular interactions that lead to the formation of ferroelectric domains or clusters. On applying the electric field, the collective alignment of domains leads to a macroscopically biaxial ordering.[18] On removal of the field the domains are destabilized, with a corresponding drop in the biaxial order parameter. It is still not clear whether such a nematic LC consists of distinguishable clusters of a lower symmetry phase, or correlated regions with a short-range order.

In spite of the obvious progress made in both experimental and theoretical studies, a number of problems remain to be solved[23] and therefore the subject of biaxial nematics continues to be a highly debated and challenging in the field of LCs. Despite numerous claims for the existence of biaxial nematic phase in different systems, electro-optic effect has so far not been demonstrated unambiguously. In this letter, we report results of the experimental study of electro-optic effect in a homeotropically aligned biaxial nematic compound. The observed electro-optic switching is explained in terms of the interaction of the ferroelectric clusters with the electric field. The bent-core LC sample under study, C_6-BAN, is synthesized in Halle, Germany. The molecular structure of the studied material is given in Fig. 1. For the optical and electro-optical studies the compound was filled in homeotropically aligned cells of different thicknesses, varying from 4 to 50 μm. The foil stripes of different thicknesses were used as electrodes in order to apply the external electric field parallel to the plane of the glass plates. The gap between the electrodes was fixed to be of the order of ~200 μm. AL60702 (JSR Japan) was used to achieve the homeotropic alignment.

The optical textures for three different thicknesses (50, 25, and 4 μm) of the sample are presented in Figs. 1(a)–1(c). On cooling from the isotropic to nematic phase in a thicker (50 μm) cell, the nematic phase is found to consist

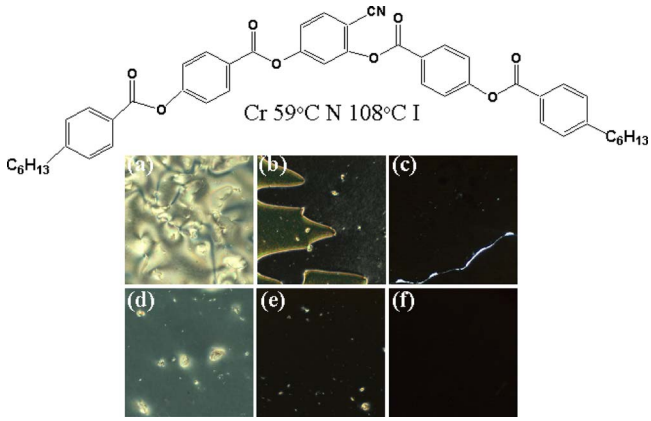

FIG. 1. (Color online) Microphotographs of the textures near T_{NI}: The cell thicknesses are d=50 μm for (a) and (d); d=25 μm for (b) and (e); and d=4 μm for (c) and (f). Textures (d), (e), and (f) are recorded after a period of 1 h from those of (a), (b), and (c).

a)Electronic mail: jvij@tcd.ie.

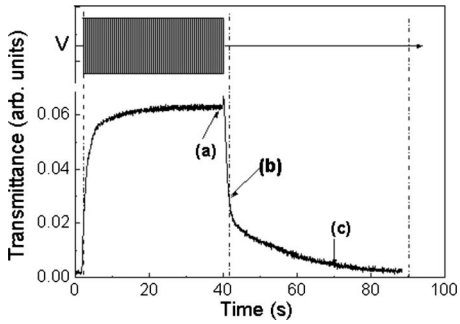

FIG. 2. The EO response in a 4 μm homeotropic cell for square-wave electric field $\mathbf{E}=1$ V/μm, 100 Hz, T=106 °C. (a), (b), and (c) on the electro-optic response refer to three states; the corresponding textures are shown in Figs. 3(a), 3(b), and 3(c), respectively.

only two-brush Schlieren texture [Fig. 1(a)] which indicates the presence of biaxial nematic phase. Nevertheless this biaxial nematic texture is not stable with time and during a period of one hour it transforms to a rather uniform dark texture [Fig. 1(d)], which nevertheless consists of very small domains of the approximate size of the wavelength of visible light. These considerably reduce the overall extinction of the texture compared with that for the isotropic phase. We assign these domains to cybotactic clusters, which are observed in this sample by x-ray diffraction.[24] It has been found that the transition from cybotactic nematic to smectic phases occurs on elongation of the chains and the clusters in this compound are observed with three to four molecules correlated in the transverse direction, and about two molecules correlated parallel to the director.[24] Textures in these samples are found to be strongly affected by surfaces. Thus a thin (4 μm) LC cell finally produces a perfect high-extinction homeotropic alignment [Fig. 1(f)]. The textures produced by the cell of intermediate thickness [Figs. 1(b) and 1(e)] are somehow between those for the two previous cells.

The effect of electric field on the textures is studied in a 4 μm cell with foil spacers as electrodes. A square-wave field 100 Hz is applied across the electrodes in the plane of a glass plate. The cell was placed between the crossed polarizers with an angle of 45° between the electric field direction and polarizer axis. Initially for a rather small electric field (<0.3 V/μm), no significant effect is observed and the LC remains optically uniaxial. On the application of a stronger electric field, the cell exhibits electro-optical switching from dark to bright state and reverse when the field is removed (Fig. 2). The electro-optic response shows dynamics with different speeds; slow and fast. These suggest coexistence of the two different processes. This suggestion is supported by observations under a polarizing microscopy (Fig. 3). Figure 3(a) shows the texture for an applied electric field of 0.5 V/μm. On the removal of the field, the cell relaxes to an

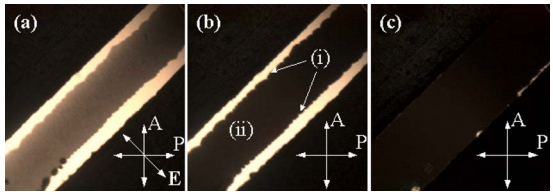

FIG. 3. (Color online) Dynamics of the induced biaxiality (a) at $\mathbf{E}=0.5$ V/μm. (b) and (c) are obtained after 1 s and 30 s on the removal of the field for T=106 °C. A, P, and **E** denote the directions of analyzer, polarizer, and electric field.

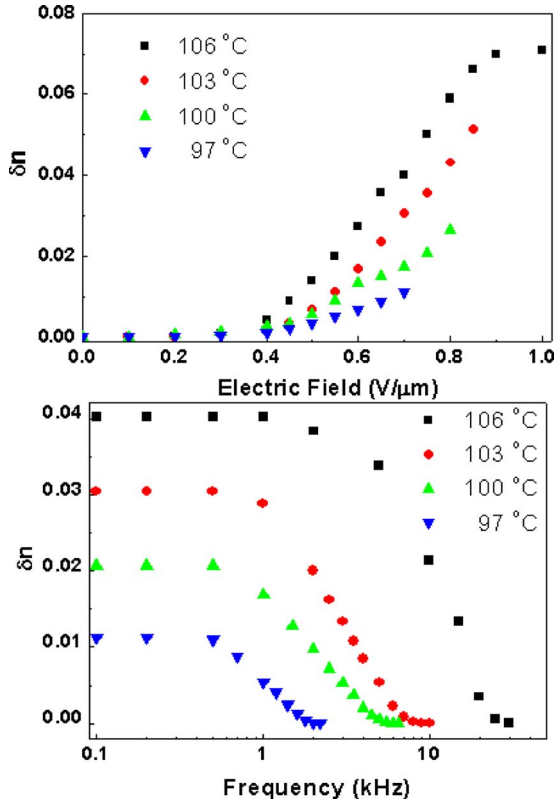

FIG. 4. (Color online) (a) Induced biaxiality (δn) vs electric field at a frequency of 100 Hz. (b) δn vs frequency for $\mathbf{E}=0.7$ V/μm.

apparently initial macroscopically uniaxial state [Fig. 3(c)]. The texture of the cell consists of two following distinct regions: (i) two bright stripes near the electrodes with slow dynamics (~10 s) and (ii) a uniform dark region between the two bright strips with fast dynamics (~1 ms) [see Fig. 3(a) and 3(b)]. A sharp border between the two regions is clearly seen. At this stage, we surmise that (i) the high-birefringent stripe region is the field induced planar (or tilt) alignment and (ii) the second region with a distinctive domain boundary is due to the field-induced biaxiality arising from the alignment of the short axes of the clusters. The fast electro-optic effect can be exploited in displays due to a fast high-contrast (Figs. 2 and 3) response. The parasitic slow response reduces the contrast ratio and the switching speed and can be overcome using molecules with a strong negative dielectric anisotropy.

The magnitude of induced biaxiality was measured using a tilting optical compensator inserted in the polarizing microscope. This allows one to measure rather small values of the optical retardation for a specific region of the cell, which in our case is the center between the electrodes of the foil (Fig. 3). Figure 4(a) shows the dependence of the induced biaxiality (δn) as a function of electric field for different temperatures using a homeotropically aligned cell of thickness 4 μm. Initially (after a threshold field of ~0.3 V/μm is applied), the induced biaxiality increases gradually with electric field and then saturates to a constant value.

The magnitude of the induced biaxiality decreases with a reduction in temperature, which shows that this phase disappears at temperatures below 97 °C. Figure 4(b) presents the dependence of the induced biaxiality (δn) as a function of frequency for an electric field of 0.7 V/μm. On cooling from 106 to 97 °C, the cut-off frequency of the electro-optic

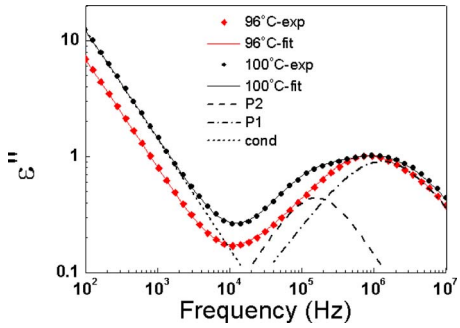

FIG. 5. (Color online) The dielectric loss spectra for two typical temperatures: (♦) 96 °C and (●) 100 °C with the fitted curves (solid lines) for a planar cell with brass electrodes for the cell thickness of 9 μm for a frequency range of 100 Hz to 10 MHz. The dashed-line denotes fitting of the two relaxation processes and the dotted-line shows the conductivity for a temperature of 100 °C.

(EO) response decreases by a factor of 10 from ~10 to 1 kHz. These frequencies are much lower than the frequency where a sign reversal from positive to negative $\Delta\varepsilon$ could occur. At the frequency range of measurements $\Delta\varepsilon$ is positive and the applied field could only induce planar alignment in the vicinity of the electrodes (Fig. 3) due to the quadratic interaction $\Delta\varepsilon \times E^2$ with the electric field. The induced birefringence in the middle area [Fig. 3(a)] therefore arises from induced biaxiality due to alignment of the short axes of the clusters by the electric field. The data on dielectric spectroscopy show this to be the polar interaction thus clearly indicating the presence of polar clusters.

The dielectric study was performed on a planar cell of 9 μm thickness using a broadband high resolution dielectric spectrometer (Novocontrol GmbH, Germany). Experiments are performed on cooling the sample from 115 to 60 °C. Figure 5 shows the dielectric loss spectra in the frequency of 10 Hz–10 MHz where the EO response disappears. Dielectric loss spectra (ε'') were fitted to the two relaxation processes. Both spectra show a relaxation process (P1) corresponding to the molecular relaxation around the short molecular axes (flip-flop mode) similar to other uniaxial nematics. The spectra at a temperature of 96 °C can well be fitted by a single relaxation process.

The second spectra for a temperature of 100 °C show an additional process (P2), Fig. 5. This process is observed in the same temperature range (97–106 °C), where the fast EO response is present. Therefore we can relate this definitely to the polar dielectrically active process observed in the EO switching. The two switched-ON states of the opposite polarity (+/−) are optically indistinguishable for the reason that the switching mechanism involves the polar reorientations of the microscopic biaxial domains in the direction of the applied electric field irrespective of its direction. Therefore the EO effect (Fig. 4) is observed between the field induced biaxial (ON) state and the uniaxial (OFF) state.

For temperatures below 97 °C, the sample exhibits neither the dielectric process (P2) nor the fast electro-optic response. This indicates the absence of the polar clusters. Nevertheless neither texture nor the DSC shows any phase transition at 97 °C. The cybotactic clusters have also been found to exist in the temperature range below 97 °C.[24] The question arises as what is the phase assignment for temperatures below 97 °C. The plausible explanation is a gradual formation of cybotactic clusters with antiferroelectric ordering as the temperature decreases. This process lowers the fraction of the clusters with ferroelectric orderings and hence the magnitude of the EO (Fig. 3) and dielectric amplitude ($\Delta\varepsilon$, Fig. 5) are reduced significantly. At a temperature of 97 °C all ferroelectric clusters transform to antiferroelectric ones. The coexistence of both ferroelectric and antiferroelectric clusters is in agreement with the results of Liao *et al.*[16] An additional (polar) relaxation process in dielectric spectra is observed even in the absence of the bias voltage (Fig. 5 and Ref. 16) and the intensity of this process increases significantly after application of large bias field due to field induced antiferroelectric to ferroelectric transition[16] and formation of ferroelectric clusters.

In summary, results on nematic phase for a bent-core LC system show that the nematic phase containing biaxial clusters is macroscopically uniaxial but the biaxiality is shown to be induced by the electric field. The electro-optic switching is shown to occur via the short axes. Such LCs, in their intermediate induced biaxial phase can be exploited for applications due to fast field-induced (~1 ms) switching between the uniaxial and biaxial states thus leading to a new concept for the devices.

The authors thank the EU Grant No. FP7-216025 BIND and SFI Grant No. RFP 06/RFP/ENE039 for funding.

[1] M. J. Freiser, Phys. Rev. Lett. **24**, 1041 (1970).
[2] L. J. Yu and A. Saupe, Phys. Rev. Lett. **45**, 1000 (1980).
[3] K. Severing and K. Saalwachter, Phys. Rev. Lett. **92**, 125501 (2004).
[4] K. Merkel, A. Kocot, J. K. Vij, R. Korlacki, G. H. Mehl, and T. Meyer, Phys. Rev. Lett. **93**, 237801 (2004).
[5] K. Neupane, S. W. Kang, S. Sharma, D. Carney, T. Meyer, G. H. Mehl, D. W. Allender, S. Kumar, and S. Sprunt, Phys. Rev. Lett. **97**, 207802 (2006).
[6] L. A. Madsen, T. J. Dingemans, M. Nakata, and E. T. Samulski, Phys. Rev. Lett. **92**, 145505 (2004).
[7] B. R. Acharya, A. Primark, and S. Kumar, Phys. Rev. Lett **92**, 145506 (2004).
[8] V. Prasad, S.-W. Kang, K. A. Suresh, L. Joshi, Q. Wang, and S. Kumar, J. Am. Chem. Soc. **127**, 17224 (2005).
[9] H. H. Wensink, G. J. Vroege, and H. N. W. Lekkerkerker, Phys. Rev. E **66**, 041704 (2002).
[10] P. I. C. Teixeira, M. A. Osipov, and G. R. Luckhurst, Phys. Rev. E **73**, 061708 (2006).
[11] D. Allender and L. Longa, Phys. Rev. E **78**, 011704 (2008).
[12] M. A. Bates and G. R. Luckhurst, Phys. Rev. E **72**, 051702 (2005).
[13] J. Peláez and M. R. Wilson, Phys. Rev. Lett. **97**, 267801 (2006).
[14] A. G. Vanakaras and D. J. Photinos, J. Chem. Phys. **128**, 154512 (2008).
[15] S. Stojadinovic, A. Adorjan, S. Sprunt, H. Sawade, and A. Jakli, Phys. Rev. E **66**, 060701 (2002); J. A. Olivares, S. Stojadinovic, T. Dingemans, S. Sprunt, and A. Jakli, *ibid.* **68**, 041704 (2003).
[16] G. Liao, S. Stojadinovic, G. Pelzl, W. Weissflog, S. Sprunt, and A. Jakli, Phys. Rev. E **72**, 021710 (2005).
[17] L. Kovalenko, M. W. Schroder, R. A. Reddy, S. Diele, G. Pelzl, and W. Weissflog, Liq. Cryst. **32**, 857 (2005).
[18] R. Stannarius, A. Eremin, M.-G. Tamba, G. Pelzl, and W. Weissflog, Phys. Rev. E **76**, 061704 (2007).
[19] J. H. Lee, T. K. Lim, W. T. Kim, and J. I. Jin, J. Appl. Phys. **101**, 034105 (2007).
[20] V. Görtz, C. Southern, N. W. Roberts, H. F. Gleeson, and J. W. Goodby, Soft Matter **5**, 463 (2009).
[21] O. Francescangeli, V. Stanic, S. I. Torgova, A. Strigazzi, N. Scaramuzza, C. Ferrero, I. P. Dolbnya, T. M. Weiss, R. Berardi, L. Muccioli, S. Orlandi, and C. Zannoni, Adv. Funct. Mater. **19**, 2592 (2009).
[22] A. De Vries, Mol. Cryst. Liq. Cryst. **10**, 219 (1970).
[23] K. V. Le, M. Mathews, M. Chambers, J. Harden, Q. Li, H. Takezoe, and A. Jákli, Phys. Rev. E **79**, 030701(R) (2009).
[24] C. Keith, A. Lehmann, U. Baumeister, and C. Tschierske, Soft Matter (to be published).