Optical confirmation of biaxial nematic (N_b) phase in a bent-core mesogen

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A bent-core mesogen with different end groups has been studied for different surface conditions in both planar and homeotropic cells using techniques for measuring biaxiality and optical switching. Biaxial nematic phase observed in between the uniaxial nematic and smectic phases is evidenced by a sharp increase in the biaxiality in a homeotropic cell measured using a photoelastic modulator. The material in this phase is switchable through the minor director with an in-plane electric field. In a planar cell, a step in the difference in the refractive indices resulting from the uniaxial to biaxial transition is also observed. © *2009 American Institute of Physics*. [doi:10.1063/1.3255013]

Since the prediction of a biaxial nematic phase (N_b) by Freiser in 1970,[1] this subject has continued to attract significant interest among scientists during the past decade for reasons of advancing fundamental science and its potential for use in displays. The switching mode in N_b is more likely to realize faster response[2,3] and wider viewing angles. For modes such as Vertical Alignment (VA), In-Plane Switching (IPS), Twist Nematic (TN), and Optically Compensated Bend (OCB) using conventional N_u to achieving wider viewing angle displays, it is necessary to use expensive optical compensation films.[4,5] However, the intrinsic biaxiality of N_b is extremely useful in reducing the light leakage for oblique viewing angle.[6] The most plausible structure for N_b device to realize both fast response and wider viewing angle is the homeotropically aligned cell with an in-plane switching of the minor director.[2] To achieve faster response, the minor director should be driven without involving the major director. If both the major and minor directors are involved in reorientation of molecules under electric field, the slower motion dominates the response time. This structure is of advantage to form a normal black state where the initial state without electric field has the darkest gray level. However, development of such a system has been hindered with a lack of materials possessing N_b and by difficulties of alignment. In this letter, we experimentally demonstrate a practical biaxial based nematic based device. In spite of a significant attention the subject has already attracted,[7–11] there is still a lack of information on driving the minor director. Lee *et al.*[12] reported fast switching of the minor director with bent core liquid crystal (LC), ODBP-Ph-C7, confirmed already by NMR and x-ray experiments,[7,8] but results of Lee at were strongly criticized by Stannarius for their incorrect interpretation.[13] Recently Le *et al.*[14] reported optical study of the bent core LC, A131, which was confirmed as showing biaxiality in its nematic phase. However, they did not find any evidence of the optical biaxiality in this material.[15] The work being reported here is timely in the continued debate as well as in providing quantitative results for biaxiality. The material under investigation, PAL1 (Fig. 1) was synthesized by the Halle group and was purified by column chromatography, followed by crystallization from a methylene chloride-methanol mixture (the detailed synthesis will be reported in a separate manuscript). This LC possesses bent-core structure and different terminal groups. It shows negative dielectric anisotropy due to the strong transverse dipole moment which also broadens the N_b.[16]

The homeotropic and planar aligned cells are shown in Fig. 2. For demonstrating the in-plane switching, a homeotropic cell is used. In the cell, a gap of ~180 μm on the indium tin oxide (ITO) coated substrate is etched lithographically. For the electrostatic screening of the cell, the second substrate coated with ITO is fixed on the top. Both glass plates of the cell are spin coated on the inside with AL60702 (JSR Corp.) polymer for homeotropic alignment. We prepared two different homeotropic cells: with and without rubbing. The rubbing direction lies at an angle of approximately 45° with respect to the two electrodes for the in-plane switching. Standard commercial cells (E.H.C. Japan) with a thickness of 5 μm and antiparallel rubbed polyimide on two substrates are used to carry out experiments in the planar geometry.

Three LC phases are observed in the unrubbed homeotropic cell by scanning with temperature as shown in Fig. 3. In the presence of the in-plane electric field, the director even if it is slightly tilted in the homeotropic alignment should stand normally to the substrate due to the negative dielectric anisotropy of the material. And in between the N_u and Sm phases, we observe another nematic phase where the minor director is switched by an electric field of 1 V/μm as shown in Figs. 3(b) and 3(c). In order to align the minor director, we

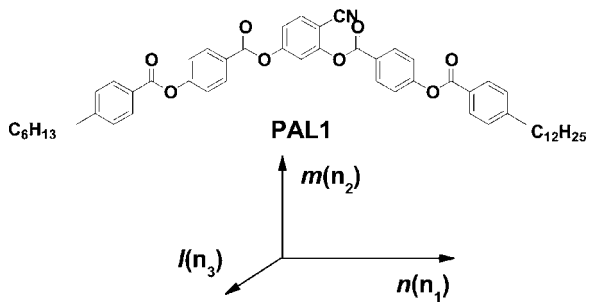

FIG. 1. Molecular structure of PAL1. The three directors and their refractive indices for N_b are denoted as $\boldsymbol{l}(n_3)$, $\boldsymbol{m}(n_2)$, and $\boldsymbol{n}(n_1)$.

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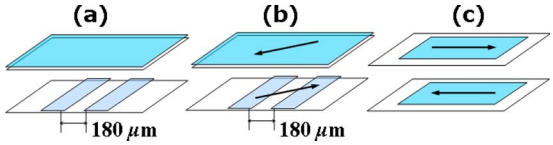

FIG. 2. (Color online) Configurations of cells used in optical study (a) homeotropic cell, cell gap=7.6 μm, (b) homeotropic cell, antiparallel rubbing, cell gap=7.2 μm. (c) Planar cell, antiparallel rubbing, cell gap =5.0 μm (E.H.C. Japan). Arrows point to the rubbing direction.

weakly rub the homeotropic cell as there can be an inhomogeneous distribution of the minor directors due to extremely small elastic constant for the deformations around the long axis. By observing a 7.2 μm thick cell in a polarizing microscope, we find a small tilt of the major director, called the pretilt angle, from the normal position toward the rubbing direction in the temperature range of the N_u [Figs. 4(a) and 4(b)]. On applying an electric field of (1 V/μm), the region between the electrodes gets darker and is independent of the cell's rotation angle [Figs. 4(e) and 4(f)]. This indicates that the director is normal to the in-plane electric field and consequently to the surface of the electrodes.

On transition from N_u to N_b, a large increase in the birefringence is observed. In the absence of electric field, the minor director aligns along the rubbing direction [Figs. 4(c) and 4(d)]. On the application of electric field of 1 V/μm, a rotation of the minor director in the N_b toward the direction of the field [Figs. 4(g) and 4(h)] is observed. Just below a temperature of 65 °C in the nematic phase the cell shows behavior similar to the IPS mode. Therefore we can clearly see a qualitative difference between the two different nematic phases.

For an accurate measurement of the retardation, a photoelastic modulator (PEM) based system is used. It provides a simultaneous measurements of both retardation (Γ) and azimuthal angle (Φ, defined as the angle between the retarder axis of the cell and the polarizer). The effective birefringence can be determined as $\Delta n_{\text{eff}}=\Gamma\lambda/2\pi d$, where d is the thickness of the cell and λ is the wavelength of the light source. We used red light emitting diode as the light source with a corresponding $\lambda=632.8$ nm narrow-band (10 nm bandwidth) optical filter. The retardation is converted into Δn_{eff}. Temperature dependence of Δn_{eff} and of Φ in homeotropic cell in the absence of the field is shown in Fig. 5. The cell is cooled at rate of 0.1 °C/min. The microscope based PEM system acquires a throughput of light from an area of approximately 150×200 μm^2 of the cell in between the electrodes. The observed Δn_{eff} and Φ correspond to their average values over several domains. In the N_u, the measured Δn_{eff} is close to zero as expected for a homeotropic cell. For a rubbed homeotropic cell, one can clearly see a jump in Δn_{eff}

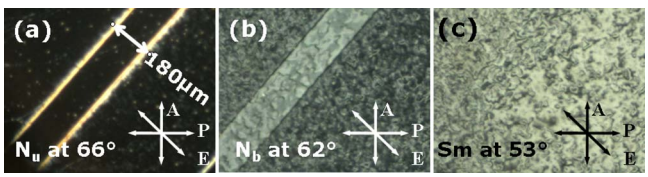

FIG. 3. (Color online) Texture of the unrubbed homeotropic cell for temperatures of (a) 68°, (b) 62°, and (c) 53 °C. Cell gap=7.6 μm, E=1.0 V/μm, 120 Hz square wave, A denotes analyzer, P denotes polarizer, R denotes rubbing direction, and E denotes electric field.

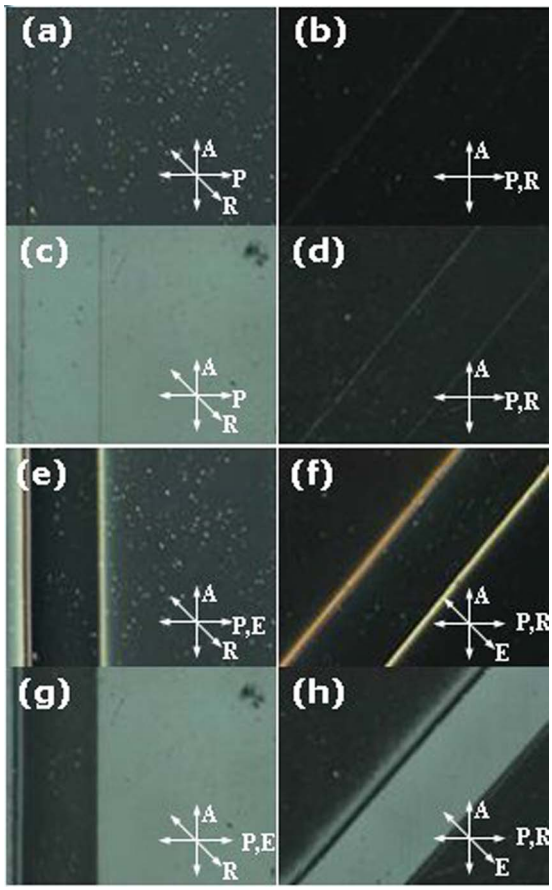

FIG. 4. (Color online) Texture of rubbed homeotropic cell. Cell gap 7.2 μm. [(a) and (b)] N_u at 66 °C, without field. [(e) and (f)] N_u with 1.0 V/μm, [(c) and (d)] N_b at 64 °C without field. [(g) and (h)] N_b, with 1.0 V/μm. 120 Hz square wave is used to drive the cell, distance between electrodes is 180 μm.

at a temperature of approximately 65 °C accompanied by a small change in Φ (Fig. 5). The minor director coincides with the rubbing direction as observed in the microscope. This increase in Δn_{eff} results from a transition to the N_b which corresponds to a biaxiality, $\delta n=(n_2-n_3)=0.0085$. To investigate the electro-optic switching, we applied 120 Hz square wave electric field with an amplitude up to 0.7 V/μm. Δn_{eff} as a function of temperature and the electric field is shown in Fig. 6. One observes that for the rubbed homeotropic cell, increasing the electric field initially results in a decrease in Δn_{eff} of both nematic phases. This is easily explained by a tilt of the major molecular directors back to the position of a perfect homeotropic alignment by electric

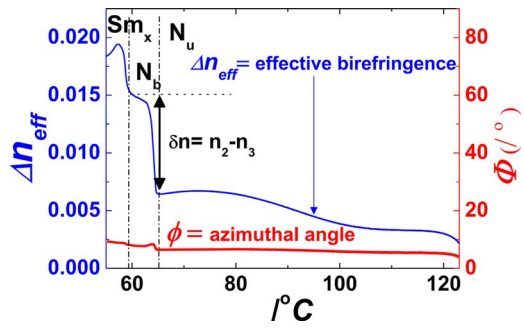

FIG. 5. (Color online) Temperature dependence of the effective birefringence in a rubbed homeotropic cell using PEM without voltage.

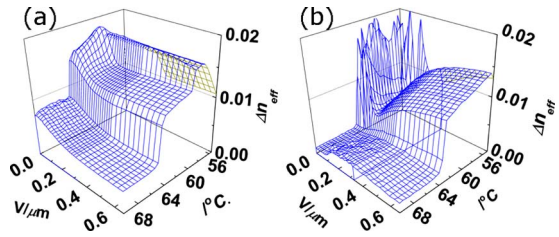

FIG. 6. (Color online) Three dimensional temperature and voltage plots of PAL1 by PEM. (a) Rubbed and (b) unrubbed homeotropic cells.

field as the material has negative dielectric anisotropy. The Φ of the retarder with electric field is found to rotate only in the N_b, since the minor director here is well defined. We thus find that the surface induced tilt can be eliminated by application of an in-plane electric field. This makes it possible to measure the optical biaxiality of N_b and to avoid problems related to the surface-induced birefringence.[15] The absence of an aligned direction of the minor director in the unrubbed cell causes a significant deterioration in the accuracy of the data. Higher fields cause a gradual alignment of the minor director in the unrubbed cell and a corresponding increase in Δn_{eff} [Fig. 6(b)].

In order to confirm N_b, we also observe an optical signal in a planar cell. Our PEM measurements with a commercial planar cell also show a similar jump in Δn_{eff} in the nematic phase (Fig. 7). The minor director in the N_b of a planar cell has been reported in the literature to be parallel to the substrate.[8,17] However in our experiment we observe increase in Δn_{eff} at the transition temperature which means that the minor director is aligned perpendicular to the substrate. On applying 2 $V/\mu m$ to the planar cell, we do not observe any measurable change in Δn_{eff} in either of the two nematic phases. This is because the minor director of the phase is already parallel to the electric field and N_b with negative dielectric anisotropy will preserve its planar alignment under electric field.

We find $n_2 - n_3 = 0.0085$ from the homeotropic cell, whereas from the planar cell, $n_2 - n_3 = 0.0023$. In both cases the resolution in retardation drawn from the signal-to-noise ratio is better than 10^{-3} rad. For the cells used here, this is better than 5×10^{-5} in birefringence. The discrepancy in between results for homeotropic and planar cells can possibly be explained by a difference in their surface conditions. However, it is reasonable that the biaxiality found in the homeotropic cell is closer to the value in reality. It must be stressed that biaxiality is not induced by the surface, however rubbing the surface breaks the symmetry and aligns the minor director along it. We find that in a planar cell the minor director is normal to the surface. Normally, the transverse dipole moments of molecules are favored normal to the surface but on the contrary, the molecular packing favors the

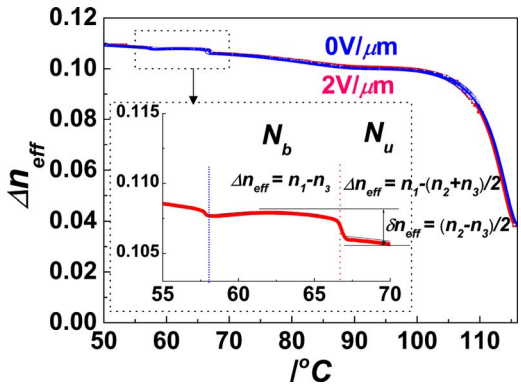

FIG. 7. (Color online) Temperature dependence of the effective birefringence in a planar cell using PEM with and without voltage. The inset magnifies dotted rectangle in the figure.

minor director lying parallel to the substrate providing a competition with an overall win for the first case. This is likely to reduce the biaxiality in a planar cell. In summary, we observe a biaxial N_b in homeotropic and planar cells using a quantitative technique where biaxiality is directly measured; we realize the most plausible device configuration for display applications.

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