Characterization of Nematic Phase of Banana Liquid Crystal

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We report the first detailed optical and electrical characterizations of the nematic (N) phase of a banana liquid crystal, i.e., pretilt angle, and optical and dielectric anisotropies, and point out the difference from those of rodlike molecules. The pretilt angle measurements using a conventional crystal rotation method show that the pretilt angle is very small (less than 1°) even in cells with a polyimide film yielding a high pretilt angle like 8° for calamitic molecules. We also measured the birefringence Δn in the N phase as a function of temperature and estimated the orientational order parameter S. The medium shows a small negative dielectric anisotropy in the N phase and the anisotropy becomes large in the B2 phase mainly because of the tilt of the molecules from the layer normal.   [DOI: 10.1143/JJAP.45.L1013]

KEYWORDS: banana liquid crystal, nematic phase, pretilt angle, birefringence, dielectric constant, order parameter

Liquid crystal is a soft matter and the soft nature of the medium couples with anisotropic optical and dielectric properties giving rise to many electrooptic effects at relatively low voltages. These are exploited in liquid crystal displays (LCDs), which are the lowest-power-consuming flat panel devices. The tremendously fast development in LCDs is due to the progress in the physics and chemistry of liquid crystals during the past three decades. Most of the display devices make use of nematic (N) liquid crystals made of rodlike molecules. The discovery of electrooptical switching in banana liquid crystals has also created enormous interest in this field.[1,2] Recently, a new liquid crystal display mode has been demonstrated by Shimbo *et al.*,[3] which appears to be promising for future display applications owing to its various advantages over all existing modes. For suitable applications, the characterization of materials is essential. So far, there are not many reports about the determination of the physical properties in terms of, for example, birefringence, elastic moduli, anchoring energy, and pretilt angle, of these materials. Measurements of these physical parameters are important from the fundamental as well as the technological point of view. The main difficulty in measuring such physical parameters in banana liquid crystal is the poor alignment. Recently, Reddy *et al.* have reported the observation of the N phase in a homologous series of banana liquid crystal.[4] The director can be well aligned in a cell treated for homogeneous alignment. In this letter, we report the measurement of pretilt angle, birefringence and dielectric constants in the N phase of a banana liquid crystal.

The chemical structure of the compound is shown in Fig. 1. The details of the synthetic scheme were reported earlier.[4] The compound exhibits the phase sequence Cry-99.6 °C-B2-114.5 °C-N-119.5 °C-Iso as observed using a polarizing microscope upon cooling. Glass plates were spin-coated with polyimide (Nissan, SE 7492) and cured at 180 °C for 30 min for homogeneous alignment. After curing, the plates were rubbed and assembled such that the rubbing directions were antiparallel. The cells were filled in the isotropic phase and cooled slowly to the N phase, resulting in a good homogeneous alignment of the director. For homeotropic alignment, glass plates were spin-coated with polyimide (JSR, JALS 204) and cured under the same
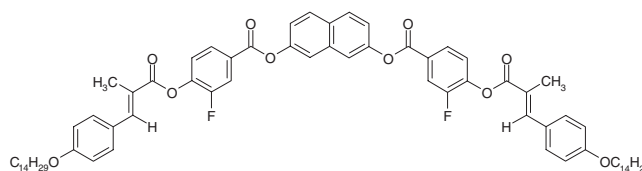

Fig. 1.   Chemical structure of compound used.

conditions. The temperature of the sample was controlled using a temperature controller within an accuracy of 0.1 °C. Texture observation was carried out using a polarizing microscope. All the measurements were made while cooling the sample from the isotropic phase.

Pretilt angle is defined as the angle of the average optical axis of the molecules relative to the substrate surface. We employed a conventional crystal rotation method (CRM) for measuring pretilt angle,[5] which is generally used for uniaxial N liquid crystals made of rodlike molecules. A He–Ne laser (632.8 nm) was used to illuminate a 40-μm-thick cell and transmitted intensity was measured as a function of incidence angle from −45 to +45° about the axis perpendicular to the light beam and rubbing direction. The transmitted intensity was fitted to a theoretical equation,[5,6] and the value of pretilt angle was obtained as a fitting parameter.

The variation in the birefringence of the sample at $\lambda = 550$ nm was measured using a polarizing spectrophotometer (ORC, TFM-120AFT-PC) as a function of temperature in the N phase. The transmittance spectra were fitted to a well-known equation for nonabsorbing birefringent media to determine Δn, where the dispersion of the refractive indices was properly taken into account. In this measurement, the cell thickness was 5.4 μm. The dielectric measurements were conducted with an impedance analyzer (Yokogawa-Hewlett-Packard, 4194A) using homogeneous ($\varepsilon_\perp$) and homeotropic ($\varepsilon_\parallel$) cells.

The textures of the N phase under cross polarizers are shown in Fig. 2. In a homogeneous cell, it was completely dark (a) when the optic axis was parallel to either of the two polarizers and gradually turned to be bright (b) when the sample was rotated. Complete darkness indicates that the
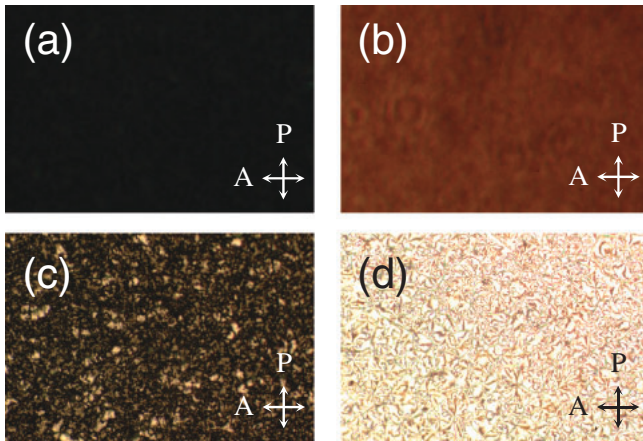
Fig. 2. Texture of homogeneously aligned 5.4-μm-thick sample at 118 °C; nematic phase under crossed polarizers with director parallel to either polarizer or analyzer direction (a) and rotated 10° from the (a) position (b). Texture of homeotropically aligned 5.7-μm-thick sample at 119 °C (N) (c) and at 111 °C (B2) (d).

Fig. 3. Incidence angle (inside cell) dependence of transmitted intensity for 40-μm-thick nematic layer at 116 °C. The pretilt angle estimated by the best fit is 0.30°. There is no temperature dependence, as shown in the inset.

Fig. 4. Variation of birefringence with temperature.

Fig. 5. Variation of order parameter with temperature.

major molecular axis aligns well along the rubbing direction. On the contrary, the brightness in Fig. 2(b) is not perfectly uniform. Because of the bent core of the molecule used, the free rotation of individual molecules is prohibited to some extent, resulting in birefringence. Hence, macroscopic biaxiality emerges and the rubbing treatment cannot align the biaxial axes. In a homeotropic cell, however, a completely dark view was not observed in the N phase (119 °C) (c). The absence of complete darkness is attributed to the molecular biaxiality and the resultant macroscopic biaxial order, as suggested by Fig. 2(b). When a layer structure was formed in the B2 phase (111 °C) (d), schlieren texture was visible owing to the biaxiality. In addition to the emergence of biaxiality, layer deformation is associated with the N–B2 phase transition. This explains why the darkness in the B2 phase is less pronounced than that in the N phase.

A representative variation in transmittance intensity in the CRM at 116 °C is shown in Fig. 3. The circles represent the experimental data points and the solid line denotes the best fit based on the theoretical equation. The pretilt angles measured at four different temperatures are plotted in the inset of Fig. 3. It is found that the pretilt angle of banana liquid crystals is extremely small with the alignment layer (Nissan, SE 7492), which generally yields large pretilt angle for calamitic liquid crystals. On the basis of our measurements using the same alignment layer and the same rubbing strength, we obtained about 8° in 5CB. Such a small pretilt angle may originate from the presence of long flexible alkyl chains on both sides of the bent core and/or from a transverse dipole. A systematic study must be performed to elucidate the real cause of the small pretilt angle.

We also measured the birefringence in the N phase as a function of temperature. The variation in birefringence is shown in Fig. 4. It is noticed that birefringence increases abruptly at the isotropic–N phase transition, indicating a first order phase transition, and gradually increases as temperature decreases in the N phase. The temperature dependence of Δn can be approximated for N liquid crystals by the formula $\Delta n = \Delta n_0 (1 - T/T_1)^\beta$, where T_1 and β are the adjustable parameters and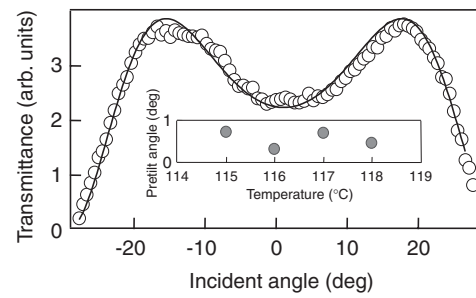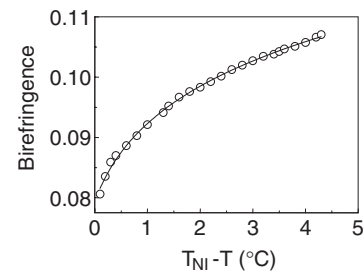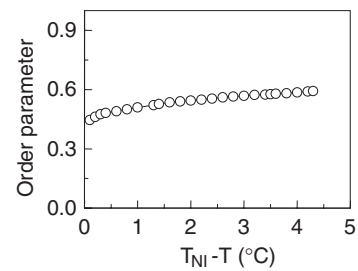 Δn_0 is the birefringence of the perfectly aligned sample. The equation fits well in the entire temperature range, as shown in Fig. 4. By least squares fitting, we obtained $\beta = 0.12$ and $\Delta n_0 = 0.18$. Similar values of β are also reported in several other nematics.[7] The order parameter S was estimated using the relation $S = \Delta n / \Delta n_0$. The temperature variation of the calculated order parameter is shown in Fig. 5. The order parameter in the N phase just below the phase transition was approximately 0.4 and increased to 0.6 before the N–B2 transition took place. The temperature dependence of S was also measured by Weissflog *et al.*[8] and Gong *et al.*[9] in the nematic phase of a banana liquid crystal by nuclear magnetic resonance spectroscopy and a similar temperature dependence with slightly smaller values of S was reported.

Finally, we show the results of the dielectric measurements in Fig. 6. In the N phase, a small negative dielectric anisotropy was obtained. The negative anisotropy originates from carbonyls and substituted F atoms. When the phase transition from N to B2 takes place, $\varepsilon_\perp$ increases, whereas $\varepsilon_\parallel$ decreases. The increase in $\varepsilon_\perp$ originates from the cooperative response of molecular dipoles due to molecular close
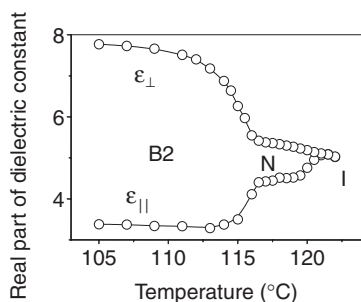
Fig. 6. Variation of real part of dielectric constant at 10 kHz with temperature.

packing in smectic layers. The decrease in $\varepsilon_\parallel$ is caused by the tilt of molecules with respect to the smectic layer normal, keeping the molecular transverse dipoles parallel to the smectic layer (perpendicular to the applied electric field).

In summary, the pretilt angle and the optical and dielectric anisotropies of a banana liquid crystal that exhibits the N phase were measured. It is found that the banana liquid crystal molecules in the N phase tend to orient parallel to the spin-coated polyimide surface, even if the polyimide producing a high pretilt angle for calamitic molecules is used. The value of the order parameter estimated from the birefringence varies slowly with temperature. The dielectric anisotropy is small and negative in the N phase and shows a large change due to N to B2 phase transition. These experimental data are useful for investigating other physical properties in terms of parameters such as elastic moduli and anchoring energies.

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