Alternating twist structures formed by electroconvection in the nematic phase of an achiral bent-core molecule

Shingo Tanaka,[1] Surajit Dhara,[2] B. K. Sadashiva, Yoshio Shimbo,[1] Yoichi Takanishi,[1] Fumito Araoka,[1] Ken Ishikawa,[1] and Hideo Takezoe[1]

[1]*Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan*

[2]*School of Physics, University of Hyderabad, Hyderabad-500046, India*

[3]*Raman Research Institute, C. V. Raman Avenue, Sadashivanagar, Bangalore-560080, India*

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We report an unusual electroconvection in the nematic phase of a bent-core liquid crystal. In a voltage-frequency diagram, two frequency regions exhibiting prewavy stripe patterns were found, as reported by Wiant *et al.* We found that these stripes never show extinction dark when cells were rotated under crossed polarizers. Based on the color interchange in between neighboring stripes by the rotation of the cells or an analyzer, twisted molecular orientation is suggested; i.e., the directors are alternately twisted from the top to the bottom surfaces with a pretilt angle in adjacent stripes, which is an analogue of the twisted (splayed) structure observed in surface-stabilized ferroelectric liquid crystal cells. The transmittance spectra calculated using the 4×4 matrix method from the model structure are consistent with the experimental observation.

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I. INTRODUCTION

It is well known that electroconvection takes place in planar cells of nematic liquid crystals with negative dielectric anisotropy depending on applied voltages and frequencies [1–3]. Since the resultant fringe pattern was first observed by Williams [4], the pattern is called the Williams domain [4]. The cause of the Williams domain was explained by Helfrich [5] and Carr [6]. Later, Penz [7] considered focusing effect due to an alignment deformation to explain the fringes observed under the polarizing microscope. Later Kondo *et al.* [8] took into account ray deflection from wave-front distortion and succeeded in explaining the details of the fringe characteristics. In addition to the typical Williams domains, a variety of electroconvection effects have been reported: grid pattern and soft-mode turbulence, and so on [9,10]. These patterns are related to the anisotropy of electric properties including dielectric constant and conductivity. In the Carr-Helfrich theory describing standard electroconvection mechanism, the dielectric anisotropy and conductivity anisotropy are assumed to be negative and positive, respectively [11]. The researches in other situations of electric anisotropies have also been made; i.e., the case of positive dielectric anisotropy and negative conductivity anisotropy or the case of both positive anisotropies [12,13]. However, most of the reported instabilities concern rodlike molecules except for a swallow-tailed molecule [12].

Recently, Wiant *et al.* [14] reported nonstandard electroconvection in the nematic (*N*) phase of a bent-core liquid crystal. However, the mechanism has not yet been understood completely, hence extensive investigations on the nematic phase of bent-core molecules with different molecular structure are necessary. Liquid crystals composed of bent-core molecules have been studied actively in recent years [15,16] since the discovery of polar switching in achiral bent-core mesogens [17]. In addition to so-called banana phases, characteristic smectic (Sm) phases consisting of bent-core molecules and being designated as $B1-B8$ [15], biaxial *N* [18,19], biaxial SmA [20,21], and randomly polarly ordered SmA [22] phases were reported. Some of them exhibit conventional *N* and SmA phases in addition to the above-mentioned phases [15,16]. A variety of interesting phenomena observed in bent-core mesogenic systems arise from polarity and chirality [15]. In this sense, unconventional electroconvection effect in the *N* phase of a bent-core mesogen has to be investigated in the light of polarity and/or chirality.

In this paper, we report electroconvection effect in a different type of a bent-core nematic liquid crystal with a very different molecular structure. We observed a similar type of instability as Wiant *et al.* [14] reported: two frequency regions showing prewavy patterns with some differences. The most important observation in our study is the alternate color change in adjacent domains of the prewavy patterns, the color interchanges under the rotation of cell or analyzer, and nonexistence of extinction position upon the cell rotation. To explain these observations, we propose a model director orientation, calculate the transmittance spectra, and compare the results with the experimental observations. Good agreement supports the proposed model structure, in which directors form twisted structures from the top to the bottom surfaces. We conclude that this structure is caused by the convection flow and the chiral nature of bent-core molecules.

II. EXPERIMENT

The compound used is a bent-core molecule shown in Fig. 1 and synthesized as described [23]. As characterized by Le *et al.* [24], the compound shows the phase sequence, crystal (102 °C) *B*2 (115 °C) *N* (119.5 °C) isotropic (Iso), where *B*2 is a typical banana phase and *N* seems to be a uniaxial nematic phase. In both liquid crystal phases, the compound shows negative dielectric anisotropy and negative conductivity anisotropy.

Glass substrate plates with electrode made of indium tin oxide (ITO) were spin coated with polyimide (JSR, AL

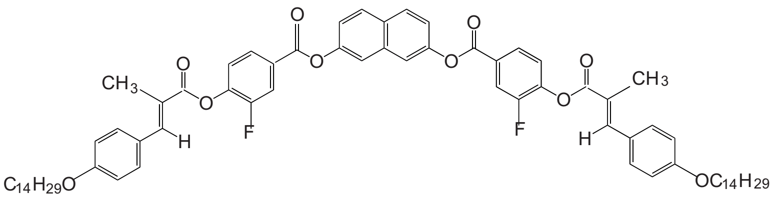

FIG. 1. Chemical structure of the compound used. The phase sequence of this compound is crystal (102 °C) *B*2 (115 °C) *N* (119.5 °C) isotropic.

1254) and baked at 180 °C for 1 h. The plates were rubbed unidirectionally and assembled to 6- or 10-μm-thick homogeneously aligned cells with antiparallel rubbing directions. The empty cell was filled with the sample in the isotropic (Iso) phase by capillary action and cooled slowly to get a well aligned *N* phase in a hot stage (Mettler FP90).

The texture was observed under a polarizing microscope (Nikon, OPTIPHOTO-POL) under the application of rectangular wave voltage of various frequencies (10 Hz–400 kHz) and amplitudes up to 80 V at 2 °C below the *N*-Iso transition temperature. It is noted that the cells showed completely dark in the absence of a field when the optic axis was parallel to either of the two polarizers.

III. EXPERIMENTAL RESULTS

Let us first show the texture caused by electroconvection observed in a 10-μm-thick cell. Figure 2 shows photomicrographs taken at various frequencies. At 10 Hz (a), the texture is polydomainlike, as observed in the isotropic electroconvection. A wavy stripe pattern due to anisotropic electroconvection gradually appeared at 60 Hz (b). At such low frequencies around 60 Hz, the direction of the stripes was not stable and not pinned in one direction, i.e., thin transverse wavy stripes were observed in addition to the longitudinal wavy stripes. Namely, the anisotropy of the electroconvection is low at this frequency region. The electroconvection pattern became distinct at 1 kHz, as shown in Fig. 2(c). The period of the patterns is about 20 μm, approximately double the cell thickness. This is the same pattern observed by Wiant *et al.* [14]. Thus isotropic electroconvection was vanished and anisotropic electroconvection called prewavy 2 grew at around 1 kHz. The prewavy pattern is different from the conventional electroconvection (Williams domain) in the sense that the former is wavy and sometimes has branches while the latter is more or less straight and rarely shows branches. Figure 2(d) shows the electroconvection at 8 kHz. The prewavy pattern became obscure compared with that seen in Fig. 2(c). Figure 2(e) shows a microphotograph at 50 kHz, where a clear prewavy pattern is observed. This pattern observed at higher frequencies is called prewavy 1, although the texture is the same as that of the prewavy 2 observed at low frequencies. The prewavy pattern disappeared at high frequencies such as 400 kHz under the same applied voltage of 80 V, as shown in Fig. 2(f). This is attributed to a dielectric heating, which is known to be serious at high frequencies and high voltages. Namely, the *N*-Iso transition occurred due to the dielectric heating.

In order to clarify the phenomenon and identify the similarities and differences between our and Wiant *et al.*'s results, we investigated a voltage-frequency diagram showing the threshold voltages for the emergence of prewavy patterns. Figure 3 shows the diagram, in which threshold voltages are shown by closed diamonds as a function of frequency in a logarithmic scale. The *N*-Iso transitions are also shown by closed squares. The diagram clearly distinguishes the two prewavy patterns 1 and 2. The threshold voltage of two prewavy patterns is discontinuous; i.e., the threshold voltage increases and decreases with increasing frequency in the prewavy 2 and 1 regions, respectively. Thus, the present diagram and that reported by Wiant *et al.* [14] apparently look similar. However, there are several important differences in their detailed structures: (1) In our polydomainlike region at low frequencies, Wiant *et al.* observed fine parallel stripes. (2) In the frequency region in between the regions showing prewavy 2 and prewavy 1, we observed the prewavy pattern, though it was obscure, whereas Wiant *et al.* suggested the existence of nonelectroconvection region. The

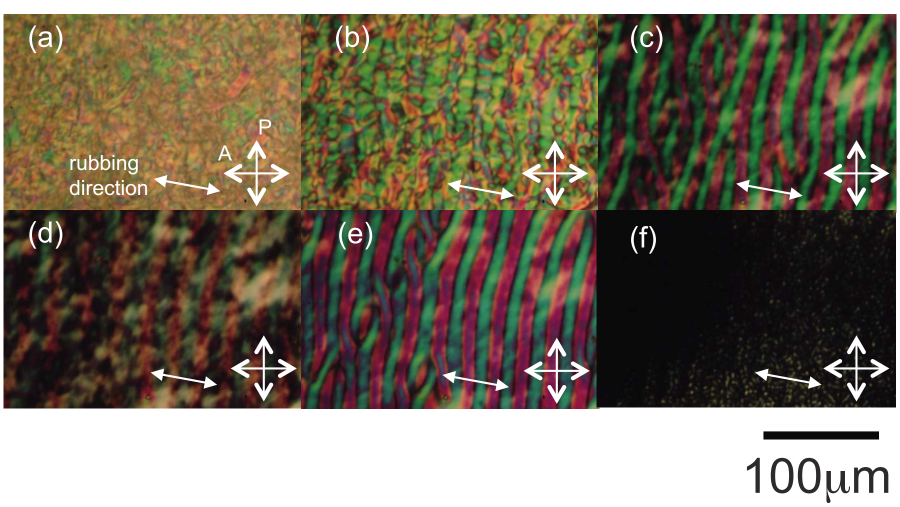

FIG. 2. (Color online) Photomicrographs showing the electroconvection under crossed polarizers (crossed white arrows) in the nematic phase (2 °C below the *N*-Iso transition) of the bent-core liquid crystal. The cell thickness was 10 μm. The cell was homogeneously aligned and the rubbing direction was 10° from a polarizer. The applied voltage was a rectangular wave of 80 V and the frequency was: (a) 10 Hz, (b) 60 Hz, (c) 1 kHz, (d) 8 kHz, (e) 50 kHz, and (f) 400 kHz.

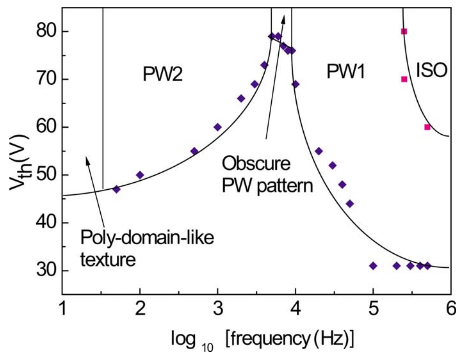

FIG. 3. (Color online) *V-f* diagram. Two regions showing prewavy patterns, prewavy 1 (PW1) and prewavy 2 (PW2) are located at high and low frequency regions, respectively, and are bordered by the region showing obscure prewavy patterns. Closed diamonds stand for the threshold voltage to show the prewavy patterns. The transition to the Iso phase caused by dielectric heating is also shown by closed squares.

applied voltage of 80 V at 8 kHz is near the threshold voltage for the emergence of the prewavy pattern, as shown in Fig. 3. (3) The effect of dielectric heating is clearly observed in our case, but not in Wiant *et al.* [14]. (4) We could find no extinction positions under sample rotation between crossed polarizers, whereas Wiant *et al.* mentioned nothing about this observation.

The most important feature we observed but was not described by Wiant *et al.* is the nonexistence of extinction conditions; we observed no extinction position for the stripes when the cell was rotated between crossed polarizers. This

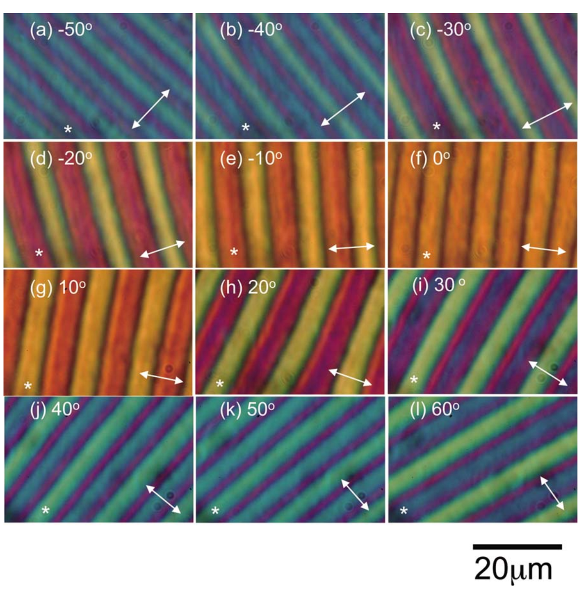

FIG. 4. (Color online) Photomicrographs showing color changes with cell rotation angle (rubbing direction with respect to polarizers) under crossed polarizers in the nematic phase (2 °C below the *N*-Iso transition) of the bent-core liquid crystal. The cell thickness was 6.0 μm. The applied voltage was a rectangular wave of 80 V and the frequency was 1 kHz. Rubbing direction is (a) −50°, (b) −40°, (c) −30°, (d) −20°, (e) −10°, (f) 0°, (g) 10°, (h) 20°, (i) 30°, (j) 40°, (k) 50°, and (l) 60° from a polarizer direction.

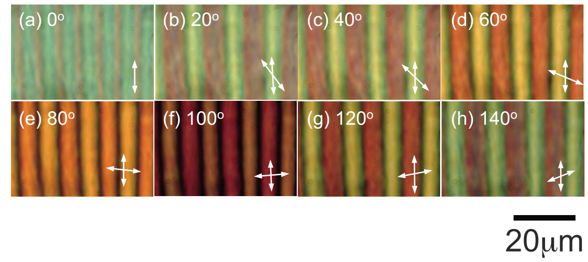

FIG. 5. (Color online) Photomicrographs showing color changes with analyzer rotation angle under crossed polarizers in the nematic phase (2 °C below the *N*-Iso transition) of the bent-core liquid crystal. The cell thickness was 6.0 μm. The applied voltage was a rectangular wave of 80 V and the frequency was 1 kHz. Rubbing directions is along the vertical direction in these photographs. The angle of analyzer is (a) 0°, (b) 20°, (c) 40°, (d) 60°, (e) 80°, (f) 100°, (g) 120°, and (h) 140° from the polarizer direction.

fact indicates that the director deformation does not occur within a single plane but the director orientation out of the plane is induced by the electroconvection. To clarify the phenomenon, texture observation was made by rotating a 6-μm-thick cell between crossed polarizers. Figure 4 shows the result observed under the condition of 80 V and 1 kHz. The period of the stripes is around 12 μm, about double the cell thickness. In the figure, the cell rotation angles between the rubbing direction (white arrow) and one of the polarizer directions are shown in the figure. Asterisks are added to identify the same striped domain. The following characteristics should be noticed: (1) Colors change alternately in adjacent striped domains, and these colors interchange at 0° and 45°, more explicitly, $0° + 90° n$ and $45° + 90° n$, where n is integer numbers. (2) The two domains never become dark at any angles. (3) The boundaries between the two domains become dark at $0° + 90° n$ and bright at $45° + 90° n$. The texture observation was also made with the rotation of the analyzer. As shown in Fig. 5 [see, for example, (d) and (g)], we find the following characteristic: (4) The colors of two domains also interchanged against the opposite rotations of the analyzer with respect to the parallel and crossed position, $90° n$. The characteristic (3) suggests that the director is parallel to the rubbing direction in the boundaries between two domains. By contrast, the characteristic (2) suggests that the director orientation is out of a plane perpendicular to the cell surface including the rubbing direction. The inversion of the

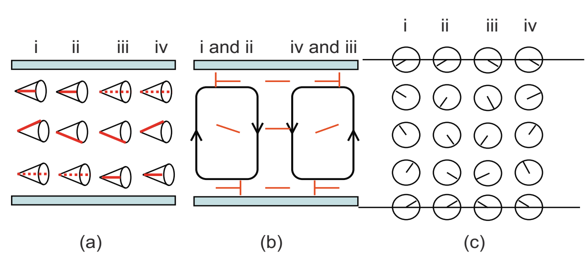

FIG. 6. (Color online) The proposed model structure. (a) Model structures proposed for left-handed and right-handed twisted (splayed) structures in SSFLC cells. (b) Electroconvection model with twisted structure. (c) *C*-director maps in twisted structures associated with surface pretilt.

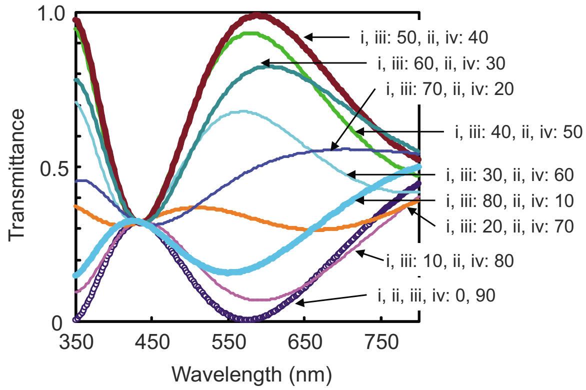

FIG. 7. (Color online) Calculated transmittance spectra by using the 4×4 matrix method. The parameters used are as follows: Refractive index of the substrate is 1.52, and those of the liquid crystal for ordinary and extraordinary light are 1.49 and 1.63, respectively. The azimuthal angle rotation of the *c* director from the surface plane is 30° and the ratio of height to radius of a tilt cone is 3 to 1. The spectra of two structures of i and iii and those of ii and iv are identical for all the sample rotation angles. The spectra at angles of opposite rotations from 45°, for instance 30° and 60°, and 20° and 70°, are the same for the former and the latter structures, consistent with the experimental observations.

colors of the two domains mentioned in the characteristics (1) and (4) may result from oppositely twisted director orientations from the top to the bottom surfaces in each domain.

IV. DISCUSSION

As mentioned in the previous section, the experimental observation suggests twisted director orientation with alternate change of the twist sense in adjacent domains. To confirm the structure we calculated transmittance spectra using the 4×4 matrix method [25]. For this purpose we need some probable models of director orientations in the prewavy pattern. Simple twisted nematic liquid crystal structures are denied, since the transmittance is identical in two oppositely twisted structures. Clear observation of periodic pattern (shadowgraph) is evidence of director modulation within a plane perpendicular to the substrates [8,26]. Therefore we need to propose a model with twist or modulation extended both in and out of a plane. A good example of such modulation is observed in surface-stabilized ferroelectric liquid crystal (SSFLC) structures, twisted or splayed orientation, as shown in Fig. 6(a) [27]. We propose the corresponding twisted structures under electroconvection, as shown in Fig. 6(b). This model can be constructed by introducing twist structures to a conventional electroconvection model structure, and has director modulation both in and out of a plane. The role of a tilt cone on which the director rotates as shown in Fig. 6(a) is played by the electroconvection flow, which induces the in-plane tilt of the director in the middle of the convection flow and the rotation of the director at surfaces. The rotation would be possible by taking into account the chiral nature of bent-core molecules [28].

Since the cause of the twisted structure in the present electroconvection is different from that of SSFLC, the cone

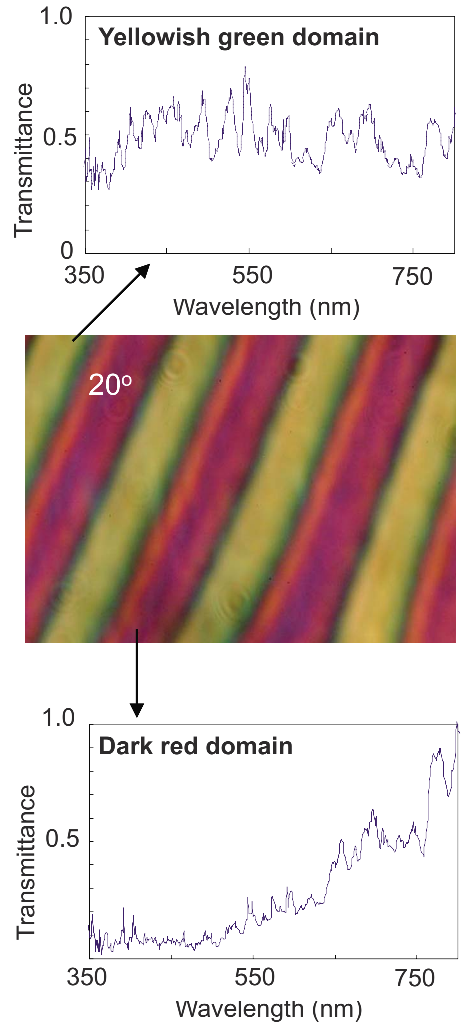

FIG. 8. (Color online) Preliminary result of transmittance spectra from adjacent stripes of a prewavy pattern.

is not defined, so that the in-plane tilt angle is not necessarily the same as the angle of the director at the surface with respect to the rubbing direction. For simplicity, however, we tested the twisted state of SSFLC. It is known in the twisted state of SSFLC cells that two twisted structures with the same twist sense give different transmittance spectra, only when surface pretilt is introduced [29]. Figure 6(c) is the model showing the *c*-director map in which pretilt (*c*-director rotation at surfaces) is added to the model shown in Fig. 6(a). The calculation was made using this model.

Figure 7 shows the transmittance spectra calculated under crossed polarizers during the sample rotation using the four models shown in Fig. 6(c). The parameters we used are azimuthal angle rotation of the *c* director from the surface plane being 30° and height to radius of tilt cone being 3 to 1, ordinary and extraordinary refractive indices of the liquid crystal being 1.49 and 1.63, respectively, and 1.52 for the refractive index of the substrate. The results for i and iii, and those for ii and iv in Fig. 6(c) are shown in Fig. 7. When the rotation sense of the *c* director is the same such as in i and iii and in ii and iv, the spectra are identical to each other. When the rotation angle is 0° and 90°, namely, the tilt-cone axis is along the polarizer direction, all the spectra are the same, as experimentally observed; i.e., the colors of the two domains are the same. It is obvious that the spectra for i and iii and those for ii and iv interchange with respect to the angles at 0°, 45°, and 90° under sample rotation. The calculated results also agree with texture observations. The transmittance spectra under the rotation of the analyzer were also calculated. We obtained qualitative agreement with the experiments, though the calculated results are not shown.

Preliminary experimental measurements of the transmittance spectra from adjacent domains were conducted. The results are shown in Fig. 8, where spectra from yellowish and reddish domains at a cell rotation angle of 20° are shown. Although quantitative agreement was not possible, we can suggest that the unique electroconvection effect in the *N* phase of a bent-core molecule is due to alternate twist molecular orientations. Further careful experiments and simulation using various parameters may give quantitative agreement, leading to a detailed director orientational model structure. We tentatively used a model structure, which is the analogue of static twisted structures of SSFLC cells [27]. It is noted, however, that the origin of the structure is totally different: Tilt of the director with respect to the layer normal in the middle of the cell corresponds to the in-plane tilt by the electroconvection flow. Twisted structures in SSFLC are caused by the surface polar interactions, whereas those between both surfaces in the present cells are caused by the molecular chirality characteristic to bent-core molecules. Thus, the electroconvection in the *N* phase of bent-core molecules provides a type of chirality-related phenomenon.

V. CONCLUSION

We observed unique electroconvections in the nematic phase of a bent-core liquid crystal. The voltage-frequency diagram for the emergence of the prewavy patterns is quite similar to the one reported by Wiant *et al.*, although a few distinct differences exist. We found that neighboring domains of the prewavy patterns show different colors and no extinction by rotating cells under crossed polarizers. Moreover, the colors interchange by oppositely rotating cells with respect to the angles 0° and 45° or an analyzer with respect to the parallel and crossed positions. These observations clearly suggest oppositely twisted director orientations from the top to the bottom surfaces in adjacent domains in the prewavy pattern. We propose a possible model director orientation analogous to the twisted (splayed) structure in SSFLC cells and calculated the transmittance spectra using the 4×4 matrix method. The calculated transmittance spectra are consistent with the experimental observations. Thus, the unique textural characteristics observed in the prewavy patterns are explained by introducing the chiral nature of bent-core molecules. Further detailed spectral measurements are necessary for quantitative comparison with the calculation. Direct observations of the structure by means of freeze fracture transmission electron microscopy and tomograms using confocal microscopy are important and are under investigation.

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