

## Induced Antiferroelectric Smectic- $C_A^*$ Phase by Doping Ferroelectric- $C^*$ Phase with Bent-Shaped Molecules

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(Received 19 January 2000)

Doping of the ferroelectric Sm- $C^*$  phase with bent-shaped molecules induces the antiferroelectric Sm- $C_A^*$  phase. The effect was observed by means of electro-optic and dielectric measurements in systems with weak interlayer interactions in which the relative strength of anticlinic-synclinic order between molecules in adjacent layers is easily controlled by external factors. Fourier-transform infrared spectroscopy studies suggest that the bent-shaped molecules are not flat. They reorient upon the electric field-induced antiferroelectric-ferroelectric transition to adopt a position in which the average direction of the carbonyl groups is in the smectic plane and a bending tip along the  $C_2$  symmetry axis.

PACS numbers: 61.30.-v

It has recently been shown that the polar properties of some liquid crystals can be easily changed from antiferroelectric (AF) to ferroelectric (FE) by interactions with sample boundaries [1–3]. This unusual behavior was found in materials with weak interlayer interactions, in which a frustration between FE and AF molecular orders occurs. Hereafter we show that the polar properties of such a system can also be tuned from FE to AF by doping with bent-shaped molecules. The anticlinic molecular order, inherent to an AF smectic phase, is apparently strengthened by steric interactions of the rodlike host molecules with bent-shaped molecules. Numerous bent-shaped molecules were found to induce an AF order and the effect does not depend on whether the dopant itself shows polar phases (Fig. 1). In contrast, dopant  $D5$ , with a thiophene ring as a central unit and a much larger bend angle of  $\alpha \sim 154^\circ$ , did not induce the AF phase. However, the induction of an AF phase is strongly dependent on the host compound. Among the several tested compounds only compounds belonging to homologous series  $M1$  (Fig. 1) show the induction of an AF phase. For this series a strong dependence of the polar properties was observed upon elongation of the nonchiral terminal alkoxy tail [4]. The short homologs ( $M1$  with number of carbon atoms  $n < 13$ ) show a broad AF phase, while longer ones display only the FE phases. For the homologs  $M1$  with  $n \geq 13$  the induction effect was observed. It was also found that doping destabilizes phases, which arise from the competition between FE and AF orders. Such intermediate phases Sm- $C_\gamma$  and Sm- $C_\alpha$  were for the first time observed in the MHPOBC compound [5]. In MHPOBC doped with  $\sim 3$  wt % of bent-shaped molecules ( $D1$ ) the direct Sm- $A$  to Sm- $C_A^*$  phase transition was observed.

In order to obtain some insight into the doping effect, the mixtures were studied by dielectric and electro-optic measurements as well as by polarized infrared spectroscopy.

Dielectric dispersion measurements were carried out using a Hewlett-Packard LF 4192A in a frequency range 1 Hz–10 MHz. The glass cells, 25  $\mu\text{m}$  thick, coated with indium-tin-oxide (ITO) transparent electrodes and parallel rubbed polyimide layer, were used. In both the smectic- $C^*$  (Sm- $C^*$ ) and hexatic- $I^*$  (Hex- $I^*$ ) phases of pure  $M1$  ( $n = 13$ ) compound, a strong phason (Goldstone) mode typical for the FE smectic phases [6,7] was detected, as shown in Fig. 2(a). In an  $M1$  ( $n = 13$ ) material doped with bent-shaped molecules ( $D1$ ) the antiferroelectric Sm- $C_A^*$  and Hex- $I_A^*$  phases appeared. This is signified by the suppressed Goldstone mode [Fig. 2(b)]. The critical dopant concentration, which induces the antiferroelectric phases, varies between 0.1–2 wt % depending on the dopant molecular structure, e.g., 0.8 wt % for  $D1$ . For a low concentration of the dopant the Sm- $C^*$ -Sm- $C_A^*$  phase transition is still visible in both dielectric measurements [Fig. 2(b)] and the observation of texture. The temperature stability of the AF phase increases quickly with increasing dopant concentration and for higher concentration direct isotropic—Sm- $C_A^*$  phase transition is observed. The electro-optic response studies also confirm changes in polar properties. In a pure FE  $M1$  ( $n = 13$ ) compound the bistable switching [8] was recorded, while the doped materials exhibited tristable switching (Fig. 3), typical for the AF phases [5]. As the concentration of the dopant increases the threshold field for AF-FE switching increases. Simultaneously, the  $P_s$  value decreases, indicating that the dipole moment of bent-shaped molecules does not participate in the ferroelectric properties. Although  $P_s$  decreases, the calculated value of  $P_s E_{\text{th}}$  increases with increasing dopant concentration, as shown in Fig. 3(c). Since the product  $P_s E_{\text{th}}$  is the electric energy necessary to break the AF interactions and induce the FE order under applying the electric field [9], its increase suggests that

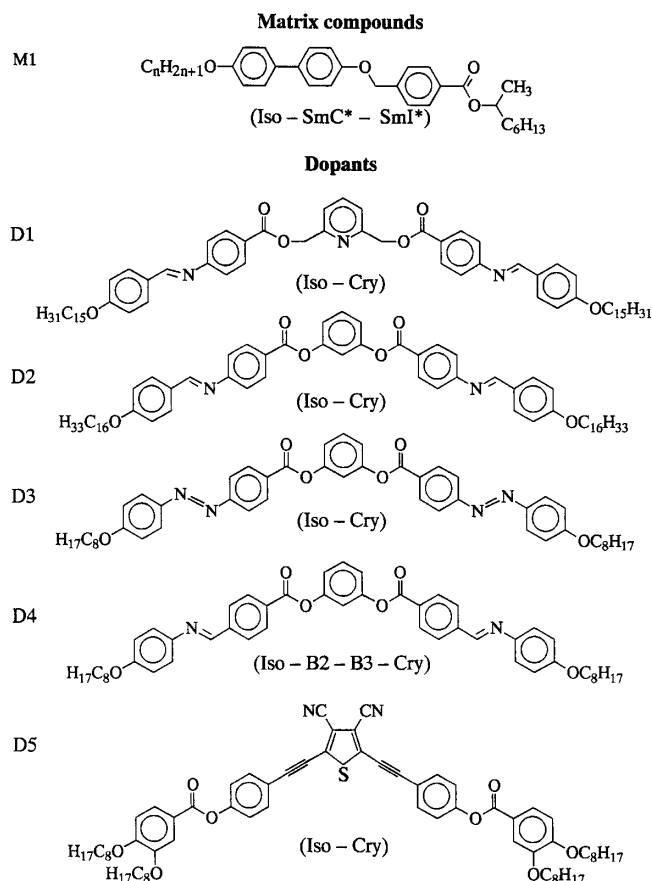


FIG. 1. Chemical structure of tested matrix and dopant molecules.

the strength of the AF interactions is controlled by the dopant concentration.

To study orientational distribution of the bent-shaped dopant and rodlike matrix molecules in the AF equilibrium state and the field-induced FE state (i.e., under dc voltage), the polarized Fourier transformed infrared spectroscopy (FTIR) measurements were performed using JOEL JIR-MICRO 6000. The  $2 \mu\text{m}$  thick cells made of  $\text{SrF}_2$ , coated with ITO and rubbed polyimide, were used. Reasonably good alignment was obtained after applying an electric field for several minutes prior to the FTIR measurements. Spectra were measured as a function of the angle  $\theta$  between polarization direction of the IR wave and the smectic layer normal. The spectral analysis was restricted to the phenyl ring stretching and C=O stretching bands. For the rodlike molecule the phenyl stretching direction is assumed to coincide with the long molecular axis, while for bent-shaped molecules it should nearly coincide with the direction of the molecule branches. For IR studies the D3 dopant was chosen, since only for this compound peaks due to the phenyl ( $1579 \pm 2 \text{ cm}^{-1}$ ) and carbonyl ( $1742 \pm 3 \text{ cm}^{-1}$ ) stretching could be separated from the corresponding peaks ( $1604 \pm 2 \text{ cm}^{-1}$ ,  $1716 \pm 2 \text{ cm}^{-1}$ ) of the host molecules M1 ( $n = 13$ ). The absorption due to the individual band was determined as the maximum absorption in the corresponding wave number region relative to

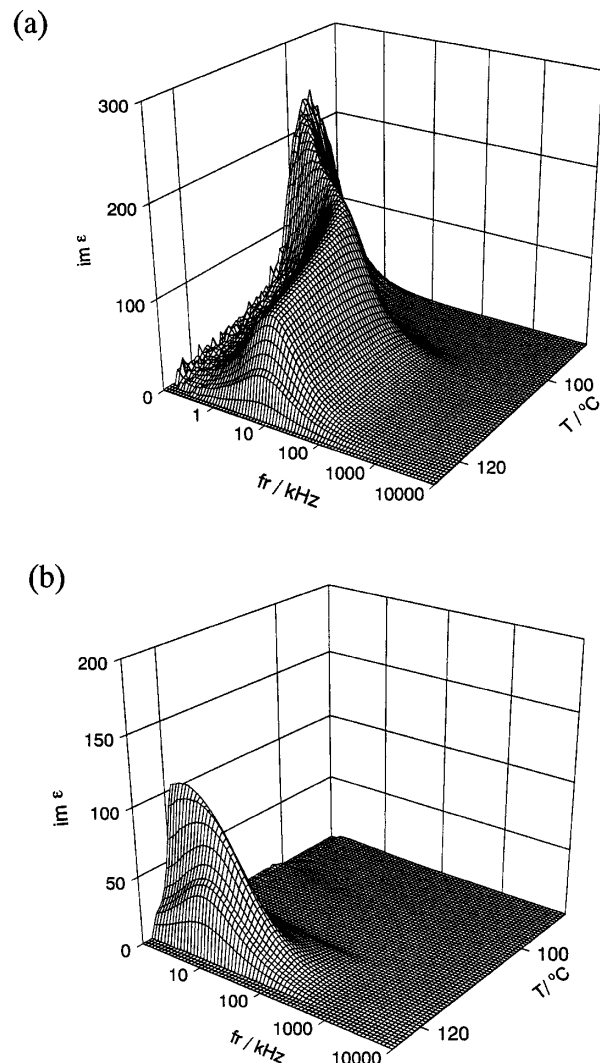


FIG. 2. Imaginary part of the dielectric constant vs frequency and temperature for a pure M1 ( $n = 13$ ) compound (a) and mixtures of M1 ( $n = 13$ ) with dopant D1 at concentration 1.2 wt % (b). In pure M1 ( $n = 13$ ) compound Hex- $I^*$ -Sm- $C^*$  phase transition is observed at  $101^\circ\text{C}$ .

an appropriate baseline. Figure 4 shows a polar plot of principal stretching bands obtained in the Sm- $C_A^*$  phase (a) without and (b) with an electric field. Fitting the absorption value for each band with the general formula

$$A(\theta) = P_1 \cos^2(\theta - \theta_0) + P_2 \sin^2(\theta - \theta_0)$$

yields the mean orientation  $\theta_0$  and dichroic ratio  $R = P_1/P_2$  for the stretching of the phenyl and the C=O groups.

With zero electric field the polar absorption pattern for both matrix and dopant exhibits symmetry about  $\theta_0 = 0$  and  $90^\circ$ , as expected for the Sm- $C_A^*$  phase [5]. Under an electric field the reorientation of host molecules from anticlinic to synclinic structure is evident. The absorption for the phenyl stretching has a dichroic ratio significantly higher ( $R = 2.5$ ) than that with zero electric field ( $R = 1.6$ ) and its maximum is at  $\theta_0 = 30 \pm 1^\circ$ . This value

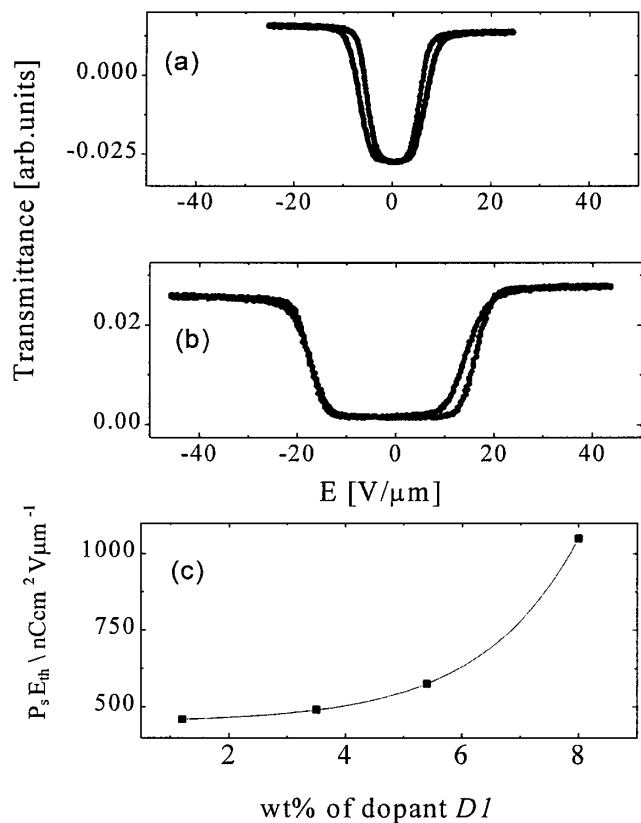


FIG. 3. Optical transmittance measured at frequency 0.1 Hz in a  $2 \mu\text{m}$  cell at  $106^\circ\text{C}$  for the mixtures of  $M1$  ( $n = 13$ ) with  $D1$  at concentrations 5.4% (a) and 7.9% (b). Plot of  $P_s E_{th}$  vs concentration (c).

of tilt agrees with the tilt angle obtained from electro-optic measurements. The analysis of the  $\text{C}=\text{O}$  vibrations shows that for the matrix molecules this moiety exhibits a smaller reorientation (ca.  $20^\circ$ ) than the mesogenic core. The average orientation  $\theta_0 = 70^\circ$  is not perpendicular to that of the phenyl stretching  $\theta_0 = 30^\circ$ ; i.e., the mesogenic core axis is not a principal axis of the carbonyl absorbance ellipsoid. This indicates that the orientational distribution of the  $\text{C}=\text{O}$  moiety around the director is not completely random over azimuthal angles but rotation along the long molecular axis is biased to give a higher probability of finding the  $\text{C}=\text{O}$  group in the smectic plane [10].

Now let us consider the orientation of dopant molecules. In the absence of a field the bent molecular plane is parallel to the tilt plane of matrix molecules, so that the dopants affect the matrix molecules to be anticlinic. In the presence of an electric field the branches of the dopant molecules also reorient, the maximum absorption for the phenyl stretching is at  $\theta_0 = 20 \pm 2^\circ$ , and the dichroic ratio for this band also slightly increases (from  $R = 2.1$  to  $R = 2.8$ ). Under supposition that molecules do not change conformation in the electric field, this situation could be explained through the rotation of a bent-shaped molecule plane as illustrated in Fig. 5. Only a small increase of dichroic ratio for the phenyl stretching band of bent-shaped molecules is observed, since the IR beam tests

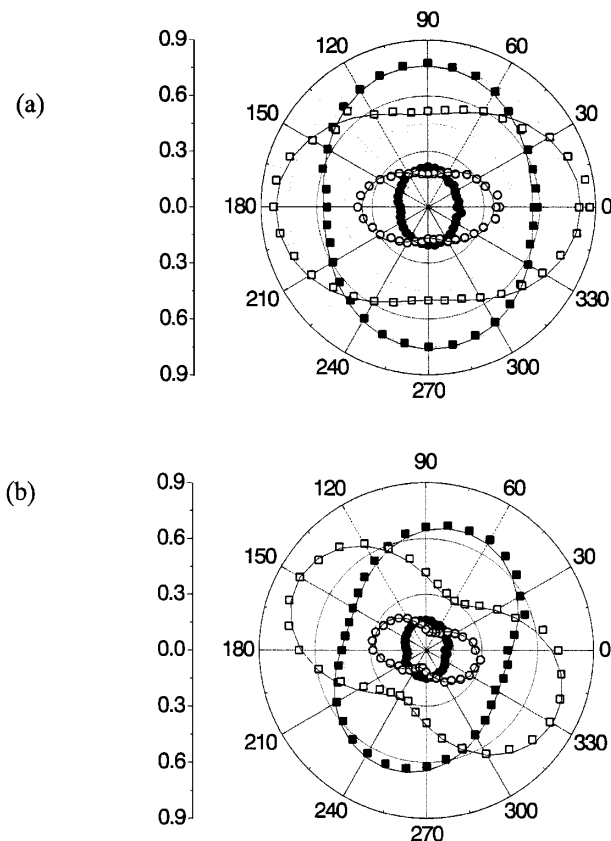


FIG. 4. Polar plot for a mixture of  $M1$  ( $n = 13$ ) doped with 10 wt % of  $D3$ . The absorption  $A(\theta)$  of phenyl (open) and  $\text{C}=\text{O}$  (solid) stretching bands for matrix (squares) and dopant molecules with zero (a) and with electric field  $15 \text{ V}/\mu\text{m}$  (b). The solid lines are fit to the formula given in the text.

projection of the tilted absorption dipoles. In contrast to host molecules, the  $\text{C}=\text{O}$  band of the dopant molecules does not show reorientation under the electric field. On average, the  $\text{C}=\text{O}$  moieties with and without the electric field are in the layer plane  $\theta_0 = 90^\circ$  or symmetrical about it,  $\theta_0 = 0^\circ$ . As suggested by Sekine *et al.* [11] and Pelzl *et al.* [12] based on NMR data taken in the *banana-B<sub>2</sub>* mesophase [2], the most stable conformation of a banana molecule is not flat, but with molecular branches twisted in respect to the plane of the central phenyl ring. Furthermore, the FTIR studies confirmed that carbonyl group rotation is strongly biased [13]. This model is also supported by detailed computer simulation [14]. For the model of such a molecule, the maximum absorption of  $\text{C}=\text{O}$  groups in the layer plane inevitably suggests a particular orientation of  $\text{C}=\text{O}$  groups, as illustrated in Fig. 5. Namely, the average direction of two  $\text{C}=\text{O}$  groups should be nearly in the smectic layer plane; i.e., the molecular orientations (A) or (C) are privileged while the orientations (B) and (D) are discouraged. The higher probability of finding  $\text{C}=\text{O}$  moiety in the smectic plane is actually observed also for rodlike molecules [10]. However, for bent-shaped molecules this effect is more pronounced since the rotation of a bent-shaped molecule in the  $\text{Sm-C}^*$  host is expected to be strongly hindered between states with the bending tip

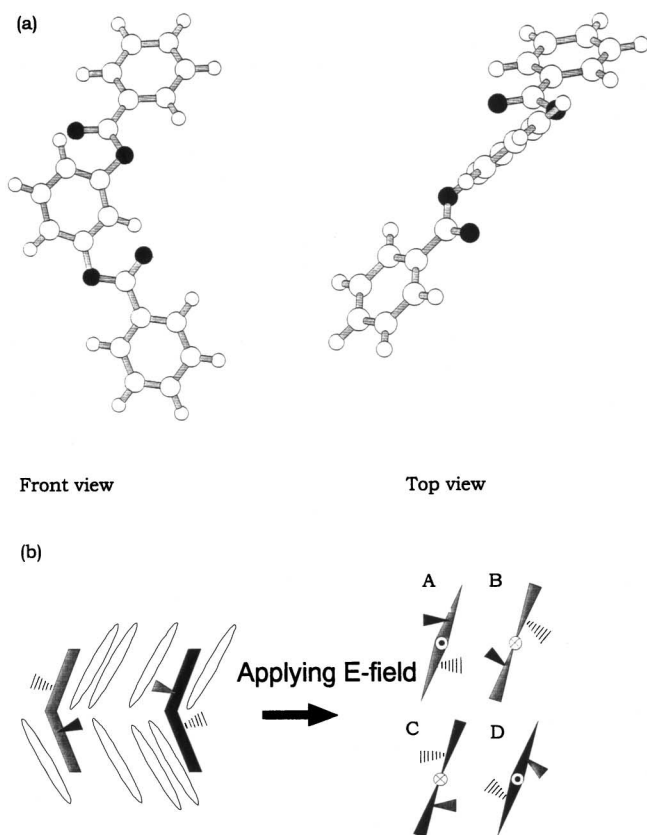


FIG. 5. Two projections of the most stable conformation of the central part of the banana molecule with twisted C=O groups (a). Schematic drawing of the bent-shaped molecules placed in the anticlinic and synclinic smectic structure (b). Note that the A conformation has opposite chirality to C; B (or D) is rotated by 180° conformer A (or C). Based on FTIR results the orientations (B) and (D) are strongly discouraged.

pointing up or down the smectic- $C_2$  symmetry axis. Summarizing, based on the IR data we have to assume that at the field-induced anticlinic-synclinic phase transition re-orientation of the bent-shaped molecular plane, as well as the special redistribution of C=O groups, takes place.

It should be noticed that the bent-shaped molecule with twisted C=O groups does not have a mirror plane, so that the overall structure of the molecule becomes chiral. However, both basic stereoisomers would fit into the Sm- $C^*$  structure (Fig. 5). Although two stereoisomeric forms (A) and (C) compatible to the IR data are present, one of the chiral molecular forms [e.g., (A)] is expected to be favored in a strongly chiral environment arising from the host molecules. This would affect other chiral properties of the Sm- $C^*$  phase, e.g., increase the chiral coefficients in the free energy. The increase of the Lifshitz term [15] in the free energy should influence the twisting power; by doping the helical pitch is expected to become shorter. This effect was indeed observed; i.e., the selective reflection peak is shifted to the shorter wavelength region by doping the

Sm- $C^*$  and Sm- $C_A^*$  materials with bent-shaped molecules, with respect to the pure host compound [16].

In conclusion, the electro-optic and dielectric measurements show the induction of the antiferroelectric Sm- $C_A^*$  phase by doping the ferroelectric Sm- $C^*$  materials with bent-shaped molecules. The polarized FTIR studies suggest that the bent-shaped molecules upon the field-induced antiferroelectric-ferroelectric transition reorient their plane and adopt the position in which carbonyl groups are sited in the smectic plane.

The stay of E.G. in TIT is supported by Venture Business Laboratory of TIT. This work is supported by NEDO International Collaboration Fund KBN Grant No. 3T09A 046 15.

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- [1] E. Gorecka, D. Pocięcha, M. Glogarova, and J. Mieczkowski, *Phys. Rev. Lett.* **81**, 2946 (1998).
- [2] S. S. Seomun, Y. Takanishi, K. Ishikawa, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys.* **36**, 3586 (1997).
- [3] P. Radquist, J. P. F. Lagerwall, M. Buivydas, F. Gouda, S. T. Lagerwall, N. A. Clark, J. E. MacLennan, R. Shao, D. A. Coleman, S. Bardon, T. Bellini, D. R. Link, G. Natale, M. A. Glaser, D. M. Walba, M. D. Wand, and X. H. Chen, *J. Mater. Chem.* **9**, 1257 (1999).
- [4] J. Szydłowska, D. Pocięcha, E. Gorecka, D. Kardas, J. Mieczkowski, and J. Przedmojski, *J. Mater. Chem.* **9**, 361 (1999).
- [5] A. D. L. Chandani, E. Gorecka, Y. Ouchi, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys.* **28**, L1265 (1989).
- [6] R. Blinc and B. Zeks, *Phys. Rev. A* **18**, 740 (1978).
- [7] I. Rychetsky, D. Pocięcha, V. Dvorak, J. Mieczkowski, E. Gorecka, and M. Glogarova, *J. Chem. Phys.* **111**, 1541 (1999).
- [8] N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.* **36**, 899 (1980).
- [9] M. Nakata, Y. Takanishi, K. Ishikawa, H. Takezoe, Y. Aoki, and H. Nohira, *Jpn. J. Appl. Phys.* **39**, L42 (2000).
- [10] K. H. Kim, K. Ishikawa, H. Takezoe, and A. Fukuda, *Phys. Rev. E* **51**, 2166 (1995).
- [11] T. Sekine, T. Niori, M. Sone, J. Watanabe, S. W. Choi, Y. Takanishi, and H. Takezoe, *Jpn. J. Appl. Phys.* **36**, 6455 (1997).
- [12] G. Pelzl, S. Diele, and W. Weissflog, *Adv. Mater.* **11**, 707 (1999).
- [13] S. V. Shilov, S. Rauch, H. Skupin, G. Heppke, and F. Kremer, *Liq. Cryst.* **26**, 1409 (1999).
- [14] T. Imase, Doctoral thesis, Tokyo Institute of Technology, 2000.
- [15] B. Zeks and R. Blinc, in *Ferroelectric Liquid Crystals*, edited by G. W. Taylor (Gordon and Breach Science Publications, Philadelphia, 1991).
- [16] M. Nakata, E. Gorecka, J. Mieczkowski, Y. Takanishi, K. Ishikawa, J. Watanabe, and H. Takezoe (to be published).