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Partial mixing of opposite chirality in a bent-shaped liquid crystal molecular system

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Layer structure and electrooptical switching were studied in a bent-shaped achiral liquid crystal molecule, P-12-PIMB. By the application of a dc field during slow cooling from the isotropic phase to the highest temperature smectic phase, B_2, large uniform domains of about 0.5 mm diameter were obtained. A tilted antiferroelectric structure was confirmed in the B_2 phase by means of texture observations and switching current measurements. The molecular tilt angle was found to be independent of temperature and was 34°. In addition, domains with a smaller apparent tilt angle were also observed, suggesting that layers with different senses of chirality coexist in the domain.

It has been considered that the introduction of chiral carbons into liquid crystal compounds is necessary to realize ferroelectricity in smectic liquid crystals. However, Niori *et al.*[1] and Sekine *et al.*[2] observed ferroelectricity by a switching phenomenon in the highest temperature smectic phase, B_2, in bent-shaped molecules with no chiral carbons. They explained that the molecules were efficiently packed with a polar C_{2v} symmetry in the smectic layer.[3] According to their model, the molecules do not tilt with respect to the smectic layer normal, like the biaxial version of the S_A phase. The fringe patterns suggested a helix along the smectic layer normal in the absence of an electric field. As a consequence, the net polarization was thought to be canceled out. Thus, the phase was considered to be ferroelectric.

In contrast, Link *et al.*[4] observed antiferroelectricity using free-suspended films and thin homogeneous cells in the B_2 phase. They showed that the molecules tilt with respect to the layer normal and the net polarization is canceled out in adjacent layers, like the orientation in the S_{CA} phase, and that there are two types of domains, homogeneously chiral and racemic domains. The tilt direction of the former is opposite in adjacent layers, and in the latter the tilt direction is uniform in the absence of a field. According to their model, fringe patterns are due to the alternation of the racemic domains with opposite tilt directions.

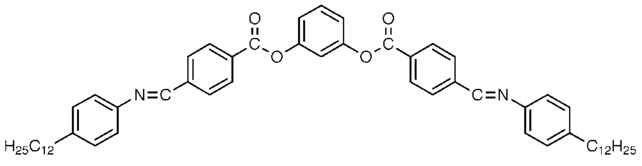
The symmetry and the antiferroelectricity in the B_2 phase were also discussed theoretically[5,6] and investigated experimentally, *e.g.*, by X-ray diffraction,[3,7,8] NMR,[3,8] electrooptic response,[4,7,8] polarization current measurements[7,8] and second harmonic generation.[9–11] Hyper-Rayleigh light scattering was performed to evaluate the molecular hyperpolarizability.[12] The anisotropic molecular orientational distribution was studied by surface second harmonic generation from a Langmuir–Blodgett film.[13]

In the B_2 phase, neither rubbing nor the application of a magnetic field was effective in making uniformly oriented homogeneous cells. Jakli *et al.*[14] reported that uniform racemic domains without fringe patterns are obtained by applying a high ac field after shearing an upper substrate parallel to the lower one in the B_2 phase. However, a large chiral domain has not yet been obtained. Recently, we succeeded in obtaining several large domains in the B_2 phase by applying a dc electric field. The large domains enable us to discuss the layer structures and the switching characteristics. The results will be reported in the following.

Experimental

The sample used was one of the conventional bent-shaped molecules, 1,3-phenylene bis[4-(4-dodecylphenyliminomethyl)-benzoate] (P-12-PIMB). The chemical structure and the phase sequence are shown in Fig. 1. The sample was sandwiched between two glass plates with a transparent indium tin oxide (ITO) electrode and without coating any polyimide layer. The thickness of the cells was controlled using polyethylene terephthalate (PET) films. In these cells, molecules aligned almost homogeneously but randomly. In order to obtain large domains, a high electric field was applied when the temperature was cooled down slowly from the isotropic phase to the B_2 phase. For texture observation and birefringence measurements, 8 μm-thick cells were used, and 2.5 μm-thick cells were used for electrooptical switching.

Texture observation was made under a polarizing microscope. Birefringence measurements were made by measuring transmittance spectra from a 10 μm × 10 μm area between crossed polarizers using a polarizing microscope spectrometer (ORC, TFM-120AFT-PC), controlled by a personal computer (NEC, PC9801-VX). The wavelength range of the incident light was from 400 to 800 nm. The switching current was measured by applying an 80 V_{pp} triangular voltage wave of 20 Hz, using a high-speed amplifier (NF Electronic Instruments, 4005) connected to a function generator (NF Electronic Instruments, 1920A). For all the measurements, the temperature of the cell was controlled by a temperature control unit (Mettler, FP-82).



$$\text{Cryst} \underset{62.6\ °\text{C}}{\rightleftharpoons} B_3 \underset{130.2\ °\text{C}}{\rightleftharpoons} B_2 \underset{156.0\ °\text{C}}{\rightleftharpoons} \text{Iso}$$

Fig. 1 The chemical structure and the phase sequence of the sample (P-12-PIMB) used.

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Results and discussion

Texture observations

When the temperature was cooled down slowly (0.5 °C min^{-1}) from the isotropic phase to the B_2 phase, only small domains aligned randomly were obtained in the absence of a field. However, by applying a high dc field larger than the threshold field during slow cooling, large uniform circular domains of about 0.5 mm diameter were obtained. Fig. 2 and 3 show the optical micrographs of P-12-PIMB in the B_2 phase under the application of an electric field of −6, 0 and 6 V μm^{-1}. As shown in Fig. 2(b), extinction directions are parallel to the transmission axes of crossed polarizers without a field, and rotate counterclockwise (Fig. 2(a)) and clockwise (Fig. 2(c)) under the application of negative and positive fields, respectively. The apparent tilt angle of the domain in Fig. 2(a) and 2(c) was 34°, which was temperature independent. It clearly indicates that molecules tilt with respect to the smectic layer normal by 34°. This value agreed with the values in previous reports,[7,8] although a smaller value (25°) was also reported.[14] The tilt angle 34° also agrees with the one determined by the ratio of the layer thicknesses of the B_2 and B_3 phases of this material.[3]

In contrast to Fig. 2, extinction directions in Fig. 3 do not change even under a field. These results are consistent with the layer structure model proposed by Link *et al.*,[4] and the domains shown in Fig. 2 and 3 correspond to the 'homogeneously chiral' and the 'racemic' ones, respectively. The birefringence of the homogeneously chiral domain in Fig. 2 was 0.156 when an applied field was zero and 0.295 when a 6 V μm^{-1} dc field was applied. For the racemic domains shown in Fig. 3, the birefringence was 0.164 without a field and 0.156 under a 6 V μm^{-1} field. The homogeneously chiral domain in the absence of a field shows the same birefringence as the racemic one under a field, since, in both domains, molecules tilt oppositely with respect to the layer normal in adjacent layers.

On the other hand, uniform domains with different apparent tilt angles were also observed. One of them is shown in Fig. 4. Extinction directions were parallel to the transmission axes of crossed polarizers without a field, like the cases of the homogeneously chiral and the racemic domains. However, they rotated clockwise (Fig. 4(a)) and counterclockwise (Fig. 4(c)) under the application of negative and positive fields, respectively. Moreover, the apparent tilt angle of the domain was 26°. Birefringence was found to be 0.157 without a field and 0.183 under a field. The apparent tilt angle and birefringence under a field were smaller than those in the homogeneously chiral domain.

Basically, tilt directional senses (tilt right or left) with respect to the smectic layer normal should be equivalent, since bent-shaped molecules do not have any asymmetric carbons. Actually, there exist two domains with opposite tilt, which correspond to two types of homogeneously chiral domains, H_+ and H_-.[4] The domain in Fig. 2 is H_+. The layer structure models corresponding to the domains in Fig. 2, 3, and 4 are shown in Fig. 5. The index ellipsoids are also shown at the bottom of the figure. It is natural from the packing entropy effect that all the molecules tilt in a certain direction in a certain layer. If the different senses of chirality are mixed at an arbitrary ratio, two types of layers with different senses of chirality, *i.e.*, different tilt directions, coexist in a domain, so that the domain is neither homogeneously chiral nor racemic. It is not known at present whether the mixing of layers with different chirality is periodic or not. However, the thickness of the H_+ and H_- domains must be smaller than the wavelength of light, since the domain is apparently uniform. If periodicity exists, the molecules under an electric field align like the molecular orientation in the ferrielectric subphases

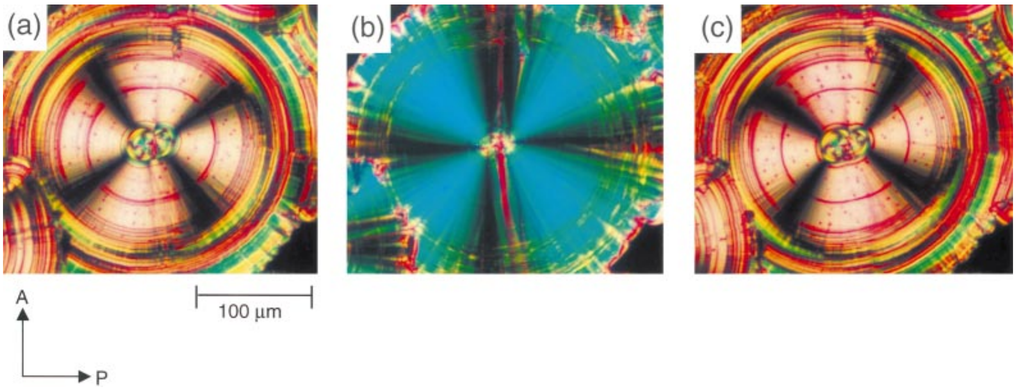

Fig. 2 Optical micrographs of the homogeneously chiral domain in the B_2 phase. Applied dc field was (a) −6 V μm^{-1}, (b) 0 V μm^{-1} and (c) 6 V μm^{-1}.

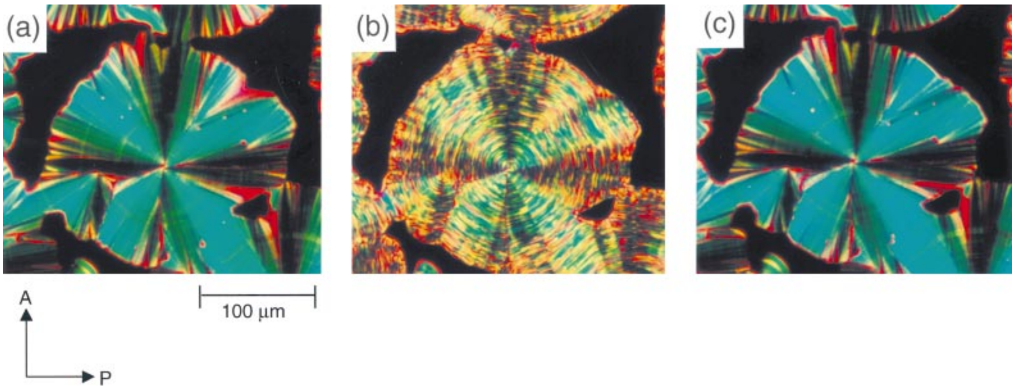

Fig. 3 Optical micrographs of the racemic domain in the B_2 phase. Applied dc field was (a) −6 V μm^{-1}, (b) 0 V μm^{-1} and (c) 6 V μm^{-1}.

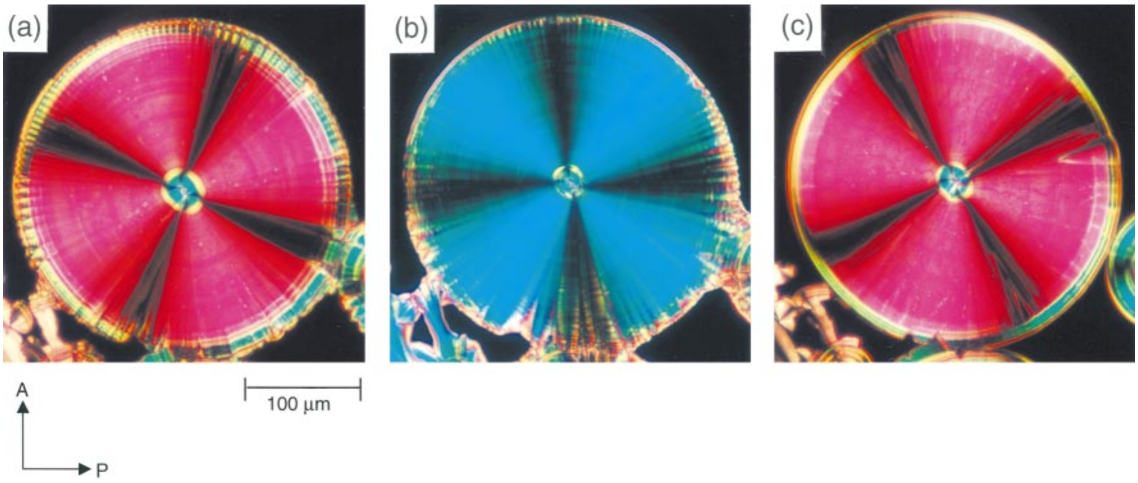

Fig. 4 Optical micrographs of the domain with smaller apparent tilt angle than that in Fig. 2 in the B_2 phase. Applied dc field was (a) -6 V μm^{-1}, (b) 0 V μm^{-1} and (c) 6 V μm^{-1}.

of antiferroelectric liquid crystals without a field,[15] though the helical structure may not exist. Using the results of the apparent tilt angle and birefringence, the mixing ratio of H_+ and H_- was estimated to be 1 : 1 (racemic) and 1 : 3 for the domains shown in Fig. 3 and 4, respectively, as shown in Fig. 5.

One of the possibilities of generating chirality in bent-shaped molecules is a particular conformational effect.[3] The two ester groups are possibly twisted, and the symmetry of the molecule is C_1. However, the relationship between the tilt direction and the conformational chirality has not been clarified yet.

Much more complicated molecular orientational structure may exist, as exemplified in Fig. 6. In these micrographs, many circular domains of the B_2 phase emerge in the isotropic phase. Under the application of an electric field, (a) -17 V μm^{-1}, (b) 0 V μm^{-1} and (c) 17 V μm^{-1}, these domains exhibit a variety of switching. Detailed observation is necessary to fully understand the molecular orientation and its switching.

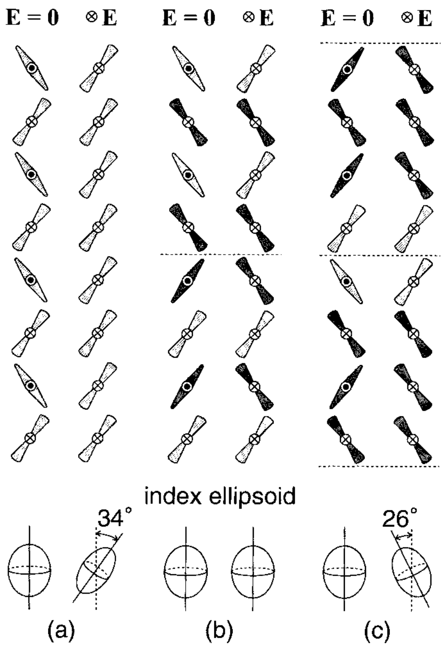

Fig. 5 The layer structure model in the B_2 phase, in the absence and the presence of an electric field. Corresponding index ellipsoids and optical axes are also shown at the bottom of the figure. To draw (c), four assumptions were made in the absence of a field: (1) the structure is periodic; (2) the mixing ratio of $H_+ : H_-$ is 1 : 3; (3) antiferroelectric structure, *i.e.*, alternation of dipoles in adjacent layers, exists; and (4) the apparent tilt angle is zero. Under the assumptions, eight layers form a unit cell, as shown in Fig. 5(c).

Switching characteristics

Fig. 7 shows the switching current profile in the B_2 phase when an 80 V_{pp} triangular voltage wave is applied. Regardless that the domain is the homogeneously chiral or racemic one and that the mixing of chirality occurs in the domain, net polarization of the domain is canceled out without a field, as shown in Fig. 5. Hence, two clear peaks were observed in every half period of the applied triangular voltage wave. It is easily recognized that the switching current peaks appear at the switching between the three stable states shown in Fig. 2, 3, and 4. This result clearly indicates that the B_2 phase is antiferroelectric. The result is consistent with those of Diele *et al.*[7] and Pelzl *et al.*[8] In the previous papers by Niori *et al.*[1] and Sekine *et al.*,[2] only a single peak was observed. The reason for the difference in the number of current peaks is not clear.

The magnitude of spontaneous polarization P_S was about 200 nC cm^{-2}. There was some sample dependence of P_S. The

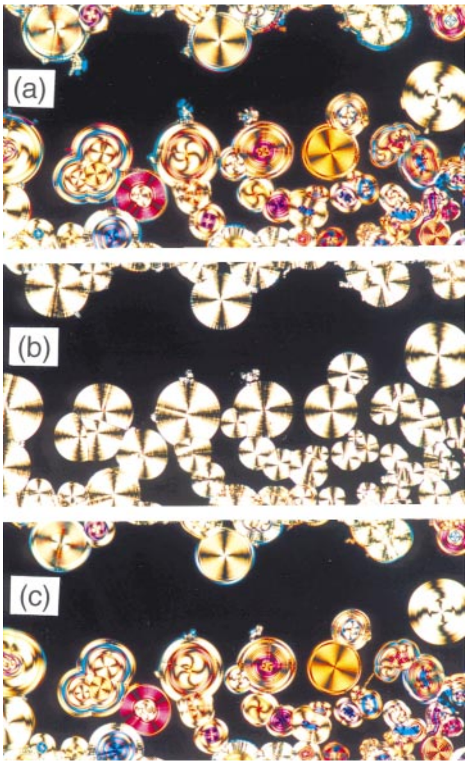

Fig. 6 Emergence of various domains at the phase transition from Iso to B_2, (a) -17 V μm^{-1}, (b) 0 V μm^{-1} and (c) 17 V μm^{-1}.

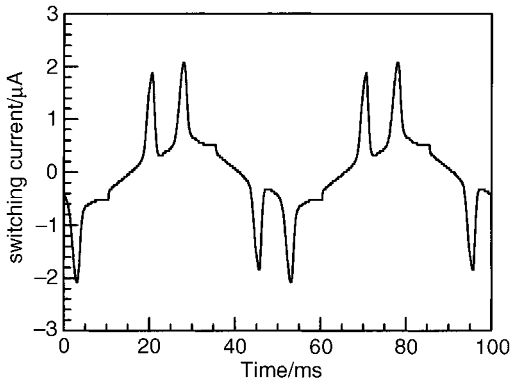

Fig. 7 The switching current profile in the B_2 phase under an 80 V_{pp} triangular voltage wave of 20 Hz.

details will be reported in a separate paper. It was found that P_S was almost independent of the temperature above the B_2–B_3 phase transition. In addition, the apparent tilt angle of a certain domain is almost independent of temperature. These results are consistent with the temperature dependence of the layer spacing, which is also constant.[3]

In the B_3 phase, no switching phenomena were observed. Although the magnitude of spontaneous polarization is not zero in the narrow temperature range just below the B_2–B_3 phase transition, it is because of the coexistence of the B_2 and B_3 phases.

Conclusions

By the application of a dc field while the temperature was cooled down from the isotropic phase to the B_2 phase, large uniform domains of about 0.5 mm diameter were obtained in the bent-shaped molecule P-12-PIMB. The tristable switching was confirmed in the texture observations and the switching current measurements, indicating antiferroelectricity in the B_2 phase. Since the extinction directions rotate under the application of an electric field, the molecules tilt with respect to the layer normal. These results are consistent with the layer structure proposed by Link *et al.*[4] The molecular tilt angle was 34°, and the birefringence was 0.156 without a field and 0.295 under a field in homogeneously chiral domains. For the racemic domain, the apparent tilt angle was almost zero. In addition to the homogeneously chiral and racemic domains, a different domain with an apparent tilt angle of 26° was observed. Based on the apparent tilt angle and the birefringence under a field, the domain was found to consist of two homogeneously chiral layers, H_+ and H_-, with the mixing ratio of 1 : 3.

Acknowledgements

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