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Molecular Chirality Due to Twisted Conformation in a Bent-Shaped Liquid Crystal Studied by Polarized FT-IR Spectroscopy

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Microscopic polarized fourier-transform infrared (FT-IR) measurements were performed in the antiferroelectric B_2 phase of a bent-shaped liquid crystal molecule. In homogeneously chiral domains, the absorbance maximum appeared when the transmission axis of a polarizer was parallel to the layer normal for the phenyl ring stretching and C-O-C asymmetric stretching and that for the C=O stretching was almost perpendicular to that for C-O-C in the absence of a field. When a dc field was applied, the maximum for C-O-C rotated by about 35°, which is almost the same as the apparent tilt angle of the molecule. In contrast, the axis of maximum absorbance for C=O was neither parallel nor perpendicular to that of C-O-C under a field. It indicates that the two ester groups are twisted with respect to the central phenyl ring and are not perpendicular to the molecular long axis. Moreover, one of the twist conformations is chosen and the rotation around the molecular long axis is strongly hindered.

Keywords: bent-shaped molecule; antiferroelectric liquid crystal; molecular chirality; twisted conformation; microscopic polarized FT-IR spectroscopy

INTRODUCTION

Bent-shaped liquid crystals show ferroelectric switching, although the molecules do not have any asymmetric carbons [1]. Bent-shaped

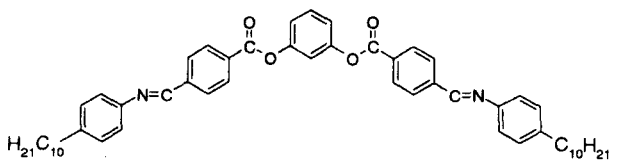
molecules construct polar smectic order due to their efficient packing with a polar symmetry of achiral molecules, as proved by Link *et al.*[2] Accoriding to their model, two tilt directional senses of the molecules (left or right) to the layer normal can introduce opposite chirality for each smactic layer. In the B_2 phase, there are two types of domains, i. e., the homogeneously chiral and the racemic ones[2]. The sense of chirality of the former is uniform and that for the latter is alternated in the neighboring layers. Although it is very difficult to obtain uniformly aligned domains in bent-shaped liquid crystals, the homogeneously chiral and racemic domains can be obtained by applying an electric field under a suitable condition [2-6]. Electrooptic [2-6] and dielectric properties [5, 6] for these specific domains thus obtained have been studied.

By using polarized FT-IR spectroscopy, the orientation of the different functional groups can be discussed. Shilov *et al.*[7] and Gorecka *et al.*[8] used this technique to show that two ester groups in the molecule are twisted in a bent-shaped molecular system and a binary mixture system consisting of rod-like SmC* molecules and bent-shaped molecules, respectively. Twisted conformation was also suggested by Sekine *et al.*[9] by NMR and by Imase [10] as a result of computer simulation. Although the twisted conformation of the molecule might induce chirality into the molecule, unambiguous evidence for the molecular chirality has not been reported. In this paper, we discuss about the molecular chirality due to twisted conformation based on microscopic polarized FT-IR spectroscopy.

EXPERIMENTAL

The sample used was one of the conventional bent-shaped molecules, 1,3-phenylene bis[4-(4-decylphenyliminomethyl)benzoates] (P-10-PIMB).

The chemical structure of the compound is shown in Figure 1.



Cryst - (68.3°C) - B_3 - (136.3°C) - B_2 - (158.5°C) - Iso

FIGURE 1 The chemical structure and phase sequence of P-10-PIMB.

The cells were sandwiched between two SrF_2 plates with transparent indium tin oxide (ITO) electrode coated with a polyimide layer (Toray, SP550). However, the polyimide layer was not rubbed since rubbing is not effective to obtain uniformly aligned domains in bent-shaped liquid crystals. The cell thickness was about 4 μm. By using these cells, molecules were aligned almost homogeneously but randomly. In order to obtain large circular domains, a dc field was applied, as reported previously [4, 6].

Polarized ir spectra were measured as a function of polarizer rotation angle, using JEOL JIR-MICRO 6000 system equipped with a microattachment and an MCT detector. A wire grid polarizer was used for obtaining polarized ir radiation, and was rotated about the axis parallel to the propagation direction of ir light. The rotation angle, ω, was defined as zero when the transmission axis of the polarizer is parallel to the smectic layer normal.

RESULTS AND DISCUSSION

For microscopic polarized FT-IR measurements, a 50 x 200 μm rectangular area in a uniform domain was selected. Since the layers are curved circularly, the dichroic ratio R ($R = A_{max} / A_{min}$: where A is the

absorbance) was smaller than what we expected. Therefore, the absolute value of R is not discussed in this paper. Figure 2 shows a typical polarized FT-IR spectrum in the B_2 phase. Three absorption peaks were analyzed: the C=O stretching at 1736 cm^{-1}, the phenyl ring stretching at 1600 cm^{-1}, and the C-O-C asymmetric stretching at 1258 cm^{-1}.

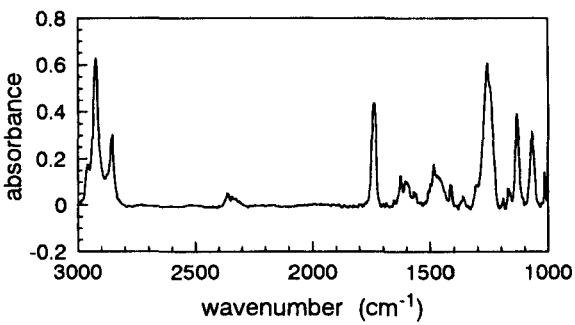


FIGURE 2 Typical FT-IR spectrum in the B_2 phase of P-10-PIMB.

Figure 3 shows the polar plot for three absorption peaks mentioned above in a homogeneously chiral domain. When an applied field was zero, the absorbance maximum appeared at polarizer rotation angle $\omega = 0°$ and 180° for phenyl ring stretching and C-O-C asymmetric stretching. This result indicates that their transition moments are parallel to the layer normal in the absence of a field. This is consistent with the observation that the extinction direction under a polarizing microscope is parallel to the layer normal in homogeneously chiral domains without a field [2], since the transition moment of the phenyl ring stretching is parallel to the molecular long axis. The anisotropy was very small because a circular domain was inevitably used.

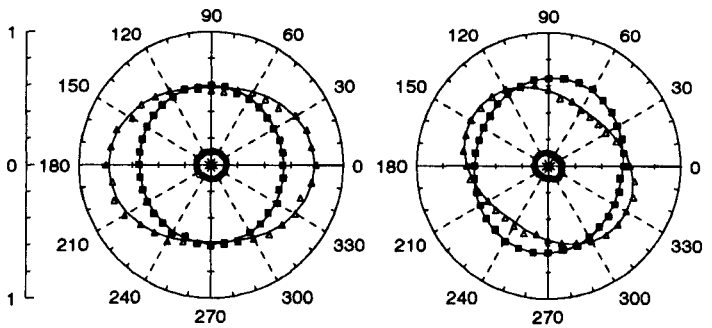


FIGURE 3 The polar plot of the absorption peaks for the C=O stretching (■), phenyl ring stretching (○), and ester C-O-C asymmetric stretching (△), against the polarizer rotation angle ω in a homogeneously chiral domain in the B_2 phase. An applied dc field was (a) 0 V/μm and (b) 11.9 V/μm, respectively.

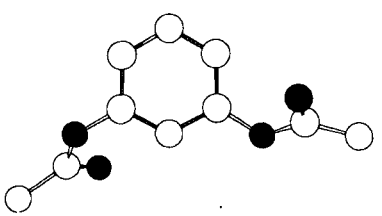


FIGURE 4 Twisted conformation of two ester groups in the molecule. For simplicity, only the central phenyl ring and two ester groups were illustrated.

When an 11.9 V/μm (50 V) dc field was applied, the maximum for the C-O-C stretching rotated by about 35° (Fig. 3(b)). The rotation angle is almost the same as the apparent tilt angle of the molecule determined by the texture observations in the B_2 phase [4,6]. In contrast, the maximum for the C=O stretching appears at ω = 80° (Fig. 3(b)), which is neither

parallel nor perpendicular to that of C-O-C under a field. This situation is possible if and only if the two ester groups are twisted with respect to the central phenyl ring and are not perpendicular to the molecular long axis (see Fig. 4), and furthermore the rotation around the molecular long axis is strongly hindered[11,12]. As a consequence, breaking of the mirror symmetry occurs due to molecular chirality in the B_2 phase.

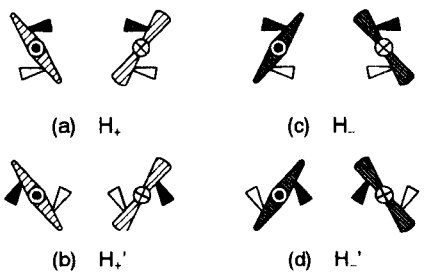


FIGURE 5 Two possible stable conformations of the ester groups. C=O groups are almost parallel to the layer plane (a) and out of the layer plane (b). (c) and (d) have the opposite sense of chirality to (a) and (b), respectively.

It is clear that there are two twisted conformations of the ester groups (Figs. 5(a) and 5(b)). In Fig. 3(b), the maximum for the C=O stretching appears at $\omega = 80°$ under a field, so that the transition moment of the C=O stretching is almost parallel to the layer plane under a field. If the ester groups were twisted oppositely (Fig. 5(b)), the transition moments of the C=O stretching would be out of the layer plane. Hence, it is concluded that the conformation shown in Fig. 5(a) is chosen in the H_+ domain. In the case of the domains with the opposite sense of chirality, H_-, the conformation shown in Fig. 5(c) will be chosen.

In the racemic domain, opposite senses of chirality (H_+ and H_-) are alternated in the neighboring layers, so that the apparent tilt angle is zero

even under a field[2]. When an applied field is zero, profiles in Fig. 6(a) are almost the same as those of the homogeneously chiral domain (Fig. 3(a)). Moreover, the absorbance maximum for every peak does not rotate even when a 10.0 V/μm (40 V) dc field was applied (Fig. 6(b)). In the racemic domain, the alternation of H_+ and H_- molecules (Figs. 5(a) and 5(c)) in the neighboring layers can explain the layer structure.

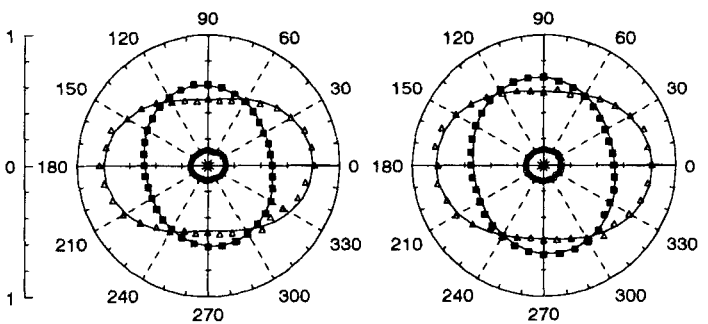


FIGURE 6 The polar plot of the absorbance versus the polarizer rotation angle ω in the racemic domain in the B_2 phase. An applied dc field was (a) 0 V/μm and (b) 10.0 V/μm.

Figure 7 shows the layer structure of the homogeneously chiral domain and the racemic domain. When the molecular twisted conformations as shown in Figs. 5(a) and 5(c) are chosen, layer structure and the rotation of the absorbance maximum can be explained at once. This layer structure model is consistent with all the electrooptic measurements[2-6]. Moreover, the molecular chirality due to twisted conformation is consistent with the results of NMR measurement[7] and computer simulation[8].

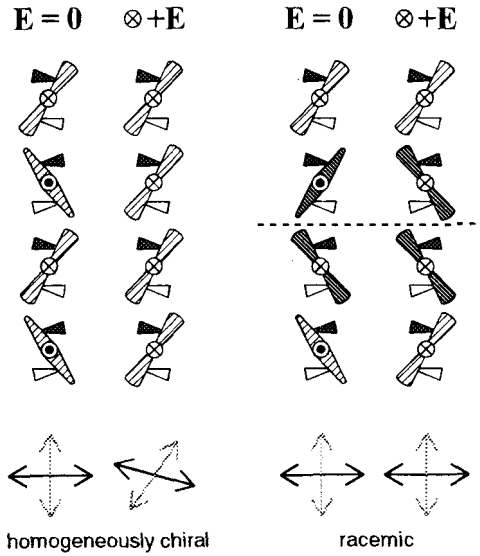


FIGURE 7 The layer structures of the homogeneously chiral domain and the racemic domain. Gray and black arrows indicate the transition moments of the C-O-C asymmetric stretching and the C=O stretching, respectively.

CONCLUSION

Polarized FT-IR measurements with a microattachment were performed in the B_2 phase of a bent-shaped liquid crystal, P-10-PIMB. In the homogeneously chiral domain, the transition moments for the phenyl ring stretching and C-O-C asymmetric stretching are parallel to the layer normal and that for the C=O stretching is almost parallel to the layer plane without a field. When a dc field is applied, the axis for the C=O stretching is neither parallel nor perpendicular to that of C-O-C. It indicates that the two ester groups are twisted with respect to the central

phenyl ring and are not perpendicular to the molecular long axis. Moreover, one of the twist conformations is chosen and the rotation around the molecular long axis is strongly hindered. As a consequence, breaking of the mirror symmetry occurs due to molecular chirality in the B_2 phase.

In the racemic domain, the alternation of H_+ and H_- molecules in the neighboring layers can explain the layer structure. The layer structure model obtained by the FT-IR measurements is consistent with the result of electrrooptic measurements.

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