Liquid Crystals

Finite Enantiomeric Excess Nucleated in an Achiral Banana Mesogen by Chiral Alignment Surfaces**

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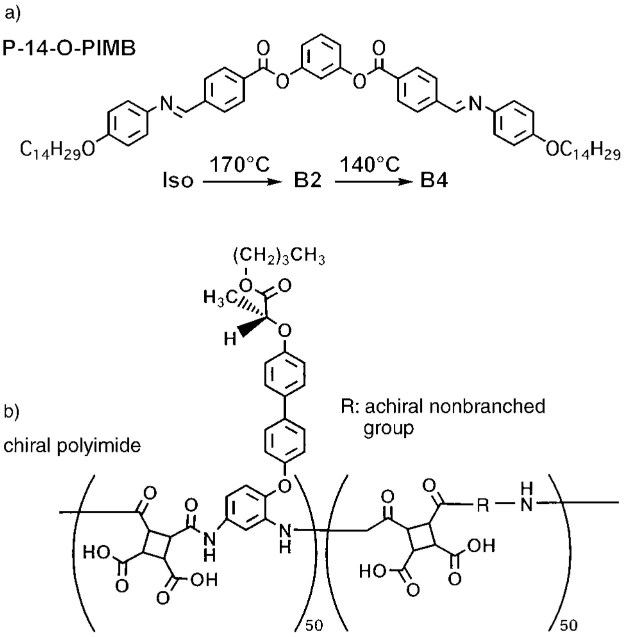
Controlling the chirality of molecular systems is important from the perspective of science as well as technology, and several methods have been adopted to achieve this. The most direct way is to dope achiral and chiral systems with chiral dopants. For example, the helical pitch of helical liquid crystals, such as cholesteric liquid crystals, can be readily tuned by the amount of dopants.[1] Another interesting and well-established method is irradiation with light of systems consisting of molecules with conformational chirality.[2] Asymmetric photoreactions, such as photoenantiomerization and asymmetric destruction, have been proposed as ways to introduce chirality. Herein we propose another method to control the chirality in a bent-core liquid-crystalline (banana mesogen) system.

The B_4 phase in achiral banana-shaped molecules is known to segregate into two chiral domains with opposite senses.[3–5] Since the two chiral domains are formed in equal probabilities, the B_4 phase has no macroscopic chirality and zero enantiomeric excess (*ee*). To produce an imbalance in the two chiral domains and nucleate a finite *ee* value in the bulk phase, we synthesized polyimides with chiral side chains and succeeded in nucleating an imbalance in the chiral domains in the B_4 phase of achiral P-14-O-PIMB (Scheme 1 a) by using cells with chiral polyimide surfaces. Rubbing the surfaces makes the domains larger and enhances the effect of the chiral polyimide and results in an *ee* value of 10%.

The discovery of ferroelectric switching and chirality in liquid-crystalline phases of achiral banana-shaped molecules[6,7] has generated a new era in liquid-crystal science. The classic banana-shaped molecules, the homologous series of 1,3-benzenebis(4-(4-*n*-alkoxyphenyliminomethyl) benzoates (P-*n*-O-PIMB; Scheme 1 a), exhibit some of the four phases B_1, B_2, B_3, and B_4. These phases are generated in this order (if all of them appear) with decreasing temperature. Antiferroelectric switching is clearly observed in the B_2 phase of P-*n*-O-PIMB.[6,8–11]



Scheme 1. Chemical structure of a) P-14-O-PIMB and b) a chiral polyimide with chiral side chains.

Herein, we focus on chirality. At least two kinds of chirality are known to exist, layer chirality[12] and conformational chirality,[5,7,13] which are closely related to each other.[5] The layer chirality appears because of a tilt in the bent-core molecules defined by a molecular long axis (*n*) and a bent direction (*b*) with respect to a layer normal (*z*). Since the molecules are achiral, two chiral domains (+ and −) appear in the B_2 phase in which the molecules tilt from the layer normal. The chiral domains are either the size of a layer or are macroscopic. For example, in the former case the layer chirality alternates from layer to layer so that the overall layer chirality is racemic, and in the latter case macroscopic homochiral domains can be observed under a polarizing optical microscope but are formed with equal probability.

Spontaneous chiral segregation also occurs in the B_4 phase, in which no layer chirality exists because of the nontilted phase. A conformational chiral structure is the origin of this type of chiral domain.[5] Some strong chiral conformations which resulted in a helical structure similar to the twist-grain boundary (TGB) phase[15] were suggested by NMR[7,14] and FTIR spectroscopic analysis,[13] and was confirmed by X-ray crystallographic analysis,[7] observation of the texture,[4] atomic force microscopy,[16] and freeze-fracture electron microscopy.[17] The spontaneous chiral segregation in the B_4 phase was easily seen by decrossing the polarizers.[3,4] In this way, local spontaneous deracemization is observed both in the B_2 and B_4 phases. However, the overall *ee* value is zero because the molecular systems are achiral. The banana-shaped molecules can be regarded as racemic mixtures rather than an achiral system because of the

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chirality mentioned above. One remarkable difference between banana-shaped molecules and racemic mixtures of columitic molecules with stereogenic carbon atom(s) is evident: both layer chirality and conformational chirality are not inherent in phases formed from banana-shaped molecules and can switch to the opposite chirality, while chiral *S* and *R* conformers cannot be interchanged. In this sense, it is possible to control the enantioselectivity in banana mesogens.

The most direct way to control the *ee* value is by molecular doping with chiral compounds, and this has been shown to be a viable method.[18,19] Doping an achiral banana mesogen with only a small amount of chiral dopant (a few wt%) nucleates with 100% *ee*. This observation suggests a possibility to control the *ee* value by using chiral surfaces. Therefore, we attempted to nucleate a finite *ee* value in banana mesogens by using a polyimide surface-alignment layer with chiral side chains to nucleate a chiral field within the achiral molecules in the bulk phase.

The alignment layer used in this study is shown in Scheme 1b. We fabricated sandwich cells with four different surfaces: 1) bare glass, 2) glass coated with achiral polyimide, 3) glass coated with chiral polyimide, and 4) glass coated with chiral polyimide and rubbed. Rubbing was carried out by using a commercial rubbing machine (EHC, Japan using velvet under a moderate rubbing strength (depth = 200 μm). Dust and contaminants were blown off the rubbed surface with dry air. We used cells of different thicknesses between 2 and 12 μm. Since no essential difference was observed in the phenomenon, we only show the data for a 2-μm cell. The banana mesogen used was P-14-O-PIMB (Scheme 1a), which was introduced into each cell and then slowly cooled from the isotropic phase to the B_4 phase. A temperature-cycling technique between the B_2 and B_4 phases was adopted to enlarge the domain size, since the chiral nature is preserved during the process.[5]

The imbalance between the two chiral domains was evaluated by means of CD spectroscopic analysis (JASCO J-720WI) and direct observation of the texture under a polarizing microscope (Nikon, OPTIPHOT-POL). The temperature-cycling technique mentioned above is also effective in removing the effect of birefringence in the CD spectra. All experiments were carried out at room temperature and atmospheric pressure.

The B_4 phase is characterized by a blue color under crossed polarizers. The existence of chiral domains was confirmed in the usual way: The two domains become apparent as bright and dark regions when one of the polarizers was rotated clockwise by a small angle (2–3°) with respect to the crossed position. The brightness of the two domains interchanges when the polarizer is rotated counterclockwise. The difference in the texture of the four different cells is shown in Figure 1. The contrast between the domains is high in the cell with rubbed chiral surfaces and the size of domains is large, thus allowing the domain boundaries to be seen clearly (Figure 1d). On the other hand, the B_4 phase exhibits grainy (bare glass, Figure 1a), low contrast (glass coated with achiral polyimide, Figure 1b), and high contrast but fine (glass coated with chiral polyimide, Figure 1c) textures in the cells with other surfaces. Thus, the rubbed chiral polyimide surface produces distinct large chiral domains in the B_4 phase compared to the other surfaces.

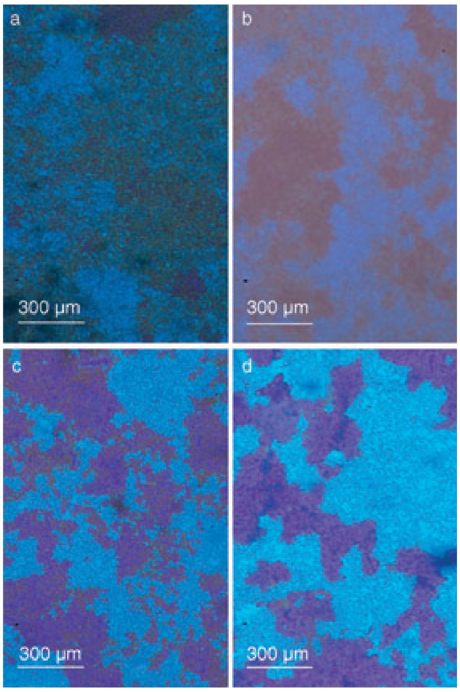

Figure 1. Optical micrographs of the B_4 phase of achiral P-14-O-PIMB under a 2°-clockwise decrossed position using cells with a) bare glass, b) glass coated with achiral polyimide, c) glass coated with chiral polyimide, and d) glass coated with chiral polyimide and rubbed.

To evaluate the effect of the chiral polyimide surfaces on the enantioselectivity we measured the CD spectra of the cells. First we confirmed that empty cells with chiral surfaces show no CD effect, and that a CD signal emerges by introducing P-14-O-PIMB. The maximum CD intensity was observed at about 400 nm in the B_4 phase (see the inset of Figure 2). Since two chiral domains generally exist within an observation area, both positive and negative signals with a maximum at 400 nm were seen at different points by moving the aperture (diameter: 6 mm) in the cells. Figure 2 shows the spatial distribution of the maximum CD signal in the cells with the four different surfaces. An equal distribution of positive and negative CD signals were found in cells with bare glass surfaces (a) and achiral polyimide surfaces (b). This observation is expected, since the molecules are achiral and form chiral domains with equal probability. Hence, the B_4 phase has no macroscopic chirality and has zero enantioselectivity in cells with these surfaces.

On the other hand, the B_4 phase in cells with chiral surfaces exhibited positive CD intensities on average, despite the molecular systems being achiral. Thus, we succeeded in nucleating an imbalance or finite enantioselectivity in the B_4 phase by using the chiral surfaces. The rubbing treatment enhanced the effect of the chiral polyimide by about a factor of four compared with the unrubbed cells. As mentioned above, rubbing enlarges the domain size. Since the formation of the chiral domain with a finite *ee* value is a sort of crystal

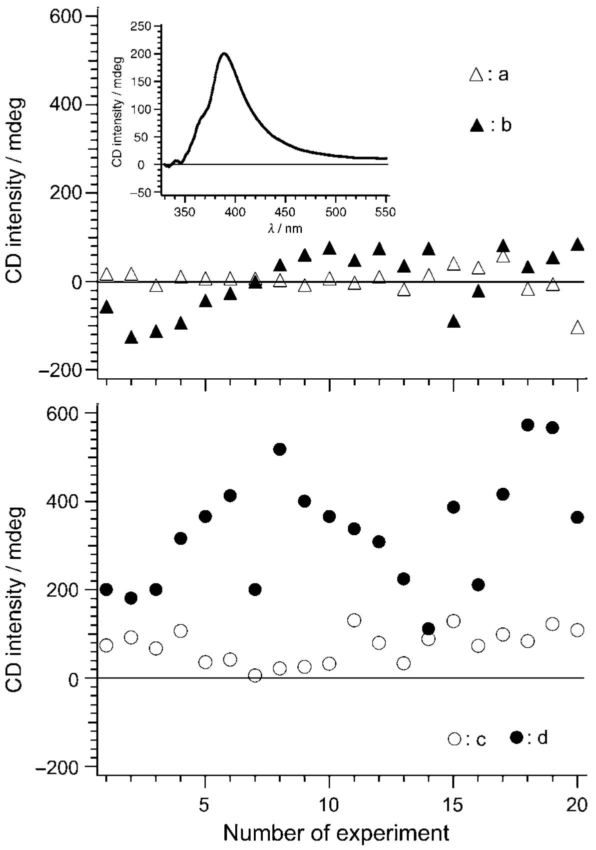

Figure 2. Spatial distribution of the maximum CD intensity in the B_4 phase of P-14-O-PIMB with a) bare glass, b) glass coated with achiral polyimide, c) glass coated with chiral polyimide, and d) glass coated with chiral polyimide and rubbed. The measurements were made by laterally shifting an aperture with a diameter of 6 mm. A typical CD spectrum of the B_4 phase of P-14-O-PIMB is also shown in the inset.

growth, the ability to form larger domains on rubbed chiral surfaces may promote enantioselectivity, although the real reason for the effect of rubbing on the domain size needs to be clarified. We confirmed that the sign of the CD signal in the B_4 phase is the same as that of the chiral polyimide.

On the basis of the results mentioned above we calculated the value of the induced enantioselectivity in the B_4 phase of P-14-O-PIMB in the cell with the rubbed chiral polyimide by two methods: 1) direct observation under a polarizing microscope and 2) measurement of the intensity of the CD signal. In the former method we took microphotographs and analyzed them using computer software packages (Photoshop and Image-J). The ratio of the + and − domains were determined over a large area and found to be 55:45, namely 10% *ee*. The maximum ratio attained if the analysis was made over a small area (1 mm diameter) in which a large imbalance was observed in a particular position was 75:25. CD measurements were made using a 1-mm aperture to enable this value to be compared with the CD signal. The spatial variation of the CD signals was much larger than the previous measurements using a 6-mm aperture. However, the average CD signals for the two aperture sizes were almost the same: 246 mdeg (1 mm) and 254 mdeg (6 mm). The maximum CD signal was 1600 mdeg in the measurement using a 1-mm aperture. If we assume that this value (1600 mdeg) corresponds to the ratio of 75:25 in the direct observation of the texture, the average ratio of 55:45 obtained over a wide area is consistent with the average CD intensity of about 320 mdeg. Thus, we can safely conclude on the basis of the two methods that 10% *ee* is nucleated under the influence of chiral surfaces.

Control of chirality by irradiation with light has only been demonstrated with a few specific molecules.[2] In the majority of molecular systems, however, the induced *ee* value was less than 1%,[20] except for diastereomeric helicenes,[21–23] which showed diastereomeric excess with a magnitude of tens of percent.[22,24] In this respect, the present *ee* value obtained in the B_4 phase of achiral P-14-O-PIMB by using cells with chiral polyimide surfaces is remarkably large and the mechanism is totally different from that ocurring under irradiation with light. The present phenomenon using chiral surfaces has not been reported. However, Jakli et al.,[25] reported macroscopic chiral induction with a nonchiral polymer network. If the polymer network is formed in cholesteric liquid crystals that are then removed after polymerization, the banana mesogen introduced into the cells with the remaining network gives rise to a chiral domain, whereas the polymerization in the isotropic phase does not give such an effect. Since chiral molecules do not exist in the cell, the chirality induced in the banana mesogen originates from polymer fibers with helical structures. Similarities and differences between the study by Jakli et al. and the present work are related to the mechanism.

The present technique is based on the different chiral interactions between the chiral side chain and bent-core molecules that form the + and − domains. These interactions are either at the molecular or macroscopic levels. In the former case, the operating interaction is essentially the same as that responsible for the effect of the chiral dopants. As a latter interaction, the possible formation of helical structures of polyimide main chains resulting as a consequence of the chiral side chains may play a role in the chiral interactions between the surfaces and bent-core molecules. This mechanism is quite similar to the phenomenon reported by Jakli et al.,[25] although the density of the helical fibrils is quite different because of their existence on the surface and in the bulk phase. Since chiral species exist only at the two surfaces in the present method, nucleation, growth, and formation of chiral domains are important factors for enhancing the *ee* value. Therefore, the following two possible ways are suggested to further enhance the enantioselectivity: 1) a chemical method: the design of chiral side chains that strengthen the chiral interactions of the bent-core molecules or by attaching chiral bent-core molecules as side chains, and 2) a physical method: the introduction of a temperature gradient to nucleate liquid-crystalline domains from the chiral surfaces that utilizes the maximum contribution from the chiral surface interactions.In conclusion, we have succeeded in obtaining finite *ee* values in the B_4 phase of an achiral bent-core molecule by using cells with polyimide layers possessing chiral side chains. The obtained *ee* value was 10% in cells with rubbed chiral polyimide surfaces. This technique opens up the possibilty for controlling the chirality in chemical and biological systems.

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