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Enhanced Optical Activity by Achiral Rod-Like Molecules Nanosegregated in the B_4 Structure of Achiral Bent-Core Molecules

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Abstract: Chirality in a mixture system consisting of bent-core 1,3-phenylene bis[4-(4−8-alkoxyphenyliminomethyl)benzoates] (P8-O-PIMB) and rod-like *n*-pentyl-cyanobiphenyl (5CB) molecules has been studied. Precise circular dichroism (CD) spectra using thin sample cells indicate mainly two characteristics: (1) the origin of CD signals is due to chiral-segregated bent-core molecules in the B_4 phase, where 5CB is in the isotropic phase; (2) the enhanced CD signal is detected in the B_X phase, where 5CB is in the nematic phase. These results suggest that 5CB molecules are embedded in the network of helical nanofilaments formed by P8-O-PIMB and form helical superstructure with the same handedness as the helical nanofilaments in the B_X phase, resulting in the giant CD signals.

1. Introduction

Since the discovery of polar switching in a bent-core liquid crystal,[1] extensive research activity has led us to a new era of liquid crystal science particularly in view of polarity and chirality.[2,3] In this paper, we focus on chirality in a mixture system consisting of achiral bent-core and rod-like molecules. Many interesting phenomena have been reported in the mixture systems of bent-core and rod-like molecules, i.e., induction of antiferroelectric phase[4] and novel smectic phases,[5] enhanced twisting power in cholecteric[6] and chiral smectic C* liquid crystals,[7] novel temperature dependence of elastic constant,[8] expansion of bent-core smectic phases,[9] etc. In 1995, Takanishi et al.[10] found that in a mixture system of a bent-core liquid crystal, 1,3-phenylene bis[4-(4−8-alkoxyphenyliminomethyl)-benzoates] (P8-O-PIMB), and a rod-like molecule *n*-pentyl-cyanobiphenyl (5CB) that the B_2 and B_3 phases readily disappear upon the addition of a small amount of 5CB, stabilizing the B_4 phase, chiral segregated domains become smooth and large, and a new B_X phase appears below B_4.

Takekoshi et al.[11] have performed ac calorimetry measurements and found that the B_4−B_X phase transition exists at nearly the same temperature as that of the isotropic−nematic (Iso-N) phase transition of 5CB, and the thermal anomaly disappears at about equiweight mixture (supercritical behavior). They considered that 5CB molecules are embedded in the twist-grain-boundary-like B_4 structure, so that the phase transition of 5CB is influenced by the confined geometry because of the environment. Quite recently, however, freeze-fractured transmittance electron micrograph (FFTEM)[12] and light scattering measurements[13] have suggested that 5CB molecules are nanosegregated from the bent-core molecules, i.e., they are not located inside the helical nanofilament formed by the bent-core molecules but outside of the helical nanofilament. Hence, the B_4 phase in the mixture is formed by the helical nanofilaments of P8-O-PIMB existing in an isotropic sea of 5CB molecules, whereas the B_X phase is formed by B_4 helical nanofilaments existing in a nematic sea of 5CB molecules. The purpose of this study is to elucidate the structures of the B_4 and B_X phases and to examine how 5CB molecules behave under the influence of the B_4 helical nanofilaments. The cartoons to show such structures are shown in Figure 1 together with the phase diagram of the mixture and the chemical structures of the two constituent molecules.

Chirality has continuously been one of the most attractive subjects in chemistry. Spontaneous chiral segregation in the B_4[2,14] and dark conglomerate[15−19] phases are some of this kind. To study such chiral structures, circular dichroism (CD) spectra

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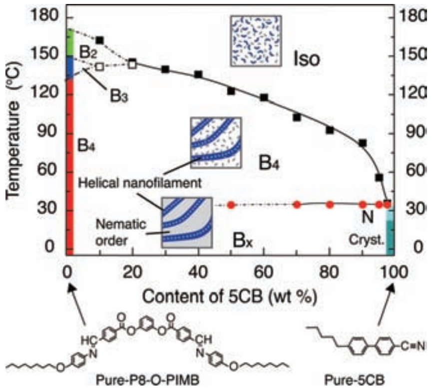

Figure 1. Phase diagram of a binary mixture of P-8-OPIMB and 5CB obtained in our previous works.[10,11] The chemical structures of the constituent molecules and cartoons of the phase structures are also shown.

have been used. In most of the cases, however, sample thickness was too thick to measure CD spectra because of the difficulty in obtaining uniform thin cells in liquid crystal samples. In such cases, artificial CD peaks due to high absorption appear and prevent us from quantitative discussion. In the present work, we prepared about 500-nm-thick cells and performed CD experiments, by which we could clearly identify the source of signals in the binary mixtures.

2. Results

2.1. Samples. The samples used were mixtures of P8-O-PIMB and rod-like 5CB (see Supporting Information 2). We made four mixtures containing 5CB of 30 wt % (57 mol %), 50 wt % (76 mol %), 60 wt % (82 mol %), and 70 wt % (88 mol %). Hereafter, for example, we call 30 wt % mixture for a mixture with 30 wt % 5CB and 70 wt % P8-O-PIMB. Particular care was taken to prepare thin and uniform cells (see Supporting Information 2 and Figure S1). We found that the absorbance of even a 1-μm cell of 50 wt % mixture was 4.9 at the absorption maximum. To keep the optical density less than 2, we used cells of 400−460 nm thick.

2.2. CD Measurements in B$_4$. UV−visible absorption and CD spectra were taken using JASCO V-560 and JASCO J-720WI CD spectrometer, respectively. The viewing field was chosen under a polarizing microscope using a pinhole of about 500 μm in diameter, and the spectra were observed using a pair of objective lenses installed in the spectrometer. Particular care was taken to eliminate the contribution from linear dichroism and birefringence. For this purpose, we always rotated the cell about the cell surface normal to confirm the independence of the rotation angle for the spectra.

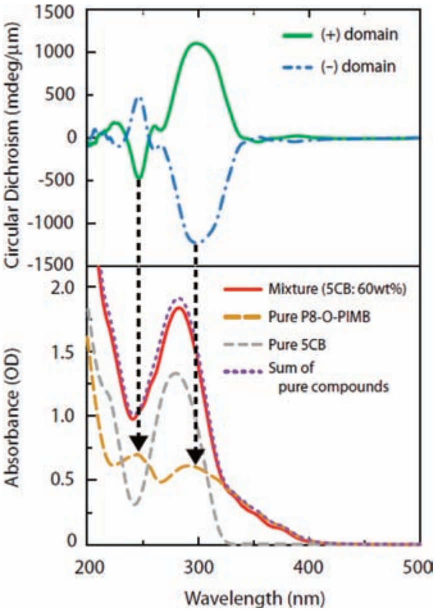

Figure 2. Absorption (lower) and CD (upper) spectra. In addition to a measured absorption spectrum (red solid line), spectra of pure 5CB (broken gray line) and P8-OPIMB (broken brown line) of equivalent thicknesses (264 and 176 nm, respectively) corresponding to the mixing ratio and the sum (dotted purple line) are shown. CD spectra are from both chiral domains.

Let us first show the absorption and CD spectra in the B$_4$ phase. The measurements were made at 10 °C below the Iso-B$_4$ phase transition after cooling from Iso with 2 °C/min. Two large (several mm^2) chiral domains are distinguishable (Figures S2a and S2b). Figure 2 (lower) shows the absorption spectra of pure 5CB (gray broken line) and pure P8-O-PIMB (brown broken line). The absolute absorbance values of 5CB and P8-O-PIMB in a 60 wt % mixture were determined so as to be 264-nm-thick 5CB and 176-nm-thick P8-O-PIMB cells by taking account of cell thickness (440 nm) and the mixing ratio (5CB:P8-O-PIMB=60:40). The sum of these spectra (purple dotted line) of pure compounds agrees well with the measured absorption spectrum (red solid line) of a 60 wt % mixture. Two CD spectra (upper in Figure 2) measured at two chiral domains (green and blue lines) are mirror images to each other. It is noted that the positions of two large CD peaks correspond to the absorption peaks of P8-O-PIMB, indicating that the CD peaks originate from induced CD due to P8-O-PIMB.

Figure 3a reveals CD spectra in different mixtures with different 5CB contents, 50, 60, and 70 wt % measured at 48 °C below the Iso-B$_4$ phase transition. The absolute intensity of the signal increases with decreasing 5CB content. The CD spectra at 38 and 58 °C below the Iso-B$_4$ transition show similar results (see Figure S4). The CD peak intensity at 300 nm observed at 38 °C, 48 °C, and 58 °C below the Iso-B$_4$ transition are summarized in Figure 3b as a function of 5CB content. At all temperatures, the CD intensity changes with 5CB wt % almost linearly. By extrapolating the data, we can estimate the CD intensities of pure p8-OPIMB as 2.2, 2.4, and 2.6 deg/μm at three temperatures (38, 48, and 58 °C below the Iso-B$_4$ transition), respectively.

2.3. CD Measurements in B$_X$. Let us first show the CD spectra in the B$_4$ and B$_X$ phases of a 50 wt % mixture. Remarkable change in the CD spectra was observed at 115 °C (B$_4$) and 30 °C (B$_X$), as shown in Figure 4; there are two CD peaks corresponding to the absorption peaks of P8-O-PIMB in B$_4$, whereas one intense peak at 292 nm is noticeable in B$_X$. The peak position approaches the absorption peak of 5CB. Therefore, the data suggest the contribution of 5CB to the CD signal in the B$_X$ phase, where 5CB is now liquid crystalline phase.

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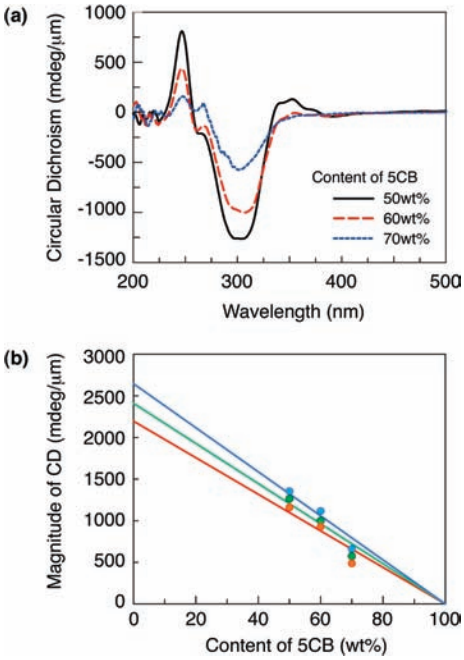

Figure 3. (a) CD spectra in the B_4 phase (48 °C below the Iso-B_4 transition) in mixtures with three different mixing ratios. (b) Magnitude of CD at 300 nm as a function of 5CB content at three temperatures (38 (orange), 48 (green), and 58 °C (blue) below the Iso-B_4 transition) in the B_4 phase.

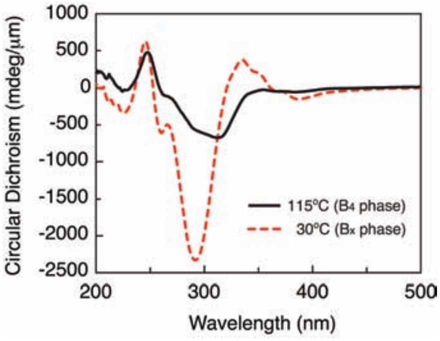

Figure 4. CD spectra in the B_4 (solid black line) and B_X (broken red line) phases of 50 wt % mixture.

In order to examine this fact more quantitatively, the temperature variations of the CD spectra in four mixtures (30, 50, 60, 70 wt % 5CB) are shown in Figure 5, where signals from both positive and negative chiral domains are shown. In every mixture, good symmetric signals are observed from both domains. In 30 and 50 wt % mixtures, only gradual changes with temperature were observed. By contrast, rapid increases were clearly seen below about 35 °C at 60 and 70 wt % mixtures. To see the behavior more clearly, the CD peak intensity is plotted as a function of temperature in four mixtures (Figure 6). Surprisingly the CD peak intensity starts to be enhanced sharply at about 35 °C, above and below which are B_4 and B_X phases, respectively. In the B_4 phase, the higher the P8-O-PIMB content, the higher the CD intensity becomes, because the CD signal originates from the helical nanofilament formed by P8-O-PIMB. However, the situation drastically changed in the B_X phase. The CD signals became more pronounced in the mixtures with a larger amount of 5CB. The CD value of 2 deg (4.5 deg/μm for a 440-nm-thick cell) is the measurable limit of our CD spectrometer. Thus, the enhancement is surely due to the formation of liquid crystalline structure of 5CB. Actually a 30 wt % mixture, which exhibits no B_4-B_X transition, gave monotonous increase of the CD intensity with decreasing temperature without showing any sign of enhancement at the B_4-B_X transition point (at about 35 °C).

One may worry about the effect of birefringence, which becomes larger in the B_X phase, on the CD signal. To confirm the lack of the contribution from the birefringence, we measured the CD spectra by rotating the cell about the cell surface normal. We observed only negligible changes in the spectra (Figure S5). Thus we confirmed no contribution of the birefringence to the CD signals. It is also worth noting that the CD enhancement is always toward the same sign of the base CD signal in the B_4 phase. Namely, if the CD signal is positive (negative) in the B_4 phase, the CD signal becomes larger toward positive (negative) directions (Figure S6).

3. Discussion

As described in the previous section, nonchiral 5CB molecules enhance the chirality in both positive and negative chiral domains, when 5CB is in the liquid crystalline state, i.e., in the B_X phase. We now discuss the origin of the phenomenon. As described in Introduction, 5CB molecules are nanosegregated from P8-O-PIMB molecules, which form a helical nanofilament structure.[12] This structure was also supported by dynamic light scattering.[13] The relaxation was observed in the B_X phase and was of the order of the orientational fluctuation mode, indicating that the 5CB molecules are in liquid crystalline order. Moreover, the scattering angle dependence of the relaxation time disappears at certain levels depending on the mixing ratio, strongly suggesting the nanosegregated structures.

The nanosegregation of 5CB molecules was also suggested in thermal measurements.[11] Pure 5CB shows the first-order Iso-N transition. With increasing P-8-O-PIMB content, the Iso-N transition continues to exist as the B_4-B_X transition; its first-order nature becomes weaker, being closer to the critical point, and the temperature dependence of heat capacity exhibits a rounded, small anomaly (supercritical) in the 50 wt % mixture. Moreover, the transition temperature shifts monotonically to a higher temperature side as P-8-O-PIMB concentration increases. The similar behavior has been observed in a smectic liquid crystal confined in silica aerogel.[20] In this case, the N-smectic A transition temperature shifts toward a lower temperature side with increasing aerogel content. The authors estimated the correlation length (confinement size). However, this method cannot directly be applied to the present system whose transition is of highly first order. The finite size effect in the first-order phase transition can be found in Monte Carlo simulation.[21] The calculated transition temperature shifts toward a higher temperature side, the same as that in the present case. Hence, the small transition temperature shift (<1 °C) and a rounded heat capacity peak actually indicate the effect of confinement. A rough estimate of the confinement size amounts to a value of the order of 100 nm, being consistent with the FFTEM observation.[12]

With such a structure in hand, we can imagine that 5CB molecules form helical structures such as a cholesteric liquid crystal or twisted nematic (TN) structure. Let us consider a simple case, where 5CB molecules are located in between two right-handed helical nanofilaments, as shown in Figure 7a. If

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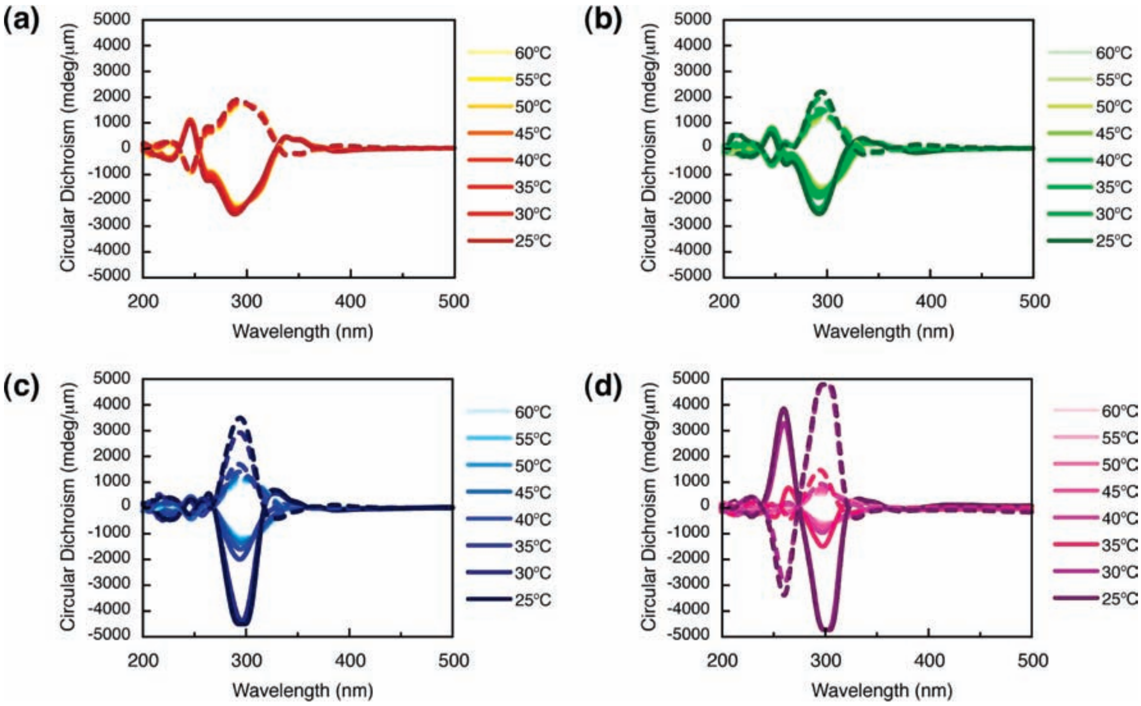

Figure 5. Temperature dependence of CD spectra in four mixtures with (a) 30, (b) 50, (c) 60, and (d) 70 wt % 5CB.

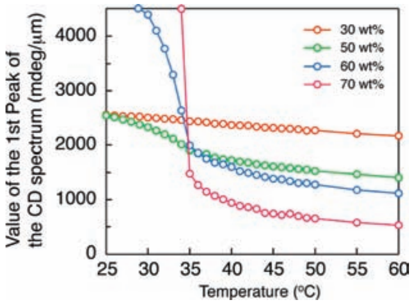

Figure 6. Peak intensity of CD spectra as a function of temperature in four mixtures (30, 50, 60, and 70 wt %).

we assume that 5CB molecules orient along the groove of the helix as suggested by Berreman,[22] 5CB molecules form a TN structure, as shown in Figure 7a, because the groove directions of the neighboring helical nanofilaments are crossed. If the opposing groove directions make less than 90° via the nanofilament axis, the helical sense of the TN structure is uniquely defined to be the same as that of the helical nanofilaments. Actually, according to FFTEM and atomic force microscopy (AFM),[12] the groove direction is about 21° with respect to the helical axis, making a 42° TN structure, if two helical nanofilaments exist parallel to each other.

The above scenario works when adjacent helical nanofilaments are almost parallel to each other. However, it is not always the case. Another idea is the induction of chiral superstructures of 5CB under the influence of helical nanofilaments of bent-core molecules. Suppose 5CB molecules orient along the groove of the helical nanofilaments as discussed above. If 5CB molecules orient parallel to each other along the direction perpendicular to the axis of the helical nanofilaments, 5CB molecules also form a helicoidal structure (Figure 7b) along the axis of the helical nanofilaments, i.e., tilt direction of 5CB molecules with respect to the axis of the helical nanofilaments precesses about the axis. Since the helical senses of 5CB helical superstructures and the helical nanofilaments are the same, we always have the enhancement of the CD signals. The enhancement effect of 5CB helical structure must overcome the decrease of the CD signal due to less helical nanofilaments. This might be possible if we take into account the long-range orientational order of 5CB molecules.

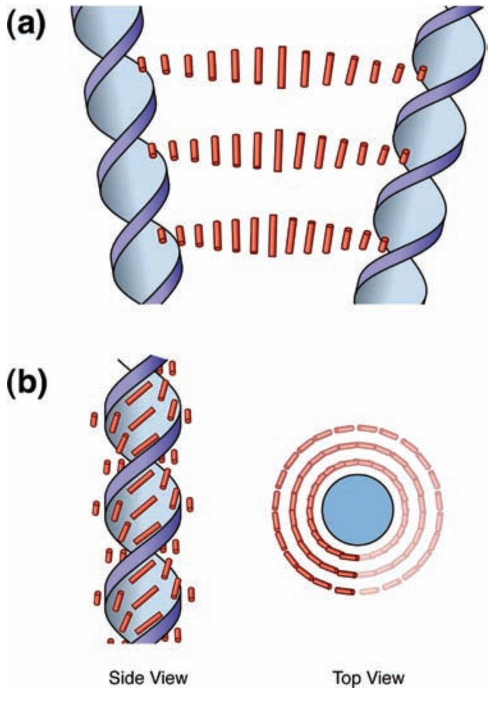

Figure 7. Models of helical superstructure of 5CB based on the assumption that 5CB molecules align parallel to the groove of helical nanofilaments. (a) 5CB molecules between two neighboring helical nanofilaments form a twisted nematic structure. (b) In the vicinity of a helical nanofilament, 5CB molecules (brown rods) also form helical structure.

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Another idea is that the helical nanofilaments act as a chiral dopant in 5CB molecules. Suppose that 5CB molecules form the cholesteric liquid crystal structure under the existence of helical nanofilaments. With increasing 5CB content, dopant (helical nanofilament) content becomes lower, so that the helical pitch becomes longer. According to the theory of the optical rotation in twisted nematic liquid crystals by de Vries[23] and Saeva,[24] the optical rotation is proportional to the helical pitch when the pitch is much larger than the wavelength used. Thus, the contribution of the 5CB helical structure to the overall CD intensity becomes larger with increasing 5CB content. If this model is correct, we can make planar alignment of 5CB molecules by surface rubbing; then 5CB forms a cholesteric-like helical structure with the helical axis along the substrate normal.

The origin of the enhanced optical activity would be a combined effect of these models mentioned above. Many types of experiments to identify the model are now in progress including the effect of an applied electric field. These results will be reported in the near future. In future research, it would also be interesting to have imbalanced chiral domains. We have succeeded in obtaining chiral domains with large imbalance, i.e., almost 100% enantiomeric excess by using circularly polarized light[25] and twisted cell geometry.[26] If we could make a single chiral domain with enhanced giant chirality by 5CB, several application can be imagined. For instance, a tunable polarization rotator would be possible by using wedge-type cells with a thickness gradient. This is our future program.

4. Conclusions

The circular dichroism (CD) spectra have been precisely measured in binary nonchiral mixtures consisting of bent-core P8-O-PIMB and rod-like 5CB molecules. In the B_4 phase, the CD signal originates only from P8-O-PIMB in the B_4 phase, since 5CB is in the isotropic phase. In contrast, a remarkably enhanced CD signal emerges mainly from 5CB in the B_X phase, where 5CB is in the nematic phase. These phenomena support the model structure, i.e., 5CB molecules are nanosegregated from P8-O-PIMB. We qualitatively discussed the possible helical superstructures of 5CB coexisting with helical nanofilaments formed by P8-O-PIMB.

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Supporting Information Available: Detailed experimental data of absorption (Figure S1), textures (Figures S2 and S3), CD spectra in mixtures with different mixing ratios (Figure S4), CD spectra at various rotation angles of sample cells about the cell surface normal (Figure S5), and CD intensity as a function of temperature (Figure S6) are available free of charge via the Internet at http://pubs.acs.org.

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