

Chiral Memory on Transition between the B2 and B4 Phases in an Achiral Banana-Shaped Molecular System

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The correlation between chirality of the B2 and B4 phases was examined by measuring the circular dichroism (CD) in the classic bent-core molecule, P-12-O-PIMB, which shows a direct B2 to B4 phase transition on cooling. Among the various structures formed in the tilted B2 phase, the homochiral $\text{SmC}_\text{S}\text{P}_\text{F}$ and $\text{SmC}_\text{A}\text{P}_\text{A}$ layer structures show a distinct CD peak at around 400 nm, while no CD effect is observed in the racemic $\text{SmC}_\text{S}\text{P}_\text{A}$ layer structure. In contrast, the lower temperature smectic B4 phase is essentially chiral and it appears to be independent of the type of layer structures of the initial B2 phase. It always exhibits a CD peak at a similar wavelength to that of the homochiral B2 phase, but with opposite sign. By incorporating the optical microscopic observation with the CD measurements, we found that once the chiral domains are formed in the B4 phase, they are conserved thereafter on successive transformation between the B2 and B4 phases. The resulting chiral structure in the B2 phase is homochiral $\text{SmC}_\text{A}\text{P}_\text{A}$. For this conservation of chirality, there must be an inherent chiral source for both the B2 and B4 phases. We propose that conformational chirality fills this role.

Introduction

The discovery of electrooptic switching by Niori et al.¹ and the suggestion of chirality by Sekine et al.² in a fluid achiral smectic phase, the B2 phase, of banana-shaped P-n-O-PIMB opened a new era in the study of polar order and chiral superstructures of liquid crystals. In these materials the polarity was considered to result from the C_{2v} symmetry due to the closed packing of bent molecules.^{3–5} In practice, however, the molecules in the B2 phase are tilted in the smectic layer,^{6,7} resulting in the layer chirality as well as polarity. This layer chirality was clearly described in the work of Link et al.⁶ who found that two distinct types of domains coexist in the B2 phase. One is anticlinic antiferroelectric known as $\text{SmC}_\text{A}\text{P}_\text{A}$ and the other is synclinic antiferroelectric designated by $\text{SmC}_\text{S}\text{P}_\text{A}$; the latter was found to be the ground-state structure. It was also pointed out that although the individual molecules are achiral, there is a chiral relationship in the B2 phase between the layer normal \mathbf{z} , the direction of the molecular tip \mathbf{b} , and the local molecular orientation director \mathbf{n} . This layer chirality is defined by $\mathbf{b} = \mathbf{z} \times \mathbf{n}/|\mathbf{z} \times \mathbf{n}|$. Consequently, it is possible for the layer chirality to be either (+) or (–) depending respectively on whether the product of the $\mathbf{z} \times \mathbf{n}$ points in the direction along \mathbf{b} or $-\mathbf{b}$ as shown schematically in Figure 1a. In addition, as the molecules are closely packed in smectic layers and rotation about their long axis is strongly hindered, each layer has a spontaneous polarization P along \mathbf{b} .

Allowing for synclinic and anticlinic stacking of tilted polar smectic layers with C_2 symmetry, there are then four possible arrangements of the polar order and layer chirality (see Figure

1b).⁶ In these structures two successive layers define the polar order (ferroelectric or antiferroelectric) and the overall layer chirality (homochiral or racemic). The term “homochiral” is used to indicate that all layers in a certain domain have layer chirality of the same sign and the term “racemic” is used to indicate an alternation of the sign of the layer chirality from layer to layer. The subscript S or A added to SmC in the nomenclature $\text{SmC}_\text{S,A}\text{P}_\text{F,A}$ defines if the relative tilt sense of adjacent layers is synclinic (S) or anticlinic (A) and the subscript F or A added to P specifies if the polar ordering is ferroelectric (F) or antiferroelectric (A). Since the tilt and polarization directions define the layer chirality, the given combination of these subscripts defines whether the overall layer chirality is racemic or homochiral; the $\text{SmC}_\text{S}\text{P}_\text{F}$ and $\text{SmC}_\text{A}\text{P}_\text{A}$ layer structures are homochiral while the $\text{SmC}_\text{S}\text{P}_\text{A}$ and $\text{SmC}_\text{A}\text{P}_\text{F}$ structures are racemic (see Figure 1b).

The B4 phase, formed on cooling the B2 phase, is also of interest.^{2,7–9} It is apparently a solid phase, and it differs from typical crystalline phases. The most striking feature of this phase is an exhibition of transparent blue color; for this reason, it was initially called “blue phase” by Sekine et al.² In addition, the B4 phase exhibits circular dichroism (CD) at about 400 nm. Hence, the blue color is attributed to the selective reflection of left- or right-handed circularly polarized light, suggesting the existence of a helical structure. In fact, detailed observations of microscopic textures and circular dichroism imply the existence of two helical domains with opposite optical rotations.^{7–9} Since these combined features are recognized only when the sample is prepared from the B2 phase with planar alignment, the helical structure is thought to be formed with the helical axis parallel to the layers such as in the twisted grain boundary (TGB) phase (Figure 18 of ref 9). The transparency is due to the twisted blocks with each block size relatively smaller than

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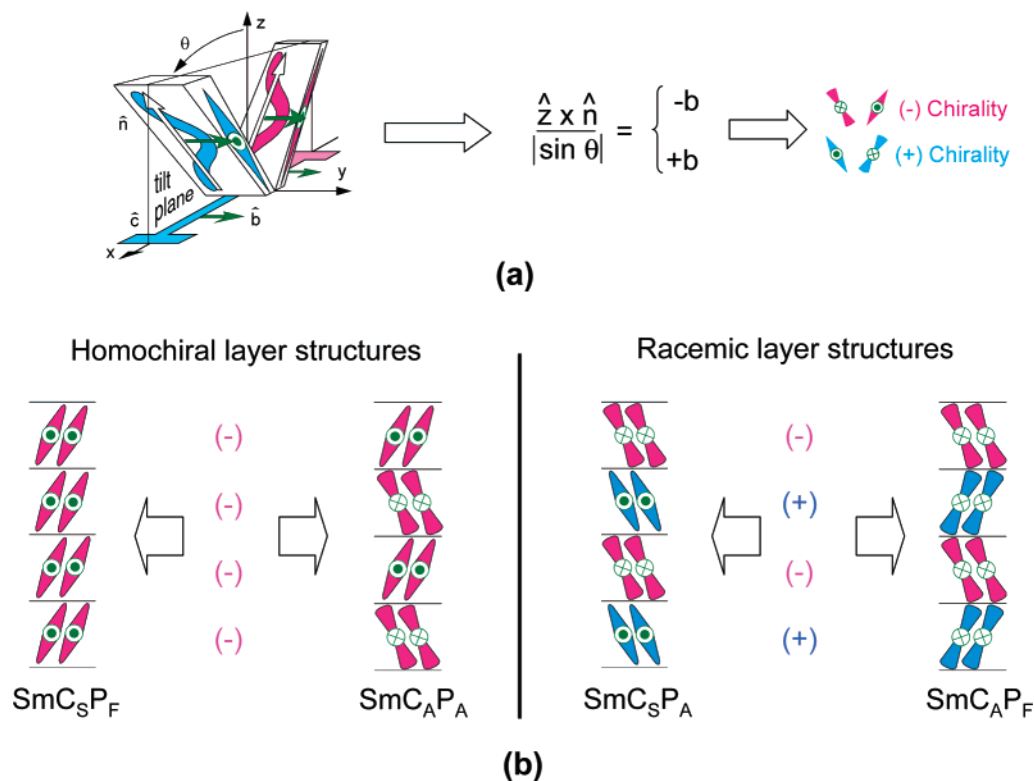


Figure 1. (a) Illustration of layer chirality as induced by molecular tilting of banana-shaped liquid crystal molecule. (b) Layer structures constructed by different molecular orientations of banana-shaped molecule: homochiral layer structures (left) and racemic layer structures (right).

the wavelength of the light. Of course, the two helical domains are formed with equal probability in an achiral molecular system, although the addition of a chiral dopant to P-n-O-PIMB removes this condition.^{9,10} As the molecules are not tilted from the layer normal in the B4 phase,⁹ we have to consider a possibility of a different origin of the chirality from that in the B2 phase. Some helical conformation characteristic of the banana-shaped molecules has been proposed.^{2,9,11,12}

The simple conclusion from the above discussion is that both the B2 and B4 phases are intrinsically chiral despite being composed of achiral molecules, but the origin of chirality is apparently different between these two phases. Our present results suggest an important relationship between the layer chirality as the molecules tilt in the layers while in the B2 phase and the conformational chirality as the molecules assume twist conformation while in the B4 phase.

In this study, we examine in detail the correlation between the chirality of these two chiral phases by using P-12-O-PIMB. For this compound, the B2 phase directly transforms to the B4 phase,² providing us a convenient way to probe its chiral interrelationship.

Experimental Section

The synthesis of P-12-O-PIMB was reported in a previous paper.² The optical microscope textures of the materials were examined using a polarizing microscope (Olympus, BX50) equipped with a hot stage (Mettler Toledo FP 90 HT). DSC thermogram data were collected using a Perkin-Elmer DSC-II differential scanning calorimeter. X-ray diffraction measurements were performed using a Rigaku-Rint-2000 diffractometer with Cu K α radiation. Circular dichroism (CD) and optical rotation (ORD) were measured using a JASCO J-720WI spectrometer.

Results

The phase sequence of P-12-O-PIMB is as follows:



On cooling from the isotropic melt, there is a transition to the B2 phase at 169 °C followed by a transition to the B4 phase at 140 °C. From the isotropic melt, the B2 phase first appears as germs throughout the entire cell, and they coalesce to form multiple types of domains (see Figure 2a). Scattering of light from the multiple domains makes this B2 phase opaque. On further cooling to the B4 phase, the sample becomes transparent and simultaneously exhibits the blue reflection color with circular dichroic nature, as stated in Introduction. The chiral domains attributable to the CD effect are also recognized by optical microscopy (Figure 2b). An unidentified and weak birefringence texture is the characteristic of the B4 phase, but two types of domains with opposite optical rotations are clearly distinguished by rotating of the polarizer or analyzer from the cross-polarization position.

In addition to these facts so far collected, we found here a new interesting fact that the size and shape of the chiral domains of the B4 phase do not change at all on heating back up to the B2 phase, even though the internal texture within the domains drastically changes. By repeating the cooling and heating cycles between the two phases, only the contrast of the two domains of the B4 phase is improved (refer to Figures 2b, 2d, and 2f). Further, the chiral domains become clearly recognized even in the B2 phase (see Figure 2e). Thus, it is likely that the chirality is completely preserved in the B2 phase once the chiral structure is constructed in the B4 phase, indicating the strong correlation of the chirality between the B2 and B4 phases. To probe this correlation, we measured the CD signal from these domains. As shown in Figure 3, the clear CD effect can be observed in

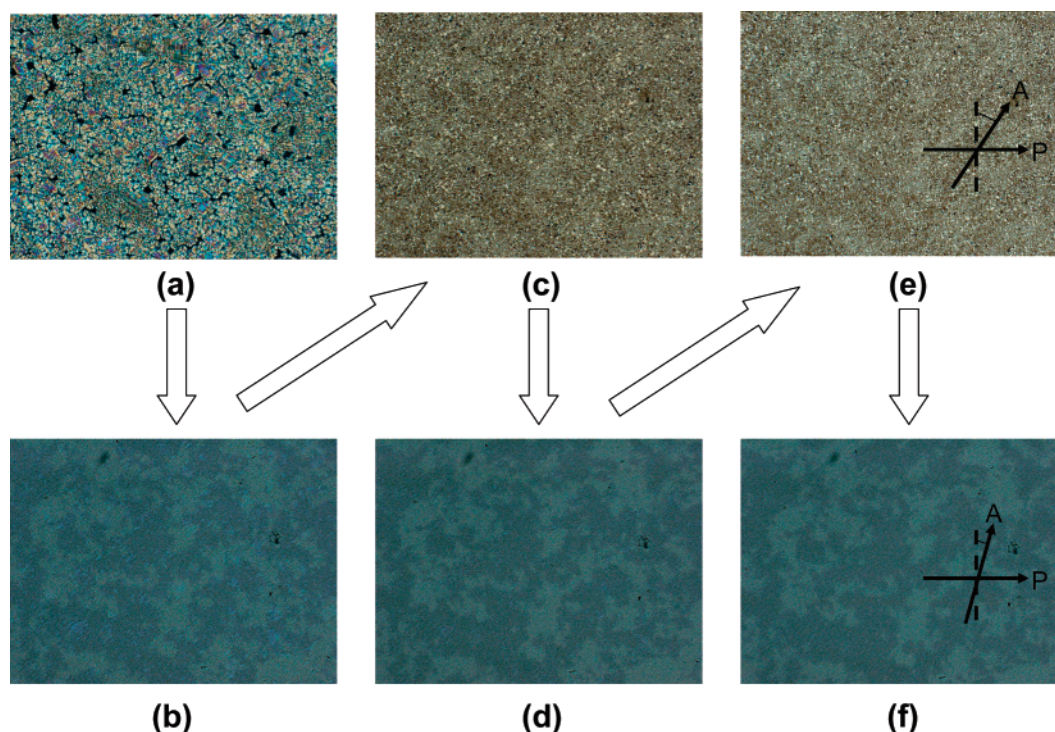


Figure 2. Optical microscopic textures observed on the transformation between the B2 (at 150 °C) and B4 phases (at 70 °C): (a and b), B2 and B4 phases on 1st cooling from the isotropic melt; (c and e), B2 phases on 2nd and 3rd heating from B4 phase, respectively; (d and f) B4 phases on 2nd and 3rd cooling from B2 phase, respectively. The textures are observed by 20° clockwise rotation of analyzer for the B2 phase and by 5° clockwise rotation for the B4 phase.

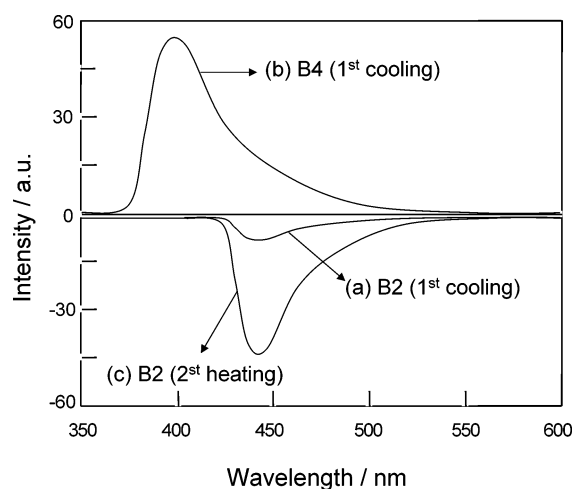


Figure 3. Typical CD spectra observed for the B2 and B4 phases of P-12-O-PIMB: curve (a), B2 phase on 1st cooling from isotropic melt; curve (b), B4 phase on 1st cooling; curve (c), B2 phase on 2nd heating from B4 phase. The same position is probed in all three measurements.

the B2 phase as well as in the B4 phase. The sign of CD in the B2 phase appears to depend on the sample preparation and position. This is due to the unbalance of the chiral domains in a limited area irradiated.^{8,9} The maximum wavelength of CD is somewhat larger than that in the B4 phase, and as a striking fact, its sign is always opposite to that of the B4 phase. The alternation of the CD sign is observed even after 20 repetitions as displayed in Figure 4.

On cooling from the isotropic melt, the B2 phase is composed of multiple domains that differ in polar order and sign of layer chirality. This heterogeneity in the B2 structures makes it difficult to understand the correlation between the chirality of the B2 and B4 phases. To avoid the complexity in forming the multiple structures of the B2 phase, we prepared uniform

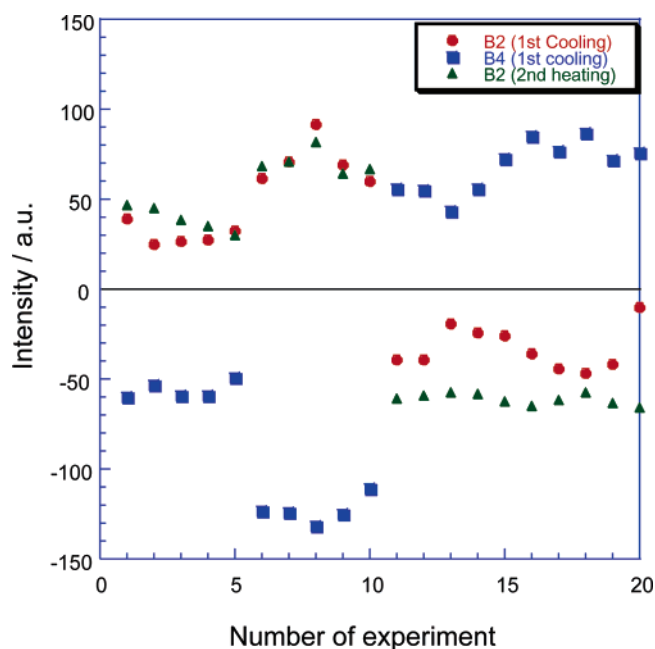


Figure 4. The intensity of CD spectra of the B2 and B4 phases taken by cycling the B2 and B4 phases. The data were collected by recording CD measurements for 20 repetitions as given in Figure 3.

domains for an initial B2 phase, which are composed of a single type of the SmCP structure, SmC_{AP}A, SmC_SP_A, or SmC_SP_F. In addition, 10 wt % of a compatible chiral material, P-8-O-PIMB6* with (s)-(+)-6-methyloctyloxy tail was used as a chiral dopant in P-12-O-PIMB to break the balance in formation of (+) and (−) chiral layer structures. The techniques we used for preparing domains of each structure are described below.¹³

Preparation of Homochiral SmC_{AP}A and SmC_SP_F. Homochiral domains of SmC_{AP}A were prepared by temperature

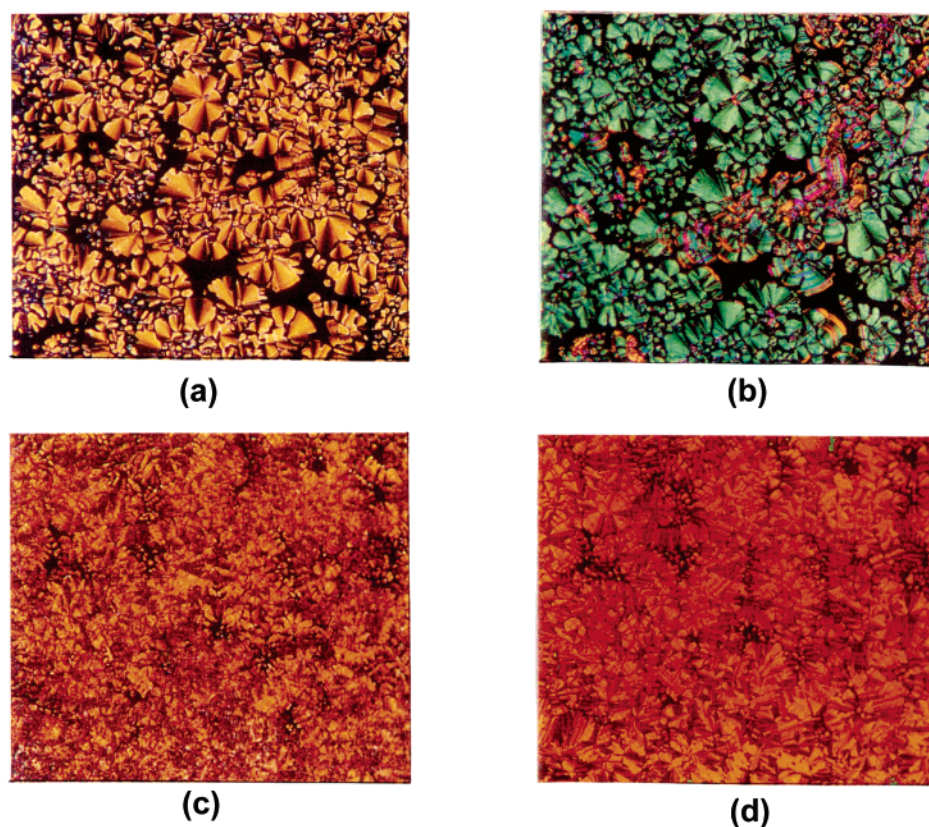


Figure 5. Optical microscopic textures in P-12-O-PIMB containing 10 wt % of chiral P-8-O-PIMB6*: (a) homochiral SmC₅P_F, (b) homochiral SmC_AP_A, (c) racemic SmC₅P_A, and (d) racemic SmC_AP_F forms of the B2 phase. The details of preparation are described in the text.

cycling between the B4 and B2 phases. Large domains can be obtained by applying a triangular wave voltage of 8 V across a 6 μm thick cell. A typical texture obtained by this technique is shown in the photomicrograph in Figure 5a taken between crossed polarizers. The extinction in nearly all of the fan or spherulite structures is found when the layer normal is along either the polarizer or analyzer. Under application of a slightly larger field (10 V/6 μm ; bipolar square wave), the extinction direction rotates 35° from the layer normal and the birefringence of the sample increases as shown in Figure 5b. From the rotation sense of the extinction direction (clockwise or counterclockwise), 70–80% of the domains are of the same sign of layer chirality.⁹ This electrooptical switching behavior confirms that the domains in Figure 5a are the homochiral SmC_AP_A and that the domains in Figure 5b are the homochiral SmC₅P_F formed due to field induced transition.

Preparation of Racemic SmC₅P_A. The racemic SmC₅P_A was prepared by continuously applying a rectangular waveform of 8 V/6 μm . A striped texture, indicative of the SmC₅P_A, can be seen in the photomicrograph of Figure 5c. Under application of a DC field above a threshold voltage, there is a field-induced transition to the SmC_AP_F state; the fringe pattern disappears and a uniform birefringence color is observed with the extinction direction along the layer normal (see Figure 5d). During this process, however, a small minority of the SmC_AP_F domains are converted to the homochiral SmC₅P_F, which makes it impossible to obtain perfect domains of the racemic SmC_AP_F structure.

The CD spectra observed for the three uniform domains (i.e. homochiral SmC_AP_A and SmC₅P_F, and racemic SmC₅P_A domains) are shown in Figures 6a, 6b, and 6c, respectively. The CD peak with the maximum wavelength of 400 nm is observed only for the homochiral structures (see Figures 6a and 6b), with

the intensity of CD in the SmC_AP_A being three to four times larger than that in the SmC₅P_F. In contrast, the racemic SmC₅P_A shows no CD peak (see Figure 6c). These results lead to a simple conclusion that the CD effect results from the layer chirality. Since the chiral dopant of P-8-O-PIMB6* is added, the homochiral domains with (–) layer chirality are formed much more than those with (+) layer chirality, resulting in the negative CD. In contrast, in the racemic domains, there are equal numbers of layers with each sign of layer chirality so that there is essentially no measurable CD. We have no interpretation to explain why the CD intensity of the homochiral SmC_AP_A structure is so much larger than that of homochiral SmC₅P_F one.

The CD spectra characteristic for respective forms do not change during annealing for prolonged times at any B2 phase temperatures. However, they do significantly change on phase transition between the B2 and B4 phases as found in Figures 7a–c. The strong negative CD of the SmC_AP_A structure (Figure 7a) changes to a strong positive CD upon cooling into the B4 phase as shown in Figure 7c. On heating again to the B2 phase, the initial negative CD is completely recovered (see Figure 7d), although an additional positive signal in the longer wavelength region emerges. Surprisingly, even if the B4 phase is formed from a racemic B2 phase with SmC₅P_A structure that shows no CD peak (see Figure 7b), there is observed a nearly identical positive peak in the CD spectrum. On heating this B4 phase back into the B2 phase, the negative CD peak begins to appear. Thereafter, the change of CD spectra on heating and cooling cycles between two phases is the same as observed in the system starting from the homochiral B2 phase. This means that the racemic SmC₅P_A structure is altered into the homochiral SmC_AP_A structure after cycling through the B4 phase. Observa-

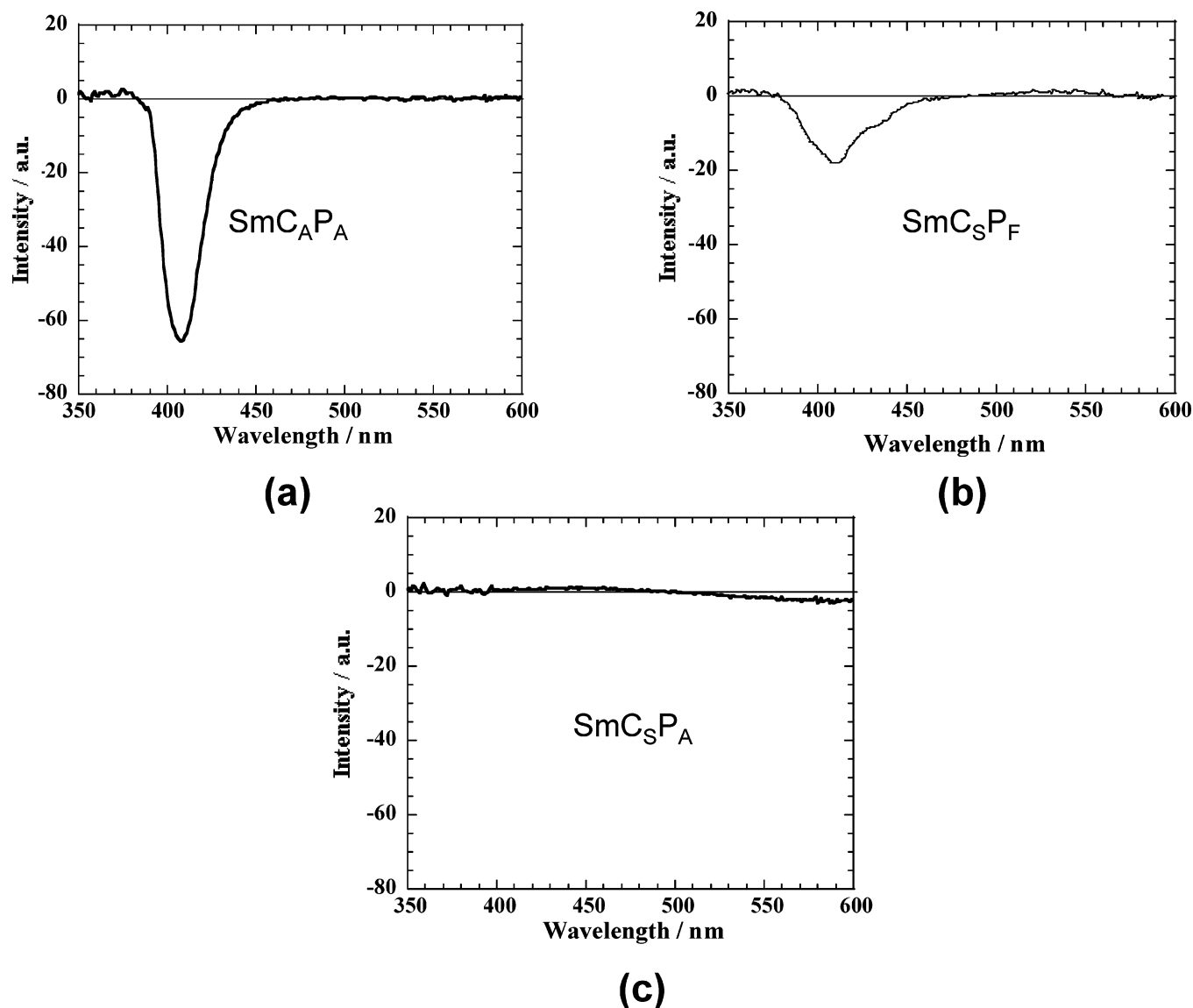


Figure 6. CD spectra observed for B2 phases of P-12-O-PIMB containing 10 wt % of chiral P-8-O-PIMB6*: (a) homochiral SmC_AP_A, (b) homochiral SmC_SP_F, and (c) racemic SmC_SP_A.

tions of optical textures also confirm this evolution in the structure. The results are clear and lead to the second conclusion that the layer structure in the B2 phase, regardless of the state it is initially prepared in, is converted to the SmC_AP_A structure after cycling through the B4 phase.

Discussion

From the above experiments using a 1:9 mixture of the chiral dopant P-8-O-PIMB6* with P-12-O-PIMB, we observed two following distinct phenomena.

(i) Any layer structures formed in the B2 phase are converted to the homochiral SmC_AP_A structure upon temperature cycling through the B4 phase.

(ii) The resulting homochiral SmC_AP_A structure is stable on repeated temperature cycling between the B2 and B4 phases. In other words, the domain size and sign of the layer chirality are completely preserved during this process.

Before further discussion of these phenomena, let us refer to the relevant question, “what is a source of the chirality to induce the TGB like helix in the B4 phase?” In the B4 phase, the molecules on average align along the layer normal as inferred from the X-ray data;⁹ thus, the breaking of symmetry due to

the tilting of molecules as in the B2 phase cannot be taken into account for the B4 phase. In our previous works,^{8,9} we have proposed that helical twist conformations of the bent-core mesogen may induce the chirality in the B4 phase. If we assume that the mesogens take up either a left- or right-handed twist conformation, then it is plausible that each layer is formed by stacking molecules with the same twist sense to achieve the more closed packing that then possess conformational chirality. In fact, the bias rotational direction of the carbonyl carbons on the ester linkages between the central core and two side wings can make such a twist conformation.¹² NMR^{2,14} and IR data^{15,16} also strongly support this assumption. This bias twisting of the carbonyl groups was also detected by time-resolved FTIR technique by Shilov et al.¹⁷ In a recent study, Jakli et al.¹⁸ have observed optically active domains with clear boundary in both anti-ferroelectric and ferroelectric transformed states in an all ester banana-shaped molecules. Importantly, he has found that this exhibition of the chiral domain is not due to the layer chirality, but the enantiomorphic property is more likely to be created by the twisted conformation in that molecule. If this is the case, the second phenomenon (ii) stated above can be explained by a simple idea: the twist conformation that is

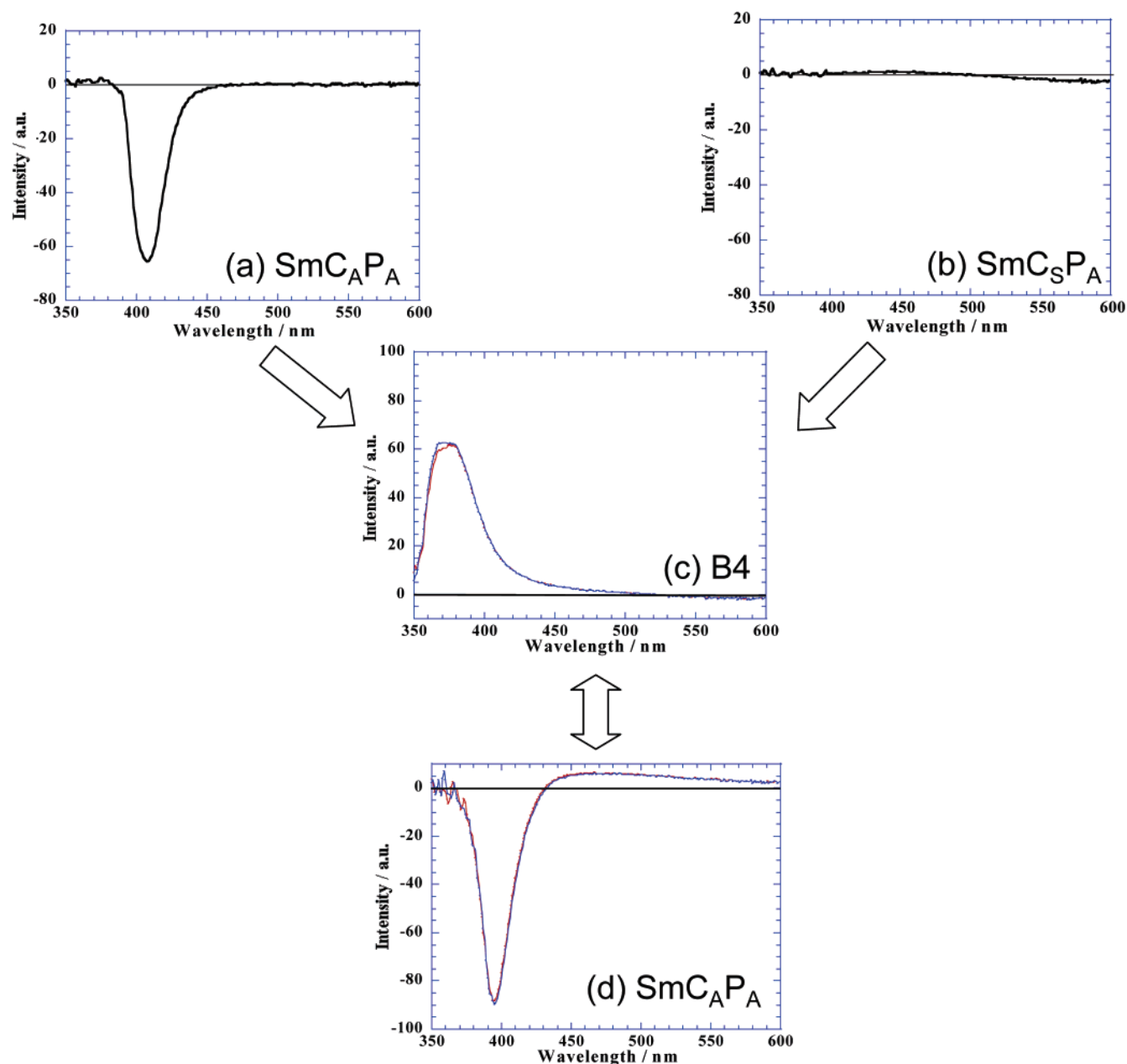


Figure 7. Change of CD spectra on the transformation between the B2 and B4 phases. Here, the spectra a and b are observed for B2 phases which are initially prepared with the homochiral SmC_AP_A and racemic SmC_SP_A structures, respectively. When either SmC_AP_A in a or SmC_SP_A in b was cooled to the B4 phase, the positive CD peak is observed at around 380 nm as in c. On heating back to the B2 phase, the strong negative CD peak characteristic of the homochiral SmC_AP_A structure is detected. Hereafter, the spectra c and d are altered upon temperature cycling between the B4 and B2 phases.

imposed in the B4 phase is kept through the B4 to B2 phase transition and then results in uniform homochiral structures of B2 phase.

One guesses that the molecules, packed laterally with the liquid nature in the fluid B2 phase, are mobile so as to have both conformational freedom and rotational freedom to some extent. In general, hence, it is unlikely that the molecules keep up the helical conformation of the same twist sense within a layer; after prolonged time, helical conformation with a certain helical sense would be converted to that with the other helical sense. However, this is not a case if the conformational chirality is closely coupled with the layer chirality, i.e., molecular tilting. In other words, the conformational chirality forces the molecules to tilt to the favorable direction of the two possible directions such that the left-handed conformation induces the tilting of

molecules to the left side while the right-handed one induces the tilting to the right (see Figure 8). According to the ref 12, the two carbonyl groups in the most stable conformation make an angle approximately of 30° to the molecular long axis (see Figure 8). Seemingly, there are two possible tilt directions, which cause the carbonyl groups to orient completely in different way. One is that the carbonyl groups are relatively parallel to the layer and the other is perpendicular. Takezoe and co-workers have proven this specific molecular orientation in the B2 phase of the P-n-O-PIMB homologues by using FT-IR spectroscopy,^{15,16} and they have found that such a molecule tilts in the layers with the carbonyl groups relatively parallel to the layer interface as shown in Figure 8d. The change of the molecular conformation by rotating of the carbonyl groups should be inevitably followed by the alternation of the tilt direction in

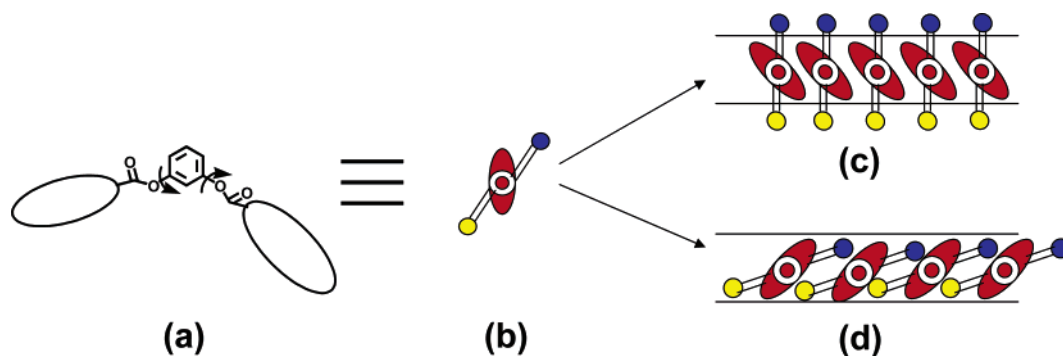


Figure 8. Illustration showing the correlation between the conformational and layer chiralities. In a is shown the most stable conformation of the P-n-O-PIMB homologues with the two carbonyl groups twisted out of molecular long axis and in b is shown its structure from the side-view. There are two possible tilted alignments of the molecule in the smectic layer. One of them is illustrated in c where the carbonyl groups lie perpendicular to the layer interface as a result of tilting of the molecules to the left-side. For the other, as sketched in d, they lie parallel to the layer by tilting to the right-side. FT-IR spectroscopic data^{15,16} indicate the preferential orientation direction, in which the carbonyl group is relatively parallel to the smectic layer as in d.

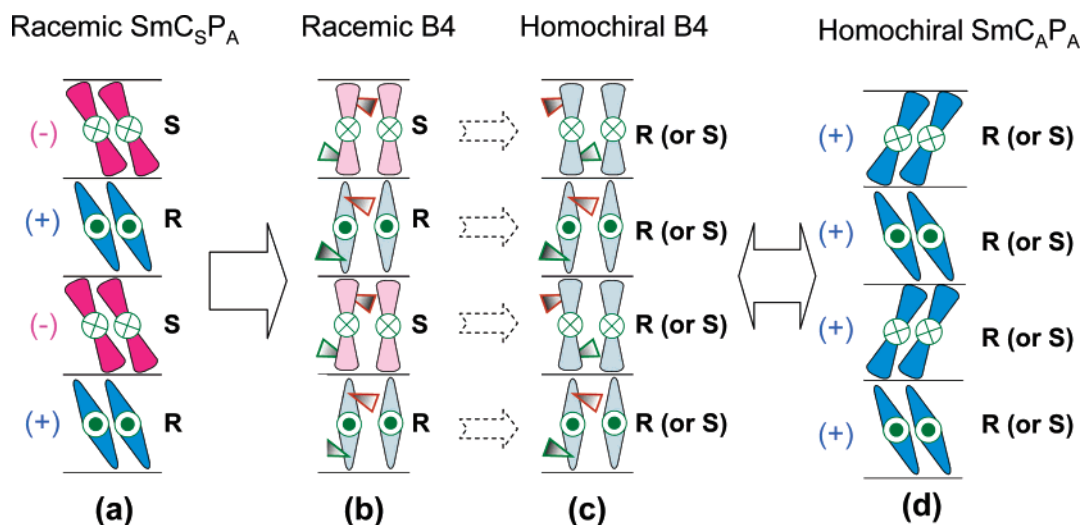


Figure 9. Proposed model explaining the phenomenon that the racemic domain of B2 phase in a is altered to the homochiral domain in d by temperature cycling through the B4 phase. In the B4 phase, the tilting disappears as in b and the molecules thermodynamically reorient into antiferroelectric order as in c, which gives rise to the formation of the homochiral SmC_AP_A structure of B2 phase on heating as in d. Here (+) and (−) indicate the layer chirality, while *R* and *S* represent the conformational chirality.

the layer, which is supposed to have a high energy barrier. This may be a reason the helical conformation is thermodynamically sustained in the B2 phase once it forms at the low-temperature B4 phase.

This correlation between the conformational chirality and layer chirality also provides a reasonable explanation for the distinct phenomenon i: that of the racemic domain of the B2 phase which is altered to the homochiral domain through the transformation to B4 phase, as shown schematically in Figure 9. In the B4 phase, the tilting disappears (see Figure 9b), which may allow molecules to change their twist conformation easier than in tilt situation by a simple cooperative rotational motion of molecules to form the most stable B4 phase. The observed data are reasonably accounted for if the most stable layer structure of the B4 phase is antiferroelectric and homochiral where all the layers within a domain possess either of (*R*) or (*S*) conformational chirality as sketched in Figure 9c. Second, for the phenomenon ii, the resulting conformational chirality is preserved when the B4 phase is heated into the B2 phase, and the molecules tilt in the direction promoted by its twist sense, giving rise to the formation of the homochiral SmC_AP_A structure as sketched in Figure 9d. Subsequent transformations between the B2 and B4 phases then occur as illustrated in Figures 9c

and 9d, under the condition that the material is not heated into the isotropic melt.

The above discussion is based on the argument that the observed CD spectra reflect the chirality in the phases. However, the basic question on the origin of the CD in these phases is still unanswered. It is known that the CD effect typically arises from two structural features:¹⁹ one is the induced CD due to the chiral structure of the absorbed chromophor within a molecule and the other is the selective reflection due to a helical superstructure as observed in the case of the cholesteric (N*) and chiral smectic C (S_C*) phases. From the above discussion, it is reasonable to expect that the CD effect observed in the B2 phase is the induced CD, as there is the intrinsic molecular chirality due to the twist conformation. This is supported by the fact that the CD peak wavelength coincides with the onset of the absorption band. In contrast, the B4 phase is considered to form a helical twist structure similar to a TGB phase,⁹ and then it is possible that the CD from the selective reflection of light coincidentally overlaps with the induced CD. This could also explain why the sign of CD in the B4 phase is opposite to that in the homochiral B2 phase. The details on these points are currently being scrutinized and should be reported soon.

Conclusion

The correlation between the chirality of the B2 and B4 phases was examined by studying the circular dichroism for P-12-O-PIMB, in which the compound exhibits the direct transition from the B2 phase to the B4 phase. To avoid the complexity from the multiple formations of the B2 structures with different chirality and polarity, we carefully prepared each of the four possible B2 layer structures and measured the CD spectra using a mixture of 10wt% P-8-O-PIMB6*/90 wt % of P-12-O-PIMB. The results simply indicate that the CD signal, at the maximum wavelength around 400 nm, is observed only for the homochiral SmC_SP_F and SmC_AP_A domains, but not for the racemic SmC_SP_A domains. This leads to the conclusion that the CD effect is attributed to layer chirality. A further interesting result is that even if any structural domains of the B2 phase initially form from the isotropic melt, they are evidently converted to homochiral SmC_AP_A after temperature cycling through the lower temperature B4 phase. In addition, the resulting chiral domains of the B2 phase perfectly correspond to those of the B4 phase, showing that chirality is conserved through the phase transformation between the B2 and B4 phases. This correlation of chirality is accounted for the existence of a common chiral source. We believe that the individual molecular chirality resulting from twist conformation plays such an important role.

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