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Effect of chiral dopant on a helical Sm1 phase of banana-shaped N-*n*-O-PIMB molecules†

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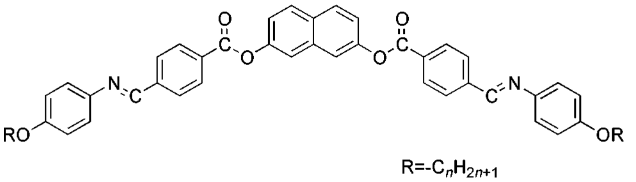
The chiral helical structures of the Sm1 phase of naphthalene-2,7-diyl bis[4-(4-alkoxyphenyliminomethyl)benzoates] (N-*n*-O-PIMB) occur with equal probability for right- and left-handed structures. In this report, we investigated the effect of chiral dopants on the formation of these structures. Two chiral homologues, N-4-O-PIMB2* with (*S*)-(+)-2-methylbutoxy tails and N-8-O-PIMB6* with (*S*)-(+)-6-methyloctyloxy tails, were synthesized for this purpose. We found that the chiral agent induces an imbalance between the two chiral domains such that the area of one of the two domains increases with chiral dopant content. The position of the chiral centre of the doping agent plays an important role in controlling the helical sense as well as the strength of the effect. A stronger effect was observed for N-4-O-PIMB2* in which the asymmetric carbon is closer to the central core. The helical pitch is not affected by the amount of chiral dopant as observed from the wavelength maximum in the CD curve. Further, it is interesting that N-4-O-PIMB2* induces preferentially left-handed helical structures, while N-8-O-PIMB6* forms right-handed structures. These unusual effects of the chiral dopant are discussed with a comparison with the conventional chiral phases such as the chiral nematic and SmC phases.

Introduction

Chirality and helicity in achiral banana-shaped molecules have generated much interest in the new sub-field of liquid crystals. Many kinds of helical phases, such as the B_4 and B_7 phases, have been found.[1–11] More interesting is the recent results on the following banana-shaped naphthalene-2,7-diyl bis[4-(4-*n*-alkoxyphenyliminomethyl)benzoates] (abbreviated as N-*n*-O-PIMB).



In the highest temperature smectic phase, Sm1, of the N-*n*-O-PIMB materials with the number of carbons *n* ranging from 8 to 16, the texture that developed from the isotropic melt was unconventional.[12,13] Although X-ray experiments indicated a liquid-like association of molecules within a layered structure similar to conventional SmA and SmC phases, in microscopic observations small fractal domains were observed which grew and then coalesced into several large domains. Very weak birefringence and a fine sandy structure without any anisotropy are characteristics of this phase. The most remarkable feature of this phase is that two distinct domains showing opposite optical rotations are detected from the polarized microscope. Further, they showed distinct circular dichroisms (CD) at around 430 nm with the opposite signs. These results suggest the natural occurrence of a helix in the Sm1 phase. Since the molecules are achiral, domains of right-handed and left-handed helices are formed with equal probabilities.

The investigation of the helical structure by techniques, such as AFM and TEM,[4,5,13] however, have not led to any further understanding of these structures. Meanwhile, alternative methods have been used to study the structure and behaviour of the helical phases. The use of chiral dopants is one reputable technique that has been employed.[14] In this work, we prepared the two chiral N-*n*-O-PIMB compounds with (*S*)-(+)-2-methylbutoxy and (*S*)-(+)-6-methyloctyloxy tail groups. N-4-O-PIMB2* and N-8-O-PIMB6* are, respectively, the mnemonics for these materials. We studied the optical microscopic textures and CD spectra of the Sm1 phases formed from these chiral materials and their mixtures with N-12-O-PIMB to clarify the influence of the chiral dopant.

Experiment

The synthesis of the chiral materials used is reported in a previous paper.[12] The optical microscopic texture of the materials was examined using a polarizing microscope (Olympus, BX50) equipped with a hot stage (Mettler FP 90 HT). DSC thermogram data were obtained using a Perkin Elmer DSC-II differential scanning calorimeter. Circular dichroic data were obtained using a JASCO, J-720WI circular dichroic spectrometer.

Results

Phase behaviour of two chiral banana-shaped molecules

We first show the phase behaviour and structure of the two chiral compounds.

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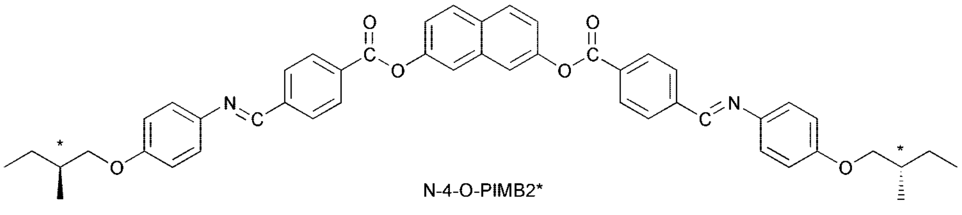
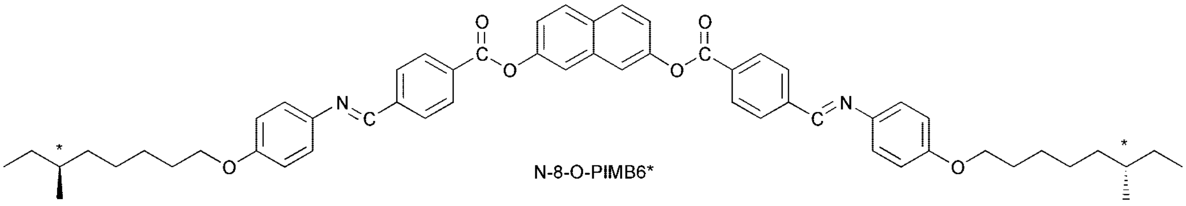


N-4-O-PIMB2*



N-8-O-PIMB6*

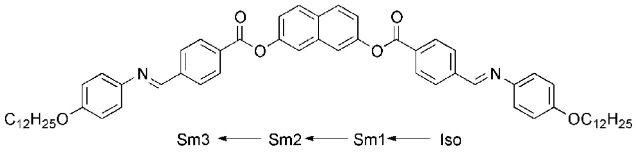
N-4-O-PIMB2*. This material does not have a liquid crystalline mesophase. Only a crystalline phase appears at 233 °C on cooling from the isotropic liquid and melts at 247 °C on heating. The absence of a liquid crystalline phases is due to the exceptionally short length of the flexible tails.

N-8-O-PIMB6*. This material exhibited an unconventional chiral Sm1 phase similar to its achiral homologous molecule, N-8-O-PIMB.[13] The Sm1 phase with a layer thickness of 40 Å was observed at 225 °C on cooling from isotropic liquid and then a Sm2 phase at 195 °C was observed. The corresponding transition temperatures on heating are 229 °C and 206 °C. The enthalpy changes are 5.4 kcal mol^{-1} and 7.8 kcal mol^{-1} respectively for the Iso–Sm1 and Sm1–Sm2 transitions.

As expected in a chiral system, a homogeneously chiral domain of the Sm1 phase is observed when it is prepared at the very slow cooling rate of 0.5 °C min^{-1} (see Fig. 1a). In curve (a) of Fig. 2, this homogeneous domain shows a large negative peak in the CD spectrum at 430 nm. The intensity and wavelength of the CD are reproducible, indicating that the right-handed helical structure is uniformly formed. On the other hand, when the phase is prepared by fast cooling, the textures of two chiral domains are observed (Figs. 1b and 1c). Annealing at any Sm1 temperature does not alter these domains at all. The relative ratio in area of the two chiral domains thus depends only on the cooling rate; a decrease in the cooling rate increases the area of the left-handed helical domain. Similar results were obtained from the CD measurement. From a comparison of curves (b) and (c) with curve (a) in Fig. 2, the intensity of circular dichroism is found to decrease with increasing cooling rate because of the compensation of the two CD effects of opposite sign. In Fig. 3, the relative intensity of the CD peak is plotted against the cooling rate. It decreases with the cooling rate and finally approaches 10% of the initial intensity observed from the homogeneous chiral domain.

Effect of chiral dopants on the phase behaviour of N-12-O-PIMB

Next we considered the effect of chiral dopants on the texture and CD spectrum exhibited by the chiral Sm1 phase. Chiral N-4-O-PIMB2* and N-8-O-PIMB6* were mixed with the following achiral material, N-12-O-PIMB.[13]



N-12-O-PIMB

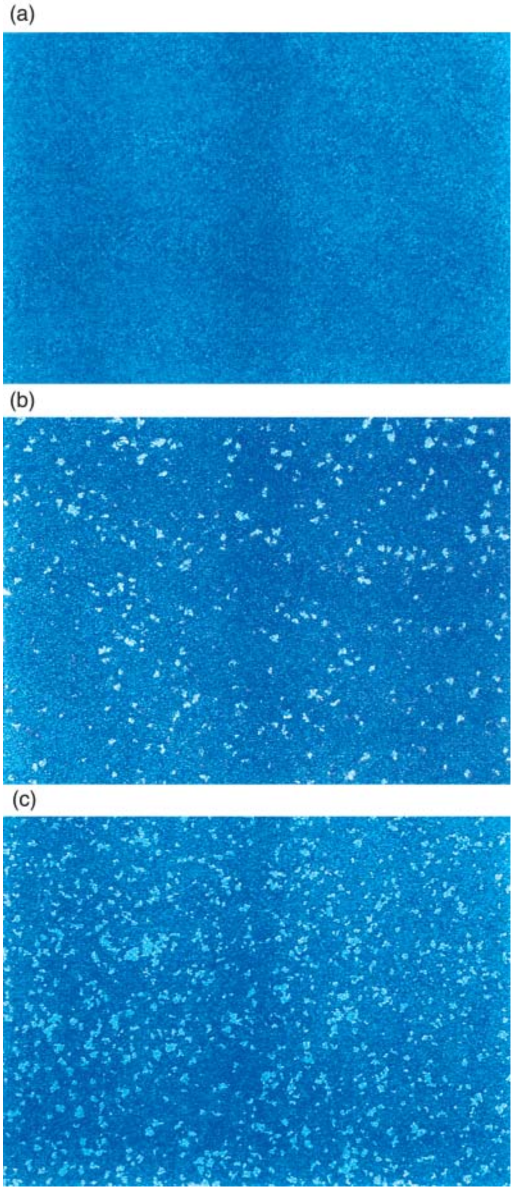


Fig. 1 The Sm1 phases of N-8-O-PIMB6*. The photomicrographs were taken on cooling from the isotropic liquid at cooling rates of (a) 0.5 °C min^{-1}, (b) 10 °C min^{-1}, and (c) 40 °C min^{-1}. The texture was observed by rotating the analyzer counterclockwise by 5° from the crossed position to distinguish the two chiral domains with opposite optical rotations.

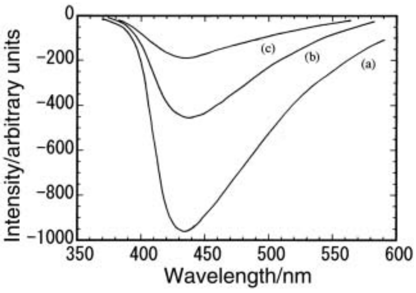


Fig. 2 CD spectra observed in the Sm1 phases. The samples were prepared by cooling from the isotropic at rates of (a) 0.5 °C min^{-1}, (b) 10 °C min^{-1}, and (c) 30 °C min^{-1}. The CD measurements were made at 210 °C in the Sm1 phases after cooling from 230 °C (10 °C higher than the Iso–Sm1 transition temperature).

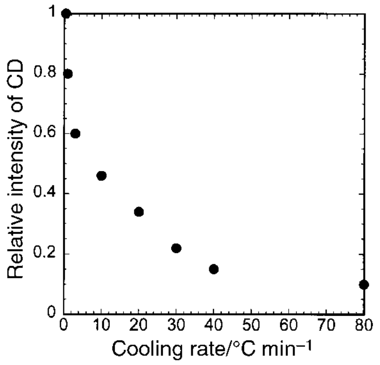


Fig. 3 Relative intensity of the CD spectra plotted against the cooling rate. The data were taken from CD spectra such as shown in Fig. 2.

All the measurements were performed in the Sm1 phase, which was prepared by cooling from the isotropic phase at a rate of 0.5 °C min^{-1}.

Mixtures with N-4-O-PIMB2*. In this system, the Sm1 phase is observed with the limited weight fractions of N-4-O-PIMB2* of 0% to 30% because of the preferential crystallization of N-4-O-PIMB2*. From the optical microscopic texture, a strong effect of the chiral dopant was observed on the helical sense of the Sm1 phase of N-12-O-PIMB. Even with the introduction of just a few percent of chiral dopant, one of the two domains increases to a great extent and the homogeneous Sm1 domain with uniform chirality was observed in mixtures with a minimum of 20% chiral content. Fig. 4a shows the CD spectra for the mixtures. As shown in the figure, all of the mixtures show a CD spectrum with a peak at around 430 nm similar to that of N-12-O-PIMB, but with a definite positive sign. The relative intensities with a positive sign averaged over 20 observations and calibrated to a standard CD intensity from the homogeneously chiral domain[13] are plotted against the chiral content in Fig. 5a. The trend is similar to that observed in the optical microscope textures; the monodomain can be obtained in the mixture only with around 20% chiral content. The positive sign of CD indicates that the left-handed helical domain is preferentially formed in this system.

Mixtures with N-8-O-PIMB6*. For the mixtures of N-12-O-PIMB and N-8-O-PIMB6*, we observed that the chiral dopant had a weaker effect. Typical photomicrographs of the observed textures are shown in Fig. 6. The imbalance between the left- and right-handed helical domains becomes remarkable with the increase in chiral content, but even with up to 90% of chiral content the texture including the two opposite optical active domains are still observed. CD measurement shows a negative sign for the CD peak for all the mixtures in Fig. 4b. Again, the relative CD intensity with a negative sign is depicted in Fig. 5b. Thus, a right-handed helical structure is preferentially formed in mixtures with N-8-O-PIMB6*.

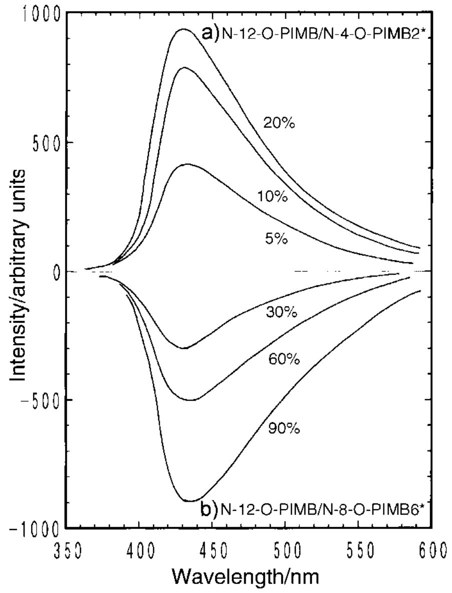


Fig. 4 CD spectra observed for the Sm1 phases in (a) the mixtures of N-O-12-PIMB and N-4-O-PIMB2* with the chiral contents of 5%, 10% and 20%, and (b) the mixtures of N-O-12-PIMB and N-8-O-PIMB6* with the chiral contents of 30%, 60% and 90%.

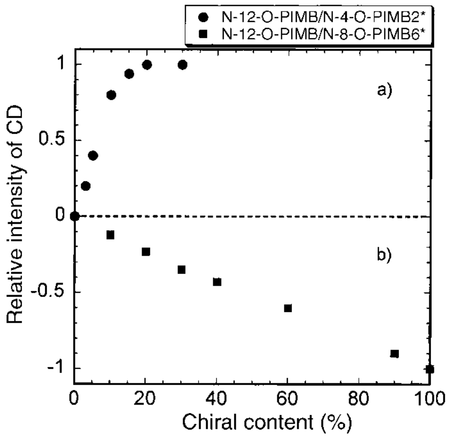


Fig. 5 Relative intensity and sign of the CD spectra, plotted against the chiral content. Shown in (a) are the mixtures of N-O-12-PIMB and N-4-O-PIMB2* and (b) the mixtures of N-O-12-PIMB and N-8-O-PIMB6*. The data were collected from the CD spectra of Fig. 4.

It is striking to note that there is no remarkable effect of the chiral dopant on the shape or maximum wavelength of CD spectra (refer to Fig. 4). In other words the doping agents do not significantly affect the helical twisting power in either system. This is significantly different from the trends observed in conventional chiral nematic and smectic phases.

Discussion

Using the geometry defined in Fig. 7 where the long axis of molecule 2 in plane 2 makes an angle φ with respect to the long axis of molecule 1 in plane 1 and considering only the nearest neighbour interaction, the potential energy $V(\varphi)$ as a function of the twist angle, φ, between the neighbouring molecules can be illustrated for the conventional liquid crystalline phases as in Fig. 8a. In achiral molecular systems, the minimum energy is located at $\varphi = 0$ and the $V(\varphi)$ curve is symmetrical. The

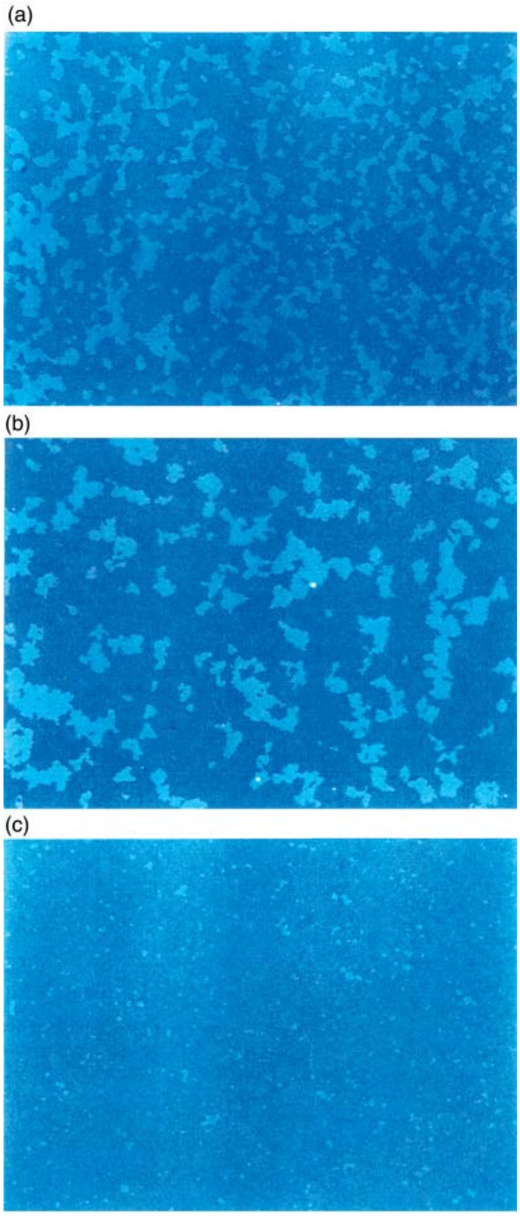


Fig. 6 Microphotographs for the Sm1 phases observed for the mixtures of N-O-12-PIMB and N-8-O-PIMB6* with (a) 20%, (b) 40%, and (c) 90% of chiral content. The textures were observed by rotating the analyzer counterclockwise by 5° from the crossed polarizer position to distinguish between the two chiral domains with opposite optical rotations.

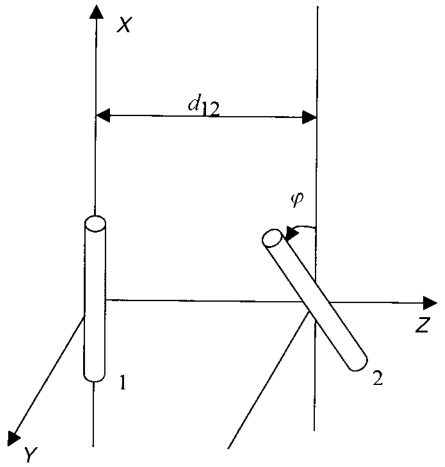


Fig. 7 Geometry of two molecules where the long axis of molecule 2 in plane 2 makes an angle φ with respect to the long axis of molecule 1 in plane 1.

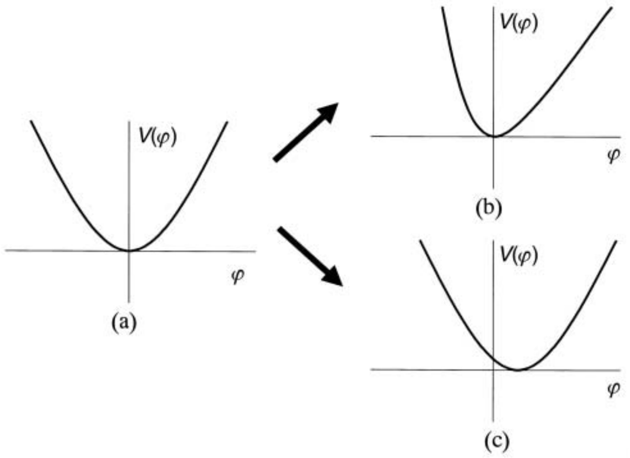


Fig. 8 Potential energy, $V(\varphi)$, as a function of twisting angle φ. In achiral system (a), and in chiral systems according to Keeting (b) and Goossens (c).

introduction of the chiral dopant changes it as illustrated in Figs. 8b and 8c. In Fig. 8b, based on Keeting's model,[15] the $V(\varphi)$ curve is asymmetrical with respect to the axis of $\varphi = 0$ while in Fig. 8c according to Goossens,[16] the $V(\varphi)$ curve is symmetrical but with respect to $\varphi \neq 0$. In both cases, the helical sense in the system is uniquely determined by the configuration of the chiral dopant and the twisting power increases continuously with increase in chiral content.

In the banana-shaped molecular system, however, the energy profile is remarkably different from those of the above-mentioned conventional systems. Since even the achiral materials exhibit the coexistence of right- and left-handed helical domains, we can draw equal energy minima for right- and left-handed helical phases. It is illustrated in Fig. 9a where the two equal energy minima appear at the positions with the same value of φ_1 but with opposite signs. Since the chiral dopant has not significantly changed the value of φ_1, it is suggested that the strong twisting power, *i.e.* the large φ_1, already exists in the achiral system. Several reasons have been proposed for this twisting power.[11,13,17,18] Thus, the incorporation of asymmetric carbon in the material causes only the imbalance of the energy minima as illustrated in Fig. 9b, which results in the imbalance of the formation of two chiral phases.

This energy profile can explain the peculiar appearance of domain structures in the Sm1 phase of N-8-O-PIMB6* prepared from the isotropic melt at different cooling rates (refer to Fig. 3). In this system, the potential energy of the right-handed helical structure is relatively lower than that of the left-handed one. The temperature dependences of the

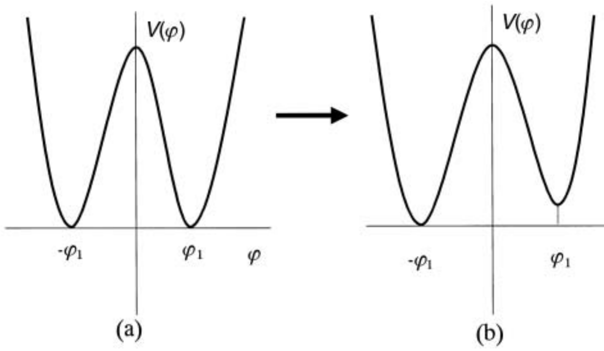


Fig. 9 Potential energy proposed in (a) the achiral and (b) chiral banana-shaped molecular systems.

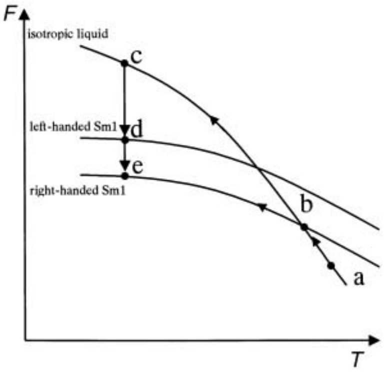


Fig. 10 Schematic diagram of the free energy as a function of temperature for the left-handed Sm1, right-handed Sm1 and isotropic liquid phases.

Gibbs energy are illustrated for the left-handed helical Sm1, the right-handed helical Sm1 and isotropic phases in Fig. 10. We can see that on slow cooling the right-handed phase is preferentially formed (refer to the process a⇒b⇒e). On fast cooling, however, the probability of the occurrence of the right-handed helical structure decreases since the isotropic phase is supercooled (the process a⇒c⇒d, e). From the data of Fig. 3, we have shown that the probability approaches 0.55 (corresponding to the relative CD intensity of 0.1) with the increase of the cooling rate. If the nucleation of the Sm1 phase takes place from the supercooled isotropic liquid with the probability according to the Boltzmann distribution, the difference in the potential energy between the left- and right-handed forms can be calculated as 0.2 kcal mol^{-1} (refer to Fig. 9b). On the other hand, from the fact that the relative ratio of the two domains never changes at all once the two domains are formed, we conclude that the energy barrier between the right- and left-handed helical structures is much higher than kT ($=1$ kcal mol^{-1}). A high energy barrier in this system may be caused by the confined packing of the banana-shaped molecules.

When we compare the two chiral systems, it is observed that N-4-O-PIMB2* has a stronger effect on the left-handed helical structure. The homogeneous left-handed helical domain was obtained in the mixture with a minimum chiral content of 20%. On the other hand, N-8-O-PIMB6* showed a weaker effect on the right-handed helical structure. Even with an increased fraction of N-8-O-PIMB6* up to 90%, we could not obtain a completely homogeneous domain. Thus, we reach the conclusion that the energy difference between the two helical structures is greater in N-4-O-PIMB2* than in N-8-O-PIMB6*. In other words, the effect of the chiral dopant decreases when the chiral centre is moved away from the central core. This is the usual trend observed in conventional chiral nematic phases,[19] but it is unusual that the helical sense is different between the two chiral systems although both of the chiral molecules have the asymmetric carbon in the absolute *S*-configuration and the branching point at an even number of carbon atoms from the core structure.

Conclusion

We have studied the effect of chiral dopants on the formation of the chiral Sm1 phase by using two chiral banana molecules, N-4-O-PIMB2* with (*S*)-(+)-2-methylbutoxy tails and N-8-O-PIMB6* with (*S*)-(+)-6-methyloctyloxy tails. The results show that doping the chiral agent induces an imbalance between the two chiral domains. An increase in the chiral content increases the relative area of one of the two chiral domains and finally results in the production of a homogeneous domain. The position of the chiral centre of the doping agent plays an important role in controlling the helical sense. A stronger effect was observed with N-4-O-PIMB2* in which the asymmetric carbon is moved near to the central core. As far as we know, from the maximum wavelength of the CD curve, the helical pitch is not affected by the chiral content. Further, we observed the unusual trend that N-4-O-PIMB2* induced preferentially the left-handed helical structure while N-8-O-PIMB6* induced the right-handed one.

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