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HELICAL STRUCTURES PRODUCED IN SOME BINARY MIXTURES BETWEEN TWIN AND MONOMERIC LIQUID CRYSTALS

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HELICAL STRUCTURES PRODUCED IN SOME BINARY MIXTURES BETWEEN TWIN AND MONOMERIC LIQUID CRYSTALS

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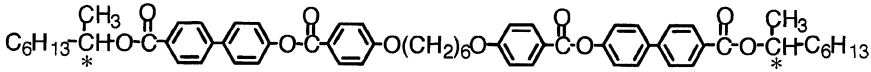
Binary mixtures between a chiral twin possessing two identical chiral moieties and the analogous parent monomeric liquid crystal were prepared, and liquid-crystalline properties investigated. TGB phase was found to be induced in some mixtures between (R, R)-twin and (R)-monomer. A mixture between (S, S)-twin and (R)-monomer showed an induced nematic phase due to the pitch compensation, however, also showed an induced TGB phase. XRD measurements showed that the intra-layer molecular distance increases by mixing the twin and monomeric compounds, which may produce a weaker layered structure, consequently, the TGB structure was stabilized.

Keywords: liquid crystal; TGB; twin; mixture; chiral; intra-layer

1. INTRODUCTION

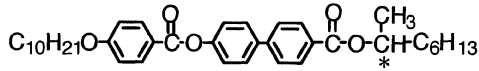
The introduction of chirality into liquid crystal phases generally produces helical superstructures. Helical structures in chiral nematic and smectic C* phases are commonly observed, however, dislocation driven twist grain boundary (TGB) structures are not always generated for chiral smectogens. So far, a few single compounds [1] and a variety of mixed systems [2] exhibiting TGB phases have been reported, however, the reason for the appearance of TGB phases has not yet been fully understood. Conversely, some binary mixtures between chiral twin and monomeric liquid crystals have been found to show induced TGB phases [3], and therefore this type

We thank Dr R.A. Lewis (Hull University) for supplying the monomeric compound, and also thank Dr M. Yoneya for MOPAC calculation.



(*R*, *R*)-**BMHBOP-6**

(*S*, *S*)-**BMHBOP-6**



(*R*)-**10B1M7**

FIGURE 1 Structures of liquid-crystalline materials.

of mixture is considered to be one of the interesting systems for studying the nature of the TGB phase.

In this study, some binary mixtures were prepared between a chiral twin (**BMHBOP-6**) and an analogous chiral monomer (**10B1M7**) [4], (see Figure 1), and the phase transition behaviour was investigated. The TGB phase was found to be induced in some binary mixtures and the structure-property correlation on the appearance, stability and structure of the TGB phase was studied.

2. EXPERIMENTAL

The chiral twin compound was obtained by the esterification between α,ω-bis-(4-carboxyphenoxy)hexane and optically active (*S*) or (*R*) 1-methylheptyl 4-hydroxybiphenyl-4′-carboxylate. Detailed preparative procedures have been reported elsewhere [5]. Phase transition behaviour was investigated by the combination of thermal optical microscopy (Nikon Optiphot-pol polarizing microscope equipped with a Mettler FP82 microfurnace and FP80 control unit), and differential scanning calorimetry (DSC) measurements using a MAC Science MTC1000S calorimeter. X-ray scattering experiments were performed by real-time diffractometer (Brucker AXS D8 Discover). The monochromatic X-ray beam (CuK α line) was generated by the 1.6 kW X-ray tube and Göbel mirror optics, where the scattered radiation was collected on a two dimensional position sensitive detector possessing 1024×1024 pixels in a $5\,\text{cm} \times 5\,\text{cm}$ beryllium window. A powder sample was introduced into a glass capillary tube (1.0 mm-diameter with 0.01 mm-thickness), which was placed into a custom-made temperature control unit (stability within $\pm$ 0.1°C). The X-ray diffraction measurement and the textural observation by the polarized light microscopy using a CCD camera on the sample in the glass capillary tube were performed simultaneously.

3. RESULTS AND DISCUSSION

Phase Transition Behaviour

Figure 2 shows a phase diagram between (*R, R*,)-**BMHBOP-6** and (*R*)-**10B1M7**. Binary mixtures containing ca. 40 ~ 55 wt% of (*R, R*)-**BMHBOP-6** exhibited an induced TGB phase. (*R, R*)-**BMHBOP-6** and (*R*)-**10B1M7** possess the identical chiral structure with the same absolute configuration, thus, the relatively strong helical structure was expected to be produced in these binary mixtures. The temperature width of the TGB phase appeared to increase with increasing the amount of (*R, R*)-**BMHBOP-6**, however, the phase separation behaviour was observed for the mixtures containing more than 60% of the twin. Therefore, properties on the mixtures richer in twins were not explored in detail.

In order to examine the effect of the strength of the helical twisting power, a binary mixture was prepared between (*S, S*)-**BMHBOP-6** and (*R*)-**10B1M7**. The absolute configuration of the chiral centre is this time opposite each other so that the compensation of the helical twisting power is more or less expected. The phase transition temperatures of the mixture between (*S, S*)-**BMHBOP-6** (50 wt%) and (*R*)-**10B1M7** (50 wt%) were found to be as follows: S_A 135.8°C TGB 139.0°C Ch 143.6°C

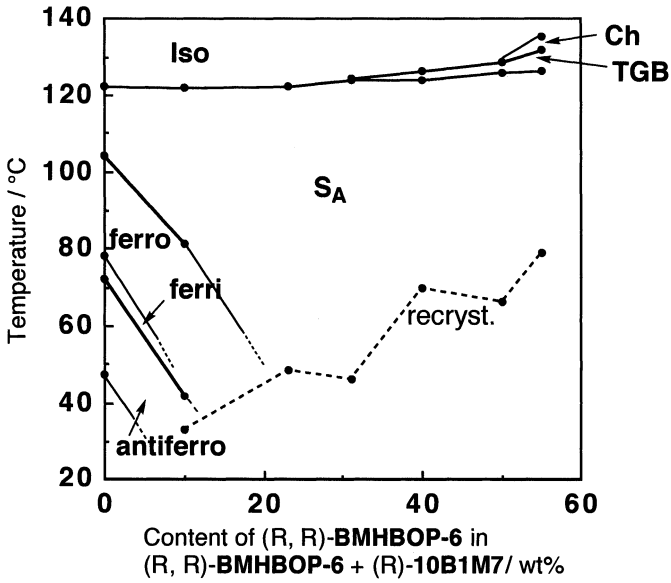


FIGURE 2 Appearance of TGB phase in mixtures between (*R, R*)-**BMHBOP-6** and (*R*)-**10B1M7**.

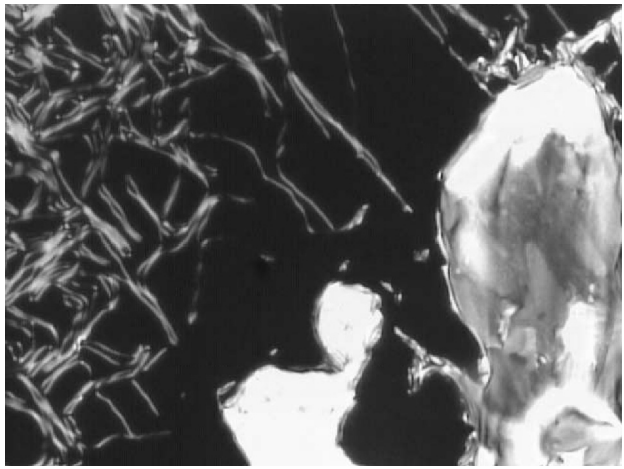


FIGURE 3 Filament and *Grandjean* textures for the TGB phase. (See COLOR PLATE I)

Iso. In the cholesteric phase, a nematic-like texture was induced at ca. 140°C. The appearance of the nematic order results from the pitch compensation in the cholesteric phase due to the opposite helical senses between (*S,S*)-**BMHBOP-6** and (*R*)-**10B1M7** as expected. Interestingly, however, this mixture also exhibited a TGB phase, even though this mixture is expected to have a relatively weak helical twisting power as indicated by the emergence of the induced nematic-like structure. Figure 3 shows the appearance of the filament texture at the S_A-TGB transition for the homeotropically aligned area and of the *Grandjean* texture for the planar alignment region, for the mixture between (*S,S*)-**BMHBOP-6** and (*R*)-**10B1M7** (50:50 wt%). These textures are typical and characteristic for the TGB phase [6]. It is also interesting that these mixtures showed the TGB phase but did not show the blue phases, which is in agreement with the study so far reported which showed that the blue phases are exhibited by the odd-membered rather than even-membered twins [7].

Differential Scanning Calorimetry Studies

Figure 4 shows DSC thermograms obtained for the mixture between (*R, R*)-**BMHBOP-6** and (*R*)-**10B1M7**. The transition from S_A to TGB phase produces a small but clear sharp DSC peak. Furthermore, a weak broad diffuse peak was observed in the isotropic region just above the clearing point, which has been reported to be characteristic for TGB materials [8]. Similarly, Figure 5 shows DSC thermograms obtained for the mixture between (*S, S*)-**BMHBOP-6** and (*R*)-**10B1M7**. DSC peaks cor-

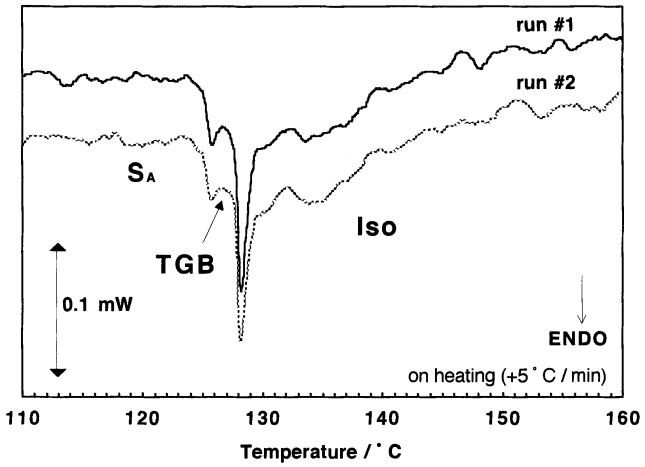


FIGURE 4 DSC thermograms of a mixture between (*R, R*)-**BMHBOP-6** and (*R*)-**10B1M7**.

responding to the S_A-TGB and Ch-Iso transitions were obtained, however, the peak corresponding to the TGB-Ch transition was found not to be clear. The peak associated with the Ch-Iso transition has a low temperature shoulder which may correspond to the TGB-Ch transition, however, this shoulder peak was not separated clearly even in measurements using a slower heating rate of +1°C/min.

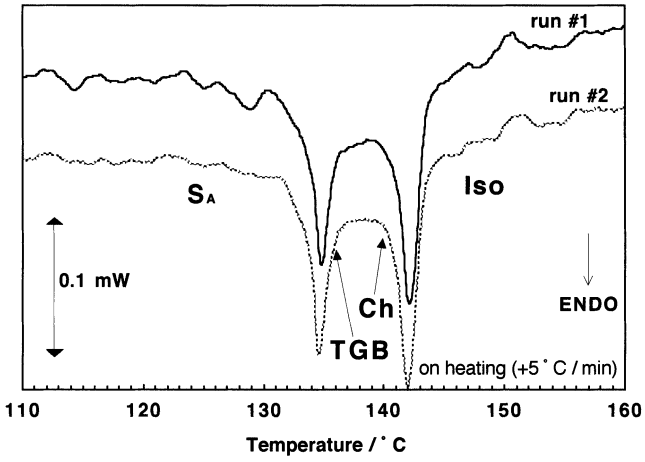


FIGURE 5 DSC thermograms of a mixture between (*S, S*)-**BMHBOP-6** and (*R*)-**10B1M7**.

X-ray Diffraction Studies

The mixture between (*R, R*)-**BMHBOP-6** and (*R*)-**10B1M7** showed a sharp peak in the small angle region of the XRD profile, corresponding to the smectic layer spacing of the S_A or TGB phase, as shown in Figure 6. The layer spacing in the S_A and TGB phases was found to be 45.6 Å.

Similarly, Figure 7 shows a small angle region of X-ray scattering of the mixture between (*S, S*)-**BMHBOP-6** and (*R*)-**10B1M7**. The S_A showed a clear sharp peak corresponding to the smectic layer spacing of 46.5 Å, however, the TGB phase this time showed a relatively broad scattering, indicating that the TGB phase produced by the mixture between (*S, S*)-**BMHBOP-6** and (*R*)-**10B1M7** possesses a weaker layered structure than that generated by the mixture between (*R, R*)-**BMHBOP-6** and (*R*)-**10B1M7**.

The molecular length of (*R*)-**10B1M7** was estimated to be 37.5 Å, based on the layer spacing obtained at the S_A phase. With respect to **BMHBOP-6**, the molecular length was estimated to be 57.2 Å by MOPAC calculation, because this twin compound shows no S_A phase. Each mixture was prepared by 50 wt% (=38 mol%) of **BMHBOP-6** and 50 wt% (=62 mol%) of **10B1M7**, and therefore, the mole-averaged molecular length of the mixture was calculated to be 45.0 Å. The obtained layer spacings of 45.6 Å and 46.5 Å for two respective mixtures are quite similar to the mole-averaged value of 45.0 Å. These results indicate that the twin and the monomeric molecules are randomly mixed and homogeneously assembled in the

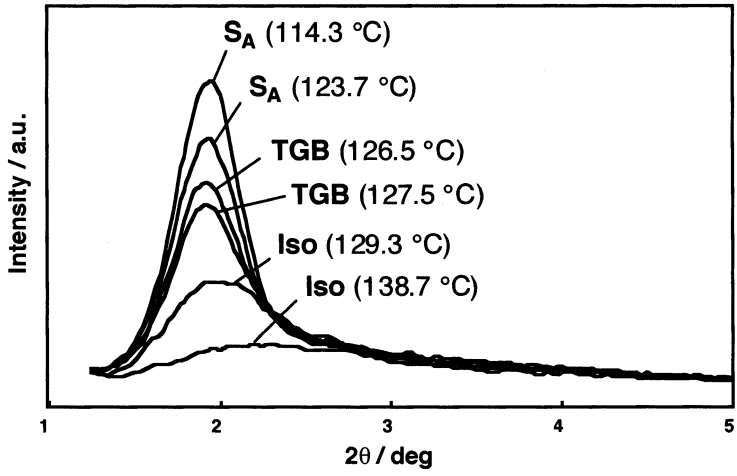


FIGURE 6 XRD profiles of a mixture between (*R, R*)-**BMHBOP-6** and (*R*)-**10B1M7**.

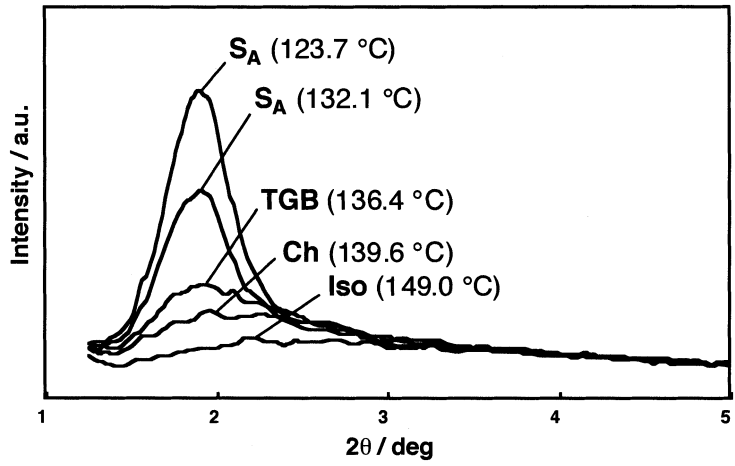


FIGURE 7 XRD profiles of a mixture between (*S, S*)-**BMHBOP-6** and (*R*)-**10B1M7**.

smectic layers of the mixtures, which may be attributable to the desire for the molecules not to make undesirable spatial vacancies or voids which are to be produced if either the twin or monomeric molecules play a dominant role in determining the smectic layer periodicity.

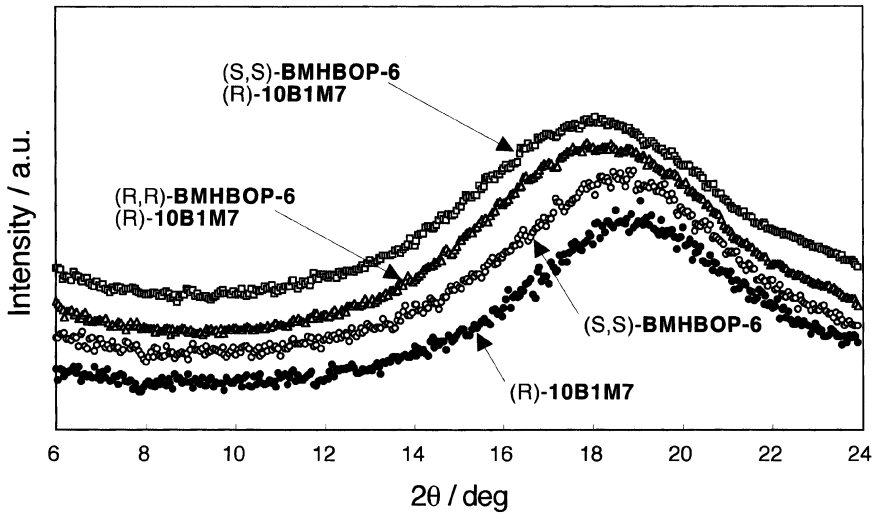


FIGURE 8 X-ray scattering profiles in a wide angle region for monomer (**10B1M7**), twin (**BMHBOP-6**), and the mixtures, obtained at 2 ~ 3 degrees below the clearing point.

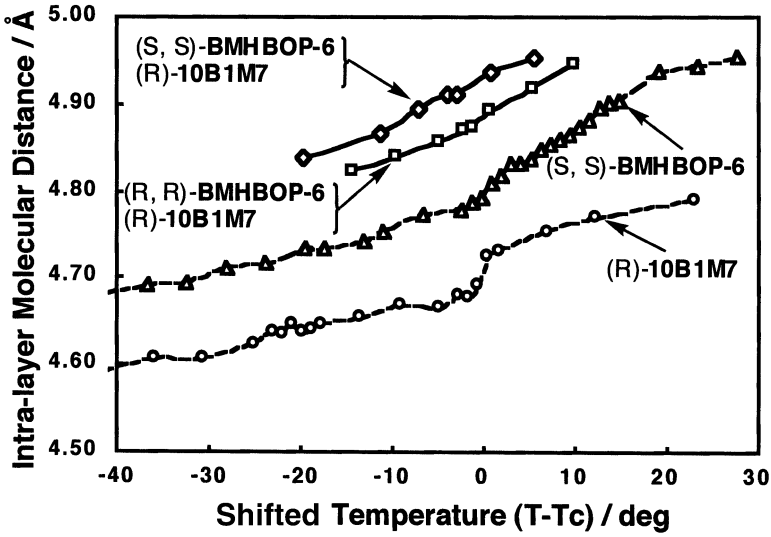


FIGURE 9 Intra-layer molecular distance of monomer (**10B1M7**), twin (**BMHBOP-6**), and the mixtures.

Unlike the layer spacing, the "intra-layer" molecular distance of the mixture, i.e., the distance between the molecules in each layer, was found not to be the average value of the intra-layer molecular distances obtained for the twin and the monomer. Figure 8 shows the broad X-ray scattering peaks observed in the wide angle region for (*R*)-**10B1M7**, (*S, S*)-**BMHBOP-6**, and the mixtures, obtained at $2 \sim 3$ degrees below the clearing point. These peaks, which are considered to correspond to the intra-layer molecular distance, showed a slight but clear low-angle shift by mixing the twin and the monomer. Figure 9 shows the intra-layer molecular distance for the twin, monomer and mixtures as a function of reduced temperature, T-Tc (Tc = the clearing point). These results clearly indicate that the intra-layer molecular distance increases by mixing the twin and the monomer. The increase of intra-layer molecular distance is expected to produce weaker packing of molecules, thus, generating a weaker smectic layer structure, which is important for the generation of the TGB phase.

4. CONCLUSIONS

A TGB phase was found to be induced in some binary mixtures between (*R, R*)-**BMHBOP-6** and the analogous parent monomer, (*R*)-**10B1M7**. A mixture between (*S, S*)-**BMHBOP-6** and (*R*)-**10B1M7** showed an

induced nematic phase due to the pitch compensation, as expected. Interestingly, however, this mixture also showed an induced TGB phase, even though the helical twisting power of the system is expected to be rather weak. XRD measurements showed that the intra-layer molecular distance increases by mixing the twin and the monomer, which may produce a weaker smectic layer structure. Thus, in this paper, the increase of the intra-layer molecular distance was reported for the first time to be important to generate the TGB phase.

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