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Chirality-induced phase transitions in some liquid crystalline binary mixtures

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Novel binary mixtures have been prepared between an optically active antiferroelectric liquid crystal, (*S*)-4-(1-methylheptyloxycarbonyl)phenyl 4′-octyloxy-biphenyl-4-carboxylate, and an optically active twin liquid crystal, (*R*)-3-methyladipic acid bis[4-(5-octyl-2-(pyrimidinyl)phenyl] ester, and the liquid crystalline properties investigated. The stability of each liquid crystal phase was found to decrease by mixing these two liquid crystalline materials. Furthermore, a phase diagram between these compounds showed a clear discontinuity in phase sequences. These results indicate that the liquid crystal phases are different in nature between these materials. The mixture consisting of the antiferroelectric material (40 per cent) and the twin material (60 per cent) shows an unusual liquid crystal phase, where the texture is similar to that reported for the twist grain boundary (TGB) phase. Related binary mixtures have been prepared between optically active or racemic materials, where the chirality of the system is expected to be altered systematically. The TGB phase was found to be induced only in the mixture between the optically active materials. Two kinds of effect on the appearance of the TGB phase, i.e. a strong helical structure induced by the optically active twin liquid crystal and a decrease of the smectic layer strength achieved by mixing between two types of liquid crystalline materials, are discussed.

1. Introduction

Chirality is currently a topical subject of study in liquid crystals [1]. A chiral twin molecule, which has the chiral centre in the central region of the molecular structure involving the bonding structure of an asymmetric carbon (see figure 1), is one of the most interesting targets for studying chirality in liquid crystals. The chiral twin molecule is expected to have a higher degree of chirality than the analogous ‘monomeric’ molecule, because the flexible spacer carrying the chiral centre is linked to two rigid cores, so that the motions of the chiral centre are more restricted, and is also expected to show special steric effects. For example, a zig–zag shape of a twin molecule has been reported to produce an antiferroelectric-like ordering [2]. Furthermore, some twin materials have been reported to exhibit a new type of ‘intercalated’ smectic phases [3], where the two rigid cores exist in adjacent layers. In the case of these intercalated smectic phases, interlayer interactions between rigid cores are expected to be increased because the cores are joined directly by the spacer. The interlayer interaction has been

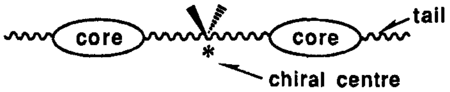

Figure 1. A schematic representation of a chiral twin molecule.

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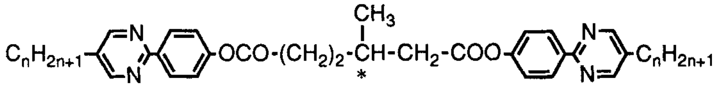
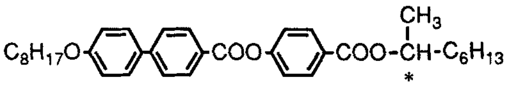


MAB-n-PYP

Figure 2. General structure of chiral twin materials.



MHPOBC

Figure 3. Structure of an antiferroelectric material, **MHPOBC**.

found, in solid state ^{13}C NMR studies reported by Yoshizawa *et al.* [4] to have a significant effect on some properties of smectic phases; thus, new effects can be seen in the smectic phases of twin materials.

So far, homologous series of twin liquid crystals, (*R*)-3-methyladipic acid bis[4-(5-alkyl-2-(pyrimidinyl)phenyl] esters (**MAB-n-PYP**) (see figure 2), have been prepared and their physical properties investigated and compared to those of analogous 'monomeric' materials [5]. Pitch measurements revealed that the twin materials induce stronger helical structures in both cholesteric (Ch) and chiral smectic C (S_C^*) phases than the analogous 'monomeric' materials. Furthermore, the strong desire for the twin materials to form a helical ordering in smectic phases was found to produce unusual smectic phases for which the texture is similar to that reported for the twist grain boundary (TGB) phases [6], in contact studies with an achiral liquid crystalline compound [5].

In the present studies, some novel mixtures have been prepared between a twin material, (*R*)-3-methyladipic acid bis[4-(5-octyl-2-(pyrimidinyl)phenyl ester (**MAB-8-PYP**) (see figure 2) and an antiferroelectric material, (*S*)-4-(1-methylheptyloxycarbonyl)phenyl 4′-octyloxybiphenyl-4-carboxylate (**MHPOBC**) [7] (see figure 3), and the liquid crystalline properties investigated. In antiferroelectric phases, molecules in neighbouring smectic layers have been proposed to tilt in opposite directions [7], whereas, in normal ferroelectric phases, the molecules are considered to tilt in the same direction. In order to create the zig–zag molecular ordering in the antiferroelectric phases, a strong layer structure, i.e. a clear periodicity of the density wave, must be produced in the system [8], or the molecules will prefer to tilt in the same direction. The clear periodicity of the density wave in the antiferroelectric phase may be broken by adding twin molecules into the system, because the twin material has a different molecular structure from the conventional molecular structure for an antiferroelectric compound. Thus, the strength of the smectic layers might be expected to be changed. Furthermore, the optically active antiferroelectric material (**MHPOBC**) is expected to have high degree of chirality, because the stability of the antiferroelectric phase of **MHPOBC** has been reported to decrease as the optical purity of **MHPOBC** decreases [9]. The chiral twin material (**MAB-8-PYP**) has also been found to have high degree of chirality [5], so that new effects may be expected to be produced by mixing these two highly chiral materials.

2. Experimental

2.1. *General synthetic procedures*

The starting materials for the compounds presented in this paper are (*R*)-(+)-3-methyladipic acid (Aldrich Chemie), (*S*)-4-(1-methylheptyloxycarbonyl)phenol (Arakawa Chemical Industries, Ltd, $[\alpha]D^{25}+37{\cdot}6°$ (c 2, $CHCl_3$)), (±)-2-octanol (Kanto Chemical Co., Ltd), 4-hydroxybenzoic acid (Kanto Chemical Co., Ltd), 4′-octyloxybiphenyl-4-carboxylic acid (Teikoku Chemical Industry Co., Ltd), 5-octyl-2-(4-hydroxyphenyl)pyrimidine (Midori Kagaku Co., Ltd), adipic acid (Tokyo Chemical Industry Co., Ltd) and pimelic acid (Tokyo Chemical Industry Co., Ltd).

The preparations and the purities of (*R*)-**MAB-8-PYP** and (±)-**MAB-8-PYP** have already been reported [5]. (*R*)-**MHPOBC** or (±)-**MHPOBC** was prepared by the esterification of 4′-octyloxybiphenyl-4-carboxylic acid with (*S*)-4-(1-methylheptyloxycarbonyl)phenol or (±)-4-(1-methylheptyloxycarbonyl)phenol. (±)-4-(1-Methylheptyloxycarbonyl)phenol was prepared starting from 4-hydroxybenzoic acid. 4-Hydroxybenzoic acid was protected with methyl chloroformate at 0°C to give 4-methoxycarbonoyloxybenzoic acid. This benzoic acid was esterified with (±)-2-octanol in the presence of triphenylphosphine and diethyl azodicarboxylate (DEAD) [10]. The carbonate ester was then converted to the corresponding phenolic ester by removal of the carbonate protecting group which was achieved by stirring at room temperature in ethanolic ammonia solution [11]. Adipic acid bis[4-(5-octyl-2-pyrimidinyl)phenyl] ester (**AAB-8-PYP**) or pimelic acid bis[4-(5-octyl-2-pyrimidinyl)phenyl] ester (**PAB-8-PYP**) was prepared by the esterification of 5-octyl-2-(4-hydroxyphenyl)-pyrimidine with adipic acid or pimelic acid. All of the final compounds were obtained by esterification [12] using *N,N*-dicyclohexylcarbodiimide (DCC), 4-dimethylamino-pyridine (DMAP) as catalyst, and dichloromethane as solvent.

2.2. *Spectroscopic analysis*

The final esters were purified by column chromatography over Kiesel gel 60 (70–230 mesh) silica gel (Merck, Darmstadt) using dichloromethane or dichloromethane ethyl acetate mixture as the eluent and then recrystallized from ethanol ethyl acetate mixture. The purities of the final products were checked by thin layer chromatography (Kiesel gel 60 F_{254}). Detection of products was achieved by UV irradiation ($\lambda = 254$ and 365 nm). The purities of all of the final compounds were also checked by reversed-phase high performance liquid chromatography, using a Waters 201 GPC-ALC. Reversed-phase chromatography was carried out over octadecylsiloxane (7 μm particle size, $25\times0{\cdot}4$ cm, ODS Lichrosorb RP-18 column) using (4/96) water methanol mixture as the eluent. Detection of the eluting products was achieved using a Hewlett–Packard 1040A ($\lambda = 260$ and 300 nm). The structures of the final products were elucidated by a variety of spectral methods. Infrared (IR) spectroscopy was carried out using a JEOL JIR-100 FT infrared spectrophotometer, proton nuclear magnetic resonance (^{1}H NMR) spectroscopy was carried out using a HITACHI R-3000 FT nuclear magnetic resonance spectrometer. Mass spectrometry was carried out using a JMS-DX 300 automated DI/MS. The analyses of the structures of the products and intermediates by spectroscopic methods were found to be consistent with the predicted structures.

2.2.1. *(S)-4-(1-methylheptyloxycarbonyl)phenyl 4′-octyloxybiphenyl-4-carboxylate (**MHPOBC**)*

^{1}H NMR (300 MHz, solvent $CDCl_3$, standard TMS) δ 8·22 (2 H, d) 8·12 (2 H, d), 7·69 (2 H, d), 7·59 (2 H, d) 7·30 (2 H, d) 6·99 (2 H, d), 5·16 (1 H, q) 4·01 (2 H, t), 1·29–1·84 (25 H, m), 0·89 (3 H, t); IR (KBr) 2940, 2850, 1730, 1715, 1600 cm^{-1}. *m/z*: 558 [M$^+$], 429. Purity: 100 per cent.

2.2.2. *(±)-4-(1-methylheptyloxycarbonyl)phenyl 4′-octyloxybiphenyl-4-carboxylate (±)-(**MHPOBC**)*

^{1}H NMR (300 MHz, solvent $CDCl_3$, standard TMS) δ 8·22 (2 H, d) 8·12 (2 H, d), 7·69 (2 H, d), 7·59 (2 H, d) 7·30 (2 H, d) 7·00 (2 H, d), 5·16 (1 H, q) 4·01 (2 H, t), 1·29–1·84 (25 H, m), 0·89 (3 H, t) 0·88 (3 H, t); IR (KBr) 2940, 2850, 1730, 1715, 1600 cm^{-1}. *m/z*: 558 [M$^+$], 429. Purity: 96·1 per cent.

2.2.3. *Adipic acid bis[4-(5-octyl-2-pyrimidinyl)phenyl]ester (**AAB-8-PYP**)*

^{1}H NMR (300 MHz, solvent $CDCl_3$, standard TMS) δ 8·60 (4 H, s) 8·44 (4 H, d), 7·21 (4 H, d), 2·68 (4 H, t) 2·62 (4 H, t) 1·92 (4 H, t), 1·60–1·68 (4 H, m) 1·27–1·33 (20 H, m), 0·88 (6 H, t); IR (KBr) 2950, 2920, 2850, 1755, 1430, 1200 cm^{-1}. *m/z*: 678 [M$^+$], 395, 284. Purity: 99·9 per cent.

2.2.4. *Pimelic acid bis[4-(5-octyl-2-pyrimidinyl)phenyl]ester (**PAB-8-PYP**)*

^{1}H NMR (300 MHz, solvent $CDCl_3$, standard TMS) δ 8·59 (4 H, s) 8·43 (4 H, d), 7·20 (4 H, d), 2·63 (4 H, t) 2·61 (4 H, t) 1·81–1·94 (4 H, m), 1·60–1·67 (4 H, m) 1·27–1·32 (22 H, m), 0·88 (6 H, t); IR (KBr) 2930, 2850, 1760, 1430, 1200 cm^{-1}. *m/z*: 692 [M$^+$], 409, 284. Purity: 100 per cent.

2.3. *Liquid crystalline properties*

The initial phase assignments and corresponding transition temperatures were determined by thermal optical microscopy using a Nikon Optiphoto POL polarizing microscope equipped with a Mettler FP 82 microfurnace and FP 80 control unit for the samples contained in a cell. The cells were made with approximately 3 μm spacings where the inner surfaces had been coated with a polyimide-(PI)-aligning agent and unidirectionally buffed (E.H.C., Co. Ltd). The heating and cooling rates were 2°C min^{-1}. The photomicrographs were taken using a camera (Nikon FX-35DX) and control unit (Nikon HFX-DX) in conjunction with the microscope and Mettler hot stage and controller. Temperatures and enthalpies of transitions were investigated by differential scanning calorimetry (DSC) using a Seiko DSC 200 calorimeter. The materials were studied at a scanning rate of 2°C min^{-1}, for both heating and cooling cycles, after being encapsulated in aluminium pans. Miscibility phase diagrams for binary mixtures were constructed by determining the transition temperatures of individual mixtures of the two components. The mixtures were prepared by weighing each component in a small sample tube and mixing the two components while they were in their isotropic liquid states. The transition temperatures for each individual mixture were then determined by thermal polarized light microscopy.

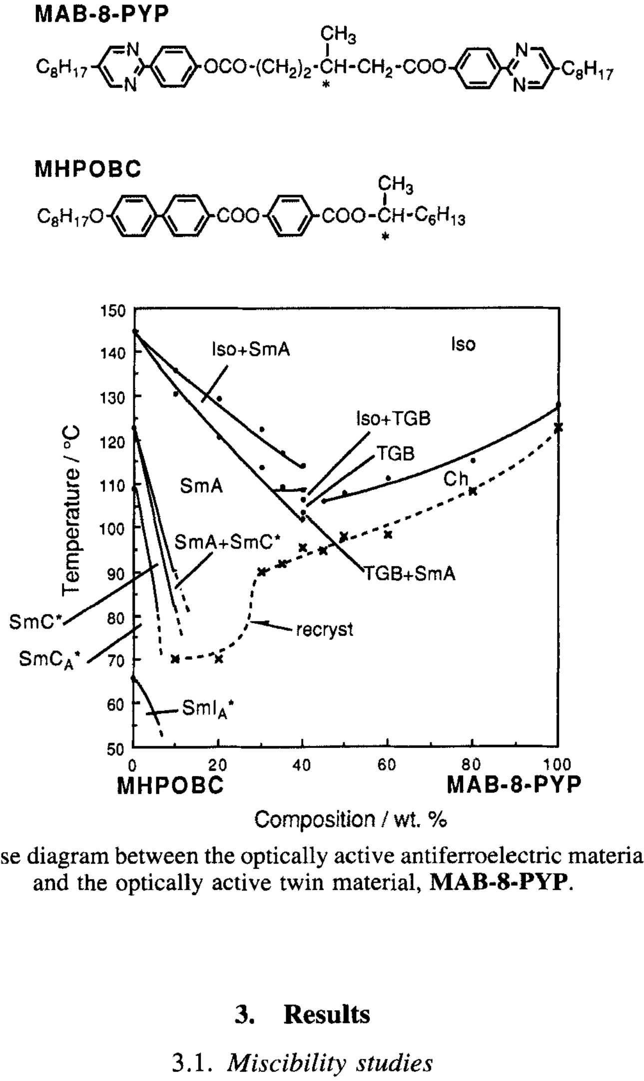
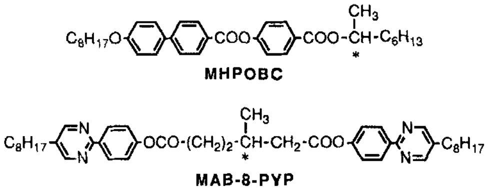


Figure 4. A phase diagram between the optically active antiferroelectric material, **MHPOBC**, and the optically active twin material, **MAB-8-PYP**.

3. Results

3.1. *Miscibility studies*

Mixtures were prepared between the optically active antiferroelectric material, **MHPOBC**, and the optically active twin material, **MAB-8-PYP**. Figure 4 shows a phase diagram between these materials. The stability of each liquid crystalline phase was found to decrease by mixing these materials, i.e. the isotropic to liquid crystalline phase transition temperatures decreased. Furthermore, the phase diagram shows a clear discontinuity in phase sequences, i.e. mixtures containing 45 per cent or more of the twin material show the cholesteric phase, whereas mixtures containing 40 per cent or less of the twin material show only smectic phases. These results indicate that the liquid crystalline phases are different in nature between the two kinds of material studied here. The mixture consisting of **MHPOBC** (60 per cent) and **MAB-8-PYP** (40 per cent) shows an unusual liquid crystalline phase of which the texture is similar to that reported for the twist grain boundary (TGB) phase [6], which will be reported in the next section in detail. With respect to the antiferroelectric and ferroelectric chiral S_C phases for **MHPOBC**, the stability of both phases substantially decreased by the addition of a small amount (10 per cent) of **MAB-8-PYP**.



Binary Mixtures	MHPOBC (60 wt%)	MAB-8-PYP (40 wt%)
A	Racemic	Racemic
B	Racemic	**Optically active**
C	**Optically active**	Racemic
D	**Optically active**	**Optically active**

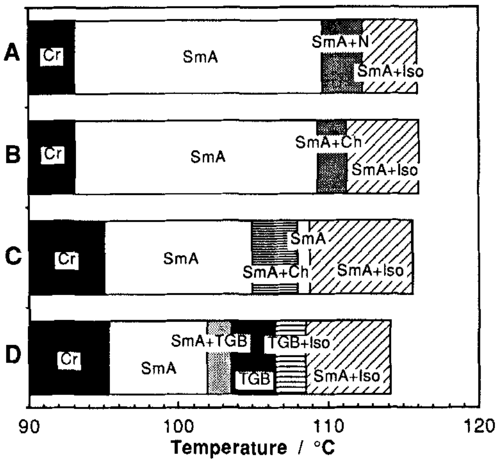


Figure 5. Transition temperatures for mixtures **A**–**D**.

3.2. *Binary mixtures between optically active or racemic **MHPOBC** and **MAB-8-PYP***

In order to investigate the effect of chirality on the appearance of the unusual liquid crystalline phase, which was reported for the mixture consisting of optically active **MHPOBC** (60 per cent) and optically active **MAB-8-PYP** (40 per cent) in the previous section, binary mixtures between the optically active or racemic materials were prepared (mixtures **A**–**D**, see figure 5). For example, mixture **B** consists of racemic **MHPOBC** and optically active **MAB-8-PYP**. Note that the mixing ratio between the two components is constant for all of the mixtures, i.e. **MHPOBC/MAB-8-PYP** = 60/40 by weight. The degree of chirality of these four binary mixtures is expected to be altered systematically. Figure 5 shows transition temperatures and phase sequences obtained for four binary mixtures. Coexistence behaviours of different phases were observed for all of the mixtures. The coexistence may be due to a kind of phase separation which can occur when two different types of liquid crystalline material are mixed [13]. The stability of the smectic phase, i.e. the highest temperature for each binary mixture where the S_A phase can coexist with the isotropic liquid phase, decreases in the order of mixtures **A**, **B**, **C** and **D**, indicating that the chirality of the system increases in this order, because the chirality has been predicted [14] and found [15, 16] to decrease the stability of smectic phases.

Mixtures **A** and **B** show similar phase transitions, indicating that, when **MHPOBC** is the racemic modification, the chirality of the twin material, **MAB-8-PYP**, has little effect on the appearance of the new smectic phases. Figures 6(*a*)–(*c*) show the temperature dependent textural changes for mixture **B** contained in a cell (3 μm spacing) and using polarized light microscopy. Figure 6 (*a*) shows the coexistence of the S_A phase (showing birefringence) with the isotropic liquid phase (showing extinction). With decreasing temperature, the isotropic liquid phase changes into the cholesteric phase so that the S_A phase coexists with the cholesteric phase (see figure 6 (*b*)). On further cooling, a texture for the normal S_A phase was obtained (figure 6 (*c*)).

Mixture **C** shows a completely different phase sequence (see figure 5). The most interesting point for the phase sequence is that the S_A phase is separated into two temperature regions by the existence of a very narrow cholesteric phase, i.e. a S_A–Ch–S_A phase sequence was obtained. This is a sort of re-entrant phenomenon [17] and those two S_A phases are expected to have different natures. Figures 7 (*a*)–(*d*) show textural changes for mixture **C** placed in a 3 μm thick cell. Figure 7 (*a*) is a texture of the first S_A phase on cooling. With decreasing temperature, the first S_A phase changes into the Ch phase (see figure 7 (*b*)) and, at the same time, the second S_A phase appears. The second S_A phase coexists with the Ch phase (see figure 7 (*c*)). Figure 7 (*d*) shows the texture of the second S_A phase. It should be noted that the layer direction of the second S_A phase is different from that of the first S_A phase (compare textures between figures 7 (*a*) and (*d*). This result indicates a rotation of molecular directions in the Ch phase existing between two S_A phases. Transition temperatures and the phase sequence of mixture **D** are quite different from that of mixture **C** (see figure 5), indicating that, when **MHPOBC** is optically active, the chirality of the twin material, **MAB-8-PYP**, has significant effect on the appearance of the new smectic phase. Mixture **D** also shows two kinds of S_A phase, but this time, the TGB phase is inserted between two S_A phases. Thus, a S_A–TGB–S_A phase sequence was obtained. Figures 8 (*a*)–(*e*) show the textural changes for mixture **D** contained in a 3 μm thick cell. Figure 8 (*a*) shows the coexistence of the first S_A phase (showing birefringence) with the isotropic liquid phase (showing extinction). With decreasing temperature, the first S_A phase changes into the TGB phase so that the TGB phase coexists with isotropic liquid phase (see figures 8 (*b*) and (*c*)). Figure 8 (*d*) shows a texture of the TGB phase. The texture is similar to the *Grandjean* texture [18] for the Ch phase; however, the characteristic filament-like texture was observed for the sample sandwiched between a microscope slide and a glass cover (see figure 9). This texture is not typical for the Ch phase, but is similar to that reported for the TGB phase [6]. Figure 8 (*e*) shows the second S_A phase which exists below the TGB phase. The alignment is not good because of the twist ordering for the molecules in the TGB phase. Figure 10 shows DSC thermograms for mixtures **A–D** on cooling cycles. Mixture **A** shows two peaks near the isotropic to liquid crystalline transition. The peak (1) in figure 10 may correspond to the gradual transition from the isotropic liquid to the S_A phase, and the peak (2) to the transition from the isotropic liquid to the nematic phase. In the case of mixture **D**, the peaks became broad, indicating the existence of the additional phase transitions. This result also supports the appearance of the TGB phase for mixture **D**.

3.3. *Binary mixtures between MHPOBC and a non-chiral twin material*

It is possible that optically active **MAB-8-PYP** exhibits two kinds of effects in the binary mixtures with antiferroelectric **MHPOBC**; one is a strong helical macrostructure and the other the steric effect. The steric effect may be mainly produced by the 'bent' shape of a twin molecule. Simple non-chiral twin materials are suitable for investigation of the effect of molecular shape, i.e. the effect of a degree of 'bentness'. The degree of 'bentness' of non-chiral twin materials has been considered to be related to several

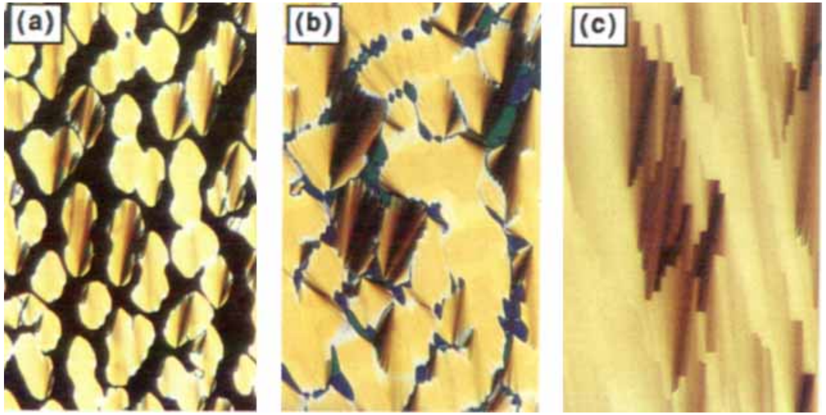


Figure 6. Photomicrographs of the liquid crystal phases of mixture **B** (racemic **MHPOBC** + optically active **MAB-8-PYP** (× 100). (*a*) Coexistence of the S_A phase with the isotropic liquid phase; (*b*) coexistence of the S_A phase with the cholesteric phase; (*c*) the S_A phase.

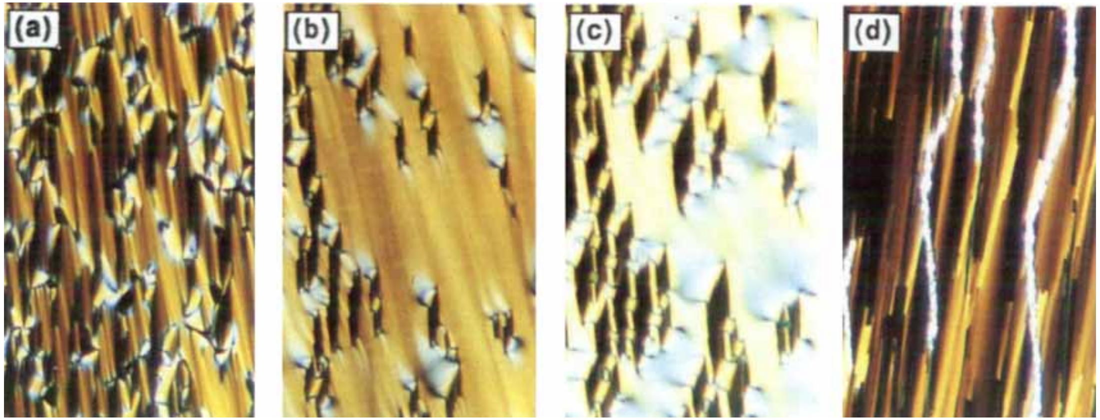


Figure 7. Photomicrographs of the liquid crystal phases of mixture **C** (optically active **MHPOBC** + racemic **MAB-8-PYP** (× 100).(*a*) The first S_A phase on cooling; (*b*) the cholesteric phase with the second S_A phase; (*c*) the cholesteric phase with the second S_A phase; (*d*) the lower S_A phase on cooling.

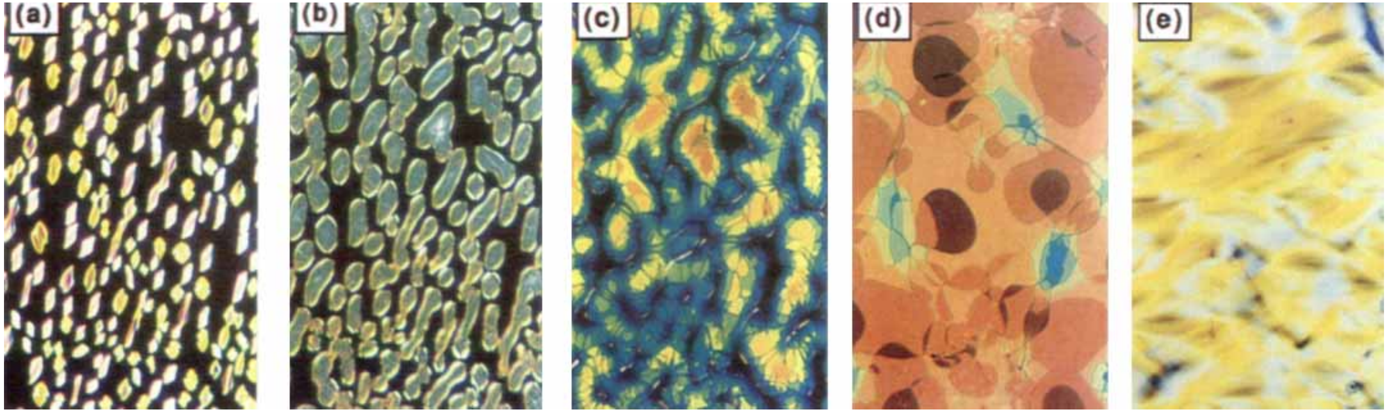


Figure 8. Photomicrographs of the liquid crystal phases of mixture **D** (optically active **MHPOBC** + optically active **MAB-8-PYP**) (× 100). (*a*) Coexistence of the first S_A phase on cooling with the isotropic liquid phase; (*b*) coexistence of the TGB phase with the isotropic liquid phase; (*c*) coexistence of the TGB phase with the isotropic liquid phase; (*d*) the TGB phase; (*e*) the second S_A phase on cooling.

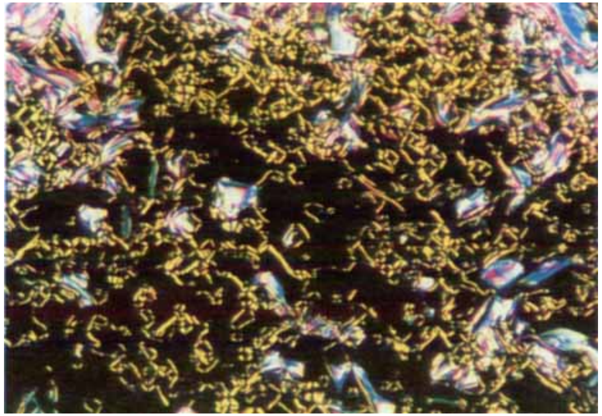


Figure 9. A photomicrograph of the liquid crystal phase of mixture **D** (optically active **MHPOBC** + optically active **MAB-8-PYP**) showing a characteristic filament-like texture (× 100). The sample was placed between a microscope slide and a glass cover.

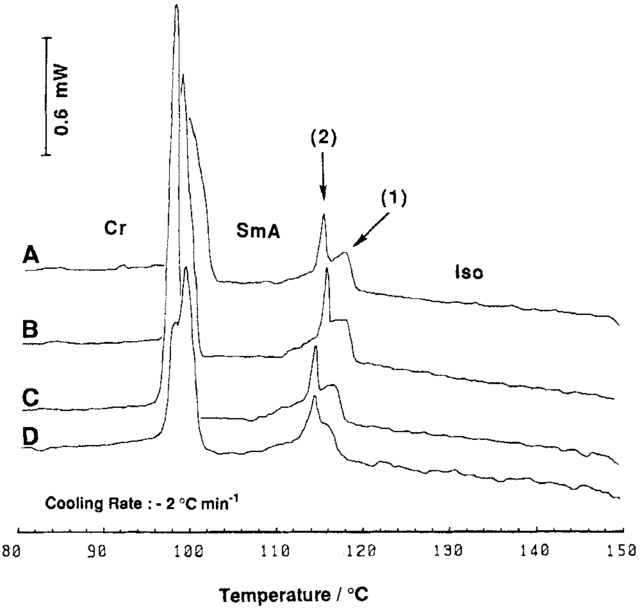
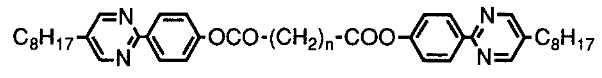


Figure 10. DSC curves for mixtures **A–D** shown for cooling at a scanning rate of 2°C min^{-1}.

factors [19, 20]: the parity of the number of atoms of the central flexible spacer (i.e. odd or even), the conformation of the alkyl chain of the central part (i.e. *trans* or *gauche*) and the type of linking group joining the core part to the central spacer.

Two related non-chiral twin compounds, adipic acid bis[4-(5-octyl-2-pyrimidinyl)-phenyl] ester (**AAB-8-PYP**) and pimelic acid bis[4-(5-octyl-2-pyrimidinyl)phenyl] ester (**PAB-8-PYP**) (see figure 11) were chosen as simple non-chiral twin materials for investigation. Similar compounds have been reported by Krone and Ringsdorf [21]. These compounds have similar structures to the chiral twin material, **MAB-8-PYP**, but do not have an asymmetric carbon in the central spacer. **AAB-8-PYP** shows a nematic phase, whereas **PAB-8-PYP** shows no liquid crystalline phases. Transition temperatures measured on cooling are also shown in figure 11.

Figure 12 shows DSC thermograms for the chiral twin material, **MAB-8-PYP**, and the non-chiral twin material, **AAB-8-PYP**, on cooling cycles. The chiral twin material, **MAB-8-PYP**, shows two peaks corresponding to the I–Ch phase transition ($\Delta H = 7{\cdot}2\,\mathrm{kJ\,mol^{-1}}$) and recrystallization ($\Delta H = 33{\cdot}6\,\mathrm{kJ\,mol^{-1}}$). Similarly, the non-chiral twin compound **AAB-8-PYP** shows two DSC peaks corresponding to the I–N phase transition ($\Delta H = 8{\cdot}3\,\mathrm{kJ\,mol^{-1}}$) and recrystallization ($\Delta H = 41{\cdot}0\,\mathrm{kJ\,mol^{-1}}$). Enthalpies for the transitions from isotropic liquid to liquid crystalline phases were found to be similar for these materials. Next, binary mixtures, mixture **E** (**MHPOBC** (60 per cent) + **AAB-8-PYP** (40 per cent)) and mixture **F** (**MHPOBC** (60 per cent) + **PAB-8-PYP** (40 per cent)) were prepared and their liquid crystalline properties investigated. The ratio between **MHPOBC** and non-chiral twin material is the same as that of mixtures **A–D**, i.e. **MHPOBC**/twin material = 60/40. Mixture **E** shows Ch and S_A phases, whereas mixture **F** shows only the S_A phase (see figure 13). Furthermore, mixture **F** shows the coexistence of the S_A phase with the isotropic liquid phase, which is similar to that observed for mixtures **A–D**. The stability of the liquid crystalline phases for mixture **F** is substantially lower than that for mixture **E**.



AAB-8-PYP (n = 4) : Isotropic liquid 157 °C Nematic 153 °C Cr
PAB-8-PYP (n = 5) : Isotropic liquid 119 °C Cr

Figure 11. Structures of non-chiral twin materials, **AAB-8-PYP** and **PAB-8-PYP**.

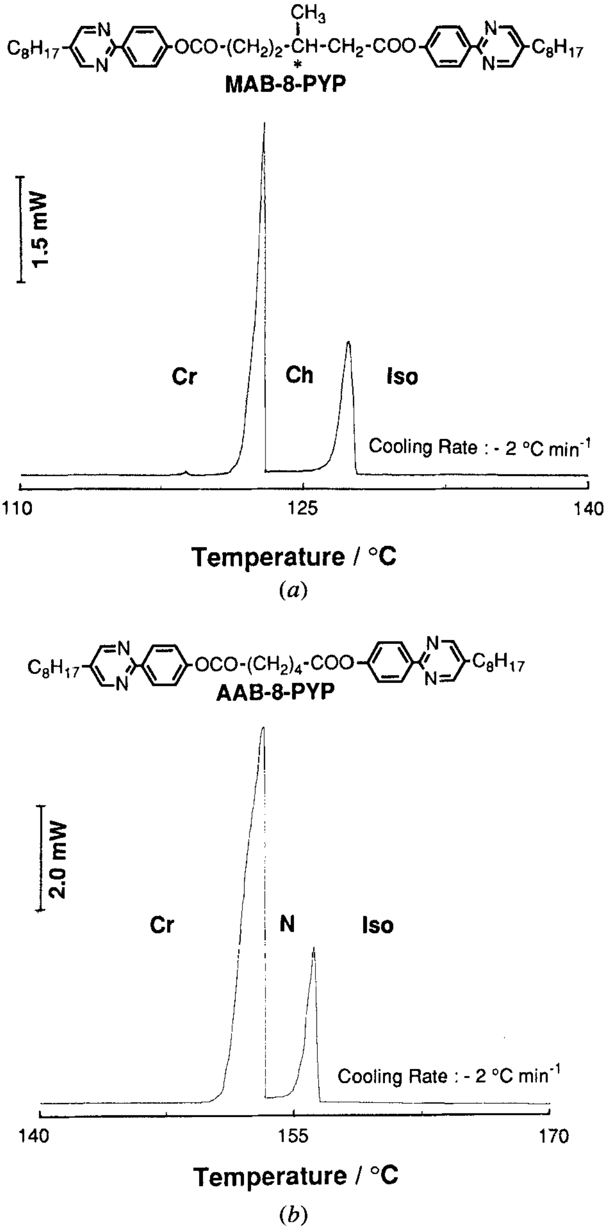
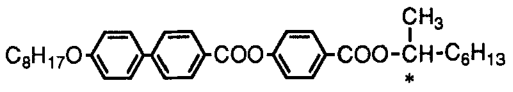
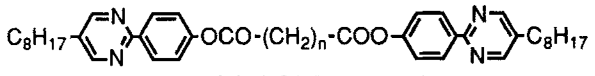


Figure 12. DSC curves for the chiral compound, **MAB-8-PYP**, and the analogous non-chiral compound, **AAB-8-PYP**, shown for cooling at a scanning rate of 2°C min^{-1}.



MHPOBC



AAB-8-PYP (n = 4)
PAB-8-PYP (n = 5)

Mixture E : **MHPOBC** (60%) + **AAB-8-PYP** (40%)
Mixture F : **MHPOBC** (60%) + **PAB-8-PYP** (40%)

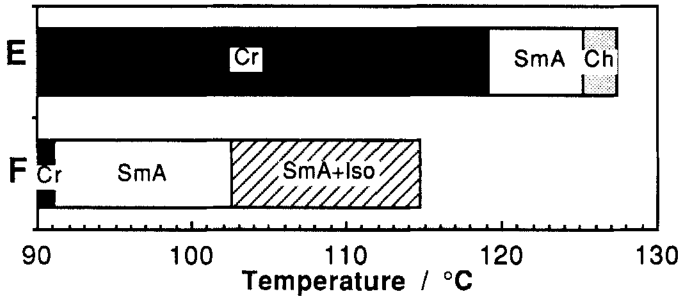


Figure 13. Transition temperatures for mixtures **E** and **F**.

4. Discussion

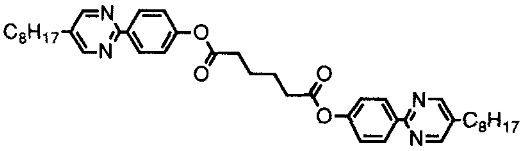
The optically active antiferroelectric material, **MHPOBC**, is considered to have a high degree of chirality [9] and a strong layer structure [8]. The strong layer structure is not suitable for producing TGB phase because the generation of the TGB phase relies on competition between layer strength and chirality [15, 16]. The layer structure of mixture **D** (optically active **MHPOBC** (60 per cent + optically active **MAB-8-PYP** (40 per cent)) is possibly weaker with respect to that of optically active **MHPOBC** itself. This is because the phase diagram between **MHPOBC** and **MAB-8-PYP** (see figure 4) shows a clear discontinuity in phase sequence, where the **MHPOBC**-rich region shows only smectic phases, whereas the **MAB-8-PYP**-rich region shows the cholesteric phase. Since the composition of mixture **D** is just on the border of these two regions, the S_A phase of mixture **D** is expected to experience fluctuations from the Ch phase. Preparation of mixtures with twin materials may be a possible new way forward for creating a fluctuating S_A phase, which has been found to be favourable for the appearance of the TGB phase [15]. It should be noted that the TGB phase for mixture **D** exists between two S_A phases, i.e. a phase sequence S_A–TGB–S_A. The difference in nature between these S_A phases is not clear at present; however, it may be expected that some kind of re-ordering of molecules occurs at the transition from one S_A to another. If this re-ordering happens, the smectic layer strength may decrease round the S_A–S_A transition which again provides conditions suitable for the appearance of the TGB phase. Two kinds of S_A phases were also observed for mixture **C** (optically active **MHPOBC** (60 per cent + racemic **MAB-8-PYC** (40 per cent)), where the phase sequence S_A–Ch–S_A was obtained. This result indicates that the smectic layer structure becomes weak between two S_A phases so that the Ch phase appears. In order to make further investigations of the nature of these S_A phases, detailed X-ray diffraction studies will be required.

The decrease of the layer strength for the mixtures may result from the difference in the liquid crystalline natures between **MHPOBC** and **MAB-8-PYP**. This difference may also induce a phase separation so that coexistence of the S_A and isotropic liquid phases was observed. Possible reasons for the phase separation are inhomogeneous mixing between these compounds, the existence of different molecular configurations for twin molecules, or the separation of (*S*) and (*R*) isomers which has been proposed to occur in the S_{C_A} phase of racemic **MHPOBC** where a molecular interaction promoting the association of each like enantiomer exists [22]. The separation of (*S*) and (*R*) isomers, however, cannot be responsible for the appearance of the various phase transitions observed for mixtures **A–D**. For instance, mixture **A** consists of racemic **MHPOBC** and racemic **MAB-8-PYP**, so that four components, i.e. (*S*)-**MHPOBC**, (*R*)-**MHPOBC**, (*S*)-**MAB-8-PYP** and (*R*)-**MAB-8-PYP**, exist in mixture **A**, whereas mixture **D** consists of only two components, i.e. (*S*)-**MHPOBC** and (*R*)-**MAB-8-PYP**. If the appearance of various phase transitions was due to the separation of the (*S*) and (*R*) isomers, mixture **A** should show more complex phase transitions than mixture **D**. In practice, however, the complex phase transitions were obtained for mixture **D** by microscopic observations and DSC measurements. Therefore, it is reasonable to conclude that the appearance of the new smectic phases is attributable to the high degree of chirality produced by the optically active materials rather than the separation of the (*S*) and (*R*) isomers.

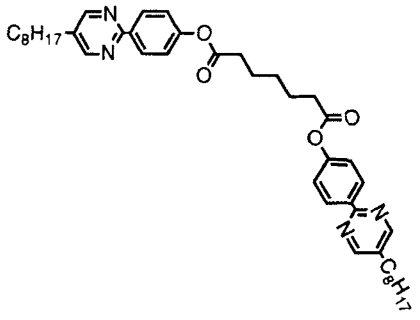
Possible configurations for **AAB-8-PYP**, **PAB-8-PYP** and **MAB-8-PYP** are shown in figures 14 (*a*), (*b*) and (*c*), respectively, where it is assumed that the alkyl chain adopts an all *trans* conformation and that the two carbonyl linking groups point in opposite directions [19]. If the molecules favour these conformations, then a greater degree of 'bentness' is obtained for **PAB-8-PYP** (see figure 14 (*b*)). The 'bent' molecular structure for **PAB-8-PYP** is considered to be undesirable for producing normal liquid crystalline phases, so that **PAB-8-PYP** shows no liquid crystalline phases. In contrast, **AAB-8-PYP** and **MAB-8-PYP** show nematic and cholesteric liquid crystalline phases, respectively, which may be attributable to the molecular structures with rather a small degree of 'bentness' (see figures 14 (*a*) and (*c*)). The enthalpy of the I–N transition for **AAB-8-PYP** ($8{\cdot}3\,\mathrm{kJ\,mol^{-1}}$) was found to be close to that of the I–Ch transition for **MAB-8-PYP** ($7{\cdot}2\,\mathrm{kJ\,mol^{-1}}$, suggesting that they have similar molecular conformations in their liquid crystalline phases. When **MAB-8-PYP** was mixed with **MHPOBC**, however, the liquid crystalline properties for the mixture were found to be similar to those for the mixture containing **PAB-8-PYP** which is supposed to have a more bent molecular structure than **MAB-8-PYP**. For instance, mixture **C** (optically active **MHPOBC** + racemic **MAB-8-PYP**) shows no cholesteric phase which is more similar to mixture **F** (optically active **MHPOBC** + **PAB-8-PYP**) than to mixture **E** (optically active **MHPOBC** + **AAB-8-PYP**). Furthermore, the coexistence of the S_A phase and isotropic liquid phase was observed for mixture **C** as well as mixture **F**. These results suggest that the molecular conformation of the chiral twin material, **MAB-8-PYP**, is more bent than expected in the mixture with **MHPOBC**.

5. Conclusions

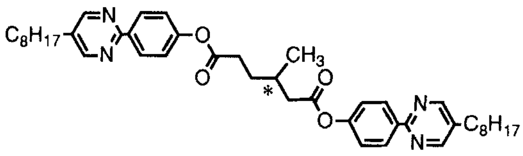
A novel smectic phase, of which the texture is similar to that reported for the twist grain boundary (TGB) phase, was obtained for the binary mixture between an optically active antiferroelectric material, (*S*)-4-(1-methylheptyloxycarbonyl)phenyl 4′-octy-



AAB-8-PYP
(*a*)



PAB-8-PYP
(*b*)



MAB-8-PYP
(*c*)

Figure 14. Possible conformations for non-chiral twin materials, **AAB-8-PYP** (*a*) and **PAB-8-PYP** (*b*), and the chiral twin material, **MAB-8-PYP** (*c*).

loxy-biphenyl-4-carboxylate (**MHPOBC**), and an optically active twin material, (*R*)-3-methyladipic acid bis[4-(5-octyl-2-(pyrimidinyl)phenyl] ester (**MAB-8-PYP**). The appearance of the TGB phase is considered to be closely related to the degree of chirality of the system rather than the separation of the (*S*) and (*R*) isomers. The liquid crystalline phases were found to be different in nature between **MHPOBC** and **MAB-8-PYC**; thus, a fluctuating S_A phase may be produced by mixing these materials, which is suitable for the appearance of the TGB phase. Two kinds of S_A phase were observed for the binary mixture, so that a novel phase sequence, i.e. S_A–TGB–S_A, was observed. The strength of the smectic layer structure is suggested to decrease between these two S_A phases, which is also favourable for producing the TGB phase.

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References

[1] Goodby, J. W., 1991, *J. mater. Chem*, **1,** 307.

[2] Takanishi, Y., Takezoe, H., Fukuda, A., Komura, H., and Watanabe, J., 1992, *J. mater. Chem.*, **2,** 71.

[3] Date, R. W., Imrie, C. T., Luckhurst, G. R., and Seddon, J. M., 1992, *Liq. Crystals*, **12,** 203.

[4] Yoshizawa, A., Nishiyama, I., Kikuzaki, H., and Ise, N., 1992, *Jap. J. appl. Phys.*, **31,** L860; Yoshizawa, A., Yokoyama, A., Kikuzaki, H., and Hirai, T., 1993, *Liq. Crystals*, **14,** 513.

[5] Yoshizawa, A., and Nishiyama, I., 1994, *J. mater. Chem.*, **4,** 449.

[6] Goodby, J. W., Waugh, M. A., Stein, S. M., Chin, E., Pindak, R., and Patel, J. S., 1989, *J. Am. chem. Soc.*, **111,** 8119.

[7] Chandani, A. D. L., Gorecka, E., Ouchi, Y., Takezoe, H., and Fukuda, A., 1989, *Jap. J. appl. Phys.*, **28,** L1265.

[8] Fukuda, A., 1990, *Abstract, 16th Japanese Liquid Crystals Conference*, Hiroshima, Japan, pp. 28–31 (in Japanese).

[9] Takezoe, H., Lee, J., Chandani, A. D. L., Gorecka, E., Ouchi, Y., Fukuda, A., Terashima, K., and Furukawa, K., 1991, *Ferroelectrics*, **114,** 187.

[10] Mitsunobu, O., 1981, *Synthesis*, 1.

[11] Chin, E., and Goodby, J. W., 1986, *Molec. Crystals liq. Crystals*, **141,** 311.

[12] Hasseni, A., and Alexanian, V., 1978, *Tetrahedron Lett.*, 4475. Kim, S., Lee, J. I., and Ko, Y. K., 1984, *Tetrahedron Lett.*, 4943.

[13] Sharma, S. R., Palffy-Muhoray, P., Bergerson, B., and Dunmur, D. A., 1985, *Phys. Rev.* A, **32,** 3752.

[14] de Gennes, P. G., 1972, *Solid St. Commun.*, **10,** 753.

[15] Goodby, J. W., Nishiyama, I., Slaney, A. J., Booth, C. J., and Toyne, K. J., 1993, *Liq. Crystals*, **14,** 37.

[16] Goodby, J. W., Slaney, A. J., Booth, C. J., Nishiyama, I., Vuijk, J. D., Styring, P., and Toyne, K. J., 1994, *Molec. Crystals liq. Crystals*, **243,** 231.

[17] Gray, G. W., and Goodby, J. W., 1984, *Smectic Liquid Crystals-Textures and Structures* (Leonard Hill Glasgow), pp. 143–148.

[18] Grandjean, F., 1921, *C. r. hebd. Séance. Acad. Sci. Paris*, **172,** 71.

[19] Slaney, A. J., 1992, Ph.D. Thesis, University of Hull.

[20] Barnes, P. J., Douglass, A. G., Heeks, S. K., and Luckhurst, G. R., 1993, *Liq. Crystals*, **13,** 603.

[21] Krone, V., and Ringsdorf, H., 1987, *Liq. Crystals*, **2,** 411.

[22] Takanishi, Y., Hiraoka, K., Agrawal, V. K., Takezoe, H., Fukuda, A., and Matsushita, M., 1991, *Jap. J. appl. Phys.*, **30,** 2023.