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Antiferroelectric Siloxane Twin Liquid Crystal

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A chiral twin liquid crystal possessing a siloxane unit in a spacer has been prepared and the properties investigated. The siloxane chiral twin showed only the antiferroelectric phase in a wide temperature range between 34 °C and 104 °C. The twin showed a high tilt angle of ca. 45 degrees, being almost temperature-independent. The siloxane twin exhibited a good miscibility with the monomer, maintaining a stable antiferroelectric phase, which is quite different from the phase transition behaviour observed for the mixtures made with the analogous non-siloxane twin and the monomer. The role of the siloxane unit was discussed in terms of the microphase segregation.

Key words: antiferroelectric, organosiloxane, twin, liquid crystal, microphase segregation

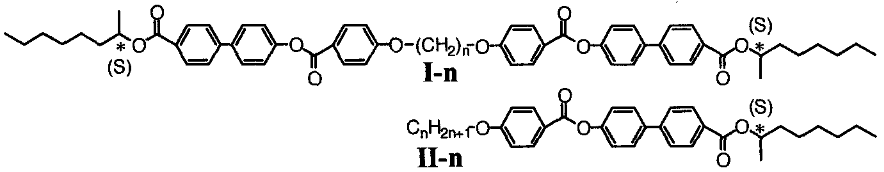
1. INTRODUCTION

Chiral twin compounds (**I-n**, figrue 1) possessing two chiral centres showed a variety of fascinating chiral smectic phases, such as ferri- and antiferroelectric phases [1-3], and the twist grain boundary and related chirality-sensitive phases [4], the phase transition behaviour of which was quite different from that of the corresponding monomer **II-n** [5]

As one of the modifications of the twin structure, the introduction of a siloxane unit in the ferroelectric and antiferroelectric twins has so far been studied [6,7]. The siloxane unit is incompatible with usual hydrocarbon components so that strong microphase segregation is induced in the molecular assemblies of chiral twin molecules [6,8]. In this study, a novel chiral twin structure, **III** (figure 2), was designed and prepared, where a siloxane unit was introduced into the central spacer part of **I-n**. The properties of mixtures made with **III** were also compared with those made with **I-n**.

2. EXPERIMENTAL

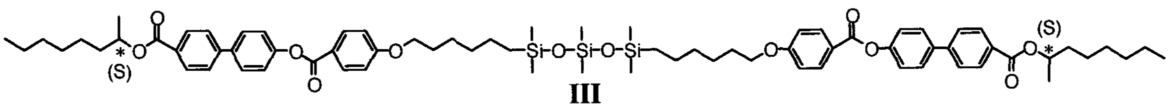
The siloxane chiral twin compound, **III**, was prepared according to the reported procedures [3,6]. The acid-based siloxane dimer (0.24 g, 0.37 mmol), (*S*)-1-methylheptyl 4-hydroxybiphenyl-4'-carboxylate (0.27 g, 0.83 mmol) and DPTS (0.03 g, 0.1 mmol) were added in dry dichloromethane (3 ml). DCC (0.17 g, 0.83 mmol) was then added and the resulting mixture was stirred at room temperature for two days. Precipitated materials were removed by filtration. After removal of the solvent by evaporation under reduced pressure, the product was purified by column chromatography using a dichrolomethane-hexane (1:1~5:1) mixture as the eluent, and recrystallized from an ethanol (20 ml), giving a colourless wax-like product. Yield = 0.42 g, (89%). The structure was confirmed by ^{1}H-NMR ((300MHz, CDC13, TMS): 8.14 (m, 8H, Ar-**H**), 7.65 (m, 8H, Ar-**H**), 7.26 (m, 4H, Ar-**H**), 6.98 (m, 4H, Ar-**H**), 5.18 (m, 2H, -C***H**(CH$_3$)-), 4.05 (t, 4H, -C**H**$_2$O-, ^3J = 6.5 Hz), 1.86-1.29 (m, 42H, aliphatic-**H**), 0.88 (t, 6H, -C**H**$_3$, ^3J = 6.7 Hz), 0.56 (t, 4H, -Si-C**H**$_2$-, ^3J = 7.9 Hz), 0.08 (s, 12H, -CH$_2$-Si(-C**H**$_3$)$_2$-O-), 0.03 (s, 6H, -O-Si(-C**H**$_3$)$_2$-O-)). The molecular weight of 1264 was confirmed by mass spectrometry. Liquid-crystalline and physical properties were studied using the methods previously reported [3].



I-n

II-n

Figure 1 Chiral twin and monomeric liquid crystals.



III

Cr 34.1 °C [13.42 kJ/mol] **antiferro** 103.6 °C [10.56 kJ/mol] **Iso**

Figure 2 Structure, transition temperatures and enthalpies for the siloxane twin.

3. RESULTS AND DISCUSSION

3.1 Phase Transition Behaviour

The transition temperatures and phase sequence of **III** are shown in figure 2. The antiferroelectric phase was observed in a wide temperature range between 34.1 °C and 103.6 °C. On cooling, the antiferroelectric phase was supercooled below room temperature, which was clearly shown in the differential scanning calorimetry (DSC) thermogram (figure 3). A broad diffuse DSC peak, so far appeared in some chiral twin materials [1,3], was not observed for **III**.

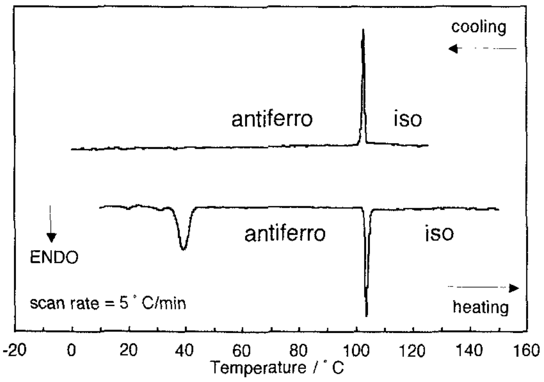


Figure 3 DSC thermogram for siloxane twin **III**.

The transition temperatures and phase sequence for the siloxane twin (**III**) are also compared with the analogous twin homologues (**I-n**) which do not possess the siloxane unit [3] (figure 4). The introduction of the siloxane unit showed a significant effect on broadening the antiferroelectric phase, and lowering the transition temperatures, especially suppressing the crystallisation. These properties are great advantages of **III** for making practical antiferroelectric liquid-crystalline mixtures.

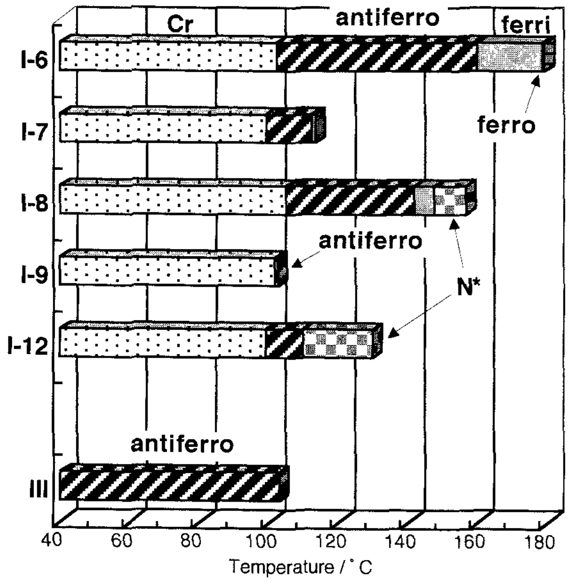


Figure 4 Comparison of the transition temperatures between **I-n** and **III**.

3.2 Electro-optical Studies

The optical tilt angle of **III** was measured for the sample contained in a commercially available evaluation cell (3 μm-thick), the inner surface of which had been polyimide-coated and buffed. Figure 5 shows the obtained tilt angle as a function of the electric field in the antiferroelectric phase at 5 °C below Tc (Tc = Iso-Antiferro phase transition). Typical threshold behaviour indicating the emergence of the antiferroelectricity was observed with a threshold electric field of ca. 3.5 Vμm^{-1}. The saturated tilt angle, corresponding to the electrically induced ferroelectric state, was found to be around 45 degrees, which was almost temperature-independent as shown in figure 6.

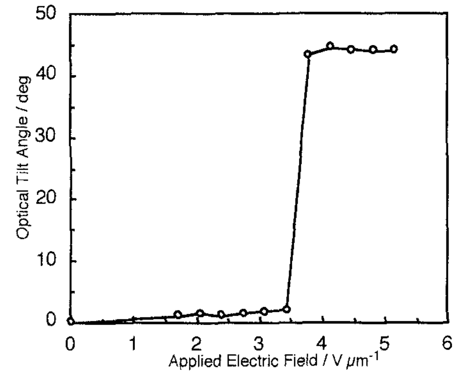


Figure 5 Applied electric field dependence of tilt angle for siloxane twin **III** in the antiferroelectric phase.

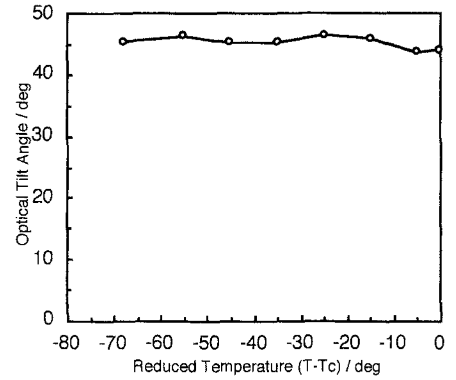


Figure 6 Temperature dependence of the saturated tilt angle for siloxane twin **III**

Figure 7 shows textural changes of **III** at 95.3 °C under the application of the electric field. The dark texture was observed without the electric field (figure 7 (a)). The dark texture may be associated with a similar phenomenon that has been reported to be produced by antiferroelectric materials where the director in alternate layers is orthogonal [9]. However, it should be noted that the cell spacing was rather large leading to the possibility of non-bookshelf alignment. Thus, it is difficult to say if orthoconic switching occurs for this material. Figure 7 (b) shows the texture just under the electrically induced transition from the antiferroelectric to ferroelectric state. A bright texture was obtained in the ferroelectric state as shown in figure 7 (c).

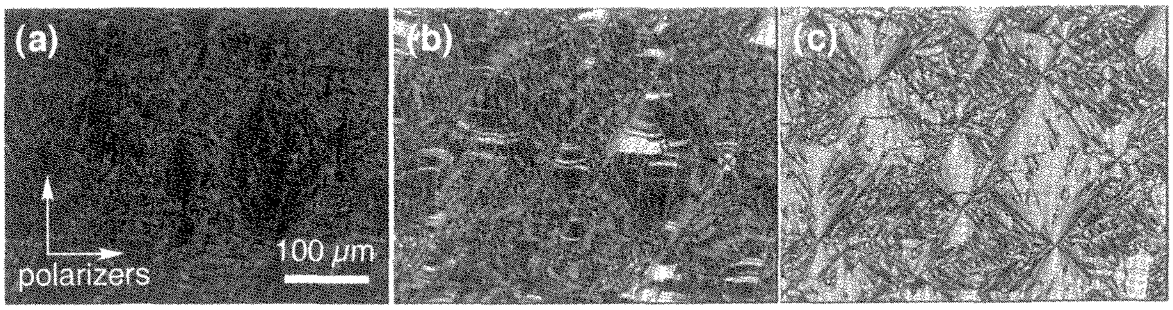
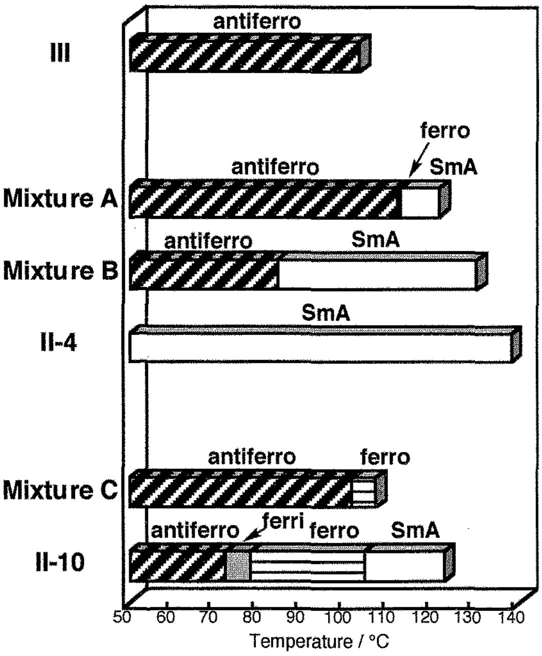


Figure 7 Textural changes under the application of the electric field: (a) 0 V μm^{-1}, (b) 3.8 V μm^{-1}, and (c) 4.5 V μm^{-1}.

3.3 Mixing Studies

Some mixtures were prepared between the siloxane twin **III** and the analogous chiral monomer (**II-4** or **II-10**) as shown in figure 8. It should be noted that, at the molar ration of 1:2 (twin:monomer), the numbers of the mesogenic core parts are the same between twin and monomeric components.

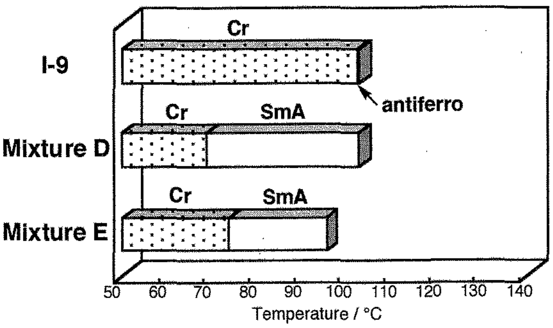


Mixture A: Twin **III** : Monomer **II-4** = 1:2 (molar ratio)
Mixture B: Twin **III** : Monomer **II-4** = 1:6 (molar ratio)
Mixture C: Twin **III** : Monomer **II-10** = 1:2 (molar ratio)

Figure 8 Transition temperatures for the mixtures between siloxane twin **III** and monomer **II-n**.

Interestingly, **Mixture A** showed a more stable antiferroelectric phase than that of the original siloxane twin **III**, although the monomeric component **II-4** used for the mixture did not show the antiferroelectric phase but just showed the smectic A (SmA) phase. This result indicates that, in **Mixture A**, the monomeric molecules are happy to exist in the over-all antiferroelectric molecular ordering produced by the siloxane twin molecules. A mixture with a higher monomer content (**Mixture B**) showed the destabilization of the antiferroelectric phase and the broadening of the SmA phase temperature range, indicating that the monomeric character was emphasized in **Mixture B**. **Mixture C** was also prepared using **II-10** as a monomer component (**III**:**II-10** = 1:2 mol). This time monomer **II-10** itself possesses the antiferroelectric phase, however, the stability of the antiferroelectric phase of **Mixture C** was slightly lower than that of **Mixture A**, indicating that the twin molecules (**III**) have a dominant role in producing the antiferroelectric structure in the mixture.

Similar mixtures were also prepared between the analogous twins possessing a hydrocarbon spacer (**I-9**) and the chiral monomer (**II-4** or **II-10**) as shown in figure 9, so that the effect of the siloxane unit on the phase transition behaviours of the mixture can be highlighted.



Mixture D: Twin **I-9** : Monomer **II-4** = 1:2 (molar ratio)
Mixture E: Twin **I-9** : Monomer **II-10** = 1:2 (molar ratio)

Figure 9 Transition temperatures for the mixtures between twin **I-9** and monomer **II-n**.

Unlike the mixtures made with the siloxane twin, **Mixture D** and **E** just showed the SmA phase, where the original antiferroelectric phase of **I-9** had been completely destroyed by the addition of the monomer **I-n**. So far, some properties of the mixtures prepared between **I-n** and **II-n** have been studied [10,11], however, the significant difference in the phase sequence between siloxane-twin-based and non-siloxane twin-based mixtures was observed for the first time. This effect may be attributed to stronger microphase segregation produced by the siloxane unit. Since the siloxane unit is incompatible with the hydrocarbon part and also has a larger excluded volume than alkyl chain, it is difficult for the monomer molecules to mix with the twin molecules randomly. Consequently, the monomer molecules tend to assemble in such a way that they stay near to one of the mesogenic parts of the twin molecules.

In this style of the molecular assembly, the monomer can stay happily with the antiferroelectric structure produced by the twin molecules, thus the antiferroelectric phase is stable for the mixtures between **III** and monomers. However, the flexible alkyl spacer of **I-9** cannot produce such strong microphase segregation when the monomer is mixed into the twins. Therefore, the molecules are considered to be mixed randomly between the twin and monomer. This random mixing does not necessarily stabilize the antiferroelectric structure originally produced by the twin molecules.

4. CONCLUSIONS

The chiral twin compound possessing the siloxane unit in the central spacer part showed a broad and low-temperature antiferroelectric phase with a high tilt angle of 45 degrees. The siloxane twin showed a good miscibility with the monomer, producing a mixture with a stable antiferroelectric phase, whereas the antiferroelectric phase of the analogous non-siloxane twin was strongly destabilized by the addition of the monomer.

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