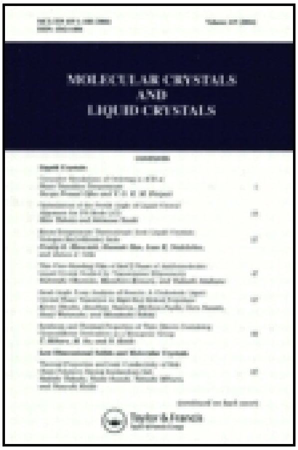

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Frustration Caused by Competition Between Interlayer and Intralayer Interactions in a Dichiral Liquid Crystal

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FRUSTRATION CAUSED BY COMPETITION BETWEEN INTERLAYER AND INTRALAYER INTERACTIONS IN A DICHIRAL LIQUID CRYSTAL

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*We reported that a dichiral liquid crystal 2-{4-[(R)-2-fluorohexyloxy]phenyl}-5-4-[(S)-2-fluoro-2-methyldecanoy]phenyl}pyrimidine (**1**) upon cooling exhibits an endothermic transition from a chiral smectic C phase to an optically isotropic phase (IsoX). We have investigated transition behaviour of a binary mixture between **1** and the corresponding monochiral liquid crystal without the IsoX phase, 2-[4-[hexyloxy]phenyl}-5-4-{[(S)-2-fluoro-2-methylnonanoyl]-phenyl}pyrimidine (**2**). In the phase diagram clear hysteresis was observed in appearance of the IsoX phase between heating and cooling.*

Keywords: chirality; frustration; liquid crystals; phase transition; smectic

1. INTRODUCTION

Recently we reported a rod-like chiral liquid crystal 2-{4-[(*R*)-2-fluoro-hexyloxy]phenyl}-5-{4-[*S*)-2-fluoro-2-methyldecanoy]phenyl}pyrimidine(**1**) upon cooling exhibits an endothermic transition from a chiral smectic C (SmC*) phase to an optically istoropic phase (IsoX) [1]. We have investigated structure-property relations for appearance of the IsoX phase. Except the tail length, a slight change of the molecular structure depressed the IsoX phase [2,3]. The diastereomers of **1**, (*R, R*) and (*S, S*), did not show the IsoX phase, however, the racemic mixture of the two enantiomers exhibited the IsoX phase. The property-structure correlations suggest that

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the IsoX phase is organized by chiral molecular recognition [1]. Recently the IsoX phase was found to have *I*432 cubic structure by X-ray analysis [4]. Furthermore, crystal structure of **1** has been determined by Matsunaga and Hori *et al.* [5]. Schematic representation of the molecular arrangement is show in Figure 1. The crystal structure has a smectic-like layer structure. Molecular long axes are parallel along the c axis and they are antiparallel along the a axis. Strong interactions between pyrimidine rings of antiparallel molecules exist, leading to the large overlapping of core moities and strong interactions between chiral groups. The results suggest that intralayer chirality-oriented electrostatic interaction contributes to appearance

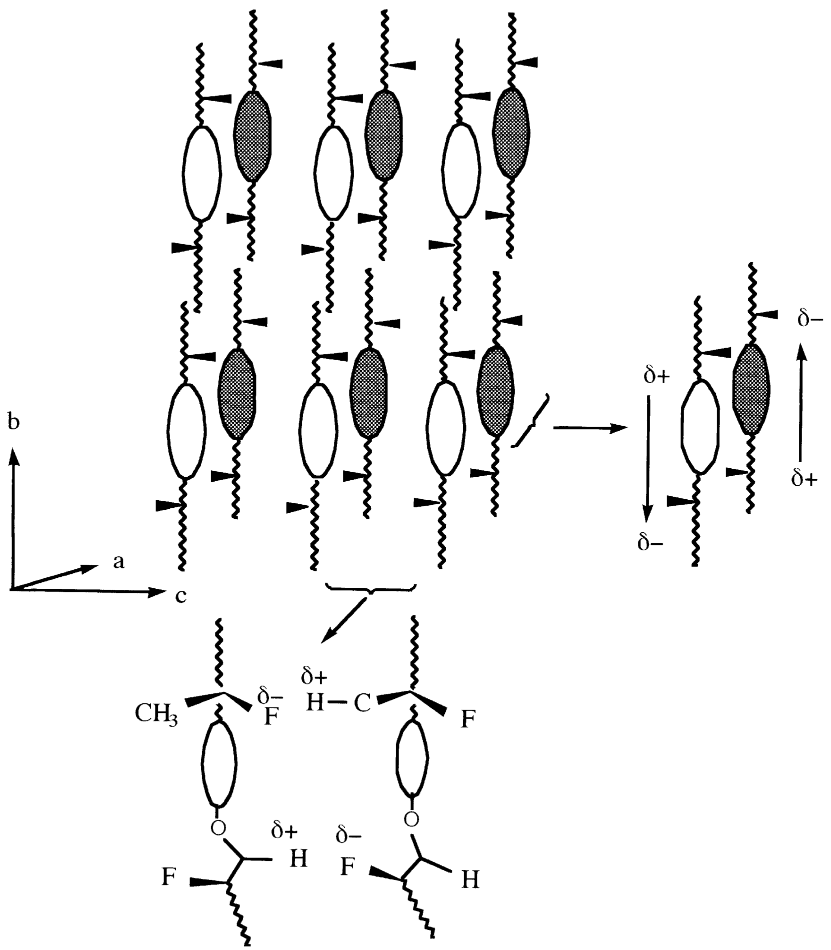

FIGURE 1 Schematic representation of crystal structure for **1**.

of the IsoX phase. On the other hand, the SmC* phase above the IsoX phase has helical structure, which is caused by interlayer chiral twist interaction. Thus the SmC* to IsoX transition is thought to be organized by competition between interlayer and intralayer chiral interactions.

In order to understand the chiral interactions for appearance of the IsoX phase, we have designed a binary system between **1** and 2-[4-[hexyloxy]-phenyl}-5-{4-[(*S*)-2-fluoro-2-methylnonanoyl]phenyl}pyrimidine (**2**) with a phase sequence of Iso Liq-SmC*-SmX*-Cryst, in which the competition is expected to cause frustrated transition behaviour.

2. EXPERIMENTAL

The samples used were a dichiral compound **1** and a monochrical compound **2** as shown in Figure 2. The enantiomeric excess of each chiral centre of **1** was determined to be over 98%*ee* by HPLC. That of the chiral centre of **2** was 75%*ee*.

The phase transition behaviour was observed by optical microscopy using a Nikon Optiphoto POL polarizing microscopy with a Mettler FP82 microscope and FP80 control unit. Temperatures and entalpies of transition were investigated by differential scanning calorimetry (DSC) using a Seiko DSC 6200 calorimeter. The heating and cooling rates were 5°C min^{-1}. The magnitude of spontaneous polarization (*Ps*) was measured for samples contained in a parallel alignment cell (purchased from E. H. C. Co., Ltd.). The cells were made with approximately 3-µm spacings,

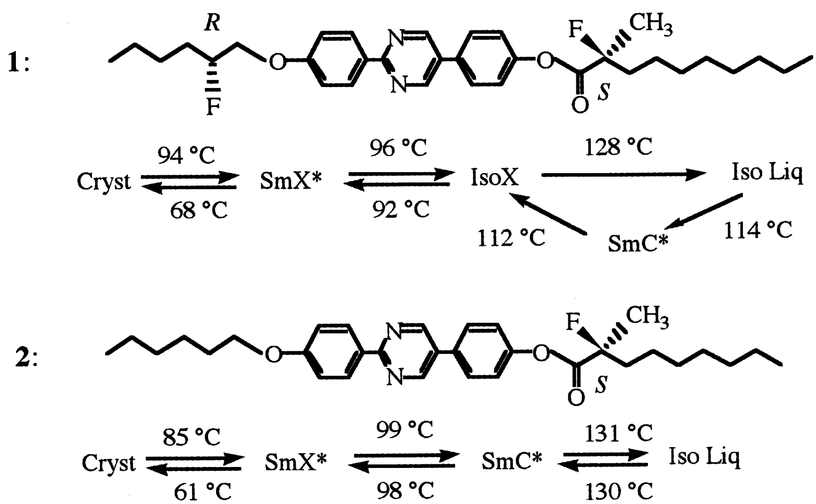

FIGURE 2 Structure and transition temperatures for **1** and **2**.

with the inner surface coated with a polyamide aligning agent and unidirectional buffed. The *Ps* values were determined using the triangle wave method.

3. RESULTS AND DISCUSSION

We have designed a binary system between the dichrial compound **1** with the IsoX phase and the mono chiral compound **2** with a phase sequence of Iso Liq-SmC*-SmX*-Cryst. Phase diagrams of binary mixtures between compounds **1** and **2** are shown in Figure 3. In the cooling phase diagram, the SmC* phase appeared above the IsoX phase, however, the SmC* phase appeared below the IsoX phase in the heating phase diagram. Another ferroelectric phase which is called as SmY* was found to be induced. Hysteresis in transition behaviour between cooling and heating was observed in a mixture between **1** (75 wt%) and **2** (25 wt%), and the IsoX phase appeared only on the heating process in the mixture. The cooling phase sequence was Iso Liq-SmC*-SmY*-SmX*-Cryst, on the other hand, the heating was Cryst-SmX*-SmY*-SmC*-IsoX-Iso Liq.

Then, we have investigated DSC thermocycle of the mixture. Cooling the mixture from Iso Liq to Cryst and them heating to Iso Liq, a thermocycle of Iso Liq-SmC*-SmY*-SmX*-Cryst-SmX*-SmY*-SmC*-IsoX-Iso Liq was observed as shown in Figure 4. The phase transition is irreversible. Cooling the mixture from Iso Liq to SmX*, and then heating to Iso Liq, a phase sequence of Iso Liq-SmC*-SmY*-SmX*-SmY*-SmC*-IsoX-Iso Liq was observed as shown in Figure 5. This phase transition is also irreversible. Cooling the mixture for Iso Liq to 110°C in the SmC* phase and then heating, the SmC* phase changed to Iso Liq with a broad exothermic peak (Fig. 6(a)). Holding the sample at 110°C for 3 h and then heating, the SmC* changed to Iso Liq without appearance of the IsoX phase. However, cooling to 100°C in the SmC* phase and heating, the SmC* to IsoX transition occurred (Fig. 6(b)). By optical microscopy, similar transition phenomena as observed by DSC measurements were obtained.

Temperature dependence of *Ps* of the mixture is shown in Figure 7. The temperature dependence of *Ps* in the SmY* and SmX* phases is different from that in the SmC* phase. The magnitude of *Ps* increases continuously in the SmC* phase as decreasing temperature, indicating that there is no discontinuous change in the ferroelectric ordering in the SmC* phase on cooling.

Let us discuss the hysteresis observed in the transition behaviour of the mixture between **1** (75 wt%) and **2** (25 wt%). Figure 8 shows a schematic illustration of Gibbs free energy for the mixture as a function of temperature. The chiral centres of **1** cause interlayer and intralayer chiral

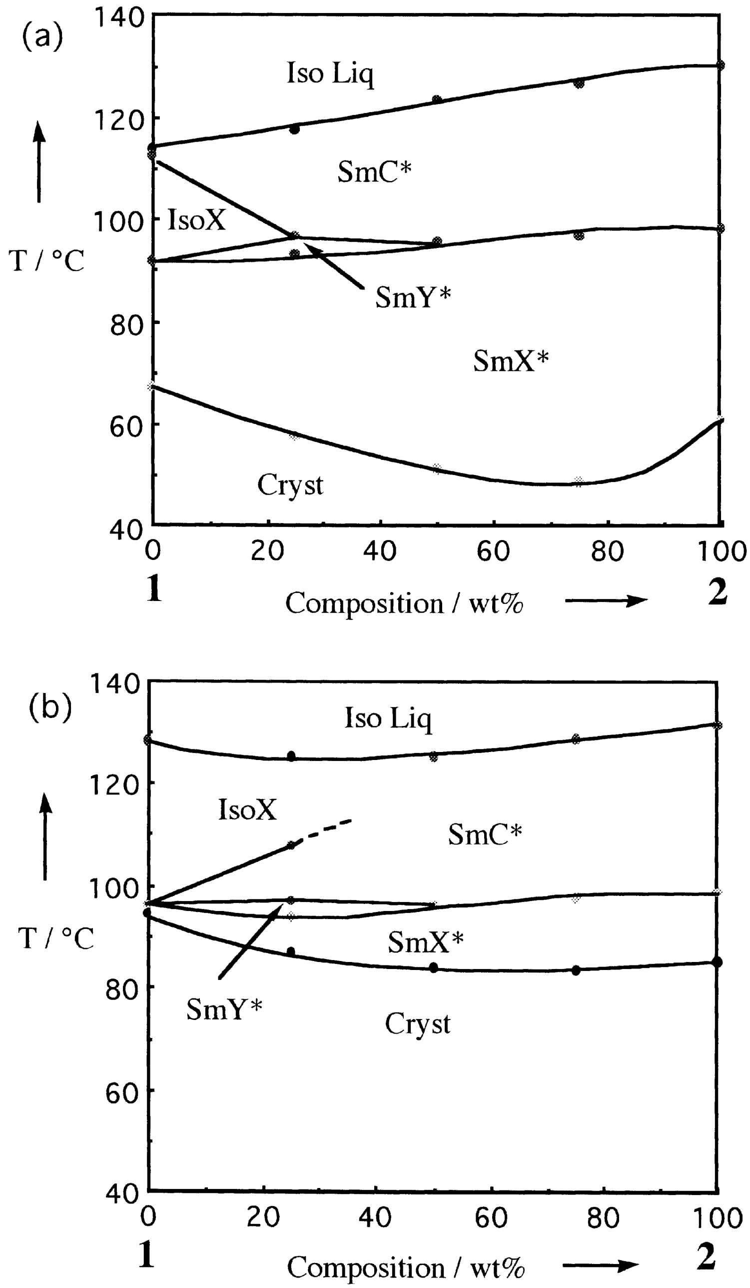

FIGURE 3 Phase diagrams of binary mixtures of **1** and **2** on cooling (a) and heating (b).

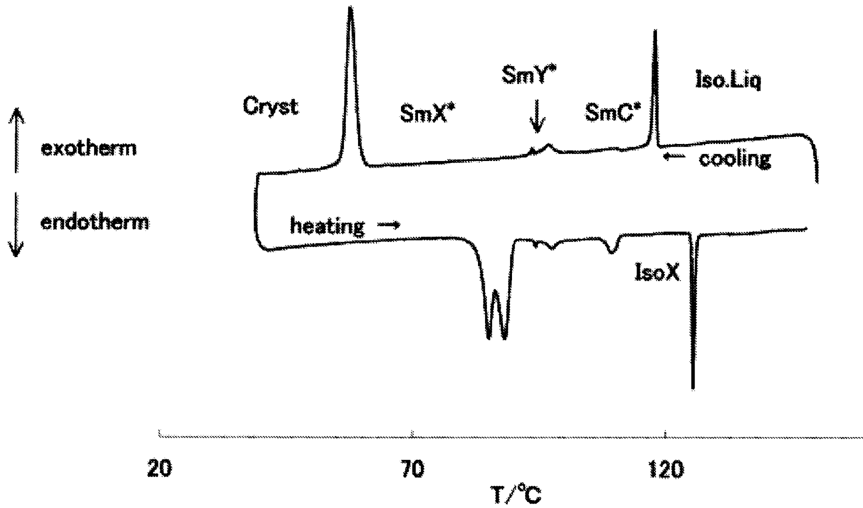

FIGURE 4 DSC thermogram of a mixture between **1** (75 wt%) and **2** (25 wt%).

interactions, and the chiral centre of **2** causes interlayer chiral interaction. Interlayer chiral interaction stabilizes the helical smectic phase on the cooling process, however, the intralayer interaction induces the IsoX phase on the heating process. The hysteresis is attributed to the competition

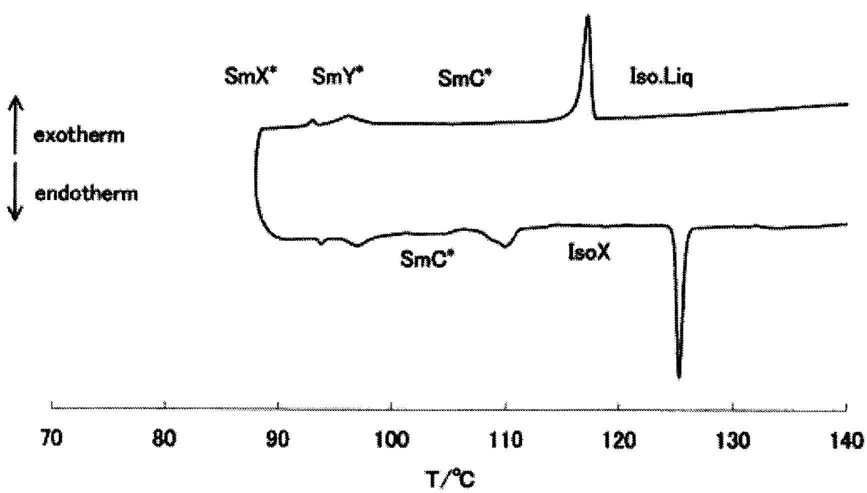

FIGURE 5 DSC thermogram of a mixture between **1** (75 wt%) and **2** (25 wt%). Cooling the mixture from Iso Liq to SmX*, and then heating to Iso Liq.

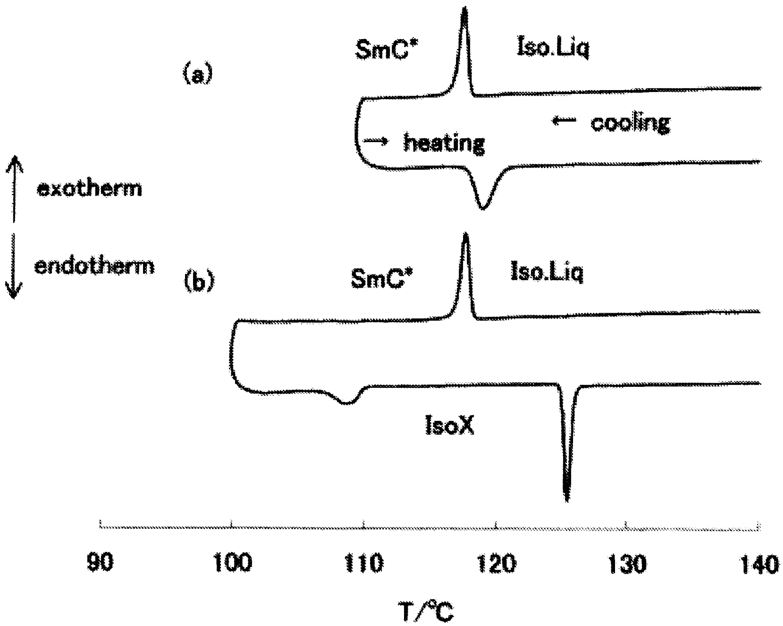

FIGURE 6 DSC thermogram of a mixture between **1** (75 wt%) and **2** (25 wt%). (a) Cooling the mixture from Iso Liq to 110°C in the SmC* and then heating to Iso Liq. (b) Cooling the mixture from Iso Liq to 100°C in the SmC* phase and then heating to Iso Liq.

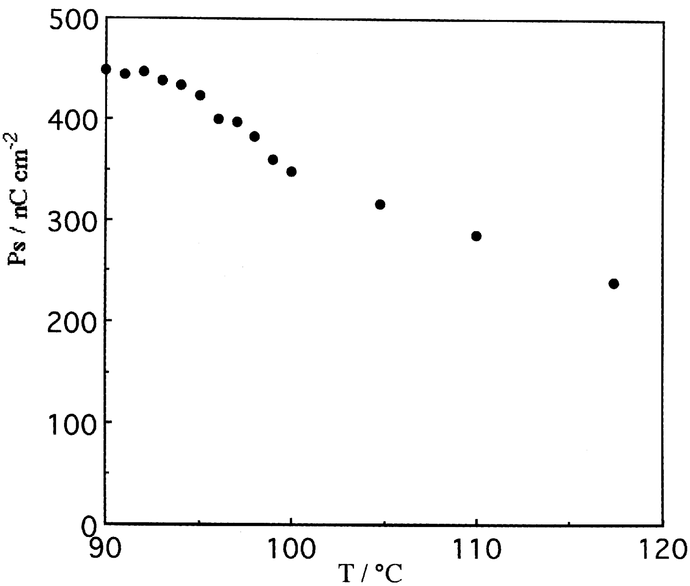

FIGURE 7 Temperature dependence of spontaneous polarization for a mixture between **1** (75 wt%) and **2** (25 wt%).

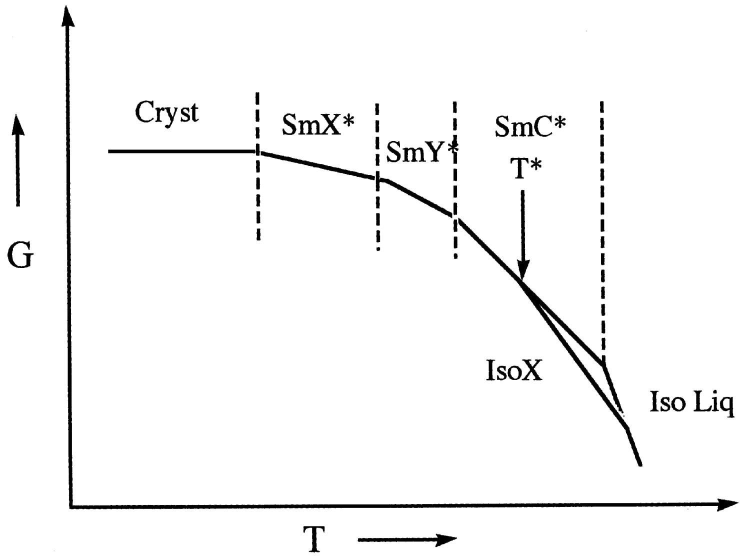

FIGURE 8 A schematic illustration Gibbs free energy as a function of temperature for transition behaviour of a mixture between **1** (75 wt%) and **2** (25 wt%).

between interlayer and intralayer chiral interactions in the SmC* phase. Cooling the mixture from Iso Liq to a certain temperature above T*, the reversible SmC* to Iso phase transition occurred. On the other hand, cooling the mixture to a certain temperature below T*, the irreversible SmC*-IsoX-Iso transition occurred. The Gibbs free energy diagram show that the SmC* phase above T* is a kinetically induced phase. Furthermore, the IsoX phase appeared from a SmC* phase both on cooling for a compound **1** and on heating for the mixture. Thus, our results suggest that kinetically favourable interlayer chiral interaction produces a layer ordering with helical structure, and then, thermodynamically favourable intralayer chiral interaction occurs in each layer and organizes the SmC* to IsoX transition.

4. CONCLUSIONS

We have investigated phase transition behaviour of a binary system of the dichiral compound with the IsoX phase and the monochrial compound without the IsoX phase. In a certain mixture the IsoX phase appeared only on heating. The frustrated transition behaviour is attributed to competition between interlayer interaction for a helical smectic phase and interlayer interaction for the IsoX phase.

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