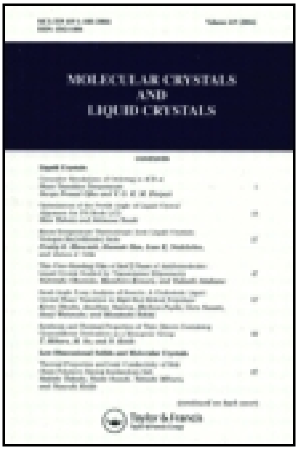

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Isotropic Cubic Phase Organized by Chiral Molecular Recognition

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Isotropic Cubic Phase Organized by Chiral Molecular Recognition

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We investigated property-structure relations in a dichiral compound which exhibits an optically isotropic phase (IsoX). Slight modification of the molecular structure except the chain length suppressed the IsoX phase. A phase diagram between enantiomers suggests that chiral recognition induces the IsoX phase. A miscibility study between the dichiral compound (**R, S**) and a hydrazine derivative (**BABH8**) with a cubic phase was performed Both the IsoX phase and the cubic phase of **BABH8** were suppressed, while the SmC* phase of (**R, S**) was miscible with the SmC phase of **BABH8**. The phase diagram reflects the competition between different intermolecular interactions. We discuss the novel chiral effect on mesophase formation.

Keywords: chirality; liquid crystals; cubic phase; molecular recognition; phase diagram

1. INTRODUCTION

We reported that a rod-like dichiral liquid crystal 2-[4-[(*R*)-2-fluorohexyl oxy]phenyl]-5-[4-[(*S*)-2-fluoro-2-methyldecanoyl]phenyl]pyrimidine **(R, S)** upon cooling exhibits an endothermic transition from a chiral smectic C phase to an optically isotropic phase (IsoX)[1, 2]. The formation of the IsoX is chirality-dependent phenomenon. Recently the structure of the IsoX phase was found to be bicontinuous cubic structure by X-ray analysis[3]. On the other hand, cubic phases have been observed in numerous substances of different structures[4]. Although some chiral compounds are known to show the cubic phase[4, 5], however, the effect of chirality on the appearance of the cubic phase has never been reported. The aim of this paper is to understand the novel chiral effect on mesophase formation.

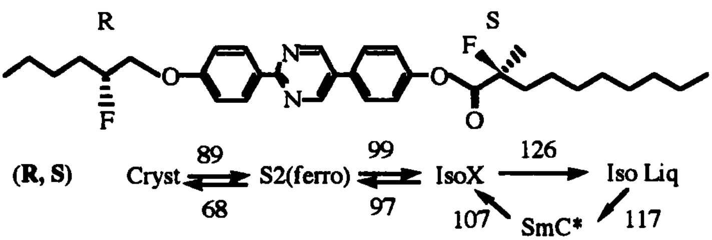


FIGURE 1 Structure and transition temperatures (°C) of **(R, S)**

2. EXPERIMENTAL

(R, S) and its derivatives were prepared according to our previous paper[2]. 1, 2-Bis-(4--octyloxybenzoyl)hydrazine **(BABH8)** [6] was also prepared in our laboratory. The purity and structure were confirmed by HPLC, thin-layer chromatography, IR, NMR and MS.

The phase transition behavior was observed by means of differential scanning calorimetry (Seiko DSC 220C) and optical microscopy.

3. RESULTS AND DISCUSSION

Property-structure Relations

We have investigated the effect of molecular structure on the appearance of the IsoX phase as shown in figure 2. Some results were already reported[1, 2].

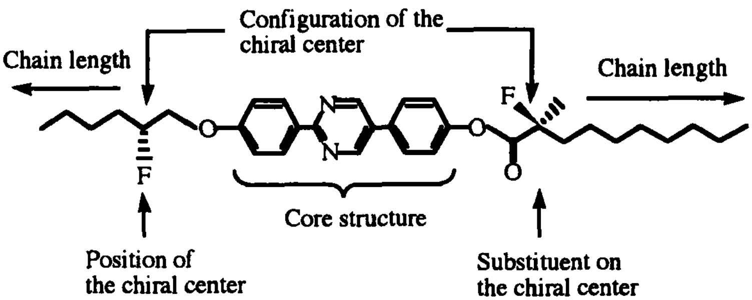
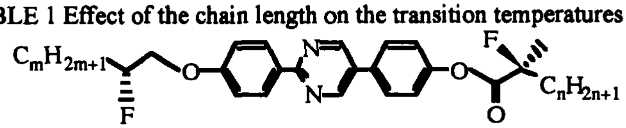


FIGURE 2 Modification of molecular structure of **(R, S)**

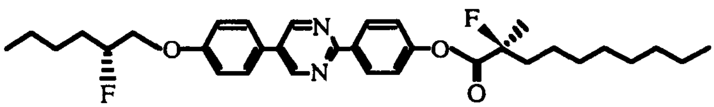
TABLE 1 Effect of the chain length on the transition temperatures (°C)



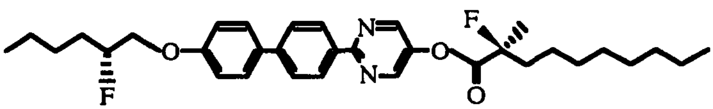
m	*n*	Cryst	S2	IsoX	SmC*	Iso Liq
3	8	• 64	• 94	• 109	• 110	•
4	8	• 68	• 97	• 107	• 117	•
5	8	• 84	• 89	•	122	•
6	8	•	95	•	127	•
4	7	• 70	• 95	•	115	•

Table 1 shows the effect of chain length on transition behavior of **(R, S)**. Chain length is known to play an important role in the formation of some frustrated phases[7]. However the chain length in this system does not have such a marked effect on the formation of the IsoX phase. Increasing carbon number *m*, the SmC* phase disappeared but the stability of the IsoX phase increased. The direct transition from Iso Liq to IsoX was observed in some compounds. The marked super cooling of the appearance of the IsoX phase of **(R, S)** is attributed to slow formation of the IsoX phase in the isotropic liquid.

On the other hand, the IsoX phase disappeared by changing the other molecular structure[2]. The slight change in the core structure suppressed the IsoX phase (figure 3).



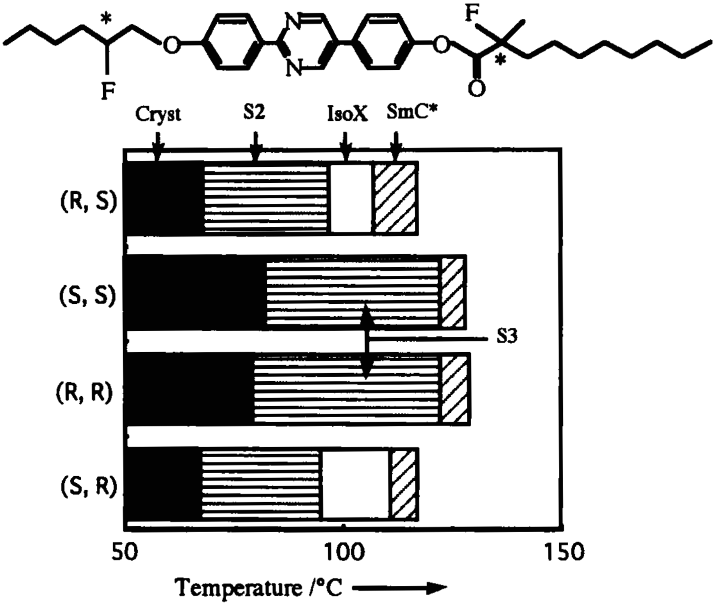
Cry 80 SmC* 101 SmA 136 Iso Liq



Cry 105 SmX 127 Iso Liq

FIGURE 3 Effect of the core structure on the transition temperatures (°C)

Figure 4 shows that the formation of the IsoX phase depends on the steric configuration of the chiral center. **(S, S)** and **(R, R)** did not show the IsoX phase. However the racemic mixture of the two enantiomers exhibited the IsoX phase (figure 5). The IsoX phase was found to be induced in the central region in the phase diagram. Furthermore the stability of the SmC* phase was depressed. This diagram indicates that: 1) chiral recognition induces the IsoX phase and 2) the recognition occurs in the isotropic liquid. The property-structure relations suggest that chirality-induced multiple interaction organizes the IsoX phase.



FGURE 4 Transition temperatures of the stereoisomers

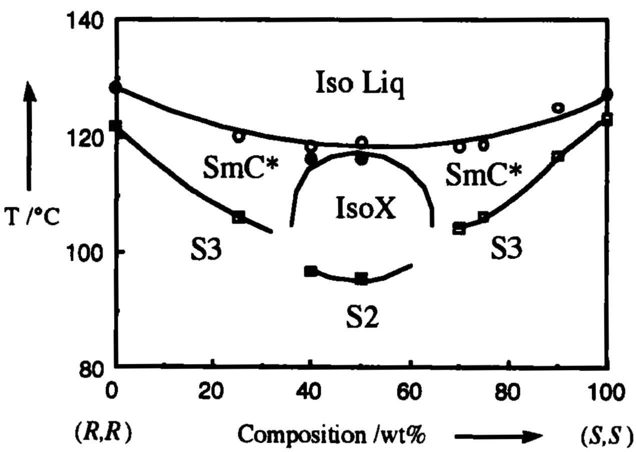
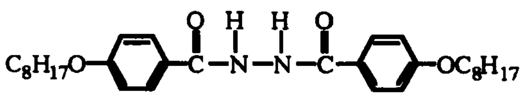


FIGURE 5 A phase diagram between (R, R) and (S, S)

Novel Chiral Effect on Formation of a Cubic Phase

Recently the IsoX phase was found to be a cubic phase with Im3m structure by X-ray analysis[3]. There are many substances with a cubic phase. Molecular aggregation via intermolecular interaction, i.e. hydrogen bonding, charge-transfer interaction and coordination to metal, is thought to be a driving force of cubic phases. We have added the chiral recognition as a novel interaction for the cubic phase.

BABH8 shows the SmC to Cub transition with exothermic enthalpy change on cooling[4]. The molecular aggregation for the cubic phase is thought to be organized by hydrogen bonding. Transition temperatures of **BABH8** by means of optical microscopy are shown in figure 6.



BABH8 Cryst $\underset{119}{\overset{136}{\rightleftharpoons}}$ Cub $\underset{155}{\overset{159}{\rightleftharpoons}}$ SmC $\underset{163}{\overset{164}{\rightleftharpoons}}$ Iso Liq

FIGURE 6 Structure and transition temperatures (°C) of **BABH8**

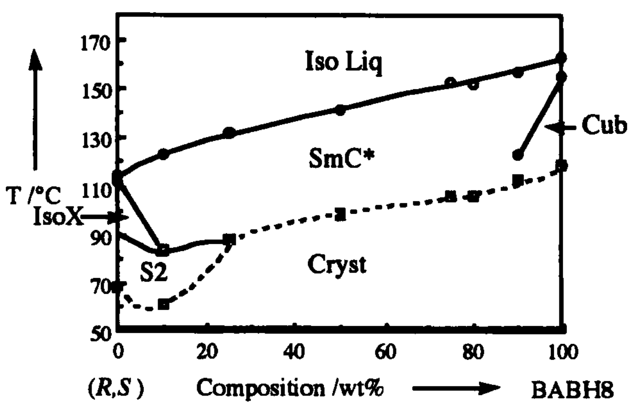


FIGURE 7 A phase diagram between **(R, S)** and **BABH8**

Figure 7 shows a phase diagram between **(R, S)** and **BABH8**. There may be three different intermolecular interactions, i.e. chiral recognition, hydrogen bonding and heteromolecular interaction. Competition between the different interactions is expected to be observed. Both the IsoX phase of **(R, S)** and the cubic phase of **BABH8** were suppressed, while, the SmC* phase of **(R, S)** was miscible with the SmC phase of **BABH8**. The results indicate that heteromolecular interaction is more favorable than homomolecular interaction via chiral recognition or hydrogen bonding in this system.

4. CONCLUSION

We would like to classify the chiral recognition as novel driving force for mesophase formation. Cubic and columnar phases appear in amphiphilic molecules or systems organized by stronger intermolecular interaction, i.e. microsegregation, hydrogen bonding, and charge-transfer interaction. Molecular aggregation via the chiral recognition was found to induce the cubic phase in the calamitic system with weak interaction.

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