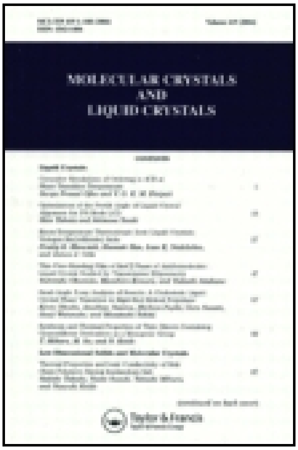

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Formation of Optically Isotropic Cubic Phase Based on Chiral Recognition in Dichiral Compounds

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Formation of Optically Isotropic Cubic Phase Based on Chiral Recognition in Dichiral Compounds

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Dielectric and ^{13}C-NMR measurements have been made to investigate the optically isotropic (IsoX) phase in dichiral compounds. The dielectric dispersions in the IsoX phase was found to be almost the same as that in the isotropic liquid (Iso) phase. The similar dynamic behavior in the Iso and IsoX phases is also observed in the ^{13}C-NMR measurement. These experimental facts suggest that the IsoX phase is not only optically isotropic but also has no cooperative motion, as in the Iso phase. An endothermic enthalpy change from the SmC* to IsoX phases associated with marked supercooling suggests that the formation and growth of the IsoX phase cannot be made in the Iso phase. Based on the phase diagrams of the binary mixtures of the stereoisomers, molecular chiral recognition was suggested to exist to form the IsoX phase.

Keywords: chirality; cubic phase; dichiral compound; dielectric dispersion; ^{13}C-NMR; phase diagram; endothermic enthalpy change; DSC

1. INTRODUCTION

Optically isotropic phases have been observed not only in lyotropic liquid crystal systems[1,2] but also in thermotropic ones[3-5] and are assigned to several kinds of cubic phases. Recently we found an optically isotropic

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phase, which was designated as IsoX, in a dichiral compound, 2-[4-[(*R*)-2-fluorohexyloxy]phenyl]-5-[4-(*S*)-2-fluoro-2-methyldecanoyloxy]phenyl]-pyrimidine ((*R*, *S*) compound)[6,7]. The IsoX phase is interesting from the following two viewpoints; (1) the IsoX phase emerges via an endothermic transition from the SmC* phase on cooling, and (2) the (*R*, *R*) and (*S*, *S*) stereoisomers of this compound do not show the IsoX phase, but the binary mixture does, suggesting chiral recognition when forming IsoX.

In this study, dielectric and ^{13}C-NMR measurements of the (*R*, *S*) compounds were made to understand the dynamic nature of the IsoX phase. Thermodynamic behavior was also discussed on the bases of DSC.

2. EXPERIMENTAL

The samples used were four stereoisomers of dichiral compounds, two of which is shown in Fig. 1. On cooling, (*R*, *S*) and (*S*, *R*) compounds show the IsoX phase below SmC*. On further cooling, some other smectic phase appears, which is called SmX*, here. On the other hand, (*S*, *S*) and (*R*, *R*) compounds show no IsoX phase, and SmC* directly changes to SmX. The

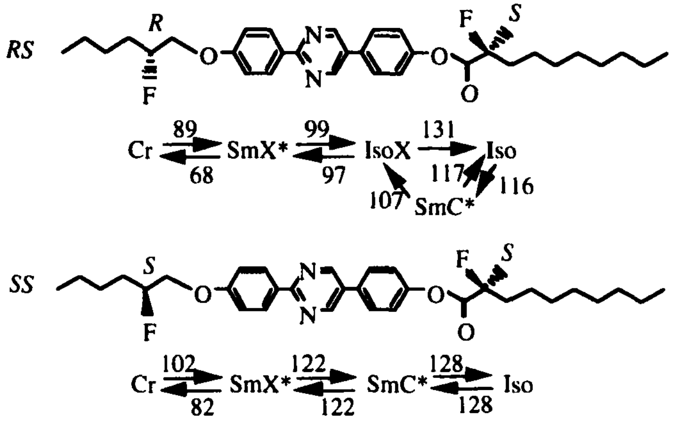

FIGURE 1 Structures and phase sequences of the stereoisomers used.

samples were sandwiched between two glass plates coated with polyimide to achieve homogeneously aligned cells for dielectric measurements.

The transition behavior was observed by means of differential scanning calorimetry (Seiko DSC 220C) and optical microscopy. The dielectric measurements were performed using an impedance analyzer (HP, LF4192A) with a temperature controller. The x-ray scattering measurements were carried out using a Rigaku RU-200 and its temperature control unit. The ^{13}C-NMR spectra were taken using a JEOL GSX-270.

3. RESULTS AND DISCUSSION

Figure 2(a) shows a DSC chart on cooling. On cooling, the SmC* phase appears monotropically, while the direct IsoX-Iso phase transition occurs on heating. Most striking feature is the endothermic peak observed at the SmC*-IsoX phase transition. On cooling a pure material, phase transitions

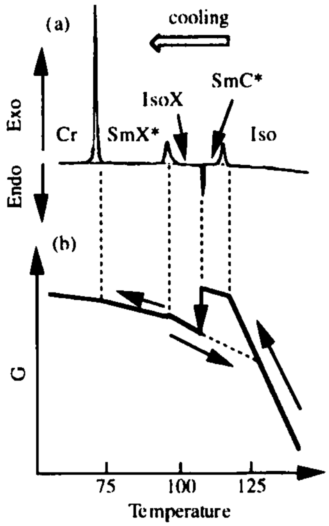

FIGURE 2 DSC chart on cooling the (*R*, *S*) compound and the schematic illustration of the Gibbs free energy as a function of temperature.

are generally accompanied by exothermic enthalpy changes. So this endothermic peak is quite interesting. However, the endothermic enthalpy change is possible and is not surprising, as shown in Fig. 2(b), where the Gibbs free energy as a function of temperature is schematically illustrated. A marked supercooling was observed for the appearance of the IsoX phase. This suggests two possibilities: (1) the formation of the IsoX phase is very slow; (2) the formation and growth of the IsoX phase cannot be made in the Iso phase. To clarify the cause, we held the sample just above the Iso-SmC* transition for 8h. However, the direct transition from Iso to IsoX phase transition did not occur but the SmC*-IsoX transition occurred with an endothermic enthalpy change. This fact indicates that the second explanation is more realistic, namely, the formation and growth of the IsoX phase cannot be made in the Iso phase.

In order to obtain structural information on the IsoX phase, ^{13}C-NMR measurements were carried out. Figure 3 shows static solid-state ^{13}C-NMR spectra in the Iso, IsoX and SmX phases[6]. The SmX phase was characterized by marked line broadening. However, the spectrum in the

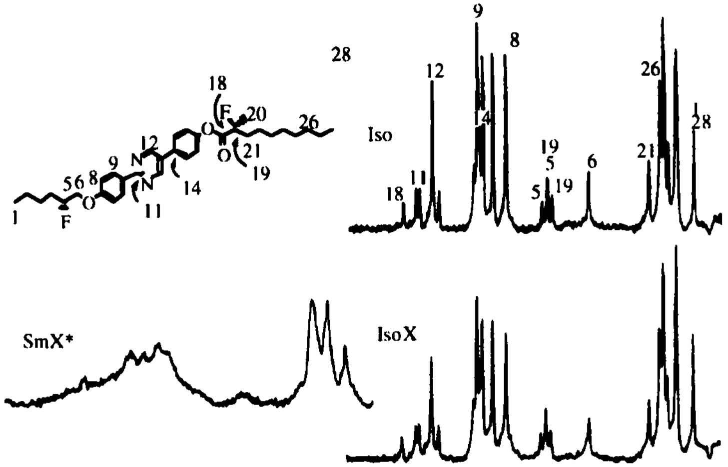

FIGURE 3 ^{13}C-NMR spectra in the Iso, IsoX and SmX* phases.

IsoX phase gave well-resolved peaks as in the Iso phase. This result indicates that fast isotropic reorientation of molecules or molecular assemblies exists in the IsoX phase.

The similar molecular dynamic properties were also observed in dielectric measurements. Figure 4 shows dielectric dispersion in each phase. The IsoX phase shows almost the same dispersion as the Iso phase does. On the contrary, a dielectric relaxation due to the Goldstone mode does exist in the SmC* phase. The relaxation attributable to the Goldstone mode was also observed in the SmX* phase. Since the electrooptic (EO) switching was also detected in this phase under an optical microscope, the

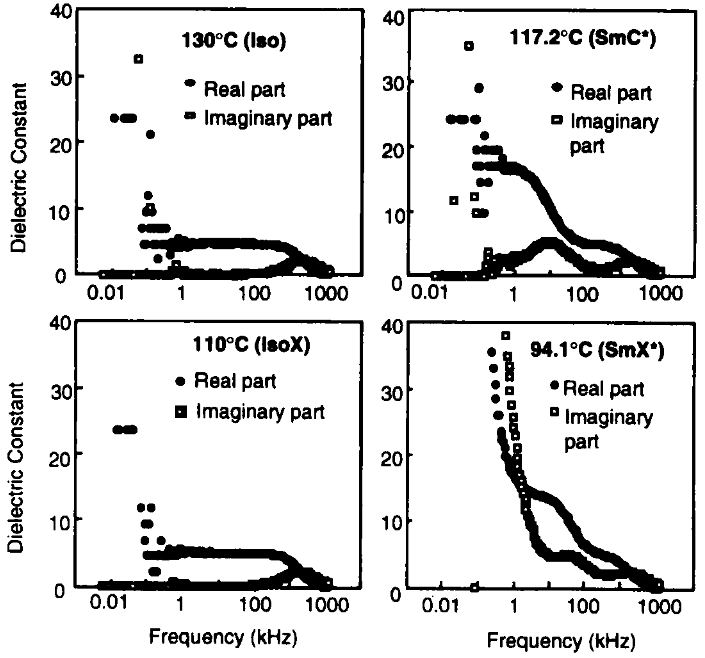

FIGURE 4 Dielectric dispersion in the (*R*, *S*) compound.

SmX* phase is also a switchable ferroelectric phase. In contrast, the IsoX phase shows neither EO response nor dielectric behavior related to ferroelectricity. Thus, it is concluded that no cooperative ferroelectric motion exists but liquid-like dynamic motion occurs in the IsoX phase.

To investigate the structure, x-ray analysis was made. Figure 5 shows the wide angle diffractions in the three phases. In addition to a main peak, a side peak appears in the IsoX and SmX* phases. However, the lack of fine structures in wide angle region suggests that both are not highly ordered phases. We also made x-ray analysis using a thick cell under reflected and transmitted geometries. By detailed comparison of all the peaks observed with those in cubic phases ever reported, the Im3m structure was suggested for the IsoX phase. The details will be reported in a separate paper.

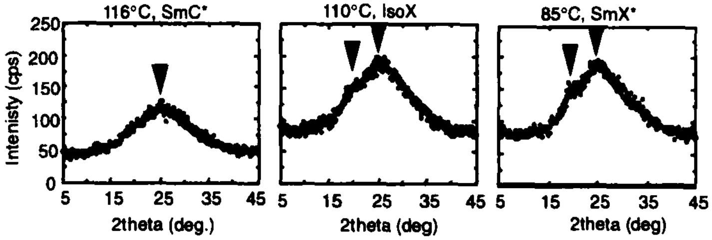

FIGURE 5 Wide angle x-ray diffraction in SmC*, IsoX and SmX* phases.

Let us show the phase diagrams in binary mixtures of the stereoisomers. The IsoX phase appears in the (*R*, *S*) and (*S*, *R*) compounds and their mixtures, as shown in Fig. 6(a). However, the IsoX phase does not emerge in the (*R*, *R*) compound, and does appear only by mixing with a large fraction of the (*R*, *S*) compound, as shown in Fig. 6(b). These phase diagrams suggest that coexistence of *R* and *S* groups is necessary to form the IsoX phase.

The most striking feature is the diagram of the binary mixture of the (*R*, *R*) and (*S*, *S*) stereoisomers. The IsoX phase is induced in the central region of the diagram, as shown in Fig. 6(d). Thus, the IsoX phase emerges only when *R* and *S* chiral groups meet each other in high probability. It should be noted that the (*R*, *R*) and (*S*, *S*) stereoisomers have larger spontaneous polarizations and short pitches than the (*R*, *S*) and (*S*, *R*) steroisomers in their SmC* phase. This means that the emergence of the IsoX phase is not simply due to high chirality but surely based on chiral recognition.

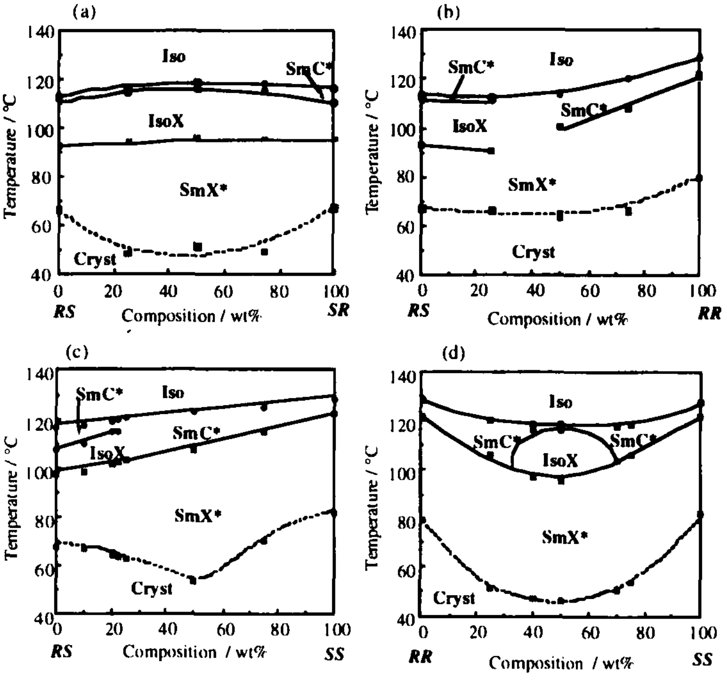

FIGURE 6 Phase diagrams of binary mixtures of stereoisomers.

6. CONCLUSION

It was found that the optically isotropic IsoX phase is very similar to the isotropic liquid phase in molecular motional and dielectric viewpoints. Phase diagrams of stereoisomeric mixtures strongly suggest that the IsoX phase is formed by molecular aggregation via chiral recognition.

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