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THE FERROELECTRICITY IN THE MIXTURES OF CHIRAL WITH NON-CHIRAL SMECTIC C

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The spontaneous polarization was measured by means of the Sawyer-Tower method in mixtures of chiral smectic C liquid crystal with smectic C liquid crystal. Induced circular dichroism in the chiral smectic C phase was also measured on the same mixtures. It was found that the magnitude of spontaneous polarization was dependent on the composition of the mixtures or the intensity of circular dichroism.

Recently, Meyer et al. have reported that (+)-p-decyloxybenzylidene p'-amino-2-methylbutyl cinnamate (DOBAMBC) is ferroelectric in the smectic C and smectic H phases.¹ Many properties of this compound have been investigated since then.²⁻¹⁰ According to the molecular statistical model of the smectic A and smectic C phases, the free rotation about the long molecular axis is generally allowed in the A and C phases.¹¹ However, free rotation is not allowed in the smectic C phase composed of chiral molecules but a chiral smectic C phase similar to the cholesteric phase is produced.

We have studied the ferroelectric effect in the binary mixtures of chiral smectic C liquid crystal: DOBAMBC, with non-chiral smectic C liquid crystal: *p,p'*-*n*-diheptyloxyazoxybenzene (DHOAB). DOBAMBC was synthesized from (+)-2-methylbutyl *p*-aminocinnamate (Eastman Kodak Co.) and *p*-*n*-decyloxybenzaldehyde (Tokyo Kasei Kogyo Co.). DHOAB was purchased from Eastman Kodak Co. Each compound was recrystallized twice from ethyl alcohol and purified by zone refining with thirty zone passes.

Ferroelectric measurement: The ferroelectric hysteresis loop of binary mixture systems are measured by the Sawyer-Tower method¹² at a frequency of 50 Hz and a voltage of 16 kV/cm (peak to peak). The sample is sandwiched between two glass slides coated with tin oxide on which SiO is evaporated at an oblique incidence. The resistivity of the sample is about $10^9 \Omega/\text{cm}$. The sample is heated to the isotropic phase and cooled to the smectic A phase at several rates in the magnetic field of about 10 kG and then to the smectic C phase. The smectic layers almost line up perpendicular to the sample walls at a very slow cooling rate ($5^\circ\text{C}/\text{hour}$). At a rapid cooling rate between about 10^0 and $1^\circ\text{C}/\text{min}$, the smectic layers no more lined up perpendicular to the sample walls and each sample has a similar texture. The degree of the sample alignment depends on the rate of decreasing temperature through the isotropic-smectic A transition point.

Figure 1 shows the temperature dependence of the spontaneous polarization in a sample of DOBAMBC

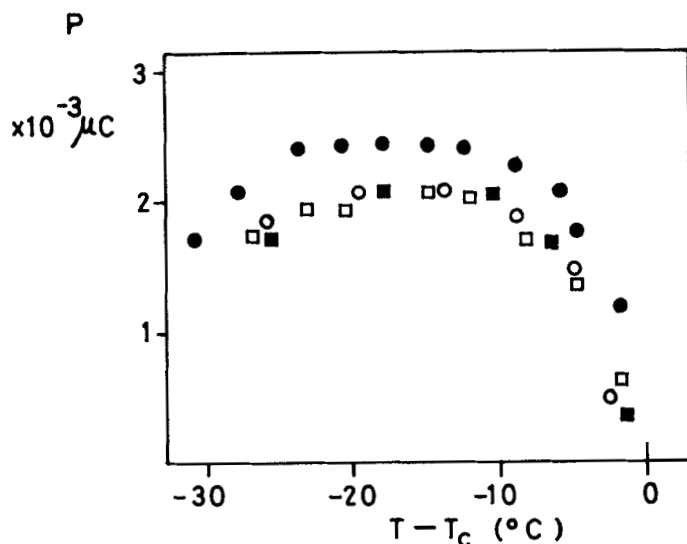


Figure 1: The temperature dependence of the spontaneous polarization in DOBAMBC 78 wt% sample prepared from cooling through isotropic-smectic A transition temperature at ●: 5°C/hour, ○: 1°C/min, ■: 4°C/min, □: 10°C/min
 T_c : smectic A-smectic C transition temperature

(78 wt%) at various cooling rates. Figure 2 shows the temperature dependence of the spontaneous polarization of the DOBAMBC-DHOAB mixtures in various compositions.

These samples are prepared by being cooled from isotropic liquid to smectic A at 4°C/min rate. The change of the spontaneous polarization of each sample shows similar temperature dependence. The value of the spontaneous polarization in a sample of DOBAMBC (71 wt%) is obviously smaller than that of the other

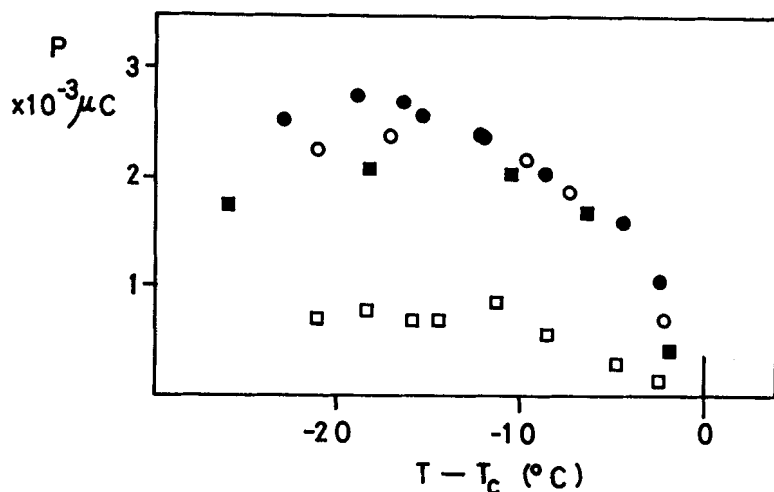


Figure 2: The temperature dependence of the spontaneous polarization in DOBAMBC
 ●: 100 wt%, ○: 89 wt%, ■: 78 wt%, □: 71 wt% samples prepared from cooling at 4 °C/min. T_c : smectic A-smectic C transition temperature

three cases. The spontaneous polarization of a sample of DOBAMBC (59 wt%) is not detected in the present experiment.

Circular dichroism measurement: The chiral smectic liquid crystal with induced circular dichroism (LCICD) in the absorption region of naphthacene was investigated. Naphthacene was purchased from Tokyo Kasei Kogyo Co. and a small amount of it was added to the liquid crystals without further purification. A single domain sample is prepared by treating the cell walls with dimethyl dichlorosilane. After this treatment, the smectic layers are parallel

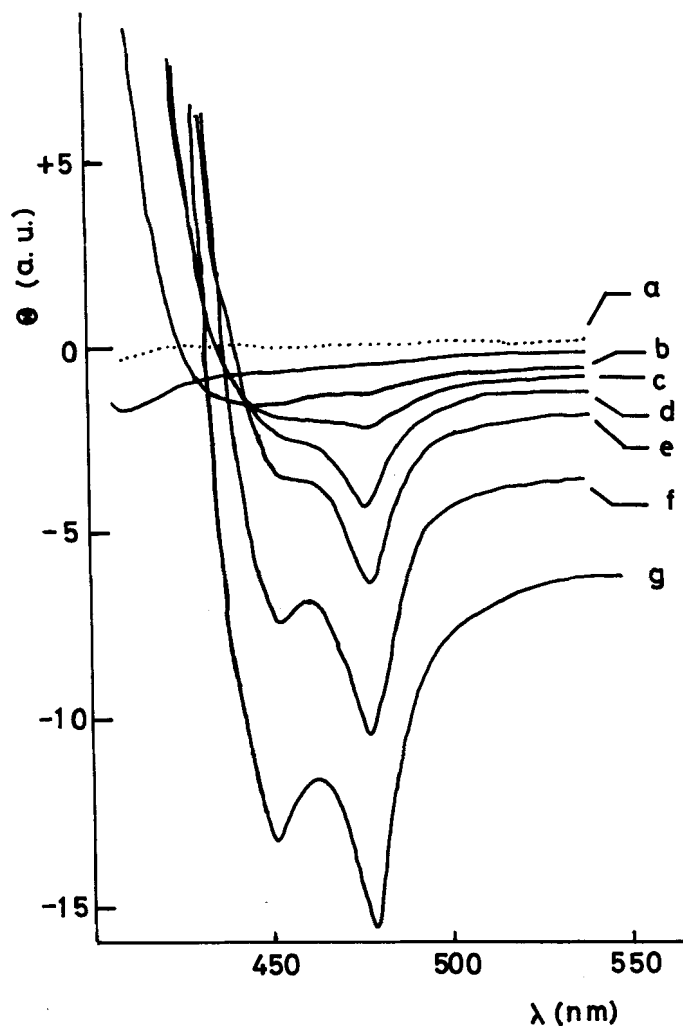


Figure 3: The temperature dependence of induced circular dichroism spectra of naphthacene at 474 nm.
 Temperature $T-T_c$: (a) $+5\text{ }^{\circ}\text{C}$
 (b) $-2\text{ }^{\circ}\text{C}$ (c) $-4.5\text{ }^{\circ}\text{C}$ (d) $-12\text{ }^{\circ}\text{C}$
 (e) $-17.5\text{ }^{\circ}\text{C}$ (f) $-21\text{ }^{\circ}\text{C}$ (g) -23°C .
 T_c : smectic A-smectic C transition temperature

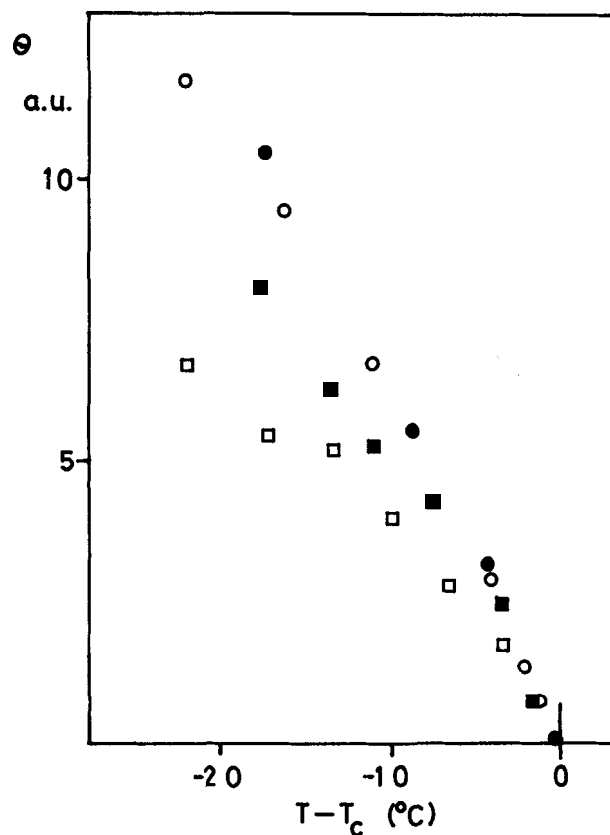


Figure 4: The intensity of LCICD at 474 nm in various mixing ratio samples DABAMBC: ●: 100 wt%, ○: 89 wt%, ■: 78 wt%, □: 71 wt% vs. temperature. T_c : smectic A-smectic C transition temperature.

to the cell walls and the optical axis is perpendicular to the cell walls. Circular dichroism spectra are recorded on a JASCO J-40 CD spectrometer. The intensity of the circular dichroism depends on the orientation of naphthacene molecules in the liquid

crystals, tilt angle of the smectic C phase and the pitch of the smectic C phase. But, it mainly represents the intensity of the twisting power of the system. Figure 3 shows the temperature dependence of the LCICD spectrum on the naphthacene in the chiral smectic C phase of DOBAMBC. The LCICD spectra are also measured for naphthacene in binary mixtures (DOBAMBC-DHOAB). The LCICD intensity of the peak at 474 nm is plotted against temperature (Fig. 4). As the DHOAB content increases, the intensity of CD decreases. In this experiment, the CD is not able to be observed in a sample of DOBAMBC (59 wt%).

Conclusion: In the binary mixtures of the chiral smectic C (ferroelectric liquid crystal) with ordinary non-chiral smectic C, it is found that the ferroelectric effect is closely related to the intensity of induced circular dichroism.

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