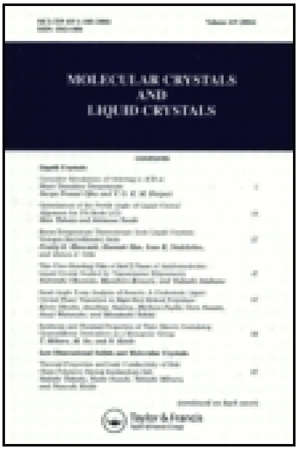

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Ferroelectric Phase Transition in Liquid Crystal

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Ferroelectric Phase Transition in Liquid Crystal†

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X-ray scattering profiles are carefully examined in a typical ferroelectric liquid crystal DOBAMBC(+) in order to clarify the mechanism of the transition. The result shows that the ferroelectricity is triggered by the tilt of the molecule through the piezoelectric coupling. Furthermore X-ray study in the racemic DOBAMBC(±) is made to verify the absence of the coupling, which shows the abrupt change of the tilt angle at the transition temperature in DOBAMBC(±), and the tricritical point may be expected in the system.

INTRODUCTION

Many attempts have been made to elucidate the molecular interaction in several liquid crystals, but the microscopic mechanism of the phase transitions has not been clear. Especially the nature of the interaction among molecules in a ferroelectric liquid crystal has not been understood explicitly.

The smectic C liquid crystals composed of chiral molecules can be expected to be ferroelectric.[1] Each layer of the chiral smectic C phase is spontaneously polarized, but there is no bulk polarization due to the helical structure in the absense of the external field. When an electric or magnetic field is applied on the specimen, the chiral smectic C phase changes into a normal ferroelectric smectic C phase.[2] Therefore the ferroelectric phase transition is considered to be a physical realization of Lifshitz point.[3]

Here we present the results of X-ray study of chiral DOBAMBC(+) and racemic DOBAMBC(±), in order to clarify the mechanism of the ferroelectric transition in liquid crystals.

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EXPERIMENT

CuKα radiations monochromatized by a graphite crystal were used throughout the measurements (60 kV, 100 mA). A divergent slit of 0.15 mm in width was set at a distance of 100 mm from the monochromator and two receiving slits of 0.30 mm and 0.60 mm in width at distances of 120 mm and 160 mm from the specimen. X-ray intensities were measured by a scintilation counter. The horizontal resolution estimated by scanning the incident beam was 0.16°.

Both specimens of chiral *p*-decyloxy benzilidene *p*-amino 2-methyl butyl cinamate, DOBAMBC(+), and racemic DOBAMBC(±) were synthesized in the almost same manner of Ref. 7. The specimen was set in a hole (0.1 × 0.2

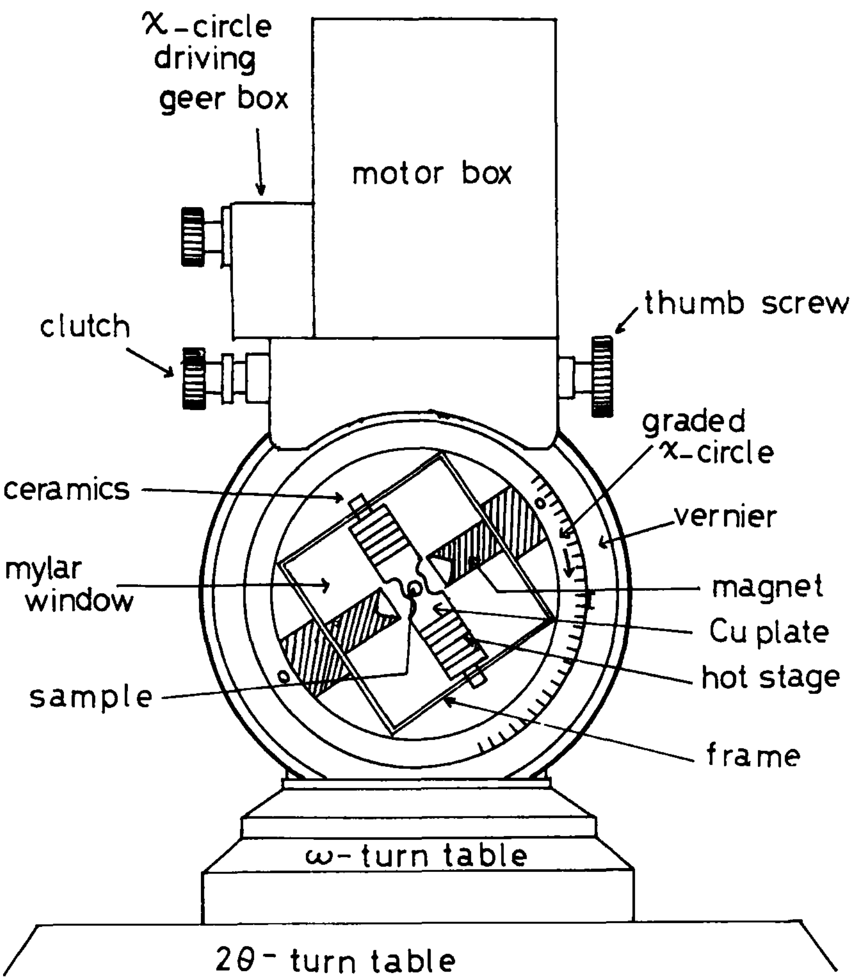

FIGURE 1 A hot stage for a specimen.

mm) drilled into a copper block (0.5 mm thick) with mylar windows (0.01 mm thick) on both sides. The sample on the hot stage was set in a magnetic field of 2.5 KOe and was rotated to give the Bragg condition in the smectic phase (See Figure 1). The temperature of the specimen was controlled within ± 0.05° C automatically. The experimental procedures are almost the same as Refs. 4, 5 and 6.

The specimens were heated to 125° C and kept under magnetic field for 2 hours. Applying the magnetic field, the temperature of the specimen was decreased very slowly. The cooling rate is about 0.1° C/min. The layer orientation is perfectly achieved in the smectic A phase and is partially achieved in the smectic C phase. The typical intensity profiles in the smectic A and C phases are given in Figure 2. The χ angle shown in Figure 1 was set to give the strongest intensity. The peak positions of the Bragg scattering, q's, were observed in the paraelectric smectic A phase and the ferroelectric smectic C phase of DOBAMBC(+). The value of q equals to $4\pi \sin \theta/\lambda$, where θ and λ are the scattering angle and the wavelength of X-ray, respectively. The tilt angle Θ of the molecules in the smectic C phases is related to q as $\Theta = \cos^{-1}(q_0/q)$, where q_0 is the position of the Bragg scattering in the smectic A phase. The temperature dependence of tilt angle Θ is shown in Figure 3. It is found that the tilt angle increases with decreasing temperature in the smectic C phase of DOBAMBC(+).

The Bragg scattering is observed in the smectic A and C phases. The intensity is almost independent of temperature just above the smectic A–C transition temperature $T_c = 93.5$°C and increases gradually with decreasing temperature in the smectic C phase. The scattering amplitude, that is, the square root of the intensity increase $\sqrt{I_C - I_A}$ in the smectic C phase is plotted as a function of temperature in Figure 3. It is found that $\sqrt{I_C - I_A}$ is proportional to the tilt angle Θ in the smectic C phase of DOBAMBC(+).

In the racemic DOBAMBC(±), the smectic A–C phase transition occurs at $T_c - 0.5$°C.[8] The temperature dependence of the peak position q or the tilt angle Θ in the racemic DOBAMBC(±) is given in Figure 4. The tilt angle is independent of temperature in the smectic C phase. The X-ray scattering intensity was carefully measured in the both smectic A and C phases. However the intensity is almost independent of temperature in the both phases of DOBAMBC(±).

DISCUSSION

A mean field expression of the free energy which involves a polarization P and a tilt angle Θ is given by

$$F = F_A + \frac{1}{2}\epsilon^{-1}P^2 + aP\Theta + \frac{1}{2}b(T - T_0)\Theta^2 + \frac{1}{4}c\Theta^4,\ c > 0, \qquad (1)$$

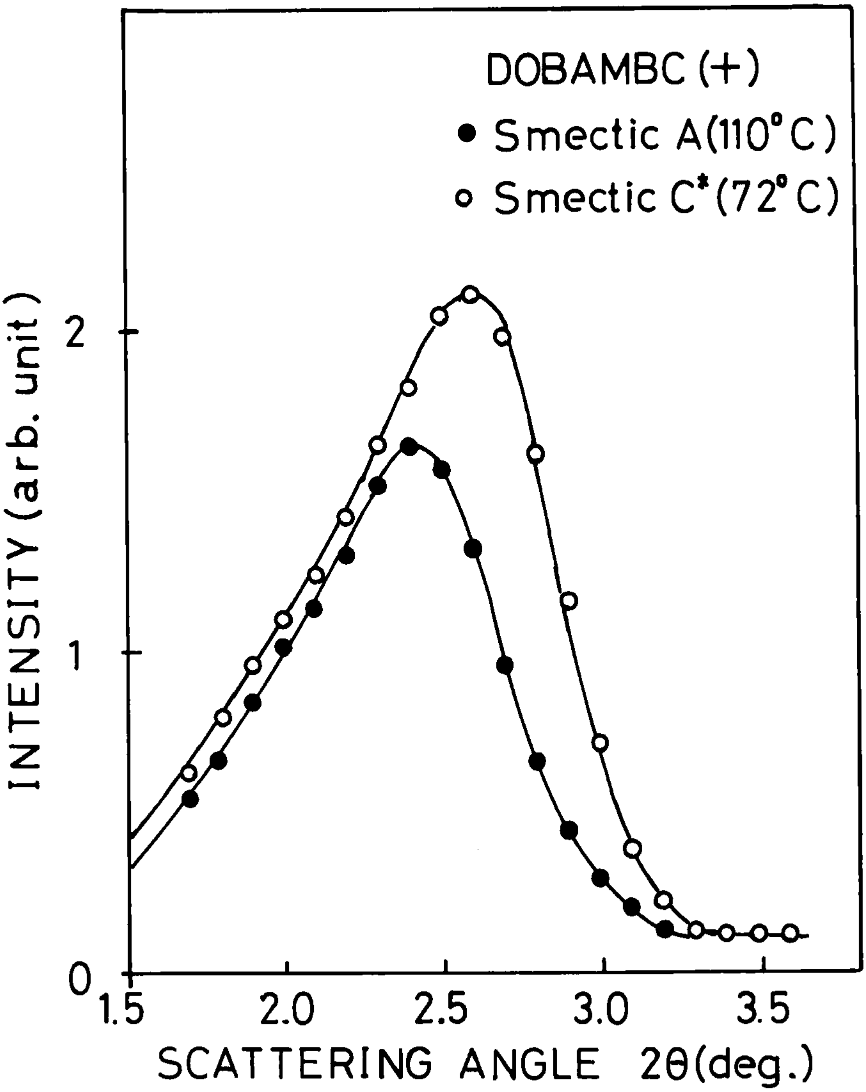

FIGURE 2 Typical intensity profiles in the smectic A phase and C phase in chiral DOBAMBC(+).

where ϵ is an electric susceptibility and a is a piezoelectric constant. The equilibrium values of the polarization and tilt angle are obtained from the relations, $\partial F/\partial P = 0$ and $\partial F/\partial \Theta = 0$ as

$$P = -a\epsilon\Theta, \tag{2}$$

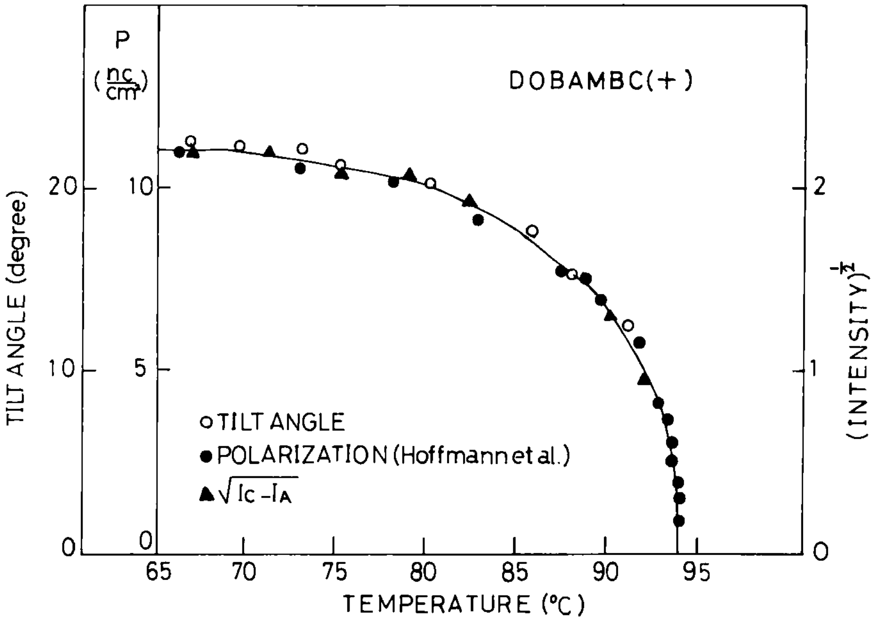

FIGURE 3 Temperature dependences of the tilt angle, the scattering amplitude and the spontaneous polarization[9] in chiral DOBAMBC(+).

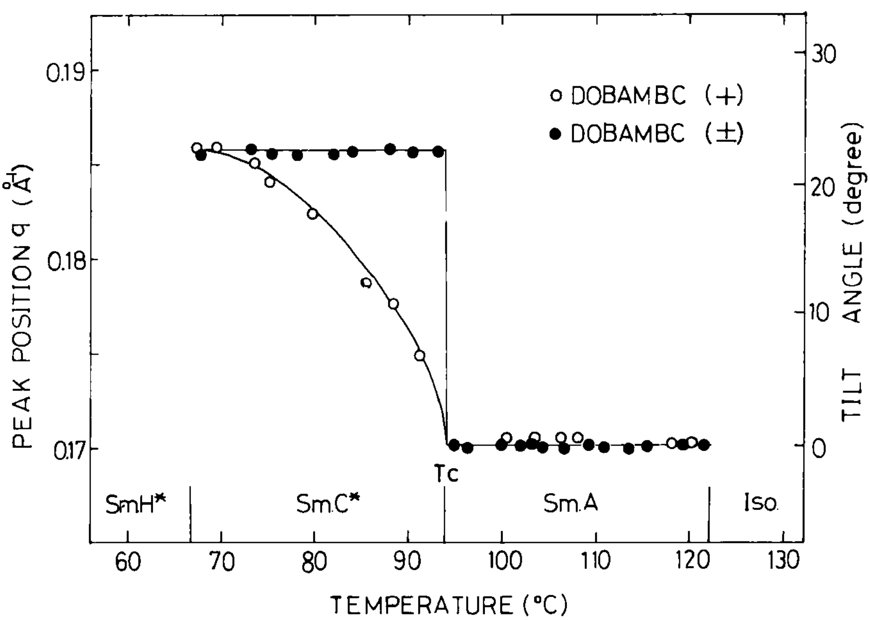

FIGURE 4 Temperature dependence of the Bragg peak position in chiral DOBAMBC(+) and racemic DOBAMBC(±).

and

$$\Theta = \{B(T_c - T)\}^{1/2}, \tag{3}$$

with $B = b/c$ and $T_c = T_0 + a^2\epsilon/b$. Eq. (2) shows that the polarization is proportional to the tilt angle below the smectic A-smectic C transition temperature T_c in DOBAMBC(+). In Figure 2 the observed tilt angle is compared with the spontaneous polarization.[9] This shows a good agreement and the temperature dependence of Θ is well established by the characteristic of Eq. (3).

In the smectic A phase the molecules are rotating freely around their long axis and the point symmetry of each layer corresponds to the group D_∞. The transition to the ferroelectric smectic phase is induced by the two dimensional representation E_1 and the point symmetry of the layer is reduced to monoclinic C_2, where a two fold axis is normal to the tilt direction.[2,10,11] The spontaneous polarization is parallel to the two fold axis. The X-ray scattering amplitude in the smectic C phase in DOBAMBC(+) is then written as[6]

$$F(q) = F_0(q) + i\Delta F(q)P, \tag{4}$$

where $F_0(q)$ and $\Delta F(q)$ are the amplitude of symmetric and asymmetric terms, respectively. The scattering intensity is $I_A = I_e N^2|F_0(q)|^2$ in the smectic A phase, where I_e is the Thomson's scattering intensity from an electron and N is a number of molecules in the specimen. In the smectic C phase the intensity increase is given by $I_C - I_A = I_e N^2|\Delta F(q)|^2 P^2$, which is proportional to the square of the polarization. The temperature dependence of the amplitude $\sqrt{I_C - I_A}$ is given in Figure 3. If the scattering vector is being maintained normal to the smectic layer planes, the imaginary part of the Eq. (4) should become zero. However our results shows that the imaginary part is almost proportional to the spontaneous polarization. The Bragg scattering in the smectic phase may be fairly different from the usual scattering in the solid phase.[2]

In racemic DOBAMBC($\pm$), the phase transition is of the first order. The free energy should be given by

$$F = F_A + \frac{1}{2}b(T - T_0)\Theta^2 + \frac{1}{4}c\Theta^4 + \frac{1}{6}d\Theta^6, \quad c < 0, \tag{5}$$

which does not involve a energy of polarization and a piezoelectric term, but involves a higher order term of the tilt angle for the abrupt change of Θ at T_c as shown in Figure 3. It is not clear why the coefficient c should change the sign in the chiral and non-chiral systems. If in racemic mixture ($\pm$) the other order parameter such as strain u can be considered, the free energy involves the terms given by $f\Theta^2 u + 1/2gu^2$ and $\partial F/\partial u = 0$ gives $u = -(f/g)\Theta^2$. The coefficient of the Θ^4 term is then written by $c' = c - f^2/g$. It is possible that c' has a negative value. However the value of u is not observed. We suggest that the tricritical point may be expected in the present system, as given in Ref. 13. The extended study on the tricritical point is in progress.

In conclusion, the tilt angle of the molecules plays a role of the primary order parameter in the smectic C phase of DOBAMBC(+). The spontaneous polarization is triggered by the tilt angle through the piezoelectric coupling. In DOBAMBC(±) the tilt angle changes abruptly at T_c. Furthermore the tricritical point may be expected in the present system, because the coefficient c of the fourth order in the free energy expression is positive in DOBAMBC(+) and negative in DOBAMBC(±). The X-ray diffuse scattering experiment is in progress in order to clarify the microscopic interaction among molecules in chiral DOBAMBC(+) and racemic DOBAMBC(±) and to determine the critical exponent. The ratent heat will be measured at T_c in DOBAMBC(±) for the first order transition. Our results will be discussed elsewhere, comparing with the heat capacity measurements, and also the optical measurements.

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After submitting the present paper, the temperature dependence of the Bragg position in racemic DOBAMBC(±) has been re-examined precisely. The abrupt change of the position at T_c as given in Figure 4 could not be detected in purified specimens.