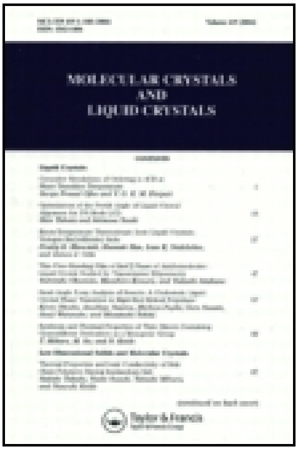

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We observed the molecular alignment in each smectic phase of an antiferroelectric liquid crystal MHPOBC under a high magnetic field using a polarizing microscope observation. The alignment in the SmC(*) phase depends on the chirality; In a racemic mixture, the molecules align parallel to the field, while the molecules tilt with respect to the field in a high optical purity compound because of the helix. On the other hand, the molecular alignment in the bulk state of the SmC_A(*) phase was independent of the optical purity and the smectic layer becomes normal to the field because of the macroscopic magnetic anisotropy of an anticlinic molecular structure in SmC_A(*).

Keywords: molecular alignment; magnetic field; optical purity; antiferroelectric liquid crystal; magnetic anisotropy

INTRODUCTION

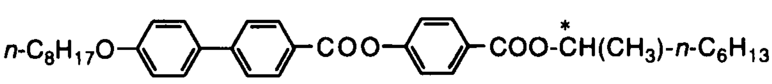
In the study of inter-molecular interaction and successive phase transition in chiral smectics, it is important to discuss the microscopic structure and dynamics. From this viewpoint, spectroscopy techniques are effective. Nuclear Magnetic Resonance (NMR) is one of them, which can clarify the molecular conformation, dynamics and the internuclear interaction using various pulse techniques. In particularly, the static broad-band NMR spectra give us much information about the molecular conformation.

When we analyze the broad-band NMR spectra using static samples, we need the macroscopic molecular alignment under a high magnetic field. In the N and SmA phases, it is easy to imagine the molecular alignment; the molecular long axis becomes parallel to the magnetic field due to the positve diamagnetic anisotropy. On the other hand, in the SmC(*) phase appearing at the lower temperature side of SmA, we can imagine two possibilities; one is that the molecular long axis remains parallel the field and the smectic layer tilts with respect to the field at the SmA-SmC phase transition, and the other is that the smectic layer remains normal to the field. Moreover, in the antiferroelectric SmC_A(*) phase, it would be more complex.

In this paper, we report the molecular alignments in the SmA, SmC(*) and SmC_A(*) phases under a high magnetic field using microscope observation. The molecular alignment in SmC(*) depends on the optical purity because of the helix. On the other hand, in the antiferroelectric SmC_A(*) phase, the layer becomes normal the magnetic field regardless of the existence of the helix and/or optical purity) because the largest macroscopic magnetic susceptibility component is parallel to the layer normal, the same as that in SmA.

EXPERIMETNAL

Samples used were 4(1-methylheptyloxycarbonyl)phenyl 4'-octyloxybiphenyl-4-carboxylate (MHPOBC)s[1] of two kinds of different optical purities. Chemical structure and the phase sequence of each mixture are as follows.



S:*R* = 8:2 Iso 148.6°C SmA 121.6°C SmC* 115.1°C SmC_A*
S:*R* = 1:1 Iso 140.0°C SmA 120.0°C SmC 113.0°C SmC_A

Each phase transition temperature was slightly shifted under the influence of a high magnetic field. We confirmed the phase transition by the texture change under the field. These mixtures were introduced in the 1 mm-thick sandwich cell in which the glass substrate was not coated with any polymers. We used the liquid helium-less super conducting magnet system (TM-5, Toshiba). This system can generate a magnetic field as high as 5 T and has a wide bore of 12 cmϕ. A heater block and a polarizing microscope were equipped in this magnet, as displayed in Fig. 1. The temperature was cotrolled using a temperature control unit (Chino, DB-1120) and the texture of each phase was observed in the cooling process from the isotropic liquid to the $SmC_A(*)$ phase. The cooling rate was less than -0.1°C/min.

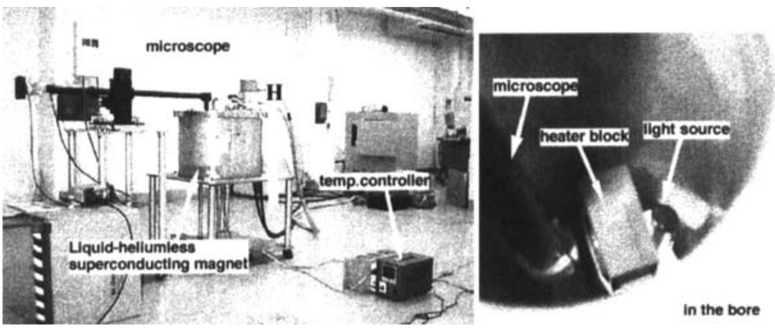


FIGURE 1 Photographs of liquid helium-less super conducting magnet. (See Color Plate XI at the back of this issue)

RESULTS and DISCUSSION

Figure 2(a) is a microphotograph of the texture just at the isotropic-SmA phase transition observed under the parallel polarizers. Large battonets appear parallel to the magnetic field and combine to make smectic layers. Figure 2(b) is a microphotograph observed in the SmA phase. Although some diamond defects were observed, the uniform alignment in which the layer normal was parallel to the magnetic field was almost attained, as already reported by many researchers[2]. In the SmA phase, we confirmed no difference of the textures between two mixtures.

When the phase transition from SmA to SmC(*) occurs, texture changes were quite different between two mixtures with different optical purities, as

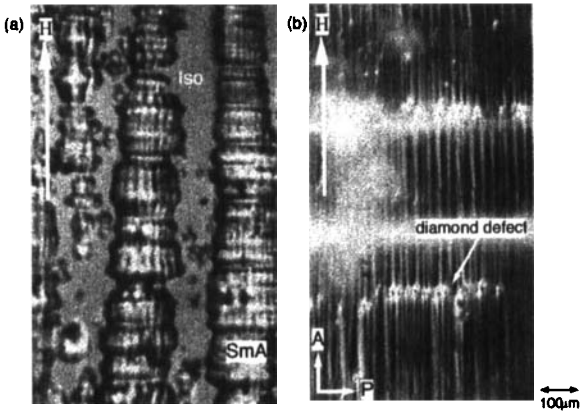


FIGURE 2 Microphotographs of the texures just at the phase transition from isotropic liquid to SmA (a) and in the SmA phase (b).
(See Color Plate XII at the back of this issue)

shown in Figs. 3(a), 3(b), 3(c) and 3(d). These textures were taken under the crossed polarizers. In the mixture with a high optical purity, the disclination lines appearing due to the helix and the ellipsoidal focal conics were observed, as shown in Fig. 3(a). The long axes of the focal conics are parallel and the disclination lines are running normal to the magnetic field. This texture clearly indicates that the smectic layer remains normal to the magnetic field even at the phase transition from SmA to SmC* because the largest macroscopic magnetic susceptibility is normal to the layer due to the helix. On the other hand, in a racemic mixture of MHPOBC, neither the disclination line nor focal conics were observed in SmC, as shown in Figs. 3(b), 3(c) and 3(d). When focused on the middle of the cell in the racemic mixture, it was found that the extinction direction under the crossed polarizers was parallel to the magnetic field, as shown in Fig. 3(b). When we shifted the focal point near the substrate surface, however, two domains whose extinction directions were tilted with respect to the field were observed, as shown in Figs. 3(c) and 3(d). These results indicate that the molecular long axis aligns parallel to the magnetic field due to the magnetic anisotropy in SmC and the smectic layer tilts with respect to the field at the phase transition from SmA to SmC in the bulk region. In contrast, the molecules are anchored to the substrate surface and the smectic layer is kept to be normal to the field at the phase transition from SmA to SmC. The similar results were assumed by Luzar et al.[3] and Yoshizawa et al.[4]

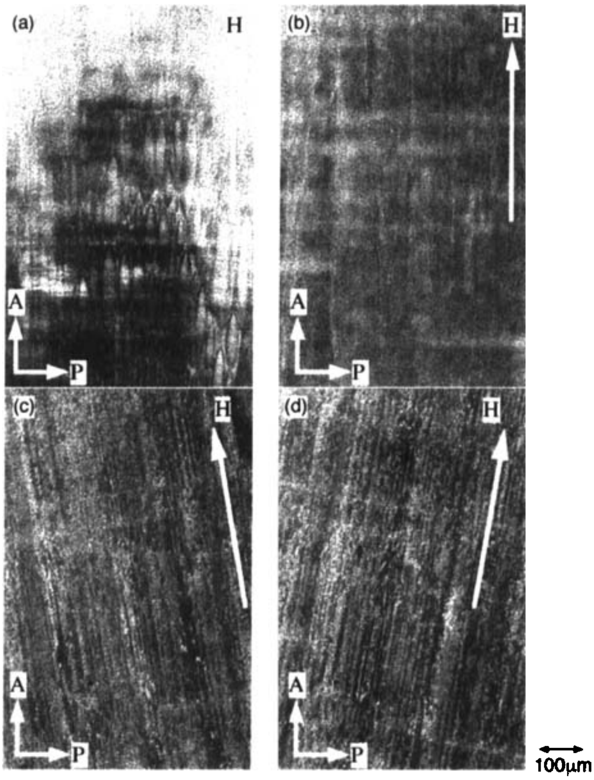


FIGURE 3 Microphotographs of the texctures in SmC* of MHPOBC (S:R=8:2) (a) and in SmC of racemic mixture of MHPOBC (b) anc (c). In SmC, different texures were taken when the focusing point was shifted in the middle of the cell (b) and at the substrate surface (c) and (d).

(See Color Plate XIII at the back of this issue)

The texture in SmC_A* of a high optical purity mixture is shown in Fig. 4(a). The extinction direction under the crossed polarizers was parallel to the magnetic field. Therefore, the smectic layer aligned normal to the magnetic field. On the other hand, to our surprise, the smectic layer realigns at the phase transition from SmC to SmC_A in a racemic mixture; the extiction direction becomes parallel to the magnetic field, as shown in Fig. 4(b). It indicates that the smectic layer aligns normal to the magnetic field. In Fig. 4(b), some defect lines are also observed, which would be caused by the layer reorientation at the SmC-SmC$_A$ phase transition. Therefore the smectic layer in a racemic mixture reorients at each phase transition of SmA-SmC and SmC-SmC$_A$. This alignment is considered to be caused by the macroscopic

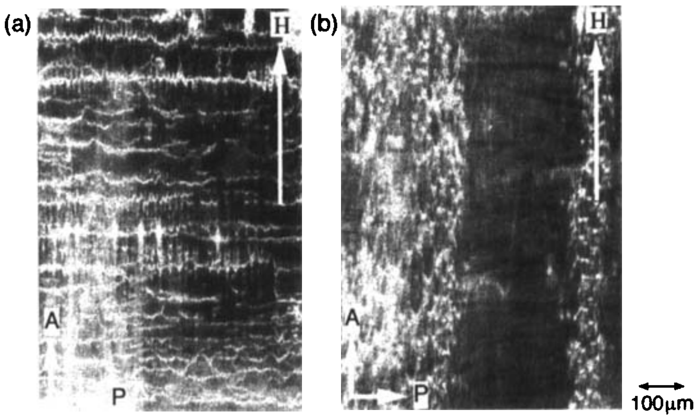


FIGURE 4 Microphotographs of the textures (a) in the SmC$_A$* of MHPOBC (S:R=8:2) and (b) in SmC$_A$ of racemic mixture of MHPOBC. (See Color Plate XIV at the back of this issue)

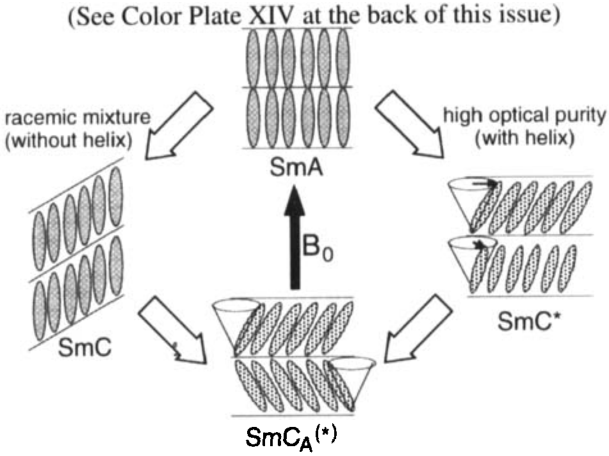


FIGURE 5 Molecular alignments under the high magnetic field of MHPOBCs with high and low optical purities.

magnetic anisotropy; since molecules tilt in the opposite sense in the neighboring layers in the $SmC_A(*)$ phase, the largest macroscopic magnetic susceptibility direct parallel to the magnetic field, the same as the largest refractive index. Thus the alignment is the same irrespective of the optical purity in the $SmC_A(*)$ phase. Molecular alignments under the high magnetic field are summerized in Fig. 5.

CONCLUSION

We studies the molecular alignment under a high magnetic field. The molecular alignment in SmC(*) depends on the optical purity, in other words, the existence or absence of the helical structure. On the other hand, the molecular alignment in the $SmC_A(*)$ phase is independent of the optical purity because of the same macroscopic magnetic anisotropy.

Acknowledgment

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