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Molecular Alignment Structure of Dimeric Liquid Crystal Having INAC$_A$ Phase Sequence

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Antiferroelectric liquid crystals (AFLCs) composed of low-mass mesogens do not show the nematic (N) phase. Recently, it has been reported that an AFLC containig dimeric molecules may show the N phase. However, it is not obvious why the antiferroelectric SmC (SmC$_A$) and N phases may coexist in the phase sequence of the dimeric LC$_S$. In this study, the molecular alignment structure has been researched with an X-ray diffractometer. It is found that a dimeric LC 8PY11OCB has a bookshelf structure in the SmA phase and a chevron structure in the SmC$_A$ phase. Moreover, the molecular alignment is an intercalated structure in both Sm phases. The bent molecular structure is stable even in the SmA phase, in which the phenylpyrimidine moieties of 8PY11OCB freely rotates due to a high thermal motion with the axis being another mesogenic part including cyano group.

Keywords: dimeric liquid crystal; nematic; smectic C$_A$; X-ray diffraction; 8PY11OCB

1. INTRODUCTION

Antiferroelectric liquid crystals (AFLCs) are attractive for LC devices because of their unique characteristics such as high-speed response and monostability [1,2]. However, it is hard to fabricate a defect-free AFLC medium owing to the phase transition from the isotropic liquid directly to the smectic (Sm) phase not via the nematic (N) phase [3,4]. Recently, it has been reported that an LC medium with dimeric molecules which take a bent molecular structure may show the N

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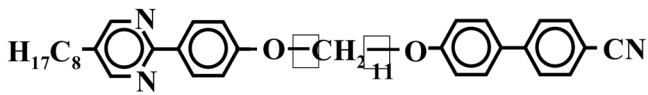
phase [5,6]. But, it has not been obvious yet why the antiferroelectric SmC (SmC_A) and N phases may coexist in the phase sequence of the dimeric LC. In this study, the molecular alignment structure of liquid-crystalline phases has been researched by the X-ray diffraction (XRD) measurement. For an investigation of the molecular periodical structure, XRD can be used as a powerful tool. A layer spacing of a dimeric LC 8PY11OCB [7] in the Sm phase can be cleared by measuring the X-ray diffraction peak. We will discuss the molecular alignment structure from the results of XRD measurement in addition to that of the polarizing FT-IR [8].

2. EXPERIMENTALS

8PY11OCB having Iso.-N-SmA-SmC_A ($INAC_A$) phase sequence was used in this research. The molecular formula and phase sequence of 8PY11OCB are shown in Figure 1. Dimeric liquid crystals may show the odd-even effect and then the bent molecular structure for 8PY11OCB would be stable. The LC alignment film used was the polyimide RN-1199 (Nissan Chemical Industries) [9,10]. A solution of polyimide was spun on glass substrate and then baked. After the thermal treatment, the substrates were rubbed. Then the LC material was injected in the isotropic phase via capillary action into an empty cell, in which the rubbing directions were set parallel.

X-ray diffraction peak was measured with X-ray diffractometer RINT2100 (Rigaku). The measuring geometry is illustrated in Figure 2. The rotation angle α was defined as about zero when the incident X-ray was vertical to the cell substrate. In order to decide the most suitable placement of counter (angle 2θ) and sample (angel α) for Bragg condition, two steps of following measurement were used. The first measurement was to decide α of sample. The counter was set a reasonable 2θ, and then the α-scan was done. The second measurement was to decide 2θ of counter. The sample was set at α which was decided in the first measurement, and then the 2θ-scan was done.

8PY11OCB



Cryst. (75) SmC_A (92) SmA (116) N (128) Iso. [°C]

FIGURE 1 Molecular formula and phase sequence of 8PY11OCB.

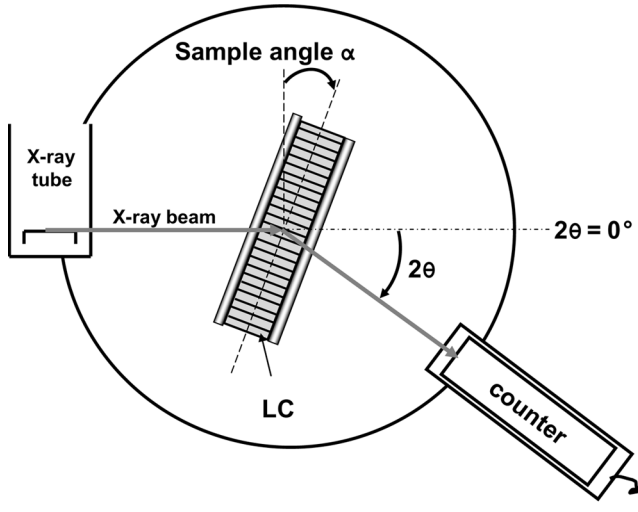


FIGURE 2 Geometry used in XRD measurement.

A half of 2θ in which XRD is highest is considered to be Bragg angle, and the layer spacing can be obtained by the Bragg angle.

3. RESULTS AND DISCUSSION

Figure 3 shows the X-ray diffraction peak of 8PY11OCB in the SmC_A phase . It is found that the double peaks appear (Fig. 3(a)), and thus 8PY11OCB has a chevron structure in the SmC_A phase. Figure 4 shows the temperature dependence of the X-ray diffraction peak of 8PY11OCB in the SmC_A phase. It is found that the chevron angle

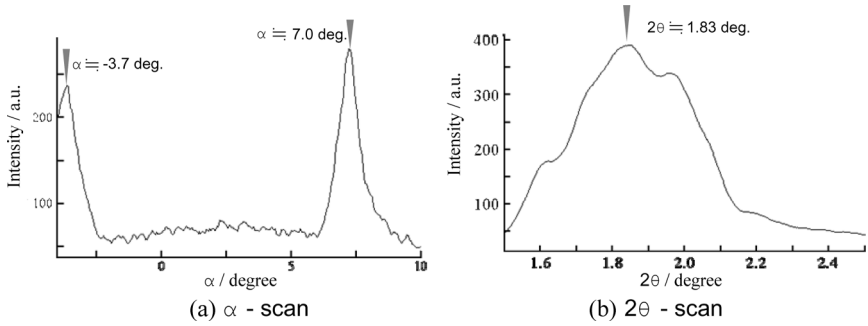


FIGURE 3 XRD patterns for 8PY11CB in SmC_A phase.

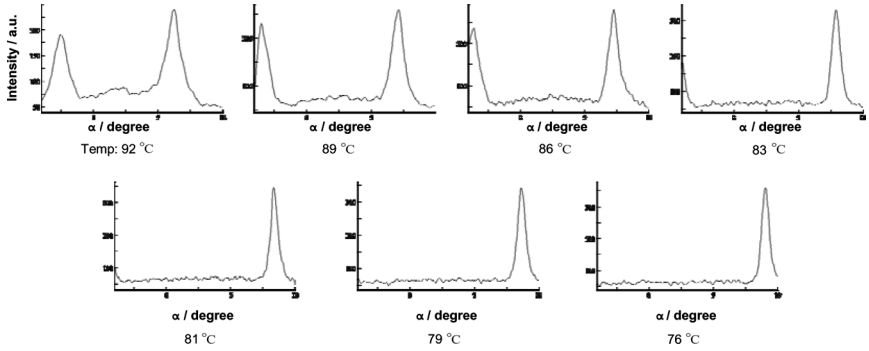


FIGURE 4 Temperature dependence of the X-ray diffraction peak of 8PY11OCB in SmC_A phase.

increases as the temperature decreases, and the maximum of cheveron angle is estimated at 6.35°. In Figure 3(b), the Bragg angle $\theta = 1.83/2$, and then the layer spacing is about 22 Å. Since the molecular length of 8PY11OCB is about 40 Å, the molecular alignment may be an intercalated structure. From the polarizing FT-IR measurement, it was found that the cyano group is directed to the rubbing direction [5], and therefore the molecular alignment structure in the SmC_A phase can be shown in Figure 5. A bent molecular conformation is stable in the SmC_A phase.

Figure 6 shows the X-ray diffraction peak of 8PY11OCB in the SmA phase. It is found that the single peak appears in the SmA phase (Fig. 6(a)). Therefore, it is confirmed that 8PY11OCB has a bookshelf-structure in the SmA phase. Furthermore, the Bragg angle is almost same as in the SmC_A phase (Fig. 6(b)), and then the layer spacing is

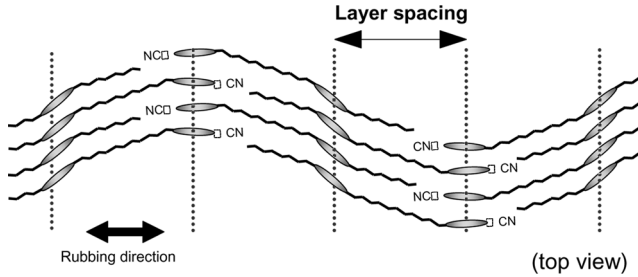


FIGURE 5 Molecular alignment structure model of 8PY11OCB in SmC_A phase.

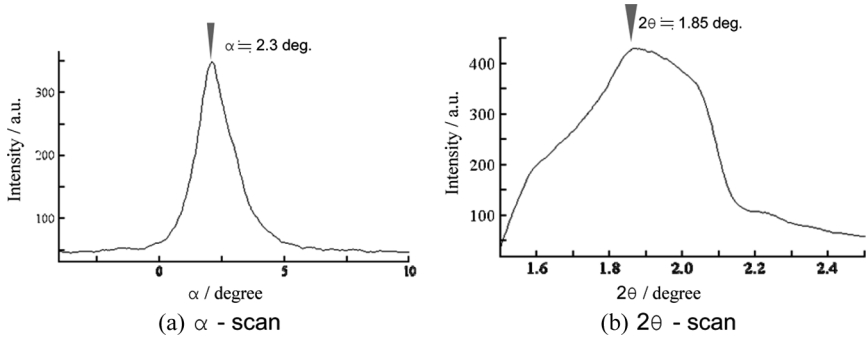


FIGURE 6 XRD patterns for 8PY11CB in SmA phase.

estimated at about 22 Å. The molecular alignment may be an intercalated structure in the SmA phase as well as in the SmC_A phase. So, the molecular alignment structure in the SmA phase can be shown in Figure 7. A bent molecular conformation is stable even in the SmA phase. However, as considering the alignment structure of SmA, it is hard to conclude that the bent molecular conformation is statically stable. Furthermore, it was confirmed that in the polarizing FT-IR measurement, the strength of the peak originated in the cyano goroup does not almost change, but that originated in the phenylpyrimidine largely decreases in the phase transition from the SmA to the SmC_A phase (see Fig. 8). Therefore, it is guessed that phenylpyrimidine moieties freely rotate and turbulent due to high thermal motion with the axis being another mesogenic part including cyano group (Fig. 7), and it looks like a cylindrical molecular shape on average. As a result, 8PY11OCB may exhibit the SmA phase and moreover the N phase even in the bent molecular conformation.

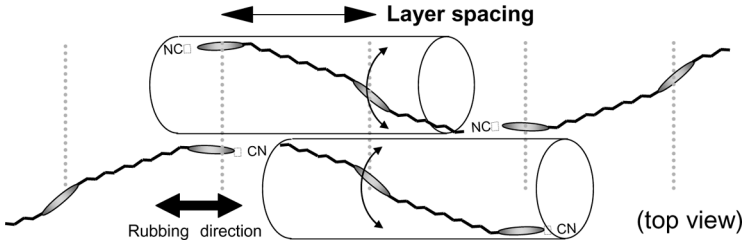


FIGURE 7 Molecular alignment structure model of 8PY11OCB in SmA phase.

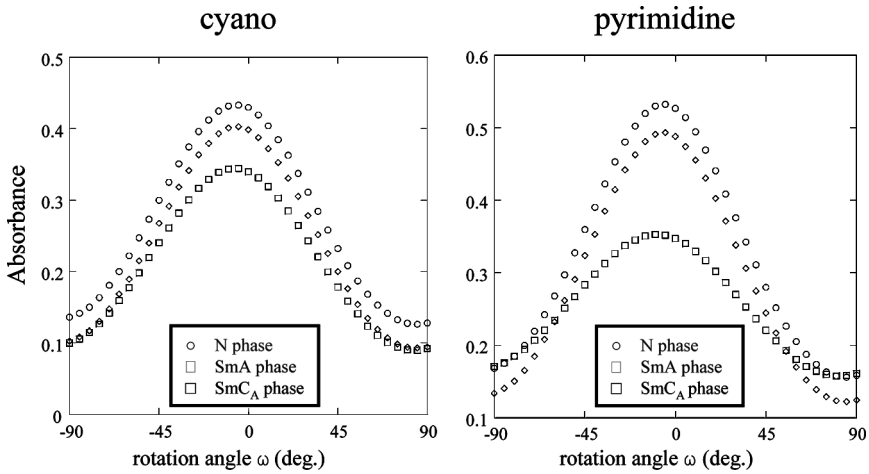


FIGURE 8 Polarized FT-IR measurement results in 8PY11OCB.

Since the main difference of the SmA phase from the N phase may be only the presence of the smectic layer structure, it is guessed that a bent molecular conformation may be stable also in the N phase. In all mesogenic phases of 8PY11OCB, the mesogenic part including cyano group orients to the rubbing direction [8]. In the SmA and N phases, the phenylpyrimdine moieties freely rotate due to high thermal motion, and therefore the SmA and N phases can appear. On the other hand, in the SmC_A phase, this rotation is suppressed due to the lower thermal motion, and then a statically alternating and herringbone alignment structure of SmC_A may appear. In this way, the SmC_A and N phases may coexist in the phase sequence of 8PY11OCB.

4. CONCLUSIONS

The molecular alignment structure of a dimeric LC 8PY11OCB was researched with XRD. 8PY11OCB has a bookshelf structure in the SmA phase and a chevron structure in the SmC_A phase. The molecular alignment is an intercalated structure and a bent molecular conformation is stable in both phases. In the SmA phase, the phenylprimidine moieties freely rotate due to higher thermal motion. So, it looks like cylindrical molecular shape on average. On the other hand, in the SmC_A phase, the rotation is suppressed due to lower thermal motion, and then a herringbone alignment structure may appear.

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