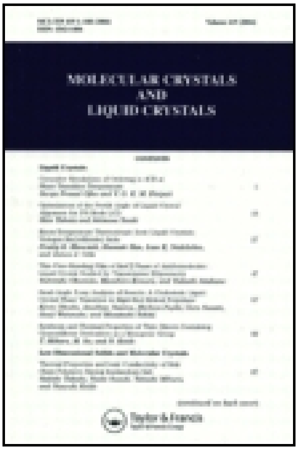

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Phase Transformation of Swollen Thermotropic Liquid Crystals Studied by X-Ray and ^{2}H-NMR Measurements

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To cite this article: Kazuyuki Hiraoka, Atsushi Kato, Hideaki Hattori, Yoshinori Sasaki, Yoshihiro Omata, Kenji Koguma, Nobuyuki Ban & Masato Oshima (2009): Phase Transformation of Swollen Thermotropic Liquid Crystals Studied by X-Ray and ^{2}H-NMR Measurements, Molecular Crystals and Liquid Crystals, 509:1, 1/[743]-8/[750]

To link to this article: http://dx.doi.org/10.1080/15421400903050970

Mol. Cryst. Liq. Cryst., Vol. 509, pp. 1/[743]–8/[750], 2009
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903050970

Phase Transformation of Swollen Thermotropic Liquid Crystals Studied by X-Ray and ^{2}H-NMR Measurements

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Molecular realignments during the successive phase transformations of a binary mixture of smectogenic and aliphatic compounds have been studied. The layer spacing, which is about 38.5A in the crystal phase, abruptly increases up to 54A during the transformation to the smectic phase, because aliphatic molecules are taken into the smectic liquid crystals during the transformation. A myelinic texture is observed in the smectic phase in which the liquid crystals are swollen with the aliphatic molecules. In addition, the quadrupolar splitting is observed in the ^{2}H-NMR spectra of the sample swollen with d_8-octane, because the aliphatic molecules are averagely oriented parallel to the director of the smectogens in the swollen smectic liquid crystals.

Keywords: ^{2}H-NMR; lyotropic; molecular orientation; order parameter; quadrupolar splitting; smectic; swollen thermotropic liquid crystals; X-ray diffraction

I. INTRODUCTION

Swollen thermotropic liquid crystals have been paid an increasing attention as a novel class of liquid-crystalline materials, because they give rise to new microscopic and macroscopic features by combining

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This work was supported by a Grant-in-Aid for Scientific Research (C) (#20550167) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), and also partially supported by the “Academic Frontier Project” for private universities (2006–2008): matching fund subsidy from MEXT.

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the thermotropic liquid crystalline structure with the lyotropic mesomorphic properties [1–10]. In this study, molecular realignments during successive phase transformations of a binary mixture of a smectogenic compound ((4-(1-methylheptyloxycarbonyl) phenyl 4′-octyloxybiphenyl-4-carboxylate: MHPOBC) and an aliphatic solvent (octane) are investigated. The crystal-to-smectic transformation is recognized by means of polarized microscope observations in which a myelinic texture appears. The layer spacing abruptly increases during the transformation, in which octane molecules are taken into the smectic structure. Additionally, the quadrupolar splitting is observed in ^{2}H-NMR spectra of the sample swollen with d_8-octane, because the octane molecules are averagely oriented parallel to the director of the smectogens in the swollen smectic liquid crystals.

II. EXPERIMENTS

We prepared a binary mixture of a smectogenic compound (x g) and an aliphatic solvent (y ml) for investigation. Concentration of the sample was fixed at 30 wt/v%. Here, we estimated the concentration in units of "(x/y × 100) wt/v%". The smectogenic compound used was a racemate of a prototype antiferroelectric liquid crystal, 4-(1-methylheptyloxycarbonyl) phenyl 4′-octyloxybiphenyl-4-carboxylate (MHPOBC), which shows the following phase sequence in cooling (°C) [11], Iso (146) SmA (116) SmC (105) SmC$_A$ (63) SmI$_A$ (50) Cryst. The synthesis of MHPOBC was done in analogy to known procedure [12]. Here, we used octane as aliphatic solvent, which was used as received from Kanto Chemical Kougyo Co.

Transition temperatures of the sample were confirmed by polarized optical microscopy and as well as by differential scanning calorimetry (DSC) at a heating and cooling rate of 10°C/min (Seiko, SSC-500). The smectic layer spacing was estimated by X-ray scattering measurements with a rotating anode X-ray system (Rigaku, RINT2500) using a Cu-K$_\alpha$ beam filtered by a confocal mirror ($\lambda = 1.54$ Å, X-ray power = 2.7 kW). The measurements were performed using a two-dimensional image plate system (2540 × 2540 pixels, 50 µm resolution). The sample was mounted in a microfurnace (Mettler, FP82HT) for temperature regulation. In order to investigate alignment of aliphatic molecules in the swollen sample, we observed the quadrupolar splitting in ^{2}H-NMR spectra of the sample swollen with d_8-octane [13,14]. ^{2}H-NMR measurements were performed using a JEOL LA-500 spectrometer. Here, we set accumulation times to 1000. The ^{2}H-NMR measurement was done after holding at the measuring temperature for at least 15 minutes.

III. RESULTS AND DISCUSSION

Figure 1 shows polarized optical micrographs of the binary mixture of MHPOBC and octane at various temperatures in heating process. Crystalline MHPOBC coexists with the octane solvent in the temperature region below 50°C, as shown in Figure 1(a) which is a photograph taken at 45°C. With increasing temperature, a myelinic texture appears at about 50°C, because the transformation to a smectic phase occurs (Fig. 1b). The smectic domain gradually transforms to the isotropic state with increasing temperature, because the smectogens are dissolved in octane. Only the isotropic phase, namely only the octane solution, is observed above 82°C. The DSC curve of the binary mixture is shown in Figure 2. The crystal-to-smectic phase transition is recognized as the sharp peak at 51.3°C in the heating process. Additionally, the smaller peak, probably due to the transformation between mesophases, is recognized at 60.9°C. Although a tiny texture change is also confirmed in the microscope observations at about 60°C (compare Fig. 1(c) with (b)), the details are not analyzed at the present stage. Instead of a smectic-to-isotropic transitional peak, we observe the broad endothermic peak extending over the temperature region from 60.9°C to 81.3°C, where the smectic and isotropic domains coexist [15,16].

Figure 3 shows the temperature dependence of the layer spacing d estimated by X-ray measurements. The layer reflection is indicated by an arrow in the X-ray images superimposed on Figure 3. d, which is about 38.5 A at room temperature, is constant in the temperature range where the crystalline MHPOBC coexists with the aliphatic solvent. The value of d, namely 38.5 A, almost corresponds to the molecular length of MHPOBC reported in previous papers [17,18]. It is noteworthy that d abruptly increases and attains at 54 A during the

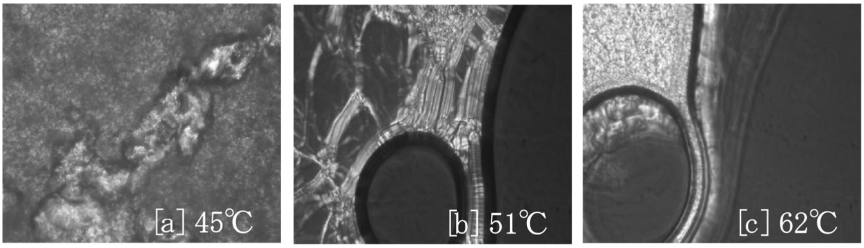

FIGURE 1 Polarized optical micrographs of a binary mixture of MHPOBC and octane. Observation was carried out in heating process. Photographs were taken at (a) 45°C, at (b) 51°C and at (c) 62°C under a magnification of 100.

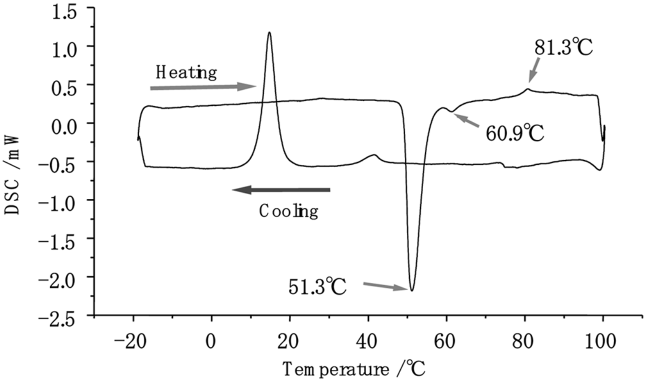

FIGURE 2 DSC curve of a binary mixture of MHPOBC and octane. The concentration of the sample was 30 wt/v%.

crystal-to-smectic phase transformation at about 50°C. This means that the aliphatic molecules, namely octane molecules, penetrate the crystalline MHPOBC and expand the layer spacing during the transformation. In other words, the crystals of MHPOBC are swollen with octane molecules, and the crystalline phase transforms into a smectic liquid-crystalline phase whose layer spacing is much larger than those of the conventional smectic phases which appear in the thermotropic phase transitions [2,11,19]. Because of good solubility between the aliphatic molecules and the flexible chains of MHPOBC, the octane

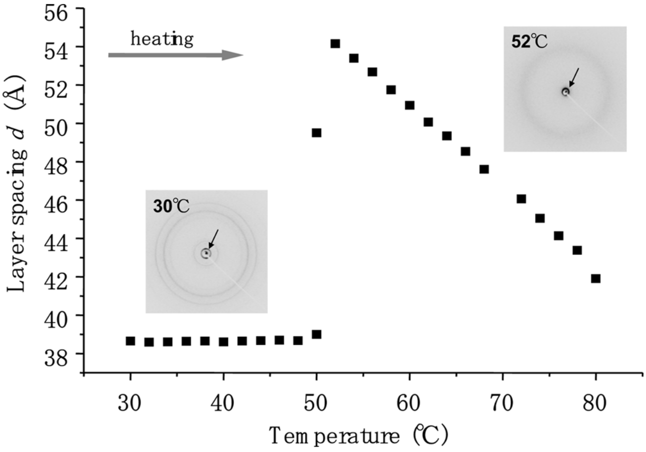

FIGURE 3 Temperature dependence of the layer spacing *d* estimated by X-ray measurements.

molecules are to be located near the flexible chains in the swollen liquid crystals. Accordingly, we easily speculate that the octane molecules, which penetrate the smectic liquid crystals, lie between the smectic layers. While the increase of *d* at the transformation (15.5 A = 54 A–38.5 A) reaches more than the length of a stretched octane molecule (about 10 A), *d* decreases with further increase in temperature above about 50°C, namely above the crystal-to-smectic phase transition temperature. The decrease of *d* indicates the octane molecules are gradually removed from the swollen smectic liquid crystals. *d* falls to less than the sum of molecular length of MHPOBC and that of octane, because the octane molecules left in the swollen smectic liquid crystals interdigitate with the flexible chains of smectogens.

We investigate the alignment of the aliphatic molecules which penetrate the smectic liquid crystals, estimating the orientational order parameter of them by means of the ^{2}H-NMR spectroscopy of the binary mixture of MHPOBC and d_8-octane. Figure 4 shows the ^{2}H-NMR spectra of the d_8-octane in various temperatures. The isotropic spectra of d_8-octane, namely the spectra with no quadrupolar splitting, are observed below 50°C, where the isotropic octane solvent coexists with the MHPOBC crystals. A quadrupolar splitting clearly appears in the spectrum measured just above the crystal-to-smectic phase transformation temperature (see the spectrum at 55°C in Fig. 4). The emergence of the quadrupolar splitting indicates that the octane molecules are uniaxially oriented probably parallel to the

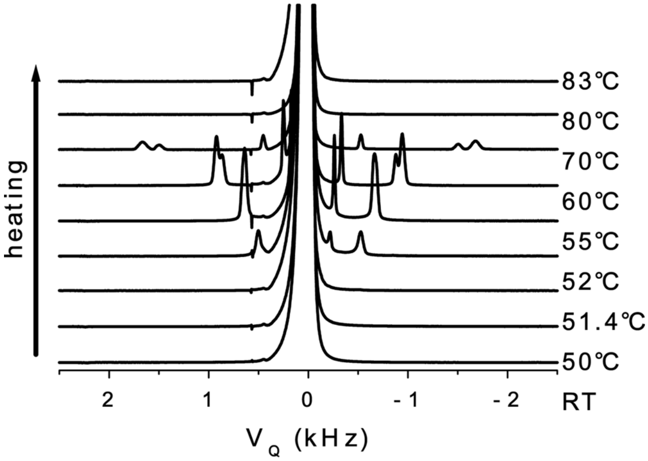

FIGURE 4 ^{2}H-NMR spectra of a binary mixture of MHPOBC and d_8-octane at various temperatures.

director of smectogens in the swollen smectic liquid crystals. In addition, the width of the splitting increases with increasing temperature, while the intensity of the splitting peaks becomes lower simultaneously. This means that a part of the octane molecules leave the liquid crystals with increasing temperature, while the orientational order of the other octane molecules which still remain in the liquid crystals becomes higher. By comparison between the X-ray and ^{2}H-NMR results, we can conclude that the removal of the octane molecules from the swollen smectic liquid crystals results in the decrease of the layer spacing. In addition, no quadrupolar splitting, which indicates the isotropic state, is observed in the ^{2}H-NMR spectra above 80°C in Figure 4, because the smectic-to-isotropic transformation is completed.

The molecular alignments speculated by means of the X-ray and ^{2}H-NMR measurements are schematically illustrated in Figure 5. The increase of d at the transformation from the crystal phase (Fig. 5a) to the swollen smectic phase (Fig. 5b), namely $15.5\,\mathrm{A} = 54\,\mathrm{A} - 38.5\,\mathrm{A}$, reaches more than the length of a stretched octane molecule (about 10 A), because an octane's multimolecular layer, in which two

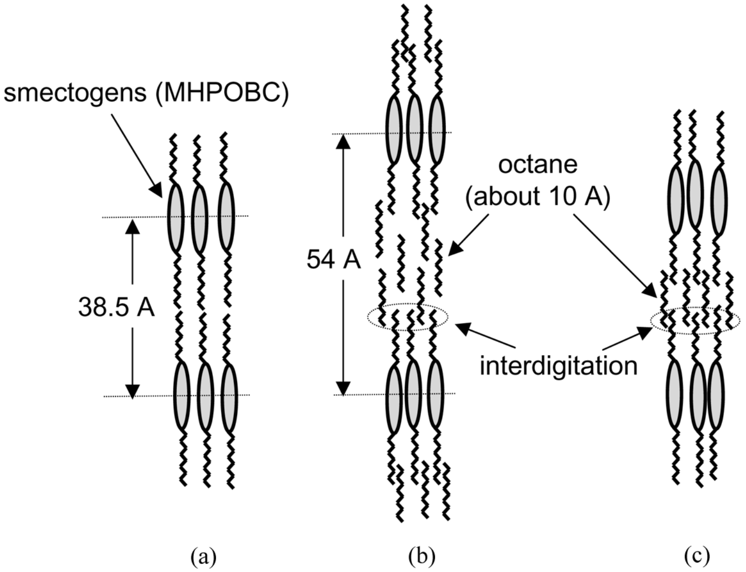

FIGURE 5 Molecular alignment speculated by means of X-ray and ^{2}H-NMR measurement. (a) At crystal phase, (b) just above crystal-to-smectic phase transformation temperature, and (c) in higher temperature region of swollen smectic phase.

or three octane molecules align along the direction parallel to the layer normal, forms between smectogenic layers. Here, the increase of d does not correspond with an integral multiple of the octane molecular length, because the octane molecules interdigitate with the flexible chains of smectogens. On the other hand, the octane molecules are gradually removed from the swollen smectic liquid crystals with increasing temperature in the temperature range of the swollen smectic phase. And then, d falls to less than the sum of molecular length of MHPOBC and that of octane, because a monomolecular layer composed of octane molecules, which interdigitate with smectogens, remains between the smectogenic layers (Fig. 5c). Because both sides of an octane molecule are fixed by the interdigitation, the orientational order parameter of the octane molecules becomes higher, as estimated by ^{2}H-NMR. In the meantime, we proceed to analyze quantitatively the orientational order and hope to show the detailed analysis in order to confirm our speculation about molecular realignment of a binary mixture of the smectogenic compound and the aliphatic solvent.

IV. CONCLUSION

Molecular realignments during the successive phase transformations of a binary mixture of a smectogenic compound ((4-(1-methylheptyloxycarbonyl) phenyl 4′-octyloxybiphenyl-4-carboxylate: MHPOBC) and an aliphatic solvent (octane), were investigated. A myelinic texture was observed above the crystal-to-smectic transition temperature which was confirmed by DSC measurements. The layer spacing, estimated by X-ray measurements, abruptly increased from 38.5 A to 54 A during the transformation from the crystal phase to the smectic phase, because the octane molecules penetrated between the smectic layers and expanded the layer spacing. In addition, the analysis of ^{2}H-NMR spectroscopy disclosed that the octane molecules were uniaxially oriented parallel to the director of the smectogens in the swollen smectic liquid crystals.

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