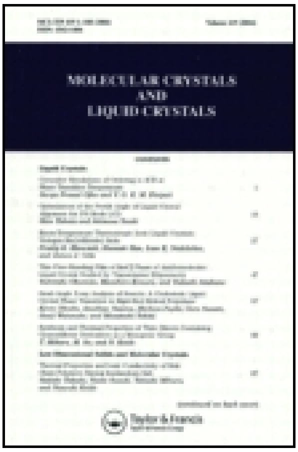

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ESR Study of Spin Probes in an Antiferroelectric Liquid Crystal MHPOBC

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ESR STUDY OF SPIN PROBES IN AN ANTIFERROELECTRIC LIQUID CRYSTAL MHPOBC

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Abstract In the liquid crystal MHPOBC (4-(1-methylheptyloxycarbonyl)phenyl 4'-octyloxybiphenyl-4-carboxylate), doxyl spin probe was dissolved and ESR spectra were observed in the antiferroelectric and ferroelectric smectic phases. The molecules of the liquid crystal in the tube- and sandwich-type cells were oriented by the static magnetic field before measurements. An anchor effect of the cell surface on the molecules of the liquid crystal was discussed. Angular variation of the spectra was discussed in connection with alignment of the spin probes in the cells and with the structure of the liquid crystal in the smectic phases.

INTRODUCTION

Liquid crystal MHPOBC (4-(1-methylheptyloxycarbonyl)phenyl 4'-octyloxy biphenyl-4-carboxylate) has been extensively studied as the first example exhibiting antiferroelectric liquid crystalline phases.[1-3] It undergoes successive phase transitions from the crystal phase through an antiferroelectric Sm C_A*, a ferroelectric Sm C*, and a Sm A phases to the isotropic phase on heating. Between Sm C_A* and Sm C*, and Sm C* and Sm A phases are observed a ferrielectric Sm C_γ* and a SmC $_\alpha$*, respectively. In addition, another antiferroelectric phase, a supercooled Sm I_A* also appears on cooling.[2] The structure of their phases, however, has not been established yet. ESR spin probe technique has been used to investigate dynamic and structural characteristics of liquid crystals and lipids.[4,5] In this paper we firstly apply the spin probe technique to the investigation on the antiferroelectric liquid crystal phase.

MATERIALS AND METHODS

Doxyl spin probe (3-doxyl-5α-cholestane (CSL)) was dissolved in MHPOBC and ESR spectra of the spin probe was observed in the smectic phases. The phase sequences of MHPOBC $C_8H_{17}O-C_6H_4-C_6H_4-COO-C_6H_4-COO-C^*H(CH_3)C_6H_{13}$ (supplied by Showa Shell Sekiyu Co. Ltd.) are as follows,

$$C \; - \; Sm\,C_A^* \; - \; Sm\,C_\gamma^* \; - \; Sm\,C^* \; - \; Sm\,C_\alpha^* \; - \; Sm\,A \; - \; I.$$

84° C m 118.3 119.2 120.7 122 148° C

The paramagnetic spin probe, 3-doxyl-5α-cholestane (CSL) was purchased from Syva Co. Ltd. The spin probe was dissolved in the liquid crystal to the concentration of about 1×10^{-3}. The sample of the liquid crystal, placed in a tube-type (diameter=5mm) or a sandwich-type glass cell (cell gap=0.1mm), was first heated to the isotropic phase and then cooled under the static magnetic field (= 0.65T) in order to align molecules of liquid crystal parallel to the magnetic field. ESR spectra were measured with magnetic field (about 0.33T) parallel and perpendicular to the initial magnetic field.

RESULTS AND DISCUSSION

The ESR spectrum of the doxyl radical CSL is composed of three lines with hyperfine constants $A_z = 3.16$, $A_x = A_y = 0.61$ mT. The principal axis (Z-axis) of the hyperfine interaction is perpendicular to the director (Y-axis) of the radical CSL. In the crystal phase, ESR spectra exhibit "powder pattern", because of the polycrystal structure of the liquid crystal. In the liquid phase ESR spectrum shows isotropic triplet. When the liquid crystal was cooled from the liquid phase into the Sm A phase under the application of the magnetic field, ESR spectra became anisotropic. Figure 1 shows ESR spectra of the sample in the Sm A phase (a): in the tube and (b): in the sandwich-type cell. The static magnetic field was initially applied perpendicular to the cylindrical axis of the tube or parallel with the surface of the cell and then ESR spectra were measured with the magnetic field parallel($\theta = 0^\circ$) or perpendicular($\theta = 90^\circ$) to the initially applied magnetic field. In Fig. 1(a), the spectra for the sample in the tube in the parallel-configuration ($\theta = 0$) show two kinds of hyperfine lines. Whereas the spectra in the perpendicular-configuration ($\theta = 90^\circ$) show a kind of the hyperfine lines. Figure 1(b) shows the spectra of samples in the cell of (θ □ 0°) and ($\theta = 90^\circ$) configurations. The hyperfine splitting in the ($\theta = 90^\circ$) configuration in Fig. 1(b) corresponds to that in the (θ □ 90°) configuration in Fig. 1(a) and the outer hyperfine splitting in the ($\theta = 0^\circ$) configuration. The hyperfine splitting in the (θ □ 0°) configuration in Fig. 1(b) corresponds to the inner hyperfine splitting in the ($\theta = 0^\circ$) configuration of Fig.1(a). The hyperfine splitting A_t in the spectrum of ($\theta = 90^\circ$) configuration is about 1.80 mT and the A_l of ($\theta = 0^\circ$) is about 0.83 mT. They are nearly equal to $(A_X + A_Z)/2$ and A_Y, respectively. These variables correspond to a situation that the spin probe CSL rotates rapidly around the Y-axis of the director of CSL and the hyperfine constants are

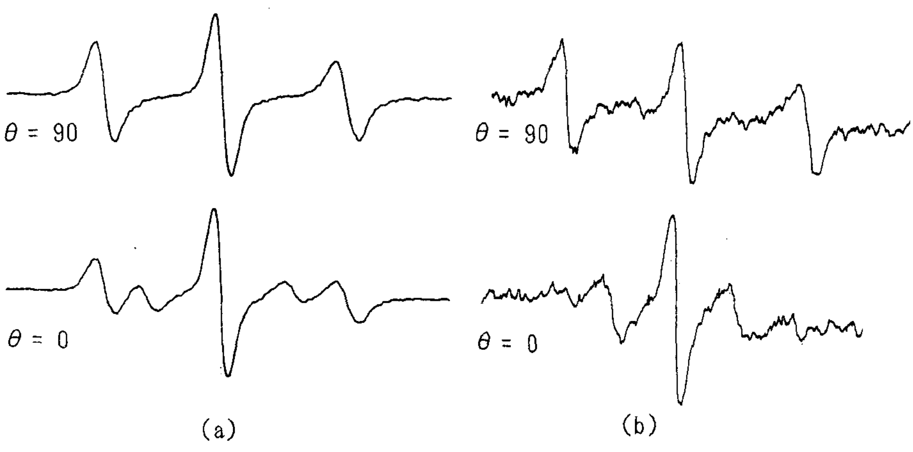

FIGURE 1 ESR spectra in the smectic A phase of MHPOBC
(a) in the tube and
(b) in the sandwich-type cell.

averaged by the rotation. The spin probe molecules are oriented in the liquid crystal whose molecules are aligned by the diamagnetic interaction with the initially applied magnetic field. From these considerations, a model is suggested for the molecular orientation of the liquid crystal in the Sm A phase in the cells. In the sandwich-type cell, the molecules of the liquid crystal are uniformly oriented parallel to the surface of the cell by the magnetic field, as shown in Fig. 2. In the tube-type cell, the molecules are thought to be oriented parallel to the cylindrical axis of the tube on the glass surface and perpendicular to the axis in the central area of the tube. Similar spectra were observed in the liquid crystals DOBAMBC and HS927SO [5] in the tube cell. The glass sample tube may have a strong anchor effect induced through a production process of the tube.

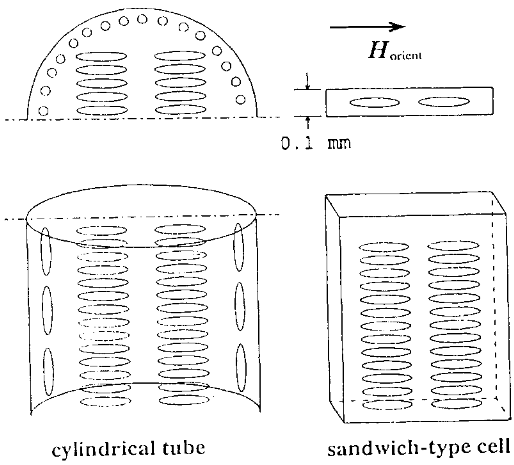

FIGURE 2 Orientation of molecules of MHPOBC
(a) in the tube and
(b) in the sandwich-type cell.

For the CSL in sandwich cell, the ESR spectra in the Sm A, Sm $C_\alpha{}^*$, Sm C^*, Sm $C_\gamma{}^*$ and Sm $C_A{}^*$ phase are shown in Fig. 3. Two traces ($\theta = 0°$, $90°$) in each smectic phase indicate spectra measured with the magnetic field parallel and perpendicular to the surface of the cell.

As mentioned previously, the hyperfine splitting A_t in the spectrum of ($\theta = 90°$)-configuration is about 1.80 mT and the A_l of ($\theta = 0°$) is about 0.83 mT in the Sm A phase. They are nearly equal to $(A_x + A_z)/2$ and A_y, respectively. These variables correspond to a situation that the spin probe CSL rotates rapidly around the Y-axis of the director of CSL and the hyperfine constants are averaged by the rotation. If the rotation axis deviates from the Y-axis by angle ϕ, the hyperfine splits A_l and A_t are represented as $A_l = A_z \cdot \sin^2\phi + A_y \cdot \cos^2\phi$ and $A_t = [A_x \cdot (2-\cos^2\phi) + A_z \cdot (1-$

$\sin^2\phi)]/2$, respectively. When ϕ is put as 26°, $A_{\parallel}$ =0.80 and $A_{\perp}$ = 1.79 mT, which arrive at a better coincidence with observed values. The result suggests a model that the spin probes rotate rapidly around an axis which exists in the cell surface plane and tilts by about 26° from the director of the probe, where the probe is supposed to be aligned in parallel to

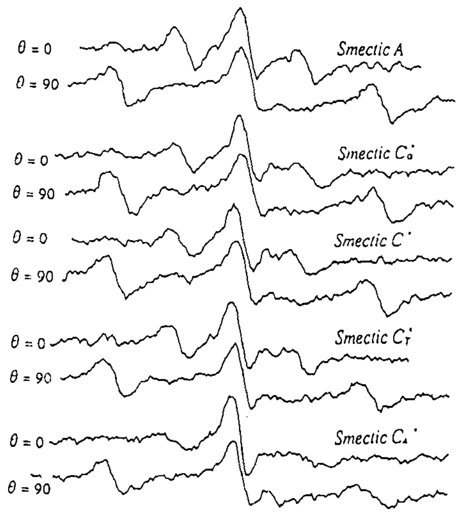

FIGURE 3 ESR spectra in smectic phases.

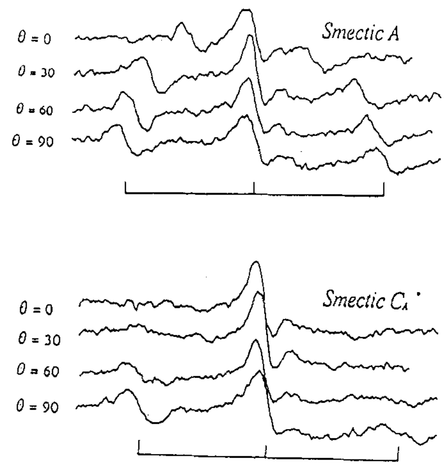

FIGURE 4 Angular variation of spectra.

the molecules of the liquid crystal aligned in the homogeneous configuration. Recently Hori and Endo [6] have carried out X-ray analysis of MHPOBC and found that the crystal phase of MHPOBC has a smectic-like layer structure composed of largely bent molecules; a chain of the chiral group is almost perpendicular (93°) to the core moiety. Under this situation necessary is further detailed investigation about actual alignment of the spin probes among the bent molecules of MHPOBC in the liquid crystalline phase.

Fig. 4 shows the angular variation of the spectra in Sm A and Sm C_A^* phases with respective to the direction of the magnetic field. The hyperfine splitting of spectra in the Sm A phase shows ordinary angular dependence. However, two hyperfine side-lines in the antiferroelectric Sm C_A^* phase become broad and disappear without variation of the hyperfine splitting, as the angle θ varies from 90° to 0°. Careful studies of the line shape of ESR spectra in Sm C_A^* phase are also necessary in connection with the chiral structure of Sm C_A^* phase, contrasting with chiral structure of Sm C^* phase.

CONCLUSIONS

In the liquid crystal MHPOBC (4-(1-methylheptyloxy carbonyl) phenyl 4'-octyloxybiphenyl-4-carboxylate), doxyl spin probes were dissolved and ESR spectra were observed in the antiferroelectric and ferroelectric smectic phases. An anchor effect of the cell surface on the molecules of the liquid crystal was discussed. Angular variation of the spectra was discussed in connection with alignment of the spin probes in the liquid crystalline structure in the smectic phases.

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