

# ESR Study of Molecular Ordering in Smectic Phase of Liquid Crystal HS927SO

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**Abstract :** Temperature dependences of the dielectric constant have been measured for (–)-4-(2'-methylbutyl) benzoate ester of 4-n-octyloxy benzoic acid (HS927SO) under a biasing electric field. ESR spectra of two doxyl spin probes (Methyl-12-doxyl-stearate and 3-doxyl-5 $\alpha$ -cholestane) dissolved in smectic A and C\* phases of HS927SO were observed, and long-range collective distortions in molecules of the liquid crystal have been found in smectic A phase in HS927SO.

## 1. Introduction

Smectic phases are intriguing liquid crystal phases of interest in various molecular conformations and extensively investigated by various methods. Among the methods, ESR spin probe technique has proved to be very useful in elucidating dynamic and structural characteristics of liquid crystals<sup>1-3)</sup>. In this paper observed were ESR spectra of two doxyl spin probes (Methyl-12-doxyl-stearate and 3-doxyl-5 $\alpha$ -cholestane) dissolved in HS927SO. The line shape of ESR spectra indicates that the molecules of HS927SO, which are macroscopically aligned along the director in the smectic A phase, bend locally.

The structure of the liquid crystal (–)-4-(2'-methylbutyl) benzoate ester of 4-n-octyloxy benzoic acid (HS927SO) is illustrated in Fig. 1. It undergoes a monotropic phase transition<sup>4)</sup>. On heating, HS927SO transforms from crystal phase into smectic A phase ( $S_A$ ) at 40°C and melts into liquid phase at 60°C. On cooling, it transforms from  $S_A$  into a ferroelectric smectic C phase ( $S_C^*$ ) at 35°C and then goes to the crystal phase at about 25°C<sup>4,5)</sup>.

## 2. Experimental

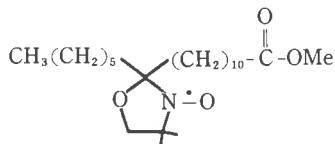
The liquid crystal HS927SO was purchased from Teikoku Chemical Co. For measurement of dielectric constant, the "sandwich geometry" sample cell was made from two 8×8 mm conducting glass plates with glass spacer (150 $\mu$ m). The dielectric constant was measured by a LCR meter (HP4274A) with various frequencies. Spin probes used in the ESR

experiment were 3-doxyl-5 $\alpha$ -cholestane (CSL ; Syva NO. 611) and Metyl-12-doxyl-stearate (M12NS ; Syva NO. 615). Their structures are illustrated in Fig. 1. The spin proves were dissolved in liquid crystals to the concentration of about  $5 \times 10^{-4}$  M. The sample placed in a glass tube ( $d=4$  mm) was first heated to the isotropic phase, and then the sample temperature was slowly lowered into  $S_A$  and  $S_C^*$  phases under the magnetic field of 6.5 KG in order to align molecules of liquid crystal parallel to the magnetic field. ESR spectra were measured by a JEOL FE-1XG spectrometer with magnetic field of about 3.3KG parallel or perpendicular to the initial magnetic field aligning the director. The temperature in the active region of the cavity was controlled within  $\pm 0.2^\circ\text{C}$  by a JEOL DVT1 variable temperature control unit.

**HS-927SO** : (-)-4-(2'-methylbutyl) benzoate ester of 4-n-octyloxy benzoic acid



**M12NS** : Methyl 12-doxyl-stearate



**CSL** : 3-doxyl-5 $\alpha$ -cholestane

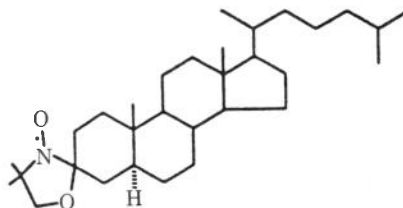


Fig. 1 Structures of liquid crystal HS927SO and spin proves M12NS and CSL.

### 3. Results and Discussion

The temperature dependences of dielectric constant ( $\epsilon$ ) of HS927SO measured with A. C. electric field of 0.67 V/cm on heating run and cooling run were shown in Fig. 2(a) and 2(b), respectively. On cooling run, the  $\epsilon$  measured with low frequency A. C. fields has large values between  $37^\circ$  and  $31^\circ\text{C}$ , which corresponds to a ferroelectric  $S_C^*$  phase in HS927SO. The dielectric constants measured under the D. C. biasing fields are shown in Fig. 3(a) and (b), respectively. When a D. C. biasing electric field of 1 KV/cm was superposed on the A. C. field, the  $\epsilon$  was not affected in the  $S_A$  phase. On the contrary,  $\epsilon$  measured with A. C. field of 100 and 200Hz were reduced in the  $S_C^*$  phase. When the D. C. field was increased to 3 KV/cm, dielectric constants were completely depressed into values in  $S_A$  phase leaving a small peak at  $S_A$ - $S_C^*$  phase transition temperature ( $37^\circ\text{C}$ ) and became similar to those with high

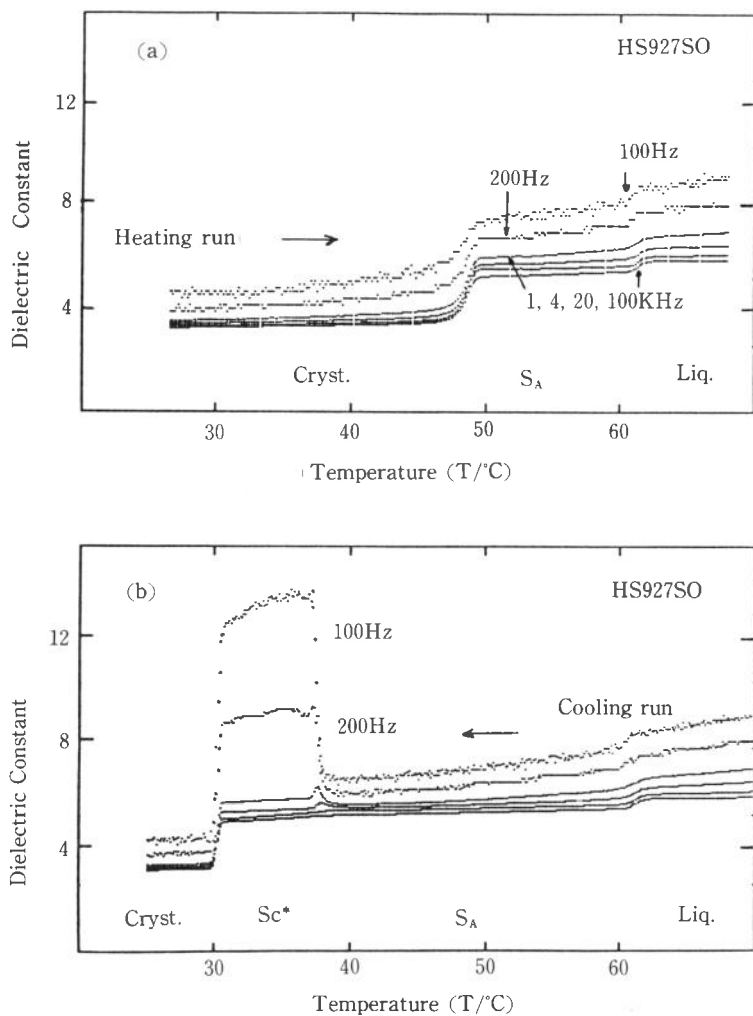


Fig. 2 Dielectric constants of HS927SO measured with frequencies of 100, 200, 1K, 4K, 20K and 100KHz, (a) : on heating run, and (b) : on cooling run,

frequency A. C. field. The facts show that the large values in the  $\epsilon$  in  $S_c^*$  phase are ascribed to flopping of the spontaneous polarization in the ferroelectric phase, motivated by the A. C. field.

The ESR spectrum of the free radical in CSL is composed of three lines caused by hyperfine interaction with nitrogen nucleus in NO-bond. In the crystal phase ESR spectra exhibit "powder pattern". ESR spectra in the liquid phase are an isotropic triplet because of rapid reorientation of the radical. From measurements in the crystal phase and the liquid phase, principal values of hyperfine interaction are determined as  $A_z=32.9$ ,  $A_x=A_y=6.8$  Gauss for CSL in HS927SO. Those of M12NS are  $A_z=32.8$ ,  $A_x=6.9$ ,  $A_y=6.4$ G. When the

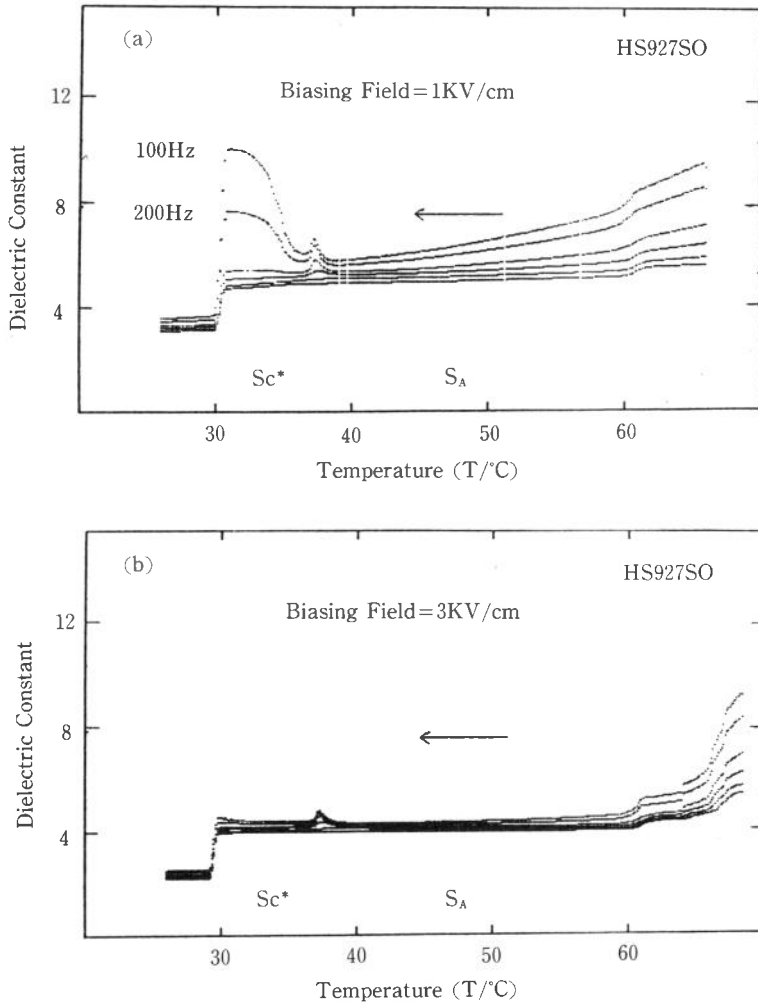


Fig. 3 Effects of D. C. biasing fields on dielectric constants on cooling run under D. C. biasing field of (a) : 1KV/cm, and (b) : 3KV/cm.

magnetic field is applied parallel to the Z-axis of the hyperfine interaction, the splitting between hyperfine lines becomes the maximum value of about 33G. The Z-axes are known to be parallel to the director of the radical M12NS and perpendicular to that of CSL<sup>3)</sup>. When the liquid crystal was slowly cooled from the liquid phase into the S<sub>A</sub> phase under the application of the magnetic field, the liquid crystal in the sample tube except near the surface of the tube was ordered along the magnetic field and then ESR spectra became anisotropic. Figure 4 shows ESR spectra of CSL and M12NS observed in S<sub>A</sub> phase of HS927SO on two orientations of the magnetic field parallel (//) and perpendicular (⊥) to the initial magnetic field for alignment. Figures 5(a) and (b) show M12NS absorption spectra obtained from integration of the "derivative" absorption spectra in Fig. 4(a). In the figures the hyperfine

splitting in ( $\parallel$ )-spectrum is larger than that in ( $\perp$ )-spectrum. It indicates that directors of molecules of HS927SO are ordered parallel to the aligning magnetic field, with fairly rapid reorientation around the direction of the mean director. The absorption spectra of CSL are computed from spectra shown in Fig. 4(b) and are shown in Figs. 5(c) and (d). we have observed an unusual spectral feature in the figures ; *i. e.*, both side hyperfine components in ( $\parallel$ )-spectrum are broaden and split. It shows that CSL radicals whose directors are locally perpendicular to the magnetic field are contained in the liquid crystal and indicates radical molecules to bend complying with a bent of molecules of HS927SO. Furthermore, a local 2-dimensional order of a distortion of the molecule of the liquid crystal is expected to occur according to the spectral shape with edge singularities. Meirovitch and Freed<sup>6)</sup> found similar ESR spectra of CSL and 12-doxyl stearic acid (12NS) in DPPC bilayers, and Meirovitch et al.<sup>7)</sup> observed them in P-probe in  $S_A$  phase of liquid crystal S2. They proposed a model of the collective distortion mode of the molecular chains : *i. e.*, the distortions of kinks in the chains propagate as a "defect wave" through lateral interactions. In Fig.6 the collective distortion mode is illustrated schematically. We may conclude that the molecule of HS927SO in  $S_A$



Fig. 4 ESR spectra of spin probes in  $S_A$  phase.

(a) : M12NS probe and (b) : CSL probe in HS927SO.

Marks ( $\parallel$ ) and ( $\perp$ ) indicate spectra measured with the magnetic field parallel and perpendicular to the field for alignment, respectively.

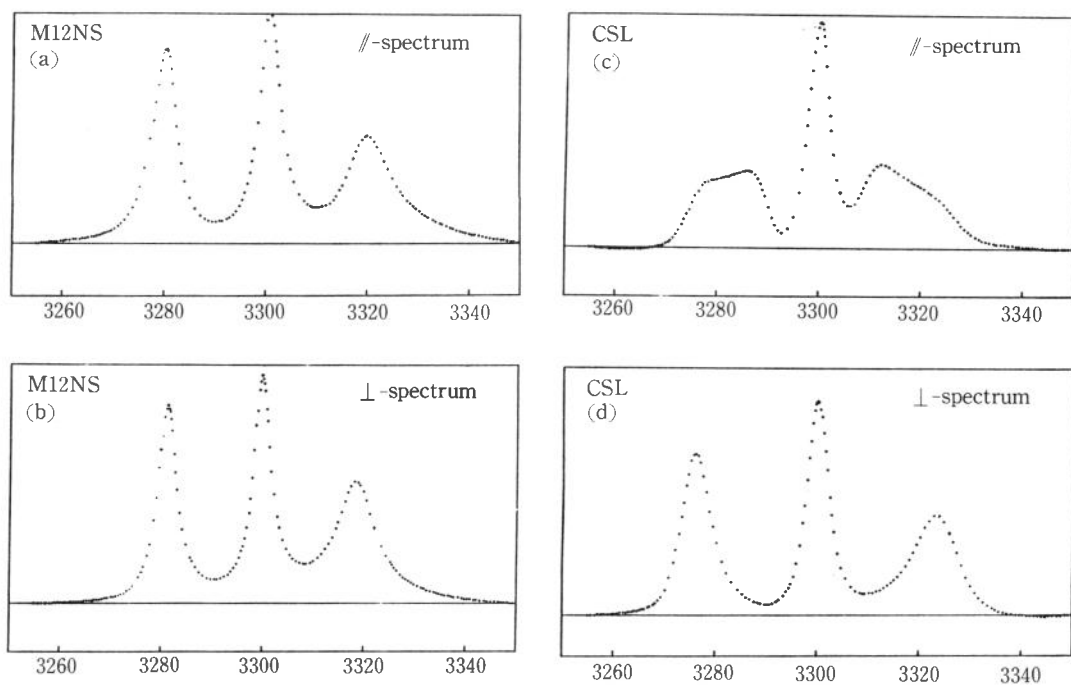


Fig. 5 ESR absorption spectra obtained from integration of the spectra in Fig. 4.

(a) : ( $\parallel$ )-spectrum of M12NS, (b) : ( $\perp$ )-spectrum of M12NS,  
 (c) : ( $\parallel$ )-spectrum of CSL and (d) : ( $\perp$ )-spectrum of CSL.

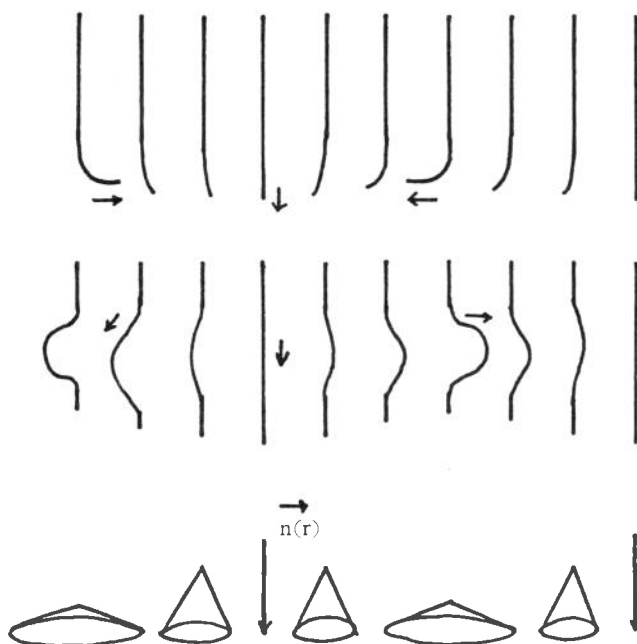


Fig. 6 Illustrative examples for a collective distortion mode. The local director  $n(r)$  lies on the surface of the cone.

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phase is straight like a "bar" at the point where M12NS is attracted, whereas it bends at CSL.

We have measured ESR spectra in Sc\* phases. The hyperfine spectra were made broader by the helical structure in Sc\* phase and it indicates the collective chain distortion exists in the Sc\* phases of HS927SO.

#### References

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