Thresholdless Antiferroelectricity in a Novel Chiral Swallow-Tailed Liquid Crystal

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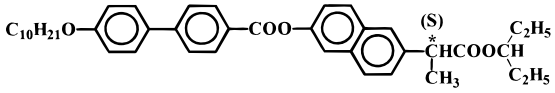
The antiferroelectric (S_{CA}*) phase in chiral liquid crystals exhibits a tristable switching property and has been extensively studied both experimentally and theoretically because of potential application in electric−optical devices.[1] Many chiral materials have been synthesized and investigated. Subsequently, a correlation between the molecular structure of the materials and the appearance of the antiferroelectric liquid crystals has been successfully reviewed.[2]

Goodby and co-workers[2] demonstrated that the formation of the S_{CA}* phase in chiral liquid crystals depends strongly on the high chirality of the molecules. The molecules possessing high chirality require that the chiral center within the molecular structure is close to the central rigid core.[2−6] Further study of some nonchiral materials with swallow-tailed terminal moieties[7−9] shows that these materials are favorable for the formation of an "antiferroelectric-like" phase, a so-called S_{Calt} phase, and can be doped by a small quantity of antiferroelectric liquid crystal to induce antiferroelectrity. This remarkable finding promotes the potential application of antiferroelectric liquid crystals in liquid crystal display devices.

More recently, Inui et al.[10] have reported that some mixtures of antiferroelectric liquid crystals exhibit the thresholdless, hysteresis-free, and V-shaped switching properties, in contrast to the normal antiferroelectric liquid crystals. The electric−optical devices constructed by applying this type of mixture have very unique properties.[11] It is unfortunate, however, that no single material has been reported that possesses chirality and a thresholdless antiferroelectric S_{CA}* phase in the chiral liquid crystals.

In this paper, we present, for the first time, a novel chiral material, 1-ethylpropyl (*S*)-2-{6-[4-(4′-decyloxyphenyl)benzoyloxy]-2-naphthyl}propionate, EP10PBNP, that has thresholdless antiferroelectricity. The characteristics of the molecular structure for this material, as depicted bellow, are that the chiral center is directly attached to the rigid core and a swallow-tailed is attached to the chiral tail. Both molecular characteristics are primarily designed to yield a material that exhibits an antiferroelectric S_{CA}* phase.



The synthetic procedures for the chiral material, derived from (S)-2-(6-methoxy-2-naphthyl)propionic acid with optical purity greater than 99% ee, are the same as previously described.[12] The purity and chemical structures of the intermediates and final product were checked by thin-layer chromatography (TLC), elemental analysis using a Perkin-Elmer 2400 spectrometer, and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy using a Bruker WP100SY FT-NMR spectrometer. The optical purity of the target material was expected to be high, since the reagents used for each synthetic procedure have been reported to be free from racemization.[12−14] The magnitudes of specific rotations were measured in dichloromethane using a JASCO DIP-360 digital polarimeter. Elemental analysis for $C_{41}H_{50}O_5$ (percent): calculated, C, 79.06; H, 8.09; found, C, 79.02; H, 8.14. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.6−1.8 (m, 29H, RCH_2CH_3), 1.6 (d, 3H, CH(CH_3)), 3.8−3.9 (q, 1H, ArC*H*COO), 4.0−4.1 (t, 2H, OCH_2), 4.8−4.9 (m, 1H, COOC*H*), 7.0−8.3 (m, 14H, Ar*H*). Specific rotation $[\alpha]^{26}_D$ (0.601 g/mL, CH_2Cl_2) = +6.62°.

Transition temperatures and enthalpies of the transition for liquid crystalline were determined by differential scanning carlorimetry (DSC) using a Perkin-Elmer DSC7 calorimeter at a rate of 5 °C/min. Mesophases were identified by the observance of the textures using a Nikon Microphot-FXA optical microscope under crossed polarizers with an INSTEC HS1 hot stage in connection with a RTC heat controller. Sample cells were purchased from Linkam Scientific Instruments, Ltd., UK and E.H.C. Co. The cells with 5 and 25 μm^2 conducting area were fabricated by coating with unidirectionally buffed polyimide film. Switching behavior and electro-optical response of antiferroelectric smectic phase were investigated by the triangular wave method.[15]

The mesophases, transition temperatures, and enthalpies of the transitions of the material were measured with the polarizing microscope in conjunction with the differential scanning calorimeter, and the results are listed in Table 1. Texture observations at a rate of 0.1 °C/min revealed that the material has a fairly rich polymorphism of mesophase. The BP_{II} phase was characterized by the appearance of iridescent platelet tex-

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Table 1. Mesophases, Transition Temperatures, and Enthalpies ΔH of Compound EP10PBNP

phase transition	T/°C	ΔH/J g^{-1}
Iso−BP_{II}	143.1	6.7
BP_{II}−N^*	134.4	[a]
N^*−TGB_A	129.0	[a]
TGB_A−S_A	128.2	[a]
S_A−S_{CA}*	102.5	0.4
S_{CA}*−Cr	54.2	28.3

[a] The enthalpies of the BP_{II}−N*, N*−TGB_A, and TGB_A−S_A transitions were added to the Iso−BP_{II} transition value.

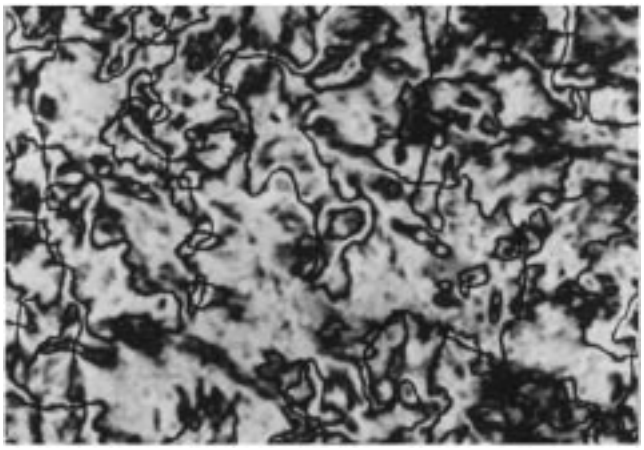

Figure 1. Schlireren texture displaying the two-brush defect of the S_{CA}* phase obtained at 100 °C (×400).

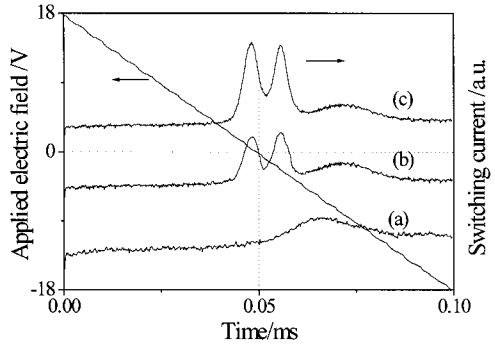

Figure 2. Switching behaviors in the S_A phase at 104.0 °C (curve a) and S_{CA}* phase at 99.5 °C (curve b) and 74.9 °C (curve c).

ture. The N^* phase displayed a typical paramorphotic texture. The TGB_A phase, mediated between the transition of the N^* and S_A phase, was primarily characterized by the formation of filament texture and was further confirmed by the appearance of Grandjean texture with selective reflecting colors in the homogeneously aligned cell. The S_A phase showed a focal-conic and homeotropic texture. The S_{CA}* phase appeared as a striated focal-conic texture and was further characterized by the appearance of the two-brush defect[16] in the pseudo-homerotropic texture, as shown in Figure 1. All mesophases are enantiotropic.

The switching behaviors of the compound in the S_A and S_{CA}* phases were measured and are presented in the Figure 2. In the S_A phase, a broad current peak was found due to the ionic effect. In the S_{CA}* phase, however, two additional switching current peaks appeared simultaneously, located approximately at the opposite sides of zero field point, and they remained unchanged in the whole temperature range of the S_{CA}* phase. This switching behavior in the S_{CA}* phase significantly differs from that in the normal S_{CA}* phase.[1]

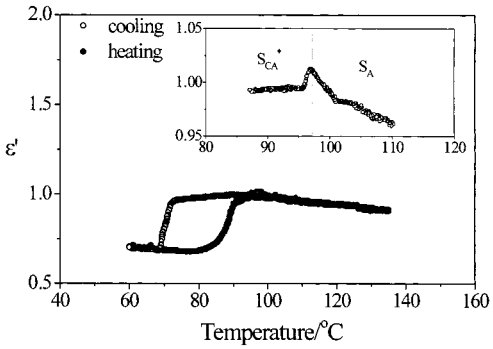

Figure 3. Temperature dependence of the dielectric constant ϵ' measured at 10 kHz.

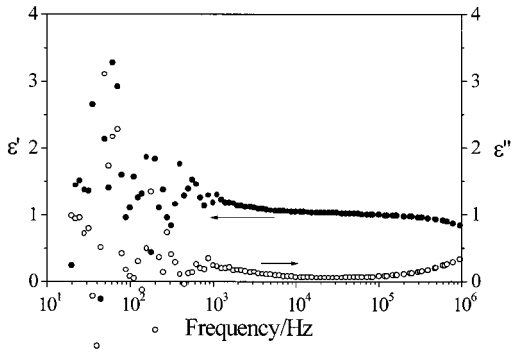

Figure 4. The dispersion and absorption curves of the compound plotted as ϵ' (●) and ϵ'' (○) versus frequency in the S_{CA}* phase at 74.9 °C.

Thus, the temperature dependence of the dielectric constant (ϵ') for the material in a 25 μm thickness of homogeneously aligned cell was investigated. The dielectric measurements were employed using an HP4284A precision LCR meter, and data were analyzed with a resistor−capacitor parallel circuit model. The results are depicted in the Figure 3. The ϵ' in the S_A phase is small and slightly increases at the S_A to S_{CA}* transition. The characteristic point corresponding to the S_A to S_{CA}* transition is seen as a small peak at approximately 92 °C. The slight enhancement of the dielectric constants in the antiferroelectric phase was proposed to result from the vibration of the azimuthal molecular motion.[17]

More detailed macro- and micromolecular motions of molecules in the S_{CA}* phase investigated by the frequency dependence of the dispersion and absorption curves are presented in Figure 4. The results show that both the real and imaginary part of the dielectric constants increase but are not quite stable at the frequency <1 kHz. It can been seen that the real dielectric constant shows a tendency to diverge (the imaginary loss consistently increases) at higher frequency, 10^5−10^6Hz. This feature has been seen from the empty cell and is presumably due to the polyimide alignment of the film. Thus, there is not any significant

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occurrence of the relaxation process in the S_{CA}* phase, similar to that detected in the MHPOBC.[18]

Furthermore, investigation of the characteristics of the S_{CA}* phase was conducted by recording the electro-optical responses of the material in a 5 μm homongeneously aligned cell at different temperatures and frequencies. During the switching process at 99.5 °C, a ferrielectric-like switching behavior appears.[19] This switching process measured at 0.5 Hz alters drastically to the thresholdless one, i.e., the V-shaped switching,[10] as shown in Figure 5 as the temperature decreases to approximately 74.9 °C. Interestingly, the V-shaped switching behavior turns to a W-shaped switching as the frequencies vary from 0.5 to 5 Hz. These observed electro-optical responses are similar to the typical characteristics of the thresholdless antiferroelectric liquid crystal mixture reported by Inui et al.

In conclusion, a novel chiral swallow-tailed material, EP10PBNP, has been demonstrated to exhibit thresholdless antiferroelectricity in the S_{CA}* phase. Thus, this material may provide a basic structure for future study of the relationship between the molecular structure and the appearance of a thresholdless antiferroelectric liquid crystal.

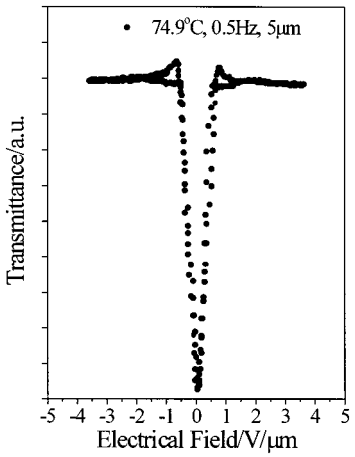

Figure 5. The electro-optical response of the S_{CA}* phase measured at a frequency of 0.5 Hz and a temperature of 74.9 °C.

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