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Terminal-Terminal Types of Liquid Crystals. I. Synthesis and Electrooptical Properties of a Ferroelectric Liquid Crystal

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Synopsis. A novel ferroelectric liquid crystal, (*S*)-bis(2-methylbutyl) 3,3′-[1,2-ethanediylbis[oxy-4,1-phenylenemethylidyne nitrilo-4,1-phenylene]]bis[2-propenoate] (EBOPBP) was prepared, which are composed of two chiral mesogenic groups interconnected by a very short flexible spacer chain. EBOPBP exhibts a chiral smectic C phase (S_c*). From an electrooptical effect due to a deformation of helical structure in the S_c* state, the rise time (τ_r) was estimated to be 240 μs at 180 °C.

Great interest has recently been shown in liquid crystals possessing ferroelectric properties in chiral smectic C (S_c*) phase which can be used as fast electrooptical elements.[1–3)] Important information about their structure and ferroelectricity has been obtained from detailed studies on thermal and electrooptical effects for various types of compounds.[4–8)] On the other hand, low molecular weight compounds composed of two terminal mesogenic groups interconnected by a flexible spacer group may be taken as models for main-chain type thermotropic liquid crystalline polymers (TLCPs) which contain core units interconnected through spacer groups.[9–13)] In spite of the great variety in chemical structure of ferroelectric liquid crystals, few terminal-terminal type compounds have so far been prepared and studied. In our previous papers,[14–16)] syntheses and electrooptical properties of polymerizable ester derivatives of a ferroelectric liquid crystalline compound 4-[(4-decyloxybenzylidene)amino] cinnamate (MBDOBAC)[17)] were described. In the course of a study on polymeric and monomeric materials with ferroelectric liquid crystalline properties, we have prepared (*S*)-bis(2-methylbutyl) 3,3′-[1,2-ethanediylbis[oxy-4,1-phenylenemethylidynenitrilo-4,1-phenylene]]bis[2-propenoate] (EBOPBP) as a prototype of ferroelectric main-chain type TLCPs. In this note, we report on thermal and electrooptical behavior of EBOPBP.

Experimental

4,4′-Ethylenedioxydibenzaldehyde. One mol of 4-hydoroxybenzaldehyde was dissolved in a mixture of 350 mL ethanol and 150 g KOH in 150 mL water. A trace of KI was added and the solution was heated and stirred while 2.2 mol of 1,2-dibromoethane was added slowly. The reaction mixture was refluxed for 10 h, the solvent was evaporated and the solid residue dissolved in 1 L of water. The solution was extracted with chloroform. The chloroform layer was then washed successively with 0.2 M (1M=1 mol dm^{-3}) HCl aqueous solution and water and evaporated to dryness. The residue was recrystallized from ethanol: 66.1% yield; mp 117—118 °C; ^{1}H NMR (CDCl$_3$) δ=4.34 (s, 4H, -C$\underline{H}_2$C$\underline{H}_2$-), 6.92—7.70 (q, 8H, aromatic), and 9.70 (s, 2H, -C$\underline{H}$O). Found: C, 71.00; H, 5.22%. Calcd for $C_{16}H_{14}O_4$ (270.288): C, 71.10; H, 5.22%.

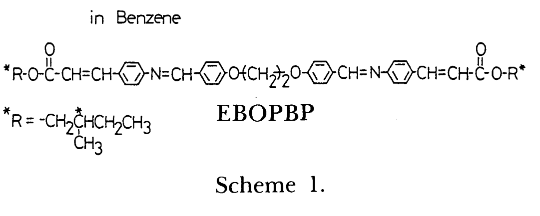
EBOPBP. One mmol of 4,4′-ethylenedioxydibenzaldehyde in 10 mL of absolute ethanol and 2 mmol of (*S*)-2-methylbutyl 4-aminocinnamate in 10 mL of absolute ethanol were mixed and allowed to stand for 2 d. The precipitate was filtered and recrystallized twice from absolute ethanol: 95.0% yield; ^{1}H NMR (CDCl$_3$) δ=0.78—1.12 (m, 12H, -C$\underline{H}_3$), 1.12—2.03 (m, 6H, -CH$_2$C$\underline{H}_3$), 4.00—4.30 (m, 6H, -C$\underline{H}_2$C$\underline{H}$(CH$_3$)C$_2$H$_5$), 4.57 (s, 4H, -O(C$\underline{H}_2$)$_2$O-), 6.24—6.48 (d, 2H, *J*=16 Hz, -C$\underline{H}$=C$\underline{H}$-), 7.15—8.09 (m, 16H, aromatic), 8.10—8.24 (d, 2H, *J*=16 Hz, -C$\underline{H}$=C$\underline{H}$-), and 8.97 (s, 2H, -C$\underline{H}$=N-). Found: C, 75.65; H, 6.95; N, 4.00%. Calcd for $C_{44}H_{48}O_6N_2$ (700.882): C, 75.40; H, 6.90; N, 4.00%.

Measurements. ^{1}H NMR measurements were carried out with a 100 MHz JEOL JNM-MH 100 spectrometer. Phase transition temperatures were determined by differential scanning calorimetry, using a Rigaku Thermoflex apparatus DSC-8230B, with almost the same heating and cooling rates (10 K min^{-1}). Sample quantities varied from 5 to 10 mg. Microscopic investigations were performed using an Olympus microscope BH-2, with a heating stage attached to a temperature controller. Thin samples were sandwiched between two glass slides, the surfaces of which had been unidirectionally rubbed with cotton wool to obtain a homogeneous alignment. The spacing between top and bottom glass plates was 50 μm, with a stretched polyester film used as the spacer material. Samples were studied at both decreasing and increasing temperatures. Electrooptical measurements were carried out as follows. Surfaces of glass plates were coated with a transparent conductive material (In$_2$O$_3$); the surface resistance was about 100 Ω m^{-2}. The spacing between top and bottom glass plates was 25 μm. The sample cell was set without polarizer in the optical path of a He-Ne laser (NEC-GLG 5313, wavelength 632.8 nm, and output power 1 mW). The incident light was damped with an attenuator and arranged with a slit. Changes in transmission by application of electric field were monitored with a photodiode and processed with a microcomputer (NEC-9801).

Results and Discussion

Thermal Properties. EBOPBP was synthesized via two kinds of reactions as follows:

EBOPBP is a pale yellow powder and is stable to air



Scheme 1.

and prolonged heating. According to differential scanning calorimetric and optical microscopic measurements, EBOPBP shows three mesophases: a transition from isotropic melt first gives a chiral nematic N* phase with a fan-shaped texture; further cooling gives a smectic A phase, followed by S_c* phase having a focal conic texture with stripes due to a helical structure. The phase transition temperatures of EBOPBP as determined by DSC are compatible with those obtained by polarizing microscopic and electrooptical measurements:

$$\text{K } 157.0 \text{ S}_c^* \text{ } 197.6 \text{ S}_A \text{ } 218.1 \text{ N}^* \text{ } 245.3 \text{ I.}$$

The pitches of the helical structure were obtained by averaging spacings of stripes at ten different places in a micrograph of the texture within the temperature range of 157.0 to 197.6 °C. The average pitch was found to be 1.9 μm as shown in Fig. 1.

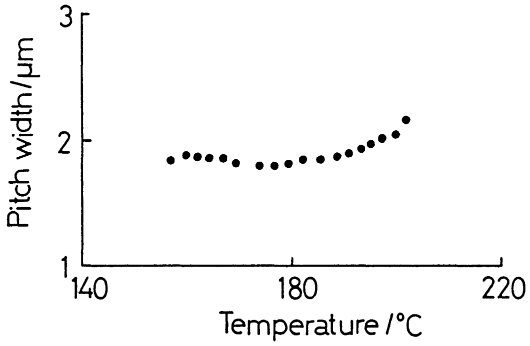


Fig. 1. Temperature dependence of the pitch width of helical structure in S_c* phase of EBOPBP.

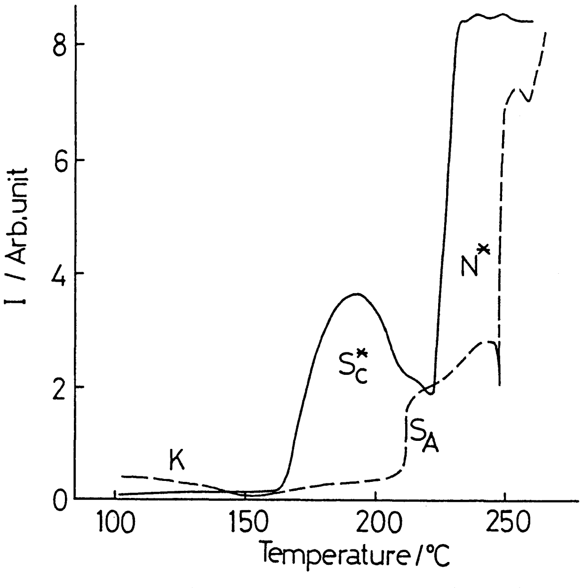


Fig. 2. Transmitted He-Ne laser light intensity (*I*) for EBOPBP on cooling cycles; (----); E=0, (——); E=16 kV cm^{-1}.

Electrooptical Properties of EBOPBP. As EBOPBP shows an S_c* phase in the range of 157.0 to 197.6 °C, two headed ferroelectric liquid crystals were subjected to electrooptical measurements, in order to obtain basic data for practical uses as optical switching and display devices. Figure 2 shows the transmission intensity (I) of the He-Ne laser through the EBOPBP cell on cooling. When no voltage is applied, the transmission intensity decreases abruptly because of a characteristic light scattering just after the transition of the isotropic liquid to the N* phase at 245.3 °C, then increasing up to ca. 30% of the original intensity as a stable N* phase followed by the S_A phase are formed at 218.1 °C. On further cooling, the transmission intensity is caused to decrease gradually by a light scattering due to wound states of the helical structure of the S_c* phase at 197.6 °C. On the other hand, upon application of voltage, the transmission intensity never decreases up to 218.1 °C because of the transformation of the N* to nematic phase caused by d.c. After the turning into the S_A phase, the transmission intensity increases again below 197.6 °C. This electrooptic effect is believed to be due to the transformation of a wound state (S_c*) to an unwound state (S_c) caused by d.c.[3] The electrooptical response time corresponding to the change in transmission caused by voltage application was then measured over the voltage range from 30 V (electric field, E=12 kV cm^{-1}) to 120 V (E=48 kV cm^{-1}) at 180 °C. Clark and Lagerwall[18] designed a surface stabilized ferroelectric liquid crystal (SSFLC) cell as a fast electrooptical element; the response time (τ_r) is associated with the inversion of directors in the surface layer of the cell. In order to know the effect of applied voltage on response time, the relation between τ_r and the electric field applied at 180 °C is plotted in Fig. 3. It shows that increase in

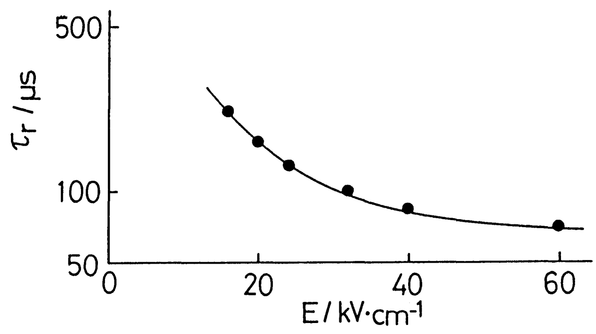


Fig. 3. Effect of electric field (E) on electrooptical response (τ_r) in ferroelectric S_c* phase of EBOPBP at 180 °C.

Table 1. Electrooptical Properties of Ferroelectric Liquid Crystals

Compound	$T_{S_A\text{-}S_C^*}$/°C	$\Delta T_{T_{S_C^*}\text{-}T_K}$/°C	Pitch width/μm	$E_{\text{thres}}^{a)}$/kV cm^{-1}	τ_r/μs$^{b)}$
EBOPBP	198	41	1.9(at 180 °C)	11.0(at 180 °C)	240(at 180 °C)
MBDOBAC	95	33	1.7(at 75 °C)	5.2(at 75 °C)	200(at 90 °C)

a) Threshold votage. b) Rise time of surface director at 16 kV cm^{-1}.

the applied voltage will shorten the optical response time. The results on the electrooptical effect are summarized in Table 1.

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References

1) J. S. Patel, *Appl. Phys. Lett.*, **47**, 1277 (1985).

2) H. Takezoe, Y. Ouchi, K. Ishikawa, and K. Fukuda, *Mol. Cryst. Liq. Cryst.*, **139**, 27 (1986).

3) S. Kishio, M. Ozaki, K. Yoshino, and A. Sakamoto, *Mol. Cryst. Liq. Cryst.*, **144**, 43 (1987).

4) T. Sakurai, N. Mikami, R. Higuchi, M. Honma, M. Ozaki, and K. Yoshino, *J. Chem. Soc., Chem. Commun.*, **1986**, 978.

5) T. Kitamura, A. Mukoh, M. Isogai, T. Inukai, K. Furukawa, and K. Terashima, *Mol. Cryst. Liq. Cryst.*, **136**, 167 (1986).

6) K. Skarp and G. Anderson, *Ferroelectrics Lett.*, **6**, 67 (1986).

7) J. W. Goodby, E. Chin, T. M. Leslie, J. M. Geary, and J. S. Patel, *J. Am. Chem. Soc.*, **108**, 4729 (1986).

8) S. Takenaka, T. Ikemoto, and S. Kusabayashi, *Bull. Chem. Soc. Jpn.*, **59**, 3965 (1986).

9) J. W. Emsley, G. R. Luckhurst, G. N. Shilstone, and I. Sage, *Mol. Cryst. Liq. Cryst. Lett.*, **102**, 233 (1984).

10) J. A. Buglione, A. Roviello, and A. Sirigu, *Mol. Cryst. Liq. Cryst.*, **106**, 169 (1984).

11) H. Toriumi, H. Furuya, and A. Abe, *Polym. J.*, **17**, 895 (1985).

12) J. C. W. Chien, R. Zhou, and C. P. Lillya, *Macromolecules*, **20**, 2340 (1987).

13) P. Esnault, D. Galland, F. Volino, and R. B. Blumstein, *Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt.*, **157**, 409 (1988).

14) K. Sugiyama, A. Sakamoto, Y. Murata, K. Shiraishi, and T. Otsu, *Nippon Kagakukaishi*, **1987**, 1064.

15) K. Shiraishi, A. Sakamoto, and K. Sugiyama, *Chem. Express*, **2**, 475 (1987).

16) K. Shiraishi and K. Sugiyama, *Makromol. Chem.*, **190**, 2235 (1989).

17) R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, *J. Phys. Lett.*, **36**, L269 (1978).

18) N. A. Clark and S. T. Lagerwall, *Appl. Phys.*, **36**, 899 (1980); *Ferroelectrics*, **59**, 25 (1984).