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Synthesis and Electrooptical Properties of Terminal-Terminal Type of Ferroelectric Liquid Crystal

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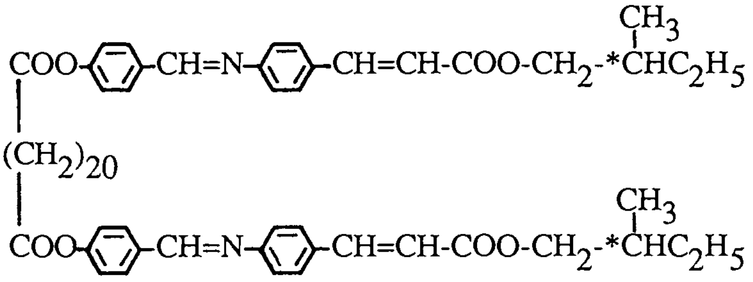
A novel terminal-terminal type of ferroelectric liquid crystal, (S)-bis(2-methylbutyl) 3,3'-[1,20-eicosanediylbis[oxy-4,1-phenylenemethylidynenitrilo-4,1-phenylene]]bis[2-propenoate] (BMBEPMNP), was prepared, which composed of two chiral mesogenic groups interconnected by a very long flexible spacer chain. From the electrooptical effect originating in deformation of helical structure at a S_c^* state, the electrooptical response time (τ_{sr}) was found to be 843 μs at 130 ℃ in 32 kV · cm^{-1}.

Great interest has been shown recently in liquid crystals possessing ferroelectric properties in a chiral smectic C (S_c^*) phase which can be used as a fast electrooptical element.[1-3] The important information about the structure and the ferroelectric properties has been obtained from a study of various types of compounds.[4-8] In spite of the great variety in chemical structure of ferroelectric liquid crystal, few compounds composed of two terminal mesogenic groups interconnected by a flexible spacer group has so far been prepared and studied. In this letter, we report on the thermal and electrooptical properties of a novel ferroelectric liquid crystal BMBEPMNP as a twin type of MBDOBAC, (S)-2-methylbutyl 4-[4-(decyloxybenzylidene)amino]cinnamate.[9] 1,20-Bis(4-formylphenoxy)eicosane dicarboxylate[10] was prepared by the reaction of 1,20-docosanedioyl chloride and double the molar quantity of 4-hydroxybenzaldehyde. BMBEPMNP[11] was prepared by the reaction of 1,20-bis(4-formylphenoxy)eicosane dicarboxylate and double the molar amount of (S)-2-methylbutyl 4-aminocinnamate in dry tetrahydrofuran. The terminal-terminal liquid crystal was pale yellow powder and was stable to air and prolonged heating. According to differential scanning calorimetry (DSC) and optical microscopy, BMBEPMNP shows two mesophases; at the transition from the isotropic melt (I) to the smectic A (S_A) phase showing a fan-shaped texture with focal conic texture first appears. On further cooling, a S_A phase and following a S_c^* phase results showing a focal conic texture with stripes due to a helical structure. The phase transition temperature of BMBEPMNP determined



BMBEPMNP

using DSC is compatible with that obtained by means of polarizing microscopy and electrooptical measurements: K 122 ℃ S_C* 139 ℃ S_A155 ℃ I. The pitches of the helical structure were obtained from averaging the spacing of the stripes at ten different places in a micrograph of the texture within the temperature ranges 123 to 138.2 ℃. The average pitch was plotted in Fig.1.

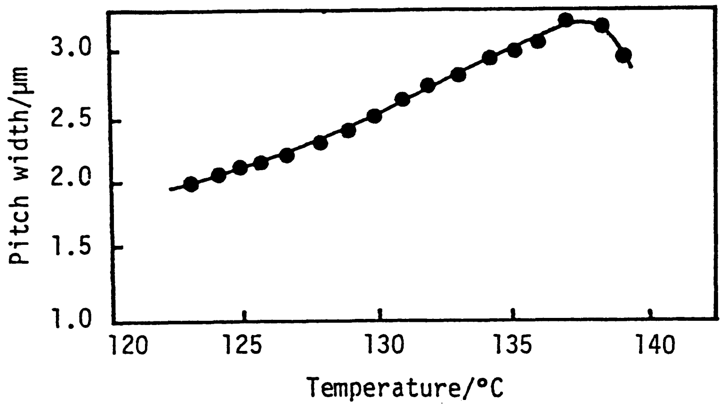


Fig. 1. Temperature dependence of the pitch width of helical structure in S_C* phase of BMBEPMNP.

As the BMBEPMNP shows the S_C^* phase, two headed ferroelectric liquid crystal was measured electrooptically,[12] in order to obtain basic data for practical uses as optical switching and display divices. Clark and Lagerwall designed the use of a surface stabilized ferroelectric liquid crystal (SSFLC) cell as a fast electrooptical element; the response time is due to the inversion of directors in the surface layer of the cell.[13] Figure 2 shows the transmission intensity (T) of the He-Ne laser through the BMBEPMNP cell on cooling. When no voltage is applied, the transmission intensity (T) decreases abruptly because of the light scattering just after the transition of the isotropic liquid (I) to S_A phase at 155 ℃, and then it increases up to ca. 60 % of the original intensity by forming a stable S_A phase. On further cooling, T decrease gradually caused by light scattering due to the wound states of a helical structure of the S_C^* phase at 139 ℃. On the other hand, upon application of voltage, T never decreases up to at 122 ℃ because of transformation of wound state (S_C^*)

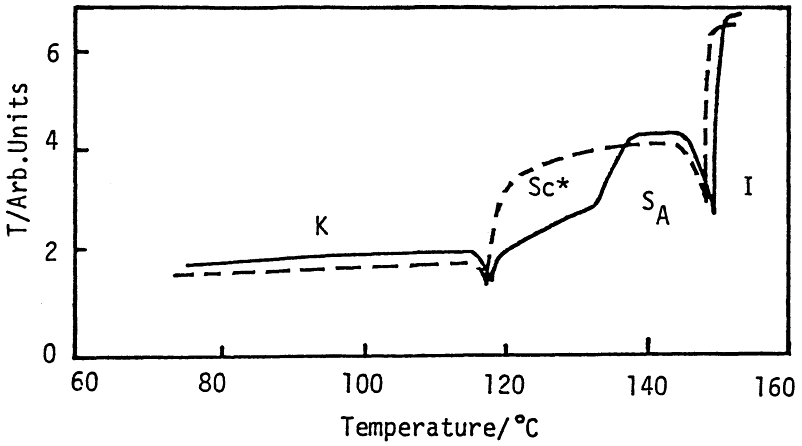


Fig.2. Transmitted He-Ne laser intensity (T) for BMBEPMNP on cooling cycle; (——); E=0, (-----); E=20 kV · cm^{-1}, cell thickness: 25 μ m.

to unwound state (S_C) caused by d.c.[3)] The electrooptical response time corresponding to the change in the transmission caused by voltage application was then measured over the electric field from 24 to 40 kV · cm^{-1} at 130 ℃ (cell thickness: 25 μm). In this case, it was found that T decreases slightly just after voltage application and then it increases remarkably. The applied field will induce a fluctuation of the boundary due to the reorientation of the surface layer, which may result in a decrease of T in a short time (τ_{sr}).[3,14)] On the other hand, the main response corresponding to the increase of T is relatively slow. This response time is due to the transition from the helical structure to a uniform monodomain structure. In order to know the effect of the applied voltage on the response time, the relation of τ_{sr} and the electric field (E) applied at 130 ℃ is shown in Fig. 3. It shows that an increase of the applied voltage results in a faster optical response time. The results of electrooptical effect of BMBEPMNP and MBDOBAC were summarized in Table 1.

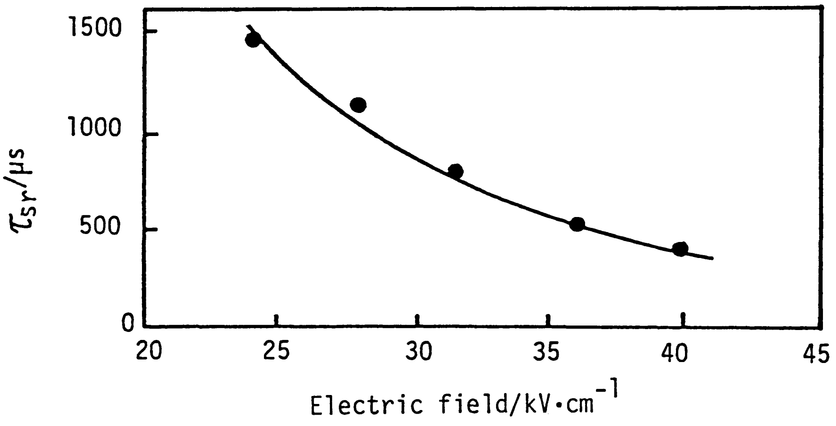


Fig. 3. Effect of electric field(E) on electrooptical response(τ_{sr}) in ferroelectric S_C* phase of BMBEPMNP at 130 ℃, cell thickness: 25 μm.

Table 1. Electrooptical properties of ferroelectric liquid crystals

Compound	$T_{S_A-S_{C^*}}$ / ℃	$\Delta T_{T_{S_C^*}-T_k}$ / ℃	Pitch width / μm	E_{thres}[a)] /kV · cm^{-1}	τ_{sr}[b)] / μs
BMBEPMNP	139	17	2.5 (at 139 ℃)	22.0 (at 130 ℃)	843 (at 130 ℃)
MBDOBAC	95	33	1.7 (at 75 ℃)	5.2 (at 75 ℃)	200 (at 90 ℃)

a) Threshold voltage of electrooptical response.

b) Rise time of surface director at 32 kV · cm^{-1}.

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10) Identification; mp 88-90 ℃, ^{1}HNMR($CDCl_3$) δ = 0.86- 2.04(m, 36H, $-CH_2\ (CH_2)_{18}CH_2-$), 2.36-2.68 (t, 4H, J=3 Hz, $-CH_2(CH_2)_{18}CH_2-$), 6.96-7.96(m, 8H, phenyl), and 9.80(s, 2H, -CHO): Calcd for $C_{36}H_{50}O_4$ (357.796); C, 74.71; H, 8.71%. Found C,74.55; H,8.79%.

11) Identification; ^{1}HNMR($CDCl_3$) δ = 0.80-1.12(m, 12H, $-CH_2CH(CH_3)CH_2CH_3$), 1.16-2.04 (m, 42H, $-COCH_2(CH_2)_{18}CH_2CO-$, $-CH_2CH(CH_3)CH_2CH_3$), 2.24-2.28 (t, J=3 Hz, 4H, $-COCH_2\ (CH_2)_{18}CH_2CO-$), 4.00-4.20(m, 4H, $-CH_2CH(CH_3)CH_2CH_3$), 6.52-6.68(d, 2H, J= 16 Hz, -CH=CH-), 8.08-8.18(d, 2H, -CH=CH-), 7.20-8.18(m, 16H, phenyl), 8.64(s, 2H, -CH=N-): Calcd for $C_{64}H_{84}O_8N_2$ (1009.391); C, 76.16; H, 8.39; N, 2.78%. Found C,76.41; H, 8.19; N, 2.70%.

12) Electrooptical measurements were carried out as follows: The surfaces of the glass plates were coated with a transparent conductive material (ITO); the surface resistance was about 100 $\Omega \cdot m^{-2}$. The spacings between top and bottom glass plates was 25 μ m. The sample cell was set without polarizer in the optical path of a He-Ne laser (NEC-GLG 5313, wavelength 632.8 nm, output power 1 mW). The incident light was performed with both an attenuator and a slit. The change in the transmission with the application of an electric field was monitored by means of a photodiode and was calculated using a microcomputer (NEC-9801).

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