

Ferroelectricity and Electro-Optical Effects in Smectic Liquid Crystals

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Ferroelectricity in D-DOBAMBC, D-OOBAMBC, D-HOBAMBC, L-DOBACPC, L-OOBACPC, L-HOBACPC and their mixtures are studied. In the mixture of D-DOBAMBC and L-DOBACPC with inverse chiralities and different dipole moments, the pitch of the helical structure is found to increase remarkably at some concentration. However, the spontaneous polarization is linear function on the concentration and any singularity is not observed in dielectric constant at this concentration. These ferroelectric liquid crystals indicate novel electro-optical effects: light switching, colour switching, hysteresis of transmission (transient memory) etc. Details of these effects and dynamic behaviour are investigated.

§1. Introduction

Recently chiral smectic liquid crystals like DOBAMBC have attracted much interest as new type of ferroelectrics.^{1~5)} Molecules which indicate ferroelectricity must have both a chiral part and a dipole moment in its structure. A tilt of molecular long axis in a layer is also essential for the appearance of ferroelectricity. Also in all these materials, a helical structure of the direction of the molecular long axis along normal of smectic layer is observed. However, it is not clear whether this helix is essential for ferroelectricity or not.

We have studied ferroelectric properties of various ferroelectric liquid crystals and also indicated several electro-optical effects characteristic for these materials.^{4~11)}

In this paper we will report detailed dielectric and optical properties of several ferroelectric liquid crystals and their mixtures.

§2. Experimental

Compounds of the series of D-p-alkoxybenzylidene-p'-amino-2-methylbutyl-cinnamate (D-AOBAMBC) and the series of L-p-alkoxybenzylidene-p'-amino-2-chloropropyl-cinnamate (L-AOBACPC) were synthesized by a modified version^{6,7)} of the method of Keller *et al.*¹²⁾ Molecular structures of the compounds synthesized and their abbreviated names are listed in Table I. Detailed sample preparation and experimental methods are re-

Table I. Molecular structures of ferroelectric liquid crystal and their names studied.

$C_nH_{2n+1}O$		D-p-alkoxybenzylidene-p'-amino-2-methylbutyl-cinnamate
n=6:	D-HOBAMBC,	n=8: D-OOBAMBC, n=10: D-DOBAMBC
n=12:	D-DOBAMBC,	n=14: D-DOBAMBC
$C_nH_{2n+1}O$		L-p-alkoxybenzylidene-p'-amino-2-chloropropyl-cinnamate
n=6:	L-HOBACPC,	n=8: L-OOBACPC, n=10: L-DOBACPC

ported in elsewhere.^{4~7)}

§3. Results and Discussion

As evident from Fig. 1, the spontaneous polarization in L-AOBACPC (L-DOBACPC, L-HOBACPC) with chlorine atom in the chiral part is much larger than that of D-AOBAMBC (D-DOBAMBC, D-HOBAMBC) with same alkoxy chain length. Dielectric constant in L-AOBACPC is extremely large compared with that of D-AOBAMBC in the smectic-C phase as indicated in the inset of Fig. 2. These facts clearly indicate that ferroelectricity increased by giving dipole moment at the chiral part in L-AOBACPC, which support the idea that the intramolecular rotation or vibration of dipole moment relative to the chiral part reduces the spontaneous polarization in D-AOBAMBC (D-DOBAMBC, D-OOBAMBC etc.).

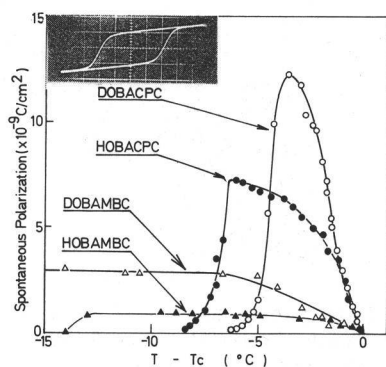


Fig. 1. Temperature dependences of spontaneous polarization in D-DOBAMBC, L-DOBACPC, D-HOBAMBC and L-HOBACPC. Inset: D-E hysteresis.

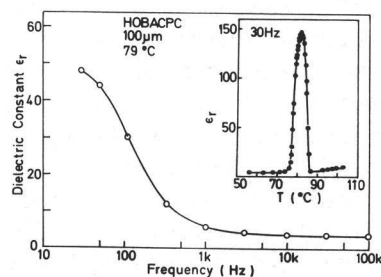


Fig. 2. Frequency dependence of dielectric constant of L-HOBACPC in the smectic-C phase. Inset: Temperature dependence of dielectric constant in L-HOBACPC.

It should be noted that the relaxation of dielectric constant appears at much lower frequency in L-AOBACPC compared with that in D-AOBAMBC as shown in Fig. 2. With increasing alkoxy chain length of the end group, this dispersion frequency also decreases (L-HOBACPC > L-OOBACPC > L-DOBACPC).

In the ferroelectric smectic-C phase, a helical structure of the arrangement of the molecular long axis along the normal to the smectic layer always appeared in these compounds.^{8,13} It is quite interesting problem whether the spontaneous polarization remains in the mixture of the chiral smectic liquid crystals with inverse chiralities and different dipole moments at the concentration where the helical structure disappears. The helical pitch can be evaluated from the distance between parallel stripes observed in the optical microscope figure (inset of Fig. 4). Figure 3 shows temperature dependence of the pitch in pure and mixed ferroelectric liquid crystals. In the mixture of D-DOBAMBC and L-DOBACPC, we found that the pitch becomes

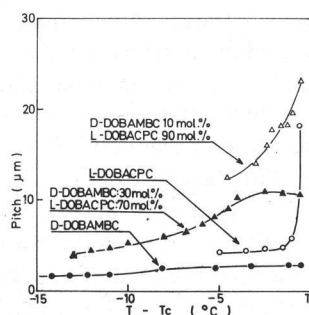


Fig. 3. Temperature dependence of observed pitch in D-DOBAMBC, L-DOBACPC and their mixture.

much longer at some concentration (around 90 mol% of L-DOBACPC in D-DOBAMBC) compared with original D-DOBAMBC and L-DOBACPC as evident in Fig. 4. However, the spontaneous polarization is nearly linear function of concentration and any singularity of dielectric constant was not observed at around this concentration (Fig. 5). Decrease of dielectric constant at high L-DOBACPC concentration is only due to lower relaxation frequency. These facts seem to support the idea that these chiral smectic liquid crystals are not the anti-ferroelectrics but the ferroelectrics.

We have already reported several novel electro-optical effects in these compounds.^{8~11} In the homogeneous cell, the transmission intensity of the light increased remarkably by the

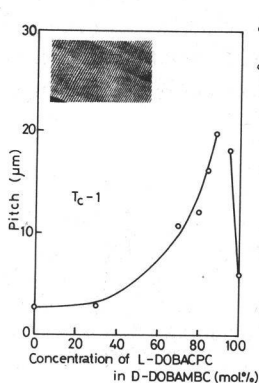


Fig. 4

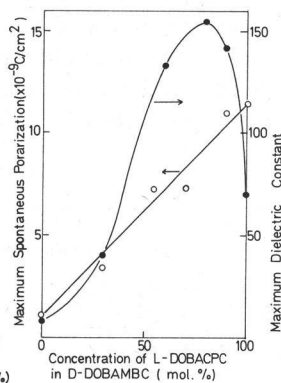


Fig. 5

Fig. 4. Dependence of observed pitch at $T_c - 1^\circ\text{C}$ in L-DOBACPC and D-DOBAMBC mixtures on the concentration. Inset: Optical microscope figure.

Fig. 5. Dependence of spontaneous polarization and dielectric constant on the concentration of L-DOBACPC in D-DOBAMBC.

application of voltage above some threshold. This can be explained in terms of disappearance of the helical structure (multi-domain $\rightarrow$ single domain transformation in some sense), and resulting decrease of the light scattering. Corresponding to the existence of D-E hysteresis, we observed also hysteresis in the light transmission in both dc and ac voltage application. However, after the removal of applied voltage, the transmission decreases to the original value slowly. This indicates that the mono-domain structure relaxes back to the original helical structure slowly due to the relatively low viscosity in liquid crystal. However, we can use this effect as temporal memory or as a memory by using a small bias voltage. Under a dc bias voltage we can obtain high and low transmission states with applying positive and negative short pulse. Figure 6 shows hysteresis of transmission at various frequencies.

The colour of the transmission light through homeotropic cell between two polarizers changes with the angle of the polarization direction of both polarizers as indicated in Fig. 7. With applying dc voltage parallel to the layer therefore glass plates, the colour of transmission changes but it is not uniform and not stable due to the non-uniformity of fields and ionic currents at high fields. Therefore it is not easy to apply this effect for practical use. On the other hand, by the application of ac electric field, wavelength dependence of transmission disappears, resulting in the white spectrum as indicated by dashed line in Fig. 7. Therefore we can use this effect as mono-colour light switch. The colour can be selected by the relative polarization angle of two polarizers.

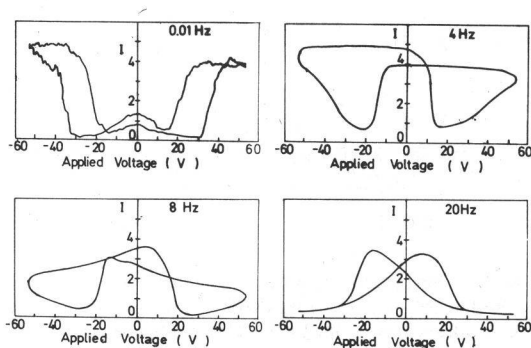


Fig. 6. Hysteresis of transmission intensity through homogeneous cell measured at various frequencies.

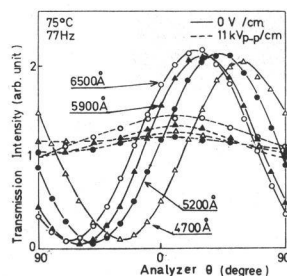


Fig. 7. Dependence of transmission of various wave length through homeotropic cell on the relative polarization angle between two polarizers with and without (dashed line) applied voltage.

Stable colour switching was observed by applying voltage on the very thin cell (several μm).^{10,11} This effect seems not to be due to the change of optical rotary power by field but due to the change of a birefringence on account of the change of the tilt angle of a molecular long axis relative to the normal of the smectic layer. The threshold field of these electro-optical effect in L-AOBACPC was much lower than that in D-AOBAMBC corresponding to the larger spontaneous polarization in the former compounds.

References

- 1) R. B. Meyer, L. Liebert, L. Strzelecki and P. Keller: *J. Phys.* **36** (1975) L69.
- 2) L. J. Yu, H. Lee, C. S. Bak and M. M. Labes; *Phys. Rev. Lett.* **36** (1976) 388.
- 3) P. Pieranski, E. Guyon, P. Keller, L. Liebert, W. Kuczynski and P. Pieranski; *Mol. Cryst. and Liq. Cryst.* **38** (1977) 275.
- 4) K. Yoshino, T. Uemoto and Y. Inuishi: *Jpn. J. Appl. Phys.* **16** (1977) 571, *Proc. FMA-1* (FMA Office, Kyoto, 1978) p. 115.
- 5) T. Uemoto, K. Yoshino and Y. Inuishi: *Jpn. J. Appl. Phys.* **18** (1979) 1261.
- 6) K. Yoshino, Y. Iwasaki, T. Uemoto, Y. Inuishi, S. Yanagida and M. Okahara; *Tech. Repts. Osaka Univ.* **30** (1980) in press.
- 7) K. Yoshino, Y. Iwasaki, T. Uemoto, S. Yanagida and M. Okahara; *Oyo Buturi* **49** (1980) 876 [in Japanese].
- 8) K. Yoshino, Y. Iwasaki, T. Uemoto, and Y. Inuishi: *Proc. 10th Conf. Solid State Devices, Tokyo 1978*, *Jpn. J. Appl. Phys.* **18** (1979) Suppl. 18-1 p. 427.
- 9) K. Yoshino, K. G. Balakrishnan, T. Uemoto and Y. Inuishi: *Jpn. J. Appl. Phys.* **17** (1978) 597.
- 10) Y. Iwasaki, K. Yoshino, T. Uemoto and Y. Inuishi; *Jpn. J. Appl. Phys.* **18** (1979) 2323.
- 11) T. Uemoto, K. Yoshino and Y. Inuishi: *Mol. Cryst. and Liq. Cryst.* submitted.
- 12) P. Keller, S. Juge, L. Liebert and L. Strzelecki: *CR. Acad. Sci. Paris* **282** (1976) 639.
- 13) Ph. Martinot-Lagade: *J. de Phys.* **38** (1977) 117.