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Effect of Hydroxyl Substituent on Ferroelectricity in Ester Type Ferroelectric Liquid Crystals

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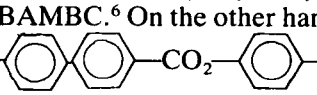
A new ester type ferroelectric liquid crystal with hydroxyl substituent on ortho-position of chiral-side phenyl group in core structure has been prepared. The spontaneous polarization of this material is much larger than that of corresponding unsubstituted material. This is interpreted in terms of the effect of intramolecular and intermolecular hydrogen bonds on ferroelectricity in liquid crystal.

INTRODUCTION

The discovery of ferroelectricity in DOBAMBC (*p*-decyloxybenzylidene-*p'*-amino-2-methylbutylcinnamate) by Meyer *et al.*[1] and proposals of various electro-optic effects in this new material have stimulated a lot of studies from both fundamental and practical viewpoints.[2–5] Many new materials with large spontaneous polarization have also been synthesized because very short response time in electro-optic effect is expected in the materials with large spontaneous polarization.[6,7]

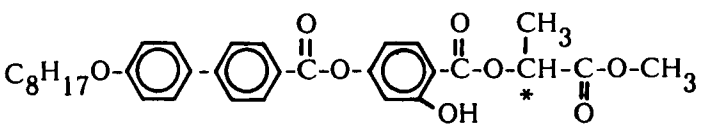
The magnitude of spontaneous polarization in ferroelectric liquid crystals is strongly related with the dipole moment perpendicular to the long molecular axis. It has been pointed out that the importance of the separation between a chiral carbon and the dipole moment must be taken into consideration to explain the larger spontaneous polarization in DOBA-1-MPC (*p*-decyloxybenzylidene-*p'*-amino-1-methylpropylcinnamate) than in DOBAMBC.[6] On the other hand, in the materials with molecular structure of R—O—  —CO_2——CO_2—R*, where R and R* are an alkyl group and a chiral group respectively, it was clarified that the C=O bond moment neighboring to the core in the chiral part contributes dominantly to spontaneous polarization.[8,9]

We prepared a new ferroelectric liquid crystal with hydroxyl substituent on the phenyl group in the core structure. In this paper, we report the effect of the hydroxyl substitution on the ferroelectricity and dielectric properties of this material and compare these properties with those of unsubstituted materials.

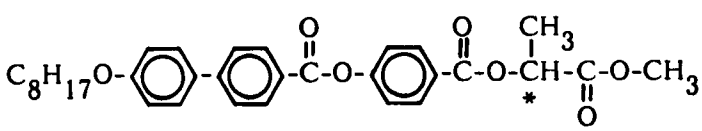
EXPERIMENTAL

The molecular structures and the abbreviated names of the materials used in this study are shown in Figure 1. The synthetic procedure of 1MC1ECPOPB (4'-(1-methoxycarbonyl-1-ethoxycarbonyl)phenyl 4-(4-octyloxyphenyl)benzoate) was described in our previous paper.[8] 1MC1ECHOPOPB was synthesized by the procedure shown in Figure 2. The carboxylic acid **1** was allowed to react with the optical active alcohol **2** in the presence of dicyclohexylcarbodiimide and 4-pyrodinopyridine in methylene chloride to give ester **3**. Selective deprotection of **3** was carried out with 5% palladium-charcoal in methanol. Subsequently, the phenol derivative **4** obtained was esterified with the carbonylchloride **5** in pyridine at room temperature. At least the optical active ester **6** was deprotected with aqueous hydrogen chloride in methanol to afford 1MC1ECHOPOPB. The molecular structure was confirmed by the elemental chemical analysis, NMR and IR spectra.

The sample was purified by liquid chromatography with silica gel and double recrystallized from ethanol solution. Then it was sandwiched between two conducting ITO (In-Sn oxide) glass plates whose surfaces had been rubbed in one direction by a cotton sheet to realize a homogeneous alignment.



(R)-4'-(1-methoxycarbonyl-1-ethoxycarbonyl)-3'-hydroxyphenyl
4-(4-octyloxyphenyl)benzoate
1MC1ECHOPOPB



(R)-4'-(1-methoxycarbonyl-1-ethoxycarbonyl)phenyl
4-(4-octyloxyphenyl)benzoate
1MC1ECPOPB

FIGURE 1 Molecular structures, their names and their abbreviated names of ferroelectric liquid crystals used in this study.

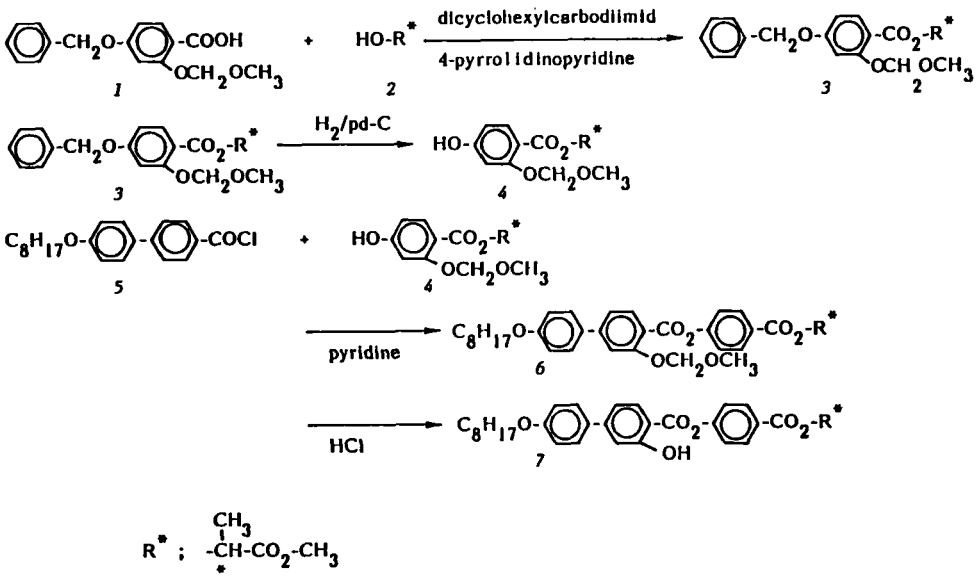


FIGURE 2 Synthetic procedure of 1MC1ECHOPOPB.

The spontaneous polarization was measured by both a triangular shaped voltage method and Sawyer-Tower method. The tilt angle and the direction of spontaneous polarization were determined by optical microscope observation of the change in the angle and direction of the long molecular axis upon field reversal. If the direction of the long molecular axis, the layer normal and the spontaneous polarization make right-hand and left-hand coordinate systems, the direction of the spontaneous polarization is expressed by $P_s(+)$ and $P_s(-)$ respectively.[10] The dielectric constant was measured by observing the current component phase shifted by 90° from the phase of applied voltage utilizing a lock-in amplifier PAR 5204.

RESULTS AND DISCUSSION

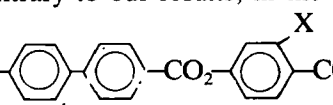
The phase transition temperatures of the materials used in this study are shown in Table I. The temperature range of the chiral smectic phase in 1MC1ECHOPOPB

TABLE I

Phase transition temperature, direction of spontaneous polarization and maximum spontaneous polarization of ferroelectric liquid crystals used in this study

	Phase transition temperature (°C)				Direction of spontaneous polarizations	Maximum spontaneous polarization (nC/cm²)
	K	SmX*SmC*	SmA	I		
1MC1ECPOPB	o 68	o 120	o 172 o		Ps(−)	65
1MC1ECHOPOPB	o 28	o 86	o 141 o		Ps(−)	180

is lower than that in 1MC1ECPOPB. The maximum value and the direction of spontaneous polarization are also shown in Table I. Figure 3 shows the temperature dependence of spontaneous polarization of these two materials. It is obvious that the magnitude of spontaneous polarization becomes twice as large without changing the direction of spontaneous polarization by substituting the hydrogen atom at ortho-position of the chiral-side phenyl group in 1MC1ECPOPB by a hydroxyl group.

Contrary to our results, in the study of materials with the molecular structure of  , where X is a halogen or a hydrogen atom, Ichihashi *et al.* reported that the spontaneous polarization of the material with a halogen was smaller than that of the corresponding one with hydrogen.[11] This result can be explained by the cancellation of the dipole moments originating from C—X and C=O bonds because they are in opposite directions due to the electrostatic repulsion, resulting in a suppression of the spontaneous polarization.

In the present study, though the molecular structure was very similar to their samples, the inverse result, enhancement in spontaneous polarization, was obtained.

Figure 4 shows the probable structures of the chiral part of 1MC1ECHOPOPB. If the electrostatic repulsion is as in halogen substituted materials, the dipole

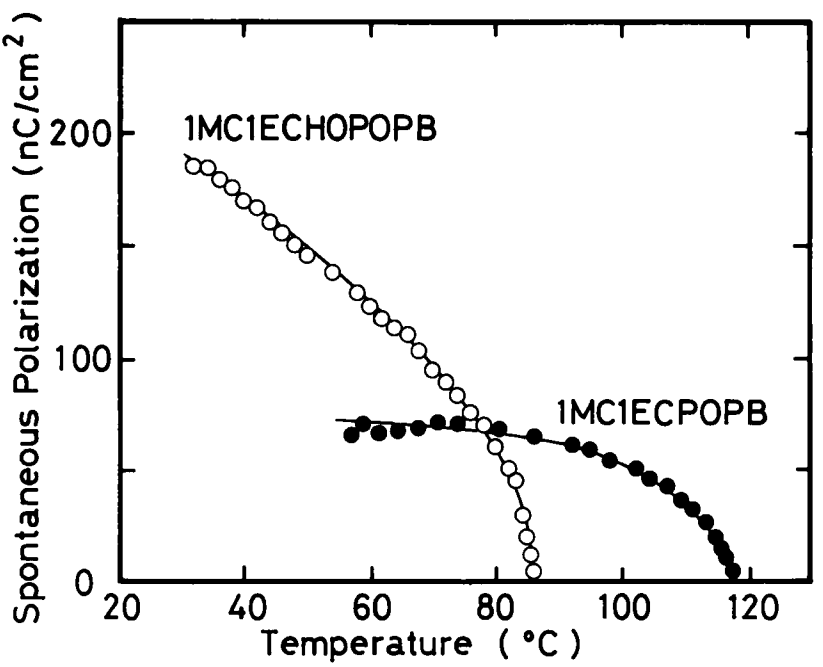


FIGURE 3 Temperature dependence of the spontaneous polarization in 1MC1ECPOPB (closed circles) and 1MC1ECHOPOPB (open circles).

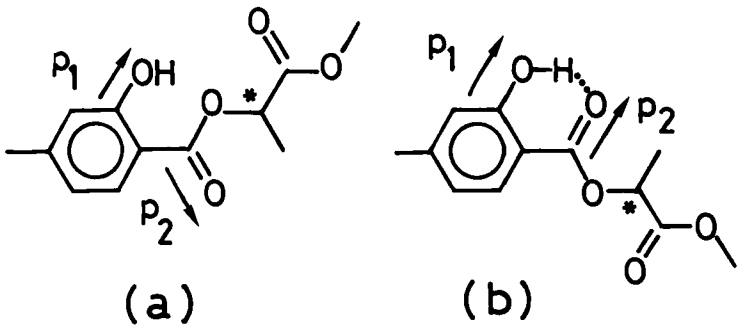


FIGURE 4 Structures of chiral parts and directions of polarization in 1MC1ECHOPOPB.

moments originating in C—OH and C=O bonds should cancel each other, resulting in the suppression of the spontaneous polarization in 1MC1ECHOPOPB (Figure 4(a)). However, the experimental results showed an enhancement of spontaneous polarization by a hydroxyl group substitution. In the case of 1MC1ECHOPOPB, the hydrogen bond can be formed, resulting in the construction of a hexagonal ring as illustrated in Figure 4(b). In this conformation, the dipole moments originating in C—OH and C=O bonds act additively and the spontaneous polarization increases. Moreover, this hydrogen bond may suppress the intramolecular rotation of the carbonyl group respect to the chiral carbon. This also enhances the spon-

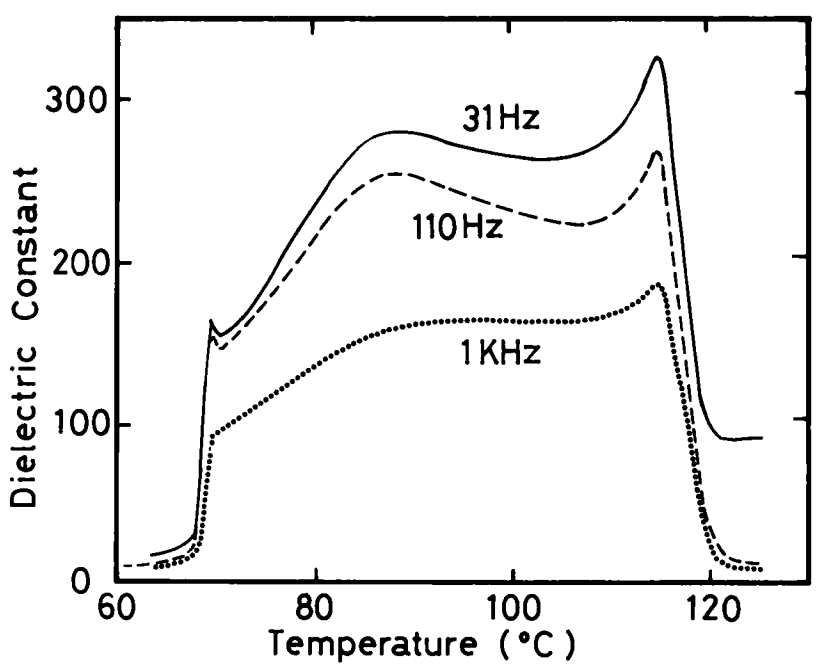


FIGURE 5 Temperature dependence of the dielectric constant in 1MC1ECPOPB.

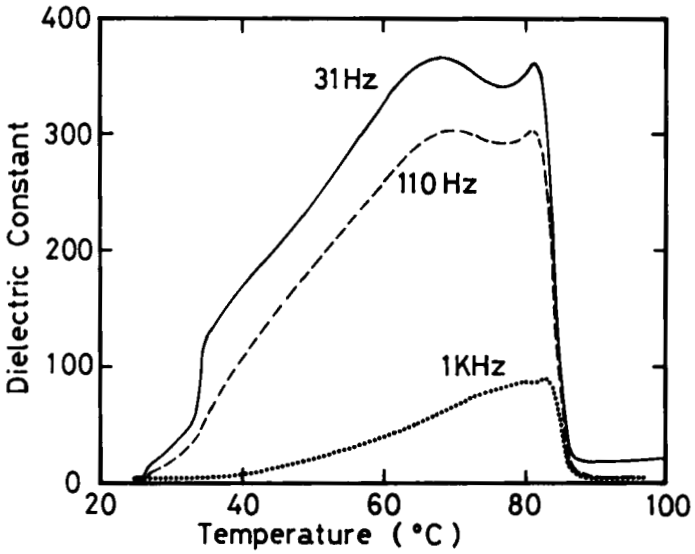


FIGURE 6 Temperature dependence of the dielectric constant in 1MC1ECHOPOPB.

taneous polarization. Therefore, the molecular conformation of Figure 4(b) is consistent with the experimental results.

Figures 5 and 6 show the temperature dependences of the dielectric constants of 1MC1ECPOPB and 1MC1ECHOPOPB, respectively. The dielectric constant of 1MC1ECHOPOPB is larger than that of 1MC1ECPOPB corresponding to

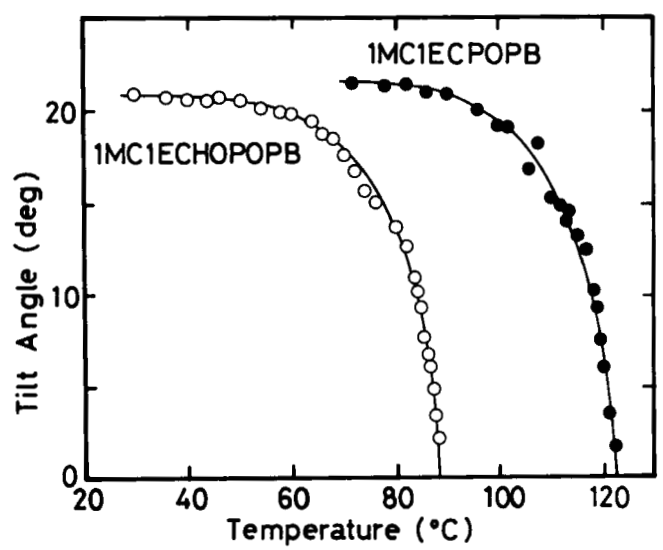


FIGURE 7 Temperature dependence of the tilt angle in 1MC1ECPOPB (closed circles) and in 1MC1ECHOPOPB (open circles).

the larger spontaneous polarization. However, the dielectric constant of 1MC1ECHOPOPB at 1 kHz was smaller than that of 1MC1ECPOPB. This means that the relaxation frequency of 1MC1ECHOPOPB is lower than that of 1MC1ECPOPB. This suggests the existence of not only intramolecular but also intermolecular hydrogen bonds in 1MC1ECHOPOPB.

Figure 7 shows the temperature dependence of the tilt angle in both materials. Almost no difference is found except for the shift in the temperature range. This means that the hydrogen bond in 1MC1ECHOPOPB influences mainly the dielectric properties and their dynamics but not so much the optical properties.

The measurements of the electro-optic effect and the studies for the effect of alkyl length and substituted positions of the hydroxyl group are now under progress.

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