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Magnitude and direction of the spontaneous polarization of ferroelectric liquid crystals with several bond moments

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The magnitude and direction of the spontaneous polarization in most ferroelectric liquid crystals have been confirmed to be determined by the location and magnitude of the bond moment around the chiral carbon and the core. In compounds with several bond moments their relative orientation is very important for obtaining a large spontaneous polarization. Compounds with benzene rings in the core substituted with OH also have a large spontaneous polarization, perhaps due to the formation of hydrogen bonds. Reversal of the direction of the spontaneous polarization with temperature has been found for EFPPOPB. This anomalous behaviour has been explained tentatively in terms of a conformation change due to the existence of a flexible $-CH_2-$ unit between the chiral carbon and the dipole moment.

1. Introduction

Ferroelectric liquid crystals have attracted great interest from both fundamental and practical points of view. Our understanding of the origin of ferroelectricity in liquid crystals has progressed considerably as a result of detailed studies of the properties of the first ferroelectric liquid crystal DOBAMBC (4-*n*-decyloxybenzylidene-4′-amino-2-methylbutylcinnamate) [1]. However, the spontaneous polarization of this material was very small compared with conventional inorganic crystalline ferroelectrics. Therefore, much effort was made to synthesize new ferroelectric liquid crystals with a large spontaneous polarization to establish a fast response for electro-optic devices [2–9]. Among these newly developed ferroelectric liquid crystals, various compounds which are quite anomalous in their characteristics, when compared with DOBAMBC, have been found.

In ferroelectric liquid crystals, both the magnitude of the spontaneous polarization, P_s, and its absolute direction are important. The sign of P_s is defined corresponding to the absolute direction of P_s as follows [9]. When the layer normal, the average direction of the molecular long axis (i.e. the director for the molecular alignment) and the direction of the spontaneous polarization form right-handed and left-handed coordinate systems, P_s is defined as positive, $P_s(+)$, and negative, $P_s(-)$, respectively. The magnitude and the direction of the spontaneous polarization depend on various factors such as the types of bond moments, the position of bond moments relative to the core and also to the chiral carbon, the relative orientation of bond moments, core structure, and so on.

Here we report the relationship between the magnitude and direction of P_s and these factors observed in several series of ferroelectric liquid crystals developed by us.

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Several anomalous dielectric properties found in these materials and their interpretation in terms of the molecular structure and their dynamics are also discussed. The effect of hydrostatic pressure on these properties is also described.

2. Experimental

The molecular structures of the ferroelectric liquid crystals used in this study and their acronyms are shown in figure 1. Details of the preparation method, synthesis and purification, of these materials have already been reported [2–8]. The sample was sandwiched between two indium–tin oxide (ITO) coated glass plates separated with polyethyleneterephthalate (PET) films as spacers.

The spontaneous polarization was measured by the modified Sawyer–Tower method (Pepinskey bridge), by applying a triangular shaped voltage, and also by a transient current measurement. The dielectric constant was measured by observing the current component whose phase was shifted by 90° from that of applied voltage with a lock-in amplifier (PAR 5204) and by an impedance analyser (YHP 4192A).

The tilt angle was evaluated by a polarized optical microscope observation, and the sign of P_s was determined by this observation upon changing the polarity of the applied D.C. bias voltage.

Hydrostatic pressure was applied to the cell, via an intensifier device with a pressure transmitting fluid (silicone oil KF-96-50cs in this case) [10].

3. Results and discussion

3.1. *Effects of bond moments around the chiral carbon*

Among various compounds, ferroelectric liquid crystals with three benzene rings in the core structure are discussed in this section.

The maximum spontaneous polarization and the direction of the spontaneous polarization for typical examples of these series of compounds are listed in the table.

Table 1. The magnitude (maximum value in the S_C^* phase) and the sign of the spontaneous polarization of typical ferroelectric liquid crystals used in this study.

	Direction of spontaneous polarization	Maximum spontaneous polarization/nC cm^{-2}
1MC1ECPOPB	$P_s(-)$	65
1BC1ECPOPB	$P_s(-)$	60
1HpC1ECPOPB	$P_s(-)$	55
1OC1ECPOPB	$P_s(-)$	56
1MC1ECPDPB	$P_s(-)$	50
2MC1PCPOPB	$P_s(+)$	15
3EC2PCPOPB	$P_s(-)$	32
1MC1EPOPB	$P_s(+)$	170
1BC1EPOPB	$P_s(+)$	240
1HpC1EPOPB	$P_s(+)$	130
1MC1EPDPB	$P_s(+)$	100
1MC1EPUdPB	$P_s(+)$	100
3B2PCPOPB	$P_s(-)$	24
1MC1EOPBB	$P_s(-)$	30
2MC1POPBB	$P_s(+)$	12
3B2POPBB	$P_s(-)$	52
1MC1ECHOPOPB	$P_s(-)$	180

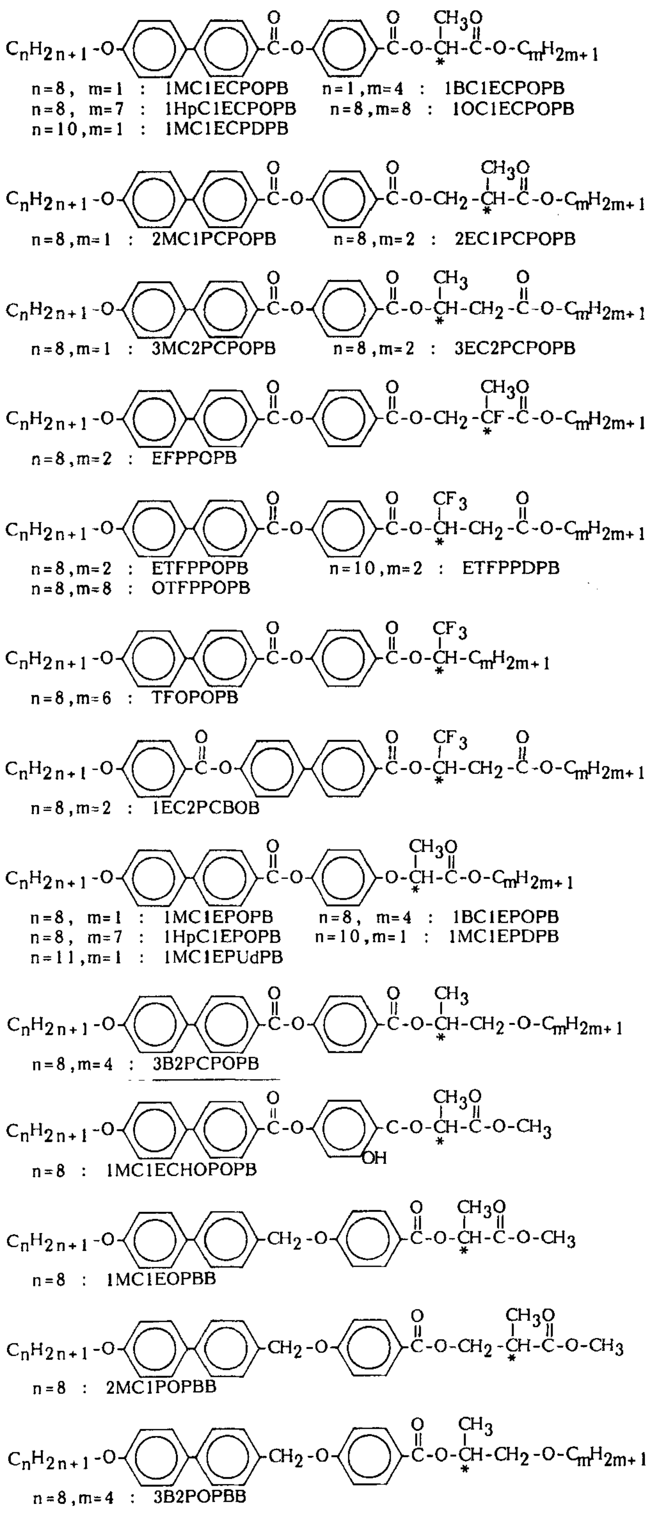


Figure 1. The molecular structures of the ferroelectric liquid crystals used in this study and their acronyms.

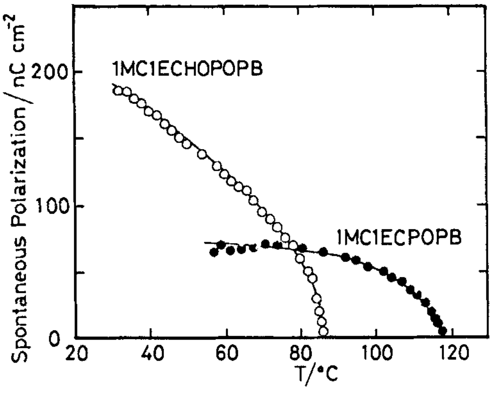


Figure 2. The temperature dependence of the spontaneous polarization of 1BC1EPOPB, 1BC1ECPOPB and 3B2PCPOPB.

It is clear from these results and figure 2 that a small modification of the molecular structure around the chiral carbon results in a drastic change of the magnitude of the spontaneous polarization [7, 8]. The position and the relative orientation of the bond moments (C = O, C–O, etc.) around the chiral carbon have a remarkable effect on the magnitude of the spontaneous polarization. That is, the magnitude of the spontaneous polarization is determined by the sum of the bond moments by taking the actual spatial configuration into consideration. This is clearly confirmed if we compare the spontaneous polarization of three compounds, 1BC1EPOPB, 1BC1ECPOPB and 3B2PCPOPB, whose molecular structures around the chiral carbon are indicated in figure 3. It should also be noted that the large spontaneous polarization was expected in the compound with the short core–chiral carbon distance. The dipole moment next to the core plays an important role. The direction of the spontaneous polarization can be also explained by taking the direction of the main bond moment and its separation from the chiral carbon into consideration.

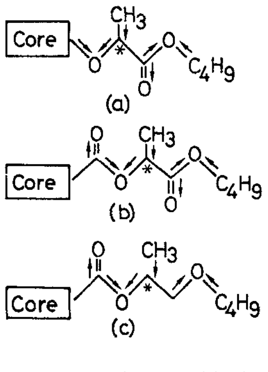


Figure 3. The molecular structures around the chiral carbon in (*a*) 1BC1EPOPB, (*b*) 1BC1ECPOPB and (*c*) 3B2PCPOPB.

The dipole moment in the core was also found to have some influence on the spontaneous polarization. If the spontaneous polarizations of 1MC1ECPOPB and 2MC1PCPOPB are compared with those of 1MC1EOPBB and 2MC1POPBB, the former materials with an ester linkage in the core exhibited larger spontaneous

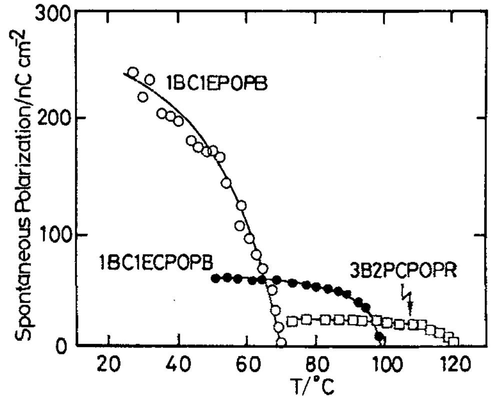


Figure 4. The temperature dependence of the spontaneous polarization of 1MC1ECHOPOPB and 1MC1ECPOPB.

polarization than those with $-CH_2O-$ in the core. However, there are some exceptions. For example, a larger spontaneous polarization was observed in 3B2POPBB (with $-CH_2O-$) than in 3B2PCPOPB (with $-CO_2-$). This anomaly seems to depend on whether the steric hindrance suppresses the intramolecular rotation of the carbonyl group in the chiral part.

In the table we do not include the spontaneous polarization of compounds with fluorine atoms at the chiral carbon. However, as we have already reported, spontaneous polarization is generally highly enhanced by replacement of C^*-CH_3 at the chiral part by C^*-CF_3 such as in ETFPPOPB, TFOPOPB, etc. [6, 11]. Therefore, the behaviour of ferroelectric liquid crystals with many fluorine atoms at the chiral part and the core are highly promising and they are now under study.

3.2. *Effect of the hydroxyl substituent*

The introduction of a hydroxyl substituent, OH, in the benzene nuclei of the core has sometimes been carried out to stabilize the nematic liquid crystal. It was observed that by the introduction of OH into the core of ferroelectric liquid crystals, spontaneous polarization can be enhanced considerably as is evident from figure 4. That is, the spontaneous polarization of 1MC1ECHOPOPB is much larger than that of 1MC1EOPOPB and approached $2 \times 10^{-7}\,C\,cm^{-2}$ [9]. The temperature range of the ferroelectricity was also lowered considerably and expanded. The enhancement of the spontaneous polarization by OH substitution can also be explained tentatively in terms of the relative orientation of the bond moments around the chiral carbon. One of the possible explanations of this effect is the formation of a hydrogen bond. Among the two possible conformations shown in figure 5, the conformation of (*b*) seems to

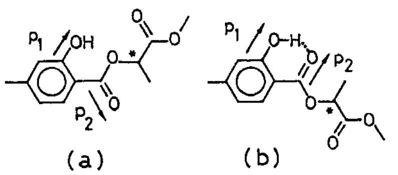


Figure 5. Two possible conformations for 1MC1ECHOPOPB.

be stabilized due to the formation of a hydrogen bond compared with the conformation of (*a*). In such a case the dipole moments originating in the C–OH and C=O bonds should act additively, resulting in the enhancement of the spontaneous polarization. The existence of the intramolecular hydrogen bond also enhances the rigidity of the molecular structure between the core and the chiral carbon, which can also result in an enhancement of the spontaneous polarization.

The meso phase with a large spontaneous polarization was confirmed to be a chiral smectic C. However, the larger viscosity compared with other compounds is consistent with the hydrogen bond formation.

3.3. *Anomalous dielectric behaviour in 3MC2PCPOPB*

In 3MC2PCPOPB ((R)-4′-(3-methoxycarbonyl-2-propoxycarbonyl) phenyl 4-[4-(*n*-alkoxy)phenyl]benzoate) in a cell 16 μm thick, an anomalous dielectric behaviour was observed as shown in figure 6. That is, two peaks of spontaneous polarization were observed at about 115 and 85°C. In the temperature range between these two peaks no spontaneous polarization was obtained. This anomaly reminds us of the case of the biphenyl ester series of ferroelectric liquid crystals such as 2MBNCBC ((S)-2″-methylbutyl 4′-*n*-nonylcarbonyloxy-(1,1′-biphenyl)-1-carboxylate) in which the sign of the spontaneous polarization is reversed at a temperature in the chiral smectic phase [12, 13]. In the optical observation by applying a pulsed voltage, the optical response was only observed at temperatures near these peaks. The direction of the spontaneous polarization was confirmed to be the same at these two peaks. Therefore, the origin of the present anomaly differs from that in 2MBNCBC. On the other hand, in 3EC2PCPOPB which has an ethyl end unit instead of a methyl group, such an anomaly was not observed as is also evident from this figure.

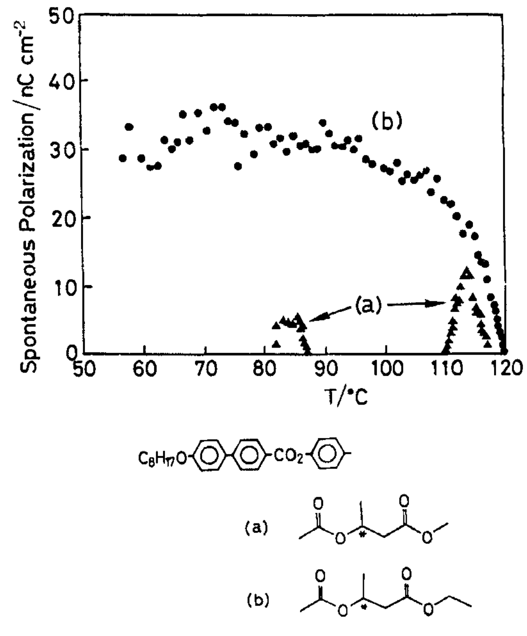


Figure 6. The temperature dependence of the spontaneous polarization of 3MC2PCPOPB and 3EC2PCPOPB in a 16 μm cell.

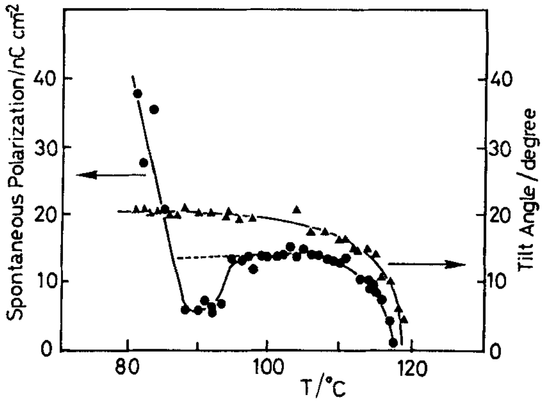


Figure 7. The temperature dependence of the spontaneous polarization and the tilt angle of 3MC2PCPOPB in a 6 μm cell.

To clarify the origin of this anomaly we have studied the response with much higher electric fields utilizing a thinner cell (6 μm). Then we confirmed that the tilt angle remains nearly constant in the temperature range between the two peaks, and the spontaneous polarization does not disappear in this range. Even the enhancement of the spontaneous polarization was observed on decreasing the temperature below the low temperature peak (see figure 7). This can be interpreted as follows. With decreasing temperature, P_s increases as is usual for ferroelectric liquid crystals. However, because of the large viscosity and/or the small pitch of helix, the molecules do not response to the electric field since it was not high enough, resulting in the apparent disappearance of the spontaneous polarization. Only at temperatures near the phase transition where the viscosity seems to be small and the pitch is large, can the molecules respond to the electric field, resulting in the peak of the spontaneous polarization. There should exist a phase transition at about 87°C. Then the second peak should be due to the much enhanced spontaneous polarization in the lower temperature phase.

It is not clear at this stage why such a small modification of the molecular structure by replacing $-C_2H_5$ with $-CH_3$ results in such a drastic change in the dielectric properties.

3.4. *Reversal of the direction of the spontaneous polarization in fluorinated ferroelectric liquid crystal with temperature*

We have already reported that the direction of the spontaneous polarization reverses with temperature in a biphenyl series of ferroelectric liquid crystals, although its mechanism has not been clarified [12, 13]. It should be also pointed out that no anomaly was observed in the helical pitch at the temperature corresponding to the reversal of the spontaneous polarization. It is not clear whether such an anomaly is special only for this biphenyl series or whether it also exists in other materials.

The temperature dependence of the dielectric constant for EFPPOPB, shown in the inset of figure 8, exhibits a small anomaly similar to the biphenyl ester series. Consequently, detailed studies of the direction of the polarization and the tilt angle in this compound were carried out. As shown in figure 9, the reversal of the tilt direction and therefore the sign of the spontaneous polarization, were clearly observed, as expected. This is similar to the anomalous behaviour observed in the biphenyl

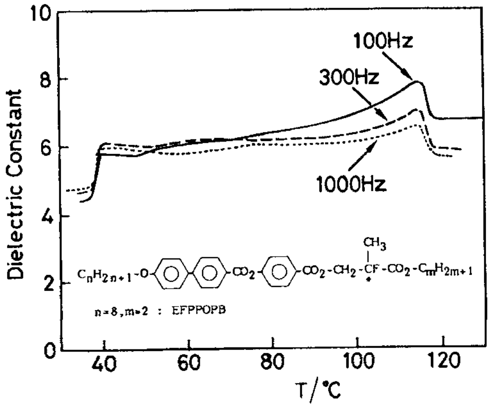


Figure 8. The temperature dependence of the dielectric constant for EFPPOPB.

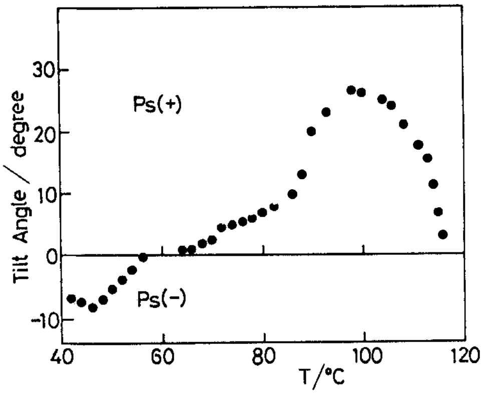
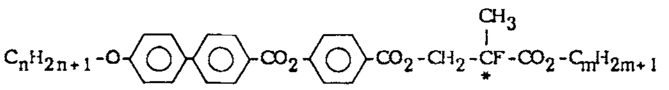


Figure 9. The temperature dependence of the tilt angle and the sign of the spontaneous polarization for EFPPOPB.

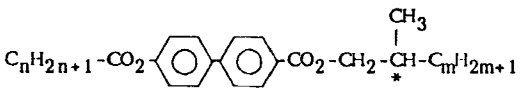
series. What is common in the structure for both materials which indicate this anomalous behaviour is the existence of a methylene unit $-CH_2-$ between the chiral carbon and dipole moment as evident in figure 10. Compounds containing such methylene units should be flexible and their conformation may change drastically with temperature as speculated also in figure 11.

In the assignment of the sign of the spontaneous polarization by Goodby [9], the rigid *trans* conformation of the molecular group at the chiral carbons was expected.



(b)

n=8,m=2 : EFPPOPB



(a)

n=9,m=2 : 2MBNCBC

Figure 10. The molecular structure of (*a*) 2MBNCBC and (*b*) EFPPOPB around the core and the chiral carbon.

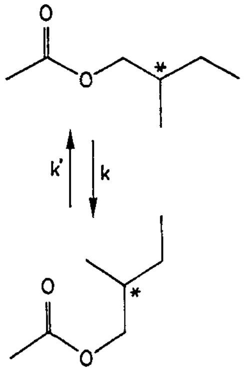


Figure 11. The proposed conformational change of EFPPOPB around the chiral carbon.

If the remarkable conformation change proposed in figure 11 occurs, the usual interpretation of the sign of the spontaneous polarization can be violated, which may result in the reversal of the directions of the tilt angle and the spontaneous polarization with temperature. Therefore, we can conclude that such an anomaly in the sign of the spontaneous polarization can also exist in many ferroelectric liquid crystals in which a flexible unit such as $-CH_2-$ is contained in their structure and a remarkable conformational change occurs in the temperature range of the chiral smectic C phase.

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