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Anomalous temperature dependence of the dielectric and optical properties in ferroelectric liquid crystals

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The anomalous temperature dependence of the sign of the spontaneous polarization in a biphenyl ester series of ferroelectric liquid crystals is reported. The reversal of the sign of the spontaneous polarization in the chiral smectic C phase of 2MBNCBC ((S)-2′-methylbutyl-4′-*n*-nonylcarbonyloxy-(1,1′-biphenyl)-1-carboxylate) is observed at T_m. This anomaly is studied in detail as functions of the length of the terminal alkyl chain, the applied electric field, the frequency and the applied hydrostatic pressure. T_m has been confirmed to depend on the length of the terminal chain and the applied pressure. However, it is independent of the applied field and the measuring frequency. In the mixture of these compounds, this anomaly is also observed.

1. Introduction

Recently, our understanding of the fundamental property of ferroelectric liquid crystals has progressed and various new ferroelectric liquid crystals have been synthesized to establish the fast response of electro-optic devices utilizing ferroelectric liquid crystals [1–3]. Among these newly developed ferroelectric liquid crystals, sometimes, compounds which show anomalous characteristics compared with those of materials known so far, are found [4].

In ferroelectric liquid crystals, not only the magnitude of spontaneous polarization, P_s, but also its absolute direction is considered to be important. The sign of P_s is defined as follows, depending on the absolute direction of this polarization [5]. When the layer normal, the director for the average molecular alignment and the spontaneous polarization form a right handed (left handed) coordinate systems, P_s is defined as positive, $P_s(+)$, (negative, $P_s(-)$). Generally, the sign of P_s is considered to be an intrinsic property of each compound, and to be determined by the structure and the position of the chiral group in the molecule. Therefore, the sign of P_s for each compound is considered to be unchanged upon varying the environmental condition. However, recently, we have reported that, in 2MBNCBC ((S)-2″-methylbutyl 4′-*n*-nonylcarbonyloxy-(1,1′-biphenyl)-1-carboxylate), the sign of P_s reverses with temperature [6]. A similar anomaly has also been observed by Goodby *et al.* [7].

In this paper, we report the anomalous dielectric and optical properties of this biphenyl series of compounds and their mixtures as functions of temperature, electric field and applied hydrostatic pressure etc. The origin of these anomalies is discussed.

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2. Experimental

Figure 1 shows the molecular structure of the ferroelectric liquid crystals used in this study and their acronyms. The synthetic procedure used to prepare these materials has been reported previously. The sample was sandwiched between ITO (In–Sn oxide) coated glass plates with a PET (polyethyleneterephthalate) film as the spacer.

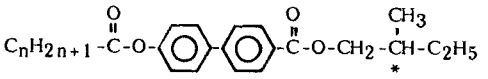

Figure 1. Molecular structure, and acronyms of the (S)-2″-methylbutyl-4′-*n*-alkylcarbonyloxy-(1,1′-biphenyl)-1-carboxylates series of ferroelectric liquid crystals used in this study. n = 7:2MBHpCBC, n = 8:2MBOCBC, n = 9:2MBNCBC, n = 10:2MBDCBC, n = 11:2MBUDCBC.

In the experiments, a sample 50 μm in thickness was mainly used. Though the spontaneous polarization evaluated sometimes depends apparently on the sample thickness, the anomaly of P_s and the tilt direction observed in this study was not dependent on the sample thickness, as discussed in §3.

The spontaneous polarization was determined both by the modified Sawyer–Tower method and by applying a triangular shaped voltage. 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).

The tilt angle was measured using polarized optical microscopy, and the sign of P_s was determined by changing the polarity of the applied D.C. bias voltage.

For the application of hydrostatic pressure to the cell, an intensifier device with a pressure-transmitting fluid (silicone oil, KF-96-50cs) was used. The pressure was monitored with a manganin gauge.

3. Results and discussion

We have previously reported that the sign of the spontaneous polarization in 2MBNCBC reverses at a temperature T_m (about 28°C in this sample), and, at this temperature, the spontaneous polarization vanishes as shown in figure 2. It has been also reported that the direction of the tilt angle reverses at T_m. That is, upon decreasing the temperature below the Curie point T_c, the tilt angle increases. However, after reaching a maximum, it decreases again approaching zero at T_m, and below T_m the direction of the tilt is reversed and again the angle increases. However, this observation was confirmed to be due to the applied field being insufficient to orient such a small spontaneous polarization near T_m. Therefore, a higher electric field was applied to a thin cell ($< 2\,\mu$m) to establish complete alignment of P_s. Then, it was found that the tilt angle did not decrease near T_m but only the direction was reversed suddenly, as shown in figure 2. In this case, the tilt angle was determined under a D.C. bias voltage. Therefore, the apparent change in the sign of tilt angle observed is due to the change in the sign of the spontaneous polarization. That is, below T_c, the tilt angle increases, tending to saturate at about 20°, and at T_m only the direction of the tilt is reversed while keeping nearly the same angle, 20°.

No anomaly was observed at T_m in the temperature dependence of helical pitch for 2MBNCBC. In the temperature dependence of the dielectric constant also two peaks can be observed in 2MBNCBC, and the value at T_m was just the same as that for the

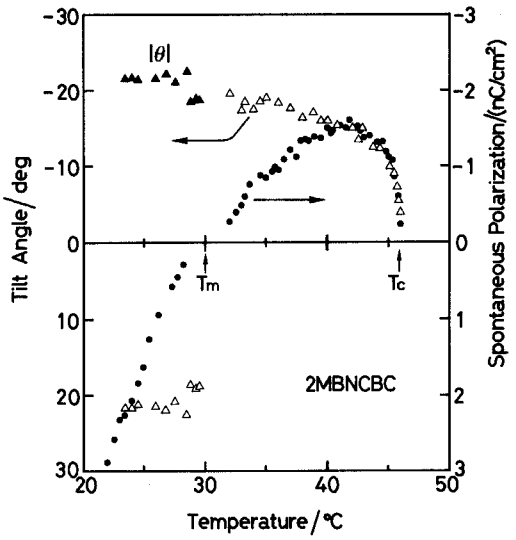

Figure 2. The temperature dependence of the spontaneous polarization and the tilt angle of 2MBNCBC. The absolute value of the tilt angle is also shown.

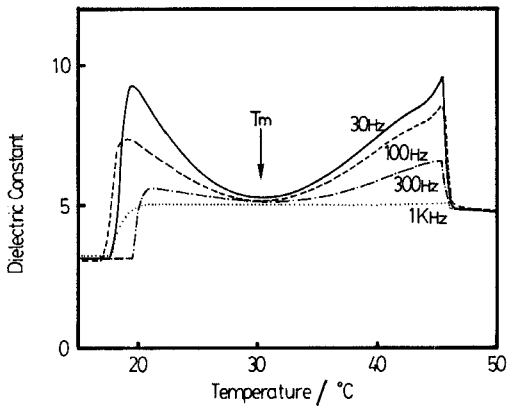

Figure 3. The temperature dependence of the dielectric constant of 2MBNCBC at various frequencies.

nonferroelectric smectic A phase. It should also be mentioned that the dielectric constant measured at low frequency (30 Hz) coincides with that at high frequency (1 kHz) at T_m, as shown in figure 3. These results clearly indicate that the contribution of the Goldstone mode to the dielectric constant is suppressed at T_m, which also corresponds to the disappearance of P_s at T_m.

Generally, the thermodynamic free energy theory predicts a similar temperature dependence for both the tilt angle and the spontaneous polarization; indeed such behaviour has been confirmed for most ferroelectric liquid crystals. However, the observations mentioned here clearly indicate that such a relationship is lost in 2MBNCBC near T_m. This may be very important in order to understand the origin of the anomaly.

A similar anomaly has also been observed in this biphenyl series of compounds, as shown in figure 4. However, depending on the length of the terminal alkyl chain

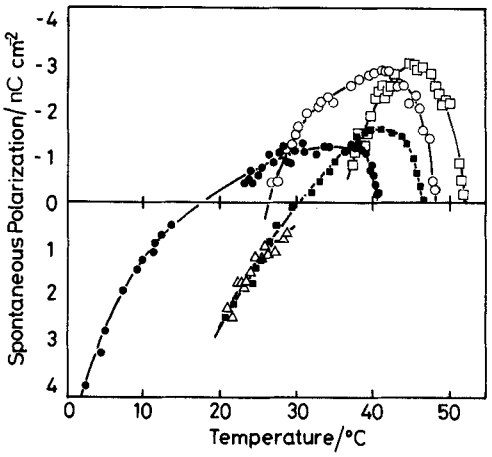

Figure 4. The temperature dependence of the spontaneous polarization for biphenyl ester series (2MBACBC). △ denotes $n = 7$; ●, $n = 8$; ■, $n = 9$; ○, $n = 10$; and □, $n = 11$.

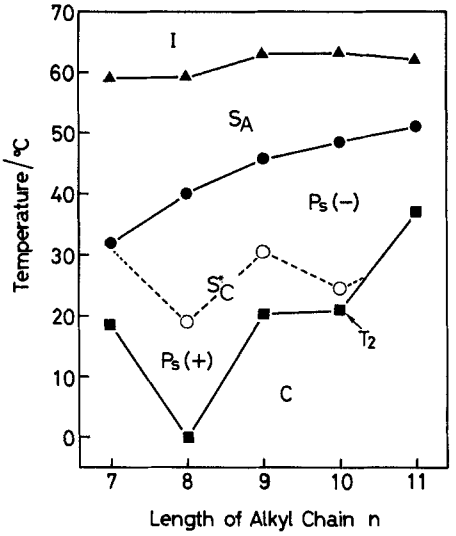

Figure 5. The transition temperatures as a function of the length of the terminal alkyl chain of the biphenyl ester series (2MBACBC). T_c is represented by ● and ○ denotes T_m.

the transition temperatures and also T_m change. These transition temperatures and T_m are summarized in figure 5. It should be noted that there is some alternation in T_m but, compared with large change in T_c, T_m is limited to a narrow temperature range. This means that the anomaly should be determined by the molecular structure around the chiral part. It is also evident that compounds which show a ferroelectric chiral smectic C (S_C^*) phase above or below T_m only show negative and positive P_s, respectively. The material which has a wide S_C^* range around 30°C shows such anomalous behaviour.

Similar anomalous dielectric behaviour was also observed in the mixture of various compounds of this biphenyl series compounds as shown in figures 6 and 7. The application of a D.C. bias electric field causes the magnitude of the dielectric constant to decrease because of the suppression of the Goldstone mode, but the anomaly near T_m does not disappear and T_m also does not shift. On the other hand,

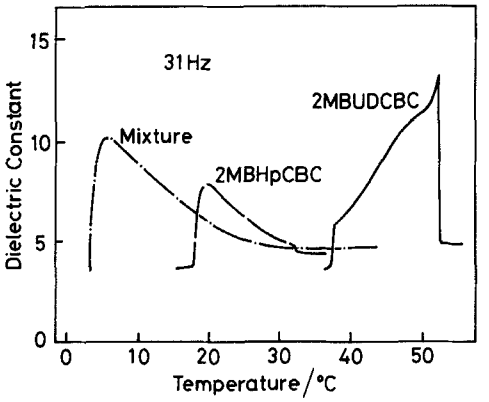

Figure 6. The temperature dependence of the dielectric constant of 2MBUDCBC (n = 11), 2MBHpCBC (n = 7) and their mixture.

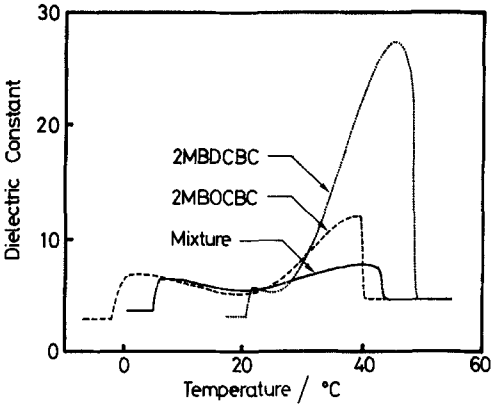

Figure 7. The temperature dependence of the dielectric constant of 2MBOCBC (n = 8), 2MBDCBC (n = 10) and their mixture.

on the application of hydrostatic pressure, the magnitude of the dielectric constant is diminished and the anomaly at T_m remains, but remarkably T_m shifts to higher temperature as evident in figure 8. The origin of this effect is not clear at this stage. However, at least this pressure effect suggests that this anomaly originates in the intermolecular effects.

Although, the origin of the anomaly at T_m is not clear at this stage, there are many possibilities which include. (1) The dipole moments of the carbonyl groups on both sides of the biphenyl unit may contribute in the opposite direction. At a higher temperature, the right hand side C = O in the molecule (see figure 1) may play a major role, resulting in the formation of the left handed coordinate system and a negative sign for P_s. On the contrary, at low temperatures the left hand side C = O may play the main contribution and prefer the right handed coordinate system, resulting in a positive P_s. (2) The other possibility is a change of the intermolecular interactions when the tilt angle exceeds some critical value, which may induce a change of the molecular interaction and the reversal of the sign of P_s. The intermolecular quadrupolar interaction may also play some role in this phenomena. Recently, Eidenschink *et al.* also discussed the parameters playing a role in the polarization sign reversal [8].

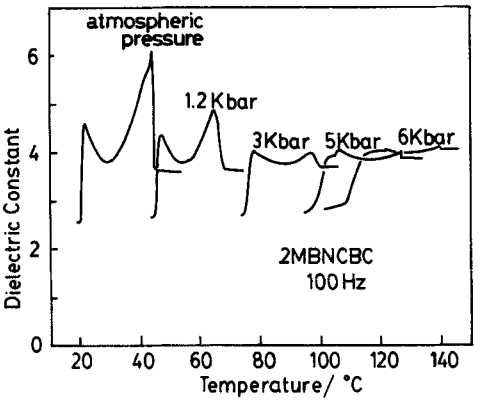

Figure 8. The temperature dependence of the dielectric constant for 2MBNCBC as a function of the applied pressure.

However, we should like to point out at this stage that there exist some possibility of conformational change near T_m. That is, in this material the $-CH_2-$ unit exists between carbonyl group and chiral carbon. Therefore, the molecule can be flexible at this $-CH_2-$. In such a core large configuration change can occur at some temperature due to some intramolecular or intermolecular interactions such as hydrogen bonding. If with their conformational change, the original Goodby rule for the sign of P_s determined by the number of carbon atoms from the core was violated or much modified, such an anomaly can be probable. To confirm this idea, more detailed studies are now in progress.

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