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The characteristic dielectric behaviour in ferroelectric liquid crystals at a phase transition and the contribution of the soft mode

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The characteristic dielectric behaviour of ferroelectric liquid crystals with a large spontaneous polarization has been studied as functions of the D.C. bias field, frequency, cell thickness and applied pressure. Under the condition in which the contribution of the Goldstone mode is suppressed, a sharp peak in the temperature dependence of the dielectric constant is clearly observed at the transition between S_A and S_C^* phases $T_{S_C^*S_A}$. The relaxation of the soft mode is observed both in the S_A and S_C^* phases by eliminating the contribution of the Goldstone mode under a D.C. bias field. Another relaxation is also observed in the S_C^* phase around several kHz in addition to that of the soft mode and the Goldstone mode. The pressure effect on the soft mode was also studied.

1. Introduction

Ferroelectric chiral smectic liquid crystals have attracted considerable attention and a great number of theoretical and experimental studies have been carried out [1]. The dielectric properties of these materials, especially, has been investigated experimentally, for example the measurement of dielectric constant [2–5], and theoretically, for example via a Landau free energy expansion [6–8]. The large dielectric constant perpendicular to the helical axis in a chiral smectic C (S_C^*) phase has been interpreted in terms of the contribution of the fluctuation of the azimuthal angle of the molecular long axis around the helical axis. This contribution is called the Goldstone mode. However, the fluctuation of the tilt angle (i.e. the soft mode) should also contribute to dielectric constant.

In conventional ferroelectric liquid crystals, below the transition temperature between the S_A and S_C^* phases, $T_{S_C^*S_A}$ the dielectric constant starts to increase with decreasing temperature, and has a maximum value a few degrees below $T_{S_C^*S_A}$. In a previous paper the appearance of a sharp peak of dielectric constant at $T_{S_C^*S_A}$ was reported for DOBAMBC (4-*n*-decyloxybenzylidene-4′-amino-2-methylbutyl-cinnamate) [2]. Because of the small peak in DOBAMBC with its small spontaneous polarization, however, its origin was not clarified at that stage. Recently, ferroelectric liquid crystals with a large spontaneous polarization have been synthesized [9–11], and interesting behaviour near $T_{S_C^*S_A}$ has been observed. Here the characteristic peak of these ferroelectric liquid crystals at $T_{S_C^*S_A}$ is described in detail as functions of the applied D.C. electric field, measuring frequency, cell thickness and applied pressure.

2. Experimental

The ferroelectric liquid crystals used in this study were 3M2CPOOB ((2S,3S)-3-methyl-2-chloropentanoic acid 4′,4″-octyloxybiphenyl ester) [9], ETFPPOPB ((S)-4′-(3-ethoxycarbonyl-1,1,1-trifluoro-2-propoxycarbonyl) phenyl 4-[4-(*n*-octyloxy)phenyl]

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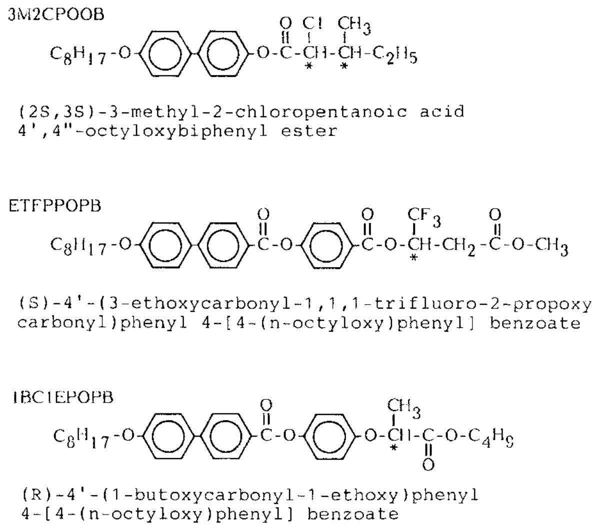

Figure 1. The molecular structures, their names and acronyms of the compounds used in this study.

benzoate [10] and 1BC1EPOPB ((R)-4′-(1-butoxycarbonyl-1-ethoxy) phenyl 4-[4-(*n*-octyloxy)phenyll benzoate) [11]. The molecular structure of these compounds are shown in figure 1. All of these liquid crystals have a large value of the spontaneous polarization, as large as 150–300 nC cm^{-2}. Details of the preparation of these liquid crystals have previously been reported [9–11]. The sample was sandwiched between indium-tin oxide (ITO) coated glass plates with polyethyleneterephthalate (PET) film as a spacer.

The dielectric constant was measured by evaluation of the current whose phase was shifted by 90° from that of the applied voltage with a lock-in amplifier (PAR, 5204), and was also measured using an impedance analyser (YHP, 4192A). The measuring applied field was sufficiently low so as not to perturb the molecular alignment.

For pressure measurement the sample was sandwiched between ITO coated glass plates with Teflon film as a spacer; the cell was sealed completely with silicone resin, taking care to eliminate small bubbles. An intensifier device with a pressure transmitting fluid, silicone oil (Shin-Etsu Chemical, KF-96-50cs) was used to apply hydrostatic pressure to the cell. The pressure was monitored with a manganin gauge.

3. Results and discussion

Figure 2 shows the temperature dependence of the dielectric constant as a function of the D.C. bias field in a 16 μm cell of ETFPPOPB. In the absence of the D.C. bias field the value of the dielectric constant is large. Under the D.C. bias field, however, the dielectric constant in the S_C^* phase decreases and only a peak at $T_{S_C^*S_A}$ remains. Such a peak in the dielectric constant is observed for all of the samples studied here.

In a thick cell the ferroelectric liquid crystal has a helicoidal structure with the helix axis perpendicular to the smectic layer. The large value of the dielectric constant in the S_C^* phase is interpreted as originating in the fluctuations of the azimuthal angle of the molecular long axis in the helicoidal structure, which is called the Goldstone mode. Under a D.C. bias field parallel to the layer the helicoidal structure is unwound,

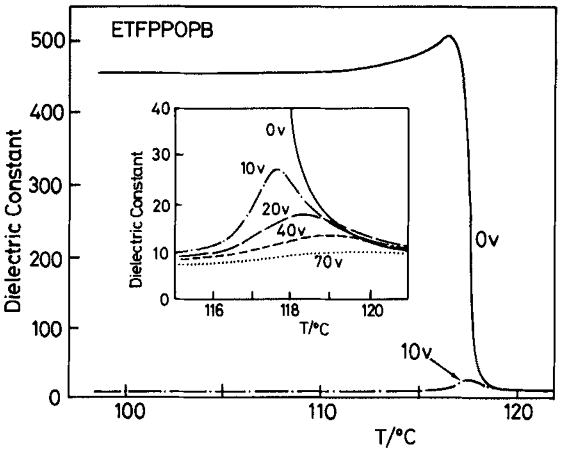

Figure 2. The temperature dependence of the dielectric constant of ETFPPOPB under various D.C. applied bias fields at 500 Hz. The cell thickness was 16 μm.

and the large dielectric constant in the S_C^* phase is suppressed by the decrease of the contribution of the Goldstone mode. As a result, a sharp peak at $T_{S_C^*S_A}$ becomes prominent as shown in figure 2. This peak may correspond to that reported in DOBAMBC [2, 12, 13].

The helicoidal structure is influenced by the surface effect of the substrates (electrodes), and can be unwound in a thin cell. Therefore, in a thinner cell the contribution of the Goldstone mode is also suppressed, and the prominence of the sharp peak in the dielectric constant at $T_{S_C^*S_A}$ can be observed. In 3M2CPOOB, especially, the helicoidal structure was unwound even in a cell as thick as several hundred μm, and the dielectric constant in the S_C^* phase was suppressed due to the decrease of the Goldstone mode contribution, resulting in the prominence of the sharp peak at $T_{S_C^*S_A}$ [14].

The relaxation frequency of the Goldstone mode is around several tens or several hundred Hz [3–5, 12] except for a special case [14]. Therefore, at high frequency the dielectric constant is found to be small because of the decrease of the Goldstone mode contribution. On the other hand, the sharp peak at $T_{S_C^*S_A}$ becomes clear at high frequency as shown in figure 3, which indicates that the relaxation frequency of this peak is high compared with that of the Goldstone mode. It should be noted that, at very high frequencies of 50 and 100 kHz, an anomalous dip just below the peak of the dielectric constant is observed. The same anomaly was observed in other liquid crystals, such as 3M2CPOOB.

Figure 4 shows the frequency dispersion of the dielectric constant in 3M2CPOOB above $T_{S_C^*S_A}$ (*a*), just below $T_{S_C^*S_A}$ (*b*) and below $T_{S_C^*S_A}$ (*c*). In the S_A phase (see figure 4 (*a*)) a single relaxation at a frequency higher than 10 kHz was observed in the frequency range in this study; this may correspond to the soft mode. As shown in figure 4 (*b*), just below $T_{S_C^*S_A}$ the lower relaxation is observed in addition to that of the soft mode, which corresponds to the relaxation of the Goldstone mode. Close to $T_{S_C^*S_A}$ both relaxations of the soft mode and Goldstone mode were observed in the S_C^* phase. However, further below $T_{S_C^*S_A}$ the relaxation of the soft mode is overlapped with the component of the Goldstone mode, and cannot be separated.

In order to eliminate the contribution of the Goldstone mode, the frequency dispersion of the dielectric constant was measured under a D.C. bias field. In this case

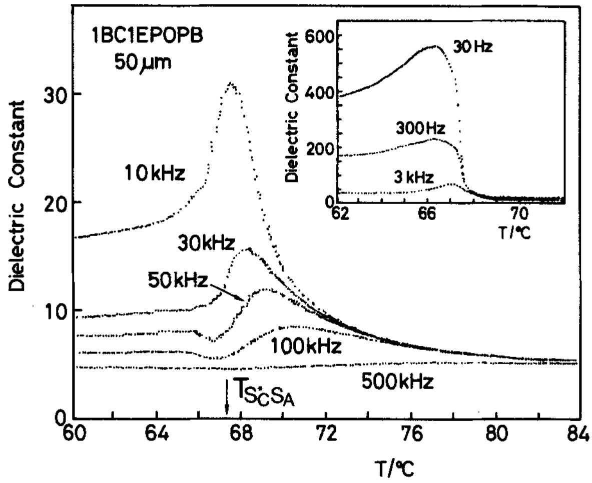

Figure 3. The temperature dependence of the dielectric constant of 1BC1EPOPB at various frequencies near the transition between the S_A and S_C^* phase. The cell thickness was 50 μm. $T_{S_C^*S_A}$ was evaluated from an optical measurement.

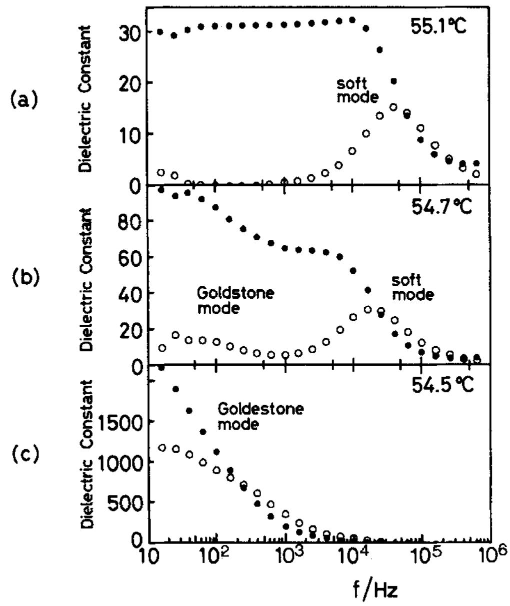

Figure 4. The dielectric relaxation of a 25 μm cell of 3M2CPOOB (*a*) above $T_{S_C^*S_A}$, (*b*) just below $T_{S_C^*S_A}$ and (*c*) below $T_{S_C^*S_A}$. The closed circles denote the real part and the open circles the imaginary part of the dielectric constant.

the contribution of the Goldstone mode was suppressed, and the relaxation of the soft mode was clearly observed apart from that of the Goldstone mode even in the S_C^* phase. Figures 5 and 6, respectively, show the temperature dependences of the relaxation frequency and the dielectric strength, $\varepsilon_s - \varepsilon_\infty$, under D.C. bias field obtained from the frequency dispersion plots of dielectric constant as shown in figure 4. Here ε_s and ε_∞ are the static and infinite frequency dielectric constant of the soft mode, respectively. It should be noted that the temperature dependence of the

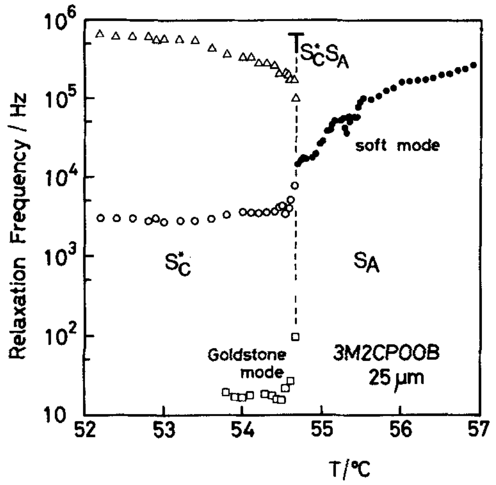

Figure 5. The temperature dependence of the relaxation frequency of the dielectric constant under a D.C. bias field of 1·2 kV cm^{-1} in a 25 μm cell of 3M2CPOOB near the transition temperature. (△) The relaxation of the soft mode and (○) the unidentified relaxation in the S_C^*.

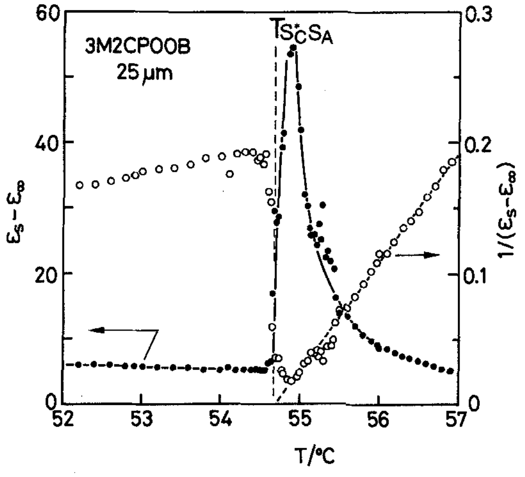

Figure 6. The temperature dependence of the dielectric strength, $\varepsilon_s - \varepsilon_\infty$, of the soft mode for 3M2CPOOB under a D.C. bias field of 1·2 kV cm^{-1}.

relaxation of the soft mode in both the S_C^* and S_A phase is clearly observed, especially, even away from $T_{S_C^*S_A}$ in the S_C^* phase, as shown in figure 5. This observation of the soft mode relaxation in the S_C^* is the first reported.

From this temperature dependence of the relaxation frequency of the soft mode, the anomalous dip of the dielectric constant at $T_{S_C^*S_A}$ shown in figure 3 can be explained as follows. In the S_A phase the relaxation frequency corresponding to the soft mode decreases with temperature as $T_{S_C^*S_A}$ is approached, and is as low as several tens kHz at $T_{S_C^*S_A}$. At close to $T_{S_C^*S_A}$, therefore, the dielectric constant should be suppressed at a frequency higher than several tens of kHz, and the dip in the dielectric constant is observed.

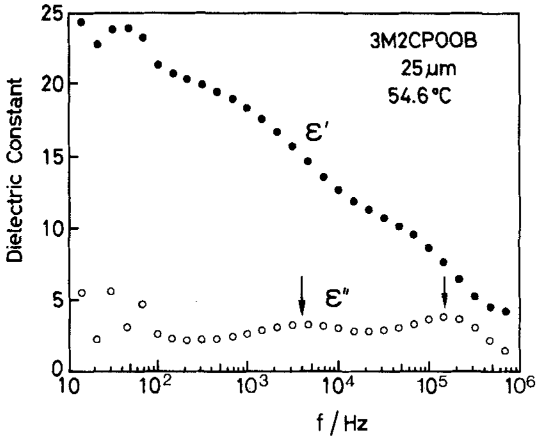

Figure 7. The dielectric relaxation of a 25 μm cell of 3M2CPOOB just below $T_{S_C^*S_A}$ under a D.C. field of 1·2 kV cm^{-1}; the closed circles are the real part, ε', and the open circles are the imaginary part, ε'', of the dielectric constant.

It should also be noted that another relaxation (around several kHz) in addition to that of the soft mode (at several hundred kHz) is recognized in the S_C^* phase as shown in figure 7, as well as that of the Goldstone mode. For reference, the relaxation frequency of the Goldstone mode obtained from the frequency dispersion plots under no D.C. bias field is also plotted in figure 5. The dielectric strength, $\varepsilon_s - \varepsilon_\infty$, of the lower relaxation is larger than that of the higher relaxation further below $T_{S_C^*S_A}$. It is found from figure 6 that $\varepsilon_s - \varepsilon_\infty$ is inversely proportional to temperature and shows a Curie-type behaviour in the S_A phase. However, at $T_{S_C^*S_A}$ the strength rapidly decreases. This shape of $\varepsilon_s - \varepsilon_\infty$ is similar to that of the peak at $T_{S_C^*S_A}$ shown in figure 3. Therefore, this confirms that the sharp peak at $T_{S_C^*S_A}$ shown by the temperature dependence of the dielectric constant is due to the contribution of the soft mode. Recently, the calculation which describes the dielectric constant peak at $T_{S_C^*S_A}$ has been reported by Levstik *et al.*; this is based on an extended Landau free energy expansion [15]. Our result shown in figures 3 and 6 agrees with their prediction.

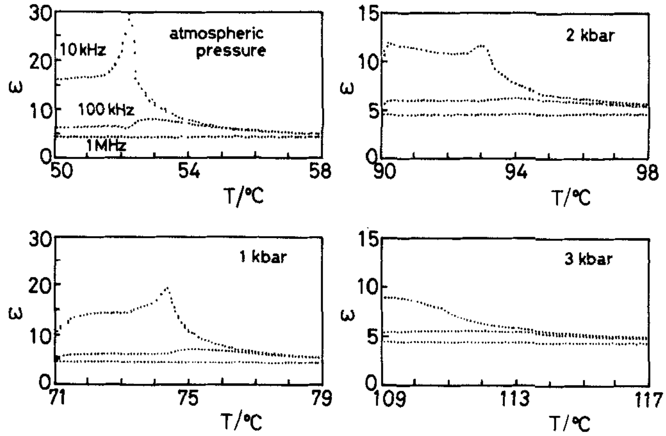

Figure 8. The temperature dependence of the dielectric constant, ε, near the transition temperature as a function of the applied hydrostatic pressure for 3M2CPOOB.

The contribution of the Goldstone mode is suppressed under a D.C. bias field, at high frequency and in a thin cell. In addition, the influence of applied hydrostatic pressure on the dielectric constant around $T_{S_C^*S_A}$ was investigated. Figure 8 shows the temperature dependence of the dielectric constant for 3M2CPOOB as a function of applied pressure. The measuring frequency was high, so that the dielectric constant peak, corresponding to the soft mode, was clearly observed at atmospheric pressure. The transition temperature $T_{S_C^*S_A}$ shifts towards higher temperature with increasing pressure with a pressure coefficient $dT_{S_C^*S_A}/dp = 20°\mathrm{C\,kbar}^{-1}$. In a previous paper it was reported that a large dielectric constant in the S_C^* phase corresponding to the Goldstone mode is suppressed, to some extent, by the application of pressure [16]. However, at a few kbar, the suppression of the contribution of the Goldstone mode seems not to be sufficient. On the other hand, the sharp peak at $T_{S_C^*S_A}$ corresponding to the soft mode becomes small with increasing pressure, and disappears completely at approximately 3 kbar. This suggests that the soft mode for the dielectric constant might be more severely influenced by applied pressure than the Goldstone mode.

4. Summary

In this study the characteristic behaviour of ferroelectric liquid crystals with a large spontaneous polarization has been reported as functions of the D.C. bias field, frequency, cell thickness and applied pressure. A sharp peak in the dielectric constant at $T_{S_C^*S_A}$ became clear under the condition that the contribution of the Goldstone mode was suppressed, such as under a D.C. bias field, at high frequency and in a thin cell. Under a D.C. bias field the relaxation corresponding to the soft mode was clearly observed both in the S_A and S_C^* phase by eliminating the component of the relaxation of the Goldstone mode. Even away from $T_{S_C^*S_A}$ in the S_C^* phase the soft mode relaxation was observed. In addition, in the S_C^* phase another relaxation (several kHz) was also recognized. The temperature dependence of the dielectric strength, $\varepsilon_s - \varepsilon_\infty$, corresponding to the soft mode, was observed separately, and it was confirmed that the sharp peak at $T_{S_C^*S_A}$ shown by the temperature dependence of the dielectric constant was due to the contribution of the soft mode. From the pressure measurement of the sharp peak at $T_{S_C^*S_A}$, it was found that the soft mode was more severely influenced by applied pressure than the Goldstone mode.

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