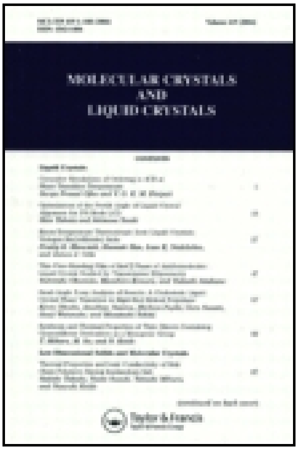

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Linear and nonlinear dielectric measurements under dc electric fields have been performed in an antiferroelectric liquid crystal MHPOCBC to obtain a deeper insight of dynamic properties related to a field-induced phase, designated as SmC_X^**, appearing when subjected to electric fields in the* SmC_α^* *phase. We observed a tricritical point in the* SmC_α^**-*SmC_X^* *phase transition. We found two low frequency modes coming from domain walls in the first-order phase transitions to* SmC_X^* *and to SmC. In the third-order nonlinear dielectric measurements another low frequency mode was observed, of which frequency decreases near the* SmC_α^**-*SmC_X^* *transition point. This may be the soft mode responsible for the field-induced transition.*

Keywords: dielectric relaxation; MHPOCBC; nonlinear dielectric response; SmC_α^*

INTRODUCTION

Recently, a precise electric field (E) – temperature (T) phase diagram of 4-(1-methyl-heptyloxycarbonyl) phenyl 4-octylcarbonyloxybiphenyl-4-carboxylate (MHPOCBC) has been obtained by optical measurements using a photoelastic modulator (PEM). A unique field-induced SmC_X^* phase and two critical points related to it were found in the low

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temperature region of the SmC^*_α phase. Numerical calculations were made based on a discrete phenomenological model. The numerical results reproduced the experimental ones and it was clarified that the phase has a three-layer structure without spatial modulation [1,2]. Now, it is time to explore the dynamic properties.

The phase sequence of MHPOCBC without electric field is SmA (105.5°C) SmC^*_α (99.5°C) SmC^*_A. Recently, on the other hand, Shtykov *et al*. have claimed that there exist two different subphases $SmC^*_{\alpha i}$ and $SmC^*_{\alpha d}$ within the SmC^*_α temperature range [3]. They found an anomaly in the birefringence at zero electric field in the *E*-*T* phase diagram. On the contrary, we have observed no anomaly [1]. The discrepancy may be ascribed to the difference in cells; homeotropic cells were used in the former experiments and homogeneous ones in the latter. In the present experiments we used homogeneous cells. We may have different results on the dynamics if we use homeotropic cells.

The dynamic properties of the SmA-SmC^*_α phase transition have been observed in detail by linear and nonlinear electrooptic and dielectric measurements [4–6]. Meanwhile, in the low temperature region of SmC^*_α phase, it was found that the frequency dispersion of the linear dielectric constant is strongly influenced by an applied dc field than in the high-temperature region near the SmA phase [7]. In the low frequency region a new relaxation mode was also found under applying dc-bias field in addition to the ferroelectric mode [8]. But there is no detailed report about the dynamic properties in this region, especially through the field-induced SmC^*_α-SmC^*_X-SmC phase transition. In this paper we have performed the linear and third-order nonlinear dielectric measurements and their dc field effects.

EXPERIMENTAL

All the measurements have been performed in commercially available EHC cells with cell gaps of 13 and 25 μm, the area of electrodes of $4 \times 4\,mm^2$, and unidirectionally rubbed polyimide coating for planar alignment.

The complex linear dielectric constants with and without dc field were calculated from the capacitance and dielectric loss measured by an impedance analyzer (Hewlett-Packard, HP4194A) in the frequency range from 100 Hz to 10 MHz. The ac electric field was kept as low as 4 mV/μm to avoid nonlinear effects on the dielectric response, and dc bias voltages up to 35 V were applied while making the measurements. In the measurements, the temperature was gradually decreased in steps and at each temperature the electric field was changed in steps.

In analysis, we fitted the frequency dispersion using the least square method to the Cole-Cole expression.

Regarding the nonlinear experiments, we used our laboratory-made measurement system which has been described in detailed in our previous paper [6]. This system utilizes the vector signal analyzer (HP89410A) which allows us to obtain the amplitudes and the phases of the linear and the third-order dielectric responses, simultaneously.

RESULTS AND DISCUSSION

Figure 1 shows the temperature and dc bias field dependences of the real part of the linear dielectric constant, ε_1', measured at 1 kHz on cooling in the 13 μm cell. We can obtain the *E-T* phase diagram by redrawing Figure 1 as a contour plot in Figure 2(a). Figure 2(b) shows the results from the 25 μm cell for comparison. The similar *E-T* phase diagram was also obtained from the simultaneous birefringence and tilt angle measurements [1]. The phase boundaries between SmA (SmC) and SmC_α^*, and SmC_α^* and SmC_A^* are clearly seen in Figure 2. Note the contour lines become dense at the boundaries. In the SmA (SmC) to SmC_α^* transition there exists a tricritical point (designated as A), where the dielectric constant begins to jump discontinuously. This tricritical point has already been found and investigated in detail

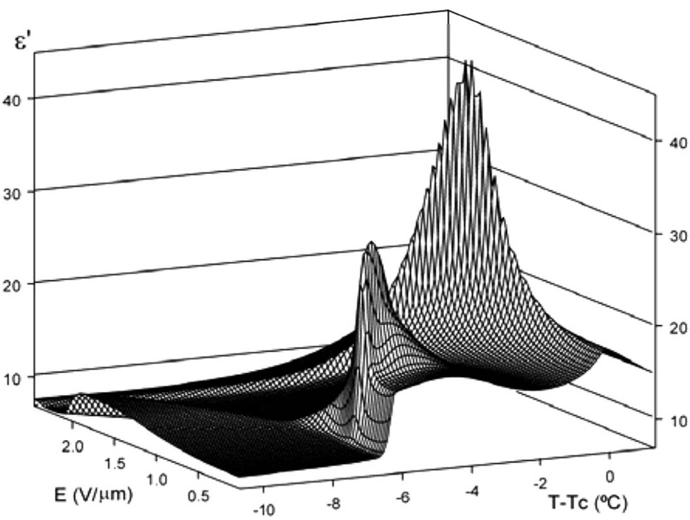

FIGURE 1 dc-bias field dependences of the 1 kHz real part of linear dielectric constant in the 13 μm thickness sample.

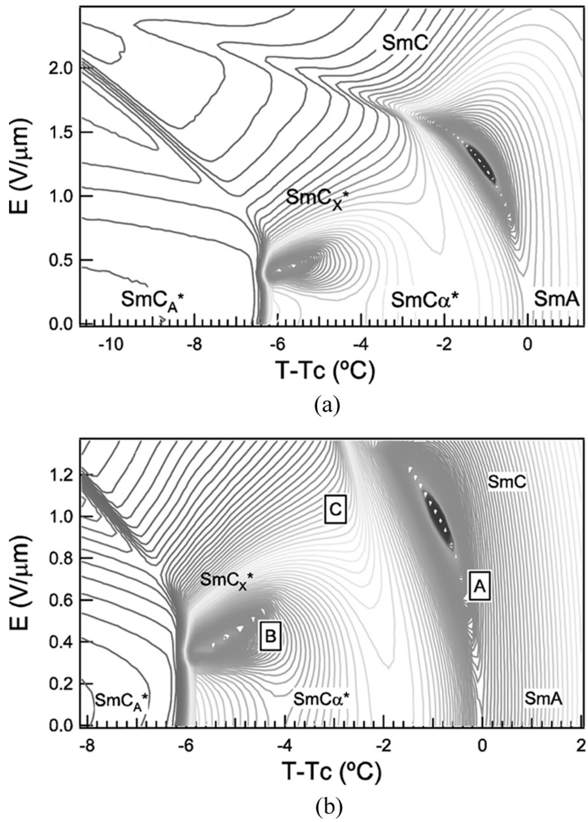

FIGURE 2 (a) The contour graph of E-T phase diagram of MHPOCBC obtained from Figure 1, and (b) the contour graph from the 25 μm thickness sample.

by Bourny *et al*. [9]. There is a transition line between SmC^*_α and SmC^*_X, where the dielectric constant steeply increases, which has been reported by Hiraoka *et al*. [8]. Orihara *et al*. mentioned that from the theoretical consideration the anomaly is due to field-induced phase transitions and the intermediate phase SmC^*_X is different from the outer phases in symmetry and showed that there is another tricritical point at the end of the line (designated as B) [1], which will be described in detail.

In order to investigate the dynamic properties in the low temperature region of SmC^*_α, we carried out the measurements of dc field dependences of linear dielectric frequency dispersion. In Figure 3, the dc-field dependences of the imaginary part of the dielectric

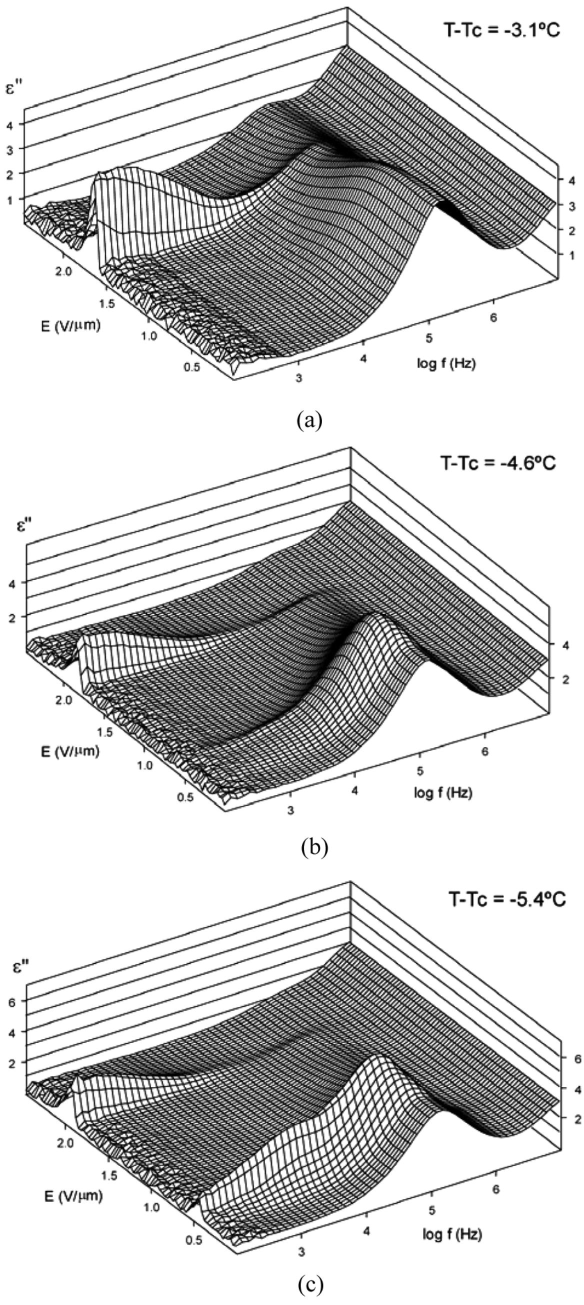

FIGURE 3 Dependence of the frequency dispersion on dc field in $\varepsilon_1''(\omega)$ at (a) $T{-}T_c = -3.1^{\circ}$C, (b) -4.6°C, and (c) -5.4°C.

constant, ε_1'', at three different temperatures are presented. At $T - T_c = -3.1°C$ (Fig. 3(a)) only one relaxation process was observed in the high frequency region. At this temperature the field-induced transition from SmC_α^* to SmC_X^* is of second order. The relaxation frequency increases and the dielectric strength decreases as the dc field is increased, as was reported by Cepic *et al*. [7]. This mode may be due to the ferroelectric mode, a homogeneously tilting mode which induces the macroscopic polarization. A low frequency mode appears at about 2 V/μm, where the first-order phase transition to SmC takes place and domain walls between the two phases may contribute to the dielectric relaxation. We also see a jump of relaxation frequency of ferroelectric mode at this transition point.

Meanwhile at $T - T_c = -4.6$ and $-5.4°C$, as the dc field is increased, the relaxation frequency of the ferroelectric mode shifts to lower frequency, and then at around the transition point SmC_X^* it turns to shift to higher frequency until the transition point to SmC phase. In Figure 3(b) the relaxation frequency of ferroelectric mode still changes almost continuously through the SmC_α^*-SmC_X^* phase transition. While in Figure 3(c) at a lower temperature the relaxation frequency of ferroelectric mode changes drastically near the transition to the SmC_X^* phase as well as the dielectric strength, indicating that the transition is of first order. In addition, a new relaxation mode appears in the low frequency region at around the transition to SmC_X^* phase. Also in Figure 3(b) this low frequency mode is slightly seen. With decreasing the temperature this mode becomes clear. Although this mode might be the soft mode inducing the SmC_X^* phase, it is more probable that it comes from the domain walls between the two phases because it appears when the transition becomes first order. These results suggest that a tricritical point should exist in the SmC_α^*-SmC_X^* transition line, where the second-order phase transition changes to the first-order one. The tricritical point is located at around $T - T_c = -4.2°C$ and $E = 0.59$ V/μm.

We have also performed the simultaneous measurements of linear and third-order nonlinear dielectric constants under dc field. The third-order nonlinear dielectric spectroscopy has a great merit that it can detect nonpolar modes. Actually, we have succeeded in observing the soft mode inducing the SmC_α^* phase from the SmA phase [5,6]. Figure 4(a) shows the temperature dependences of the real parts of linear dielectric constant $\varepsilon_1(\omega)$ and third-order nonlinear dielectric constant $\varepsilon_3(\omega)$ measured simultaneously at 1 kHz without dc field. Due to the limitation of applying dc field to the sample in our laboratory-made measurement system, we were only able to make the observation slightly above the SmC_α^*-SmC_X^* phase

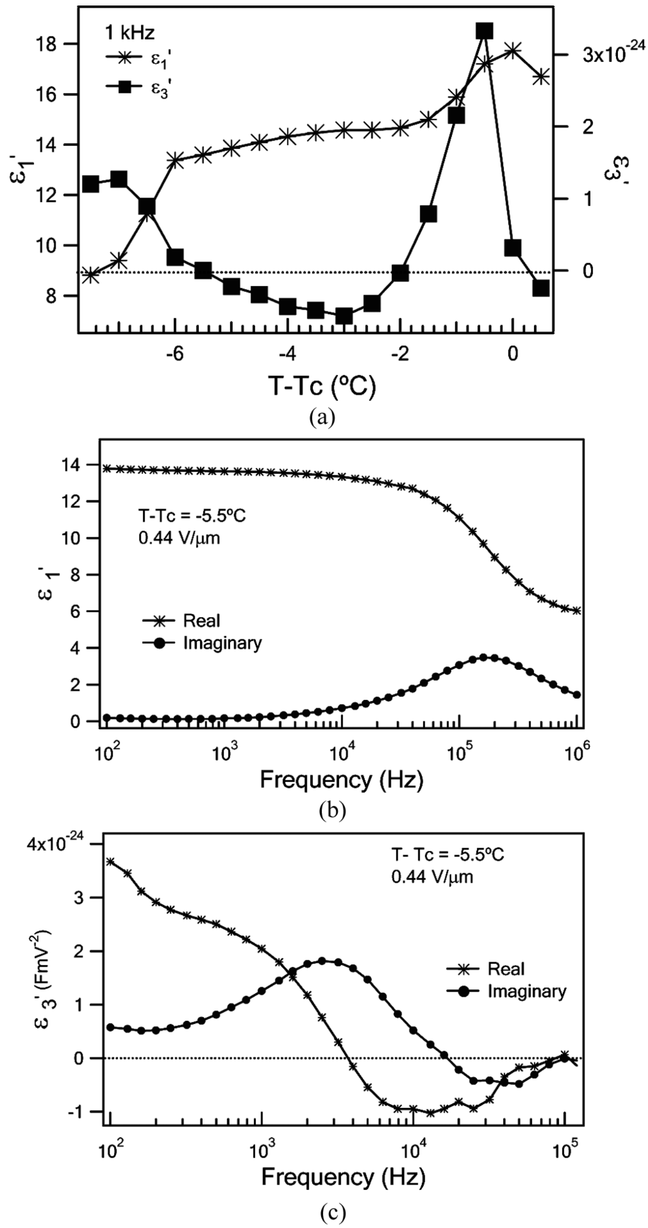

FIGURE 4 (a) Temperature dependence of linear and third-order nonlinear dielectric constants at 1 kHz without dc field, and frequency dispersion of (b) linear dielectric response and (c) the third-order nonlinear dielectric response at $T - T_c = -5.5^{\circ}C$ under dc field of $0.44\,V/\mu m$.

transition point. Figures 4(b) and 4(c) show the typical frequency dispersions of the linear dielectric constants, ε_1, and the third-order dielectric constants, ε_3, respectively, at $T - T_c = -5.5°C$ under a dc field of $0.44\,V/\mu m$. It can be seen that one relaxation process is involved in the linear dielectric frequency dispersion in Figure 4(b), which is the above-mentioned ferroelectric mode. On the other hand, as shown in Figure 4(c), the frequency dispersion of third-order response is completely different from that of the first-order one. We observe a new low frequency relaxation mode. This mode can be observed also at weaker electric fields, though the relaxation strength is small. By utilizing the equation expressing the contribution of ferroelectric mode to the third-order response derived in the previous report [6],

$$\varepsilon_3(\omega) = \frac{A_f}{(1 + i3\omega\tau_f)(1 + i\omega\tau_f)^3}, \tag{1}$$

we confirmed that the observed low frequency relaxation mode does not come from the ferroelectric mode observed in the linear dielectric measurements.

Figures 5 shows the frequency dispersions of $\varepsilon_3''(\omega)$ at different dc electric fields in the raising process of the field at $T - T_c = -4.5°C$,

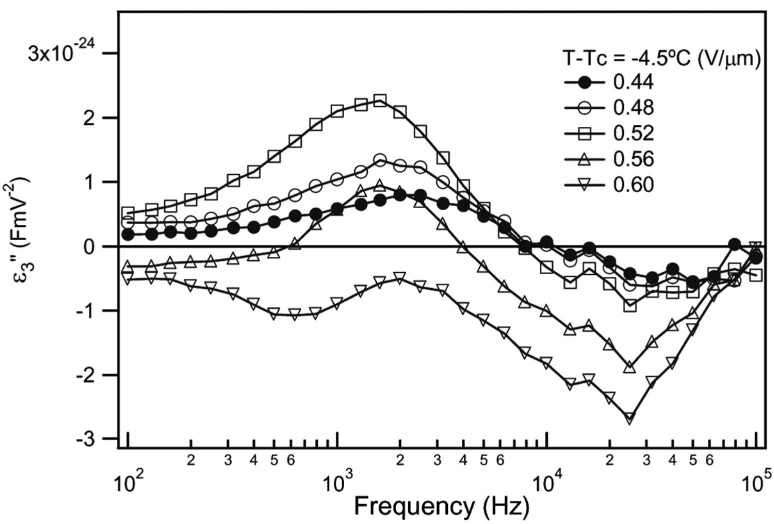

FIGURE 5 Dependence of the imaginary part of frequency dispersion on dc field in $\varepsilon_3''(\omega)$ at $T - T_c = -4.5°C$.

which is above the tricritical point in temperature. It is clearly seen that first the peak frequency of the low relaxation mode becomes lower and the relaxation strength becomes higher with increasing the dc field up to 0.52 V/μm (the SmC_{α}^{*}-SmC_{X}^{*} phase transition point). Further increasing the dc field, the peak frequency becomes higher and the relaxation strength becomes smaller. This result indicates that this low frequency mode is responsible for the SmC_{α}^{*}-SmC_{X}^{*} phase transition, i.e., it should be the soft mode. However, we have no expression for the third-order dielectric constant to obtain the relaxation frequency.

CONCLUSIONS

We have performed the linear and third-order nonlinear dielectric measurements under dc field in the low temperature region of SmC_{α}^{*} phase. From the linear dielectric measurements under dc field, we observed a tricritical point in the SmC_{α}^{*}-SmC_{X}^{*} phase transition line. The ferroelectric mode behaved in different ways below and above the tricritical point. We found two low frequency modes coming from domain walls in the first-order phase transitions to SmC_{X}^{*} and to SmC. From the third-order nonlinear dielectric measurements another low frequency mode was observed, of which frequency decreases near the SmC_{α}^{*}-SmC_{X}^{*} transition point. This may be the soft mode responsible for the field-induced transition. Theoretical consideration based on the Landau-type free energy and the detail measurements of the third-order nonlinear dielectric constants under dc field in the vicinity of the SmC_{α}^{*}-SmC_{X}^{*} phase transition point are needed to clarify the behavior of the low frequency mode.

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