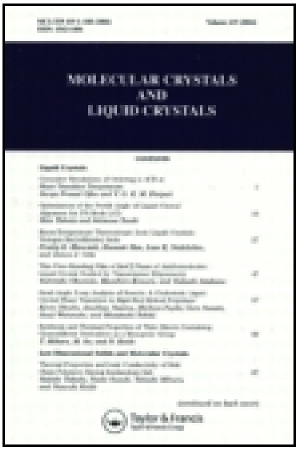

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Dielectric Studies on Antiferroelectric Liquid Crystals

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Dielectric Studies on Antiferroelectric Liquid Crystals

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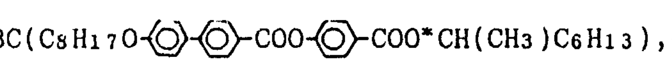
The dielectric behavior in the first and the second order phase transitions between paraelectric SmA and antiferroelectric SmC_A^* has been explored using three substances having trifluoromethyl group. The soft mode contribution to the dielectric constants was easily obtained in both phases having no spontaneous polarization. The temperature dependences of the inverse dielectric strength $1/\Delta\varepsilon$, determined by the Cole-Cole plot clearly reveal the variety of the transition order such as the first-order and the second-order phase transition. The temperature dependences of the relaxation frequency also show the characteristics of these transition order.

Keywords: ferroelectric liquid crystals, ferroelectricity, antiferroelectricity, dielectric constants, ferrielectricity

1. INTRODUCTION

Since an antiferroelectric smectic phase was discovered in

MHPOBC  ,[1]

considerable attention has been paid to antiferroelectric liquid crystals because of the characteristic tristable switching[2] applicable for display devices.[3–5] The antiferroelectric liquid crystals so far synthesized,[6–9] are classified into three types of phase sequences;

1. SmC$_A^*$—SmCγ*—SmC*—SmCα*(SmA$_b^*$)—SmA—Iso,
2. SmC$_A^*$—SmC*—SmA—Iso,
3. SmC$_A^*$—SmA—Iso.

Here, SmC$_A^*$ and SmCγ* are the antiferroelectric[1,10] and the ferrielectric phase,[11,12] respectively. The SmCα* is supposedly biaxial SmA* (SmA$_b^*$) phase.[13,14] The phase sequence (**1**) has been so far observed only in MHPOBC with extremely high optical purity.[1,10,15,16] The SmCγ* and the SmCα* phases in MHPOBC disappear by slightly decreasing the optical purity,[10,15,16] resulting in the phase sequence (**2**). The fluorinated compounds such as TFMHPOBC (see below)[7] show also the phase sequence (**2**) in their low optical purity compounds.[4,17,18]

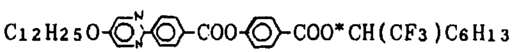
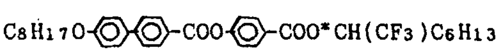
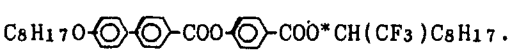
In this paper, we will report the transition behavior of the sequence (**3**) by means of dielectric measurements. This phase sequence is very attractive from the viewpoint of dielectric measurements, since there is no spontaneous polarization; the soft mode behavior is expected to be easily observed around the SmC$_A^*$—SmA phase transition temperature without applying any biased field. We will show the characteristic behaviors of the first and the second order phase transitions on the basis of the temperature dependences of the dielectric strength and the relaxation frequency.

2. EXPERIMENTAL

The samples used were listed in Table I. These substances undergo a phase transition directly from SmA to SmC$_A^*$. The materials were sandwiched between glass plates separated by 12–16 μm thick spacers. The homogeneous alignment was obtained by coating the glasses with polyimide (Toray Industry, SP550) and rubbing unidirectionally.

TABLE I

List of samples used

	SmCA*	SmA	Iso
(S)-TFMHPDOPB[9]			
	97 °C	104 °C	
(S)-TFMHPOBC[7,17,18]			
	108 °C	121 °C	
(S)-TFMNPOBC[5,7]			
	103 °C	114 °C	

The dielectric measurements were carried out using an impedance analyzer (YHP, LF4192A) as described in our previous paper.[13] The measuring field was 0.1Vpp and no biased field was applied. The temperature was controlled by a temperature control unit (Chino, Model-DB) within $\pm 0.03°C$.

3. RESULTS AND DISCUSSION

The study of the dielectric relaxation is a powerful method for investigating the phase transition. In order to investigate the soft mode behavior in the SmA—SmC* phase transition, a biased field has to be imposed to suppress the Goldstone mode.[19–22] In the case of the SmC_A^*—SmA phase transition, however, we can deduce the soft mode contribution easily in the dielectric permittivities measured without a biased field, since there are no spontaneous polarization in both phases.

The temperature dependences of the real part of the dielectric constant are shown in Figure 1 for (a) TFMHPDOPB, (b) TFMHPOBC and (c) TFMNPOBC. The discontinuous change of ε at the transition point clearly reveals the first order phase transition in TFMHPDOPB.[9] The transition is of the second order in TFMNPOBC.[17] It is impossible to judge the transition order in TFMHPOBC only by Figure 1.

The Cole-Cole diagrams were used to determine the dielectric relaxation strength, $\Delta\varepsilon = \varepsilon_0 - \varepsilon\infty$. Figure 2 shows those at some different temperatures in SmA and SmC_A^* phases. From these diagrams we see that the only one relaxation, i.e., the soft mode, is involved in the dielectric constant of all the compounds at least except for higher frequency region than 1 MHz. $\Delta\varepsilon$ was determined as the length of the abscissa cut by the circle.

Figure 3 shows the temperature dependences of the inverse dielectric strength, $1/\Delta\varepsilon$, of (a) TFMHPDOPB, (b) TFMHPOBC and (c) TFMNPOBC. As mentioned in Figure 1, the transitions are of the first order in TFMHPDOPB and of the second order in TFMNPOBC. In all the paraelectric SmA phases, it is found that $1/\Delta\varepsilon$ varies linearly with the temperature, so that the Curie-Weiss law,

$$\Delta\varepsilon = \frac{C_P}{T - T_P}, \tag{1}$$

is hold. In the antiferroelectric SmC_A^*, $\Delta\varepsilon$ also follows the Curie-Weiss law,

$$\Delta\varepsilon = \frac{C_A}{T_A - T}, \tag{2}$$

at least in the vicinity of the transition point.

The obtained constants, C_P, C_A, $T_P - T_c$ and $T_c - T_A$, are summarized in Table II, where T_c is the transition point between SmA—SmC_A^*. The Curie-Weiss constants in the paraelectric phase, C_P, are of the order of 10K, which is comparable with those for the SmA—SmC* phase transition; 11.4 K for

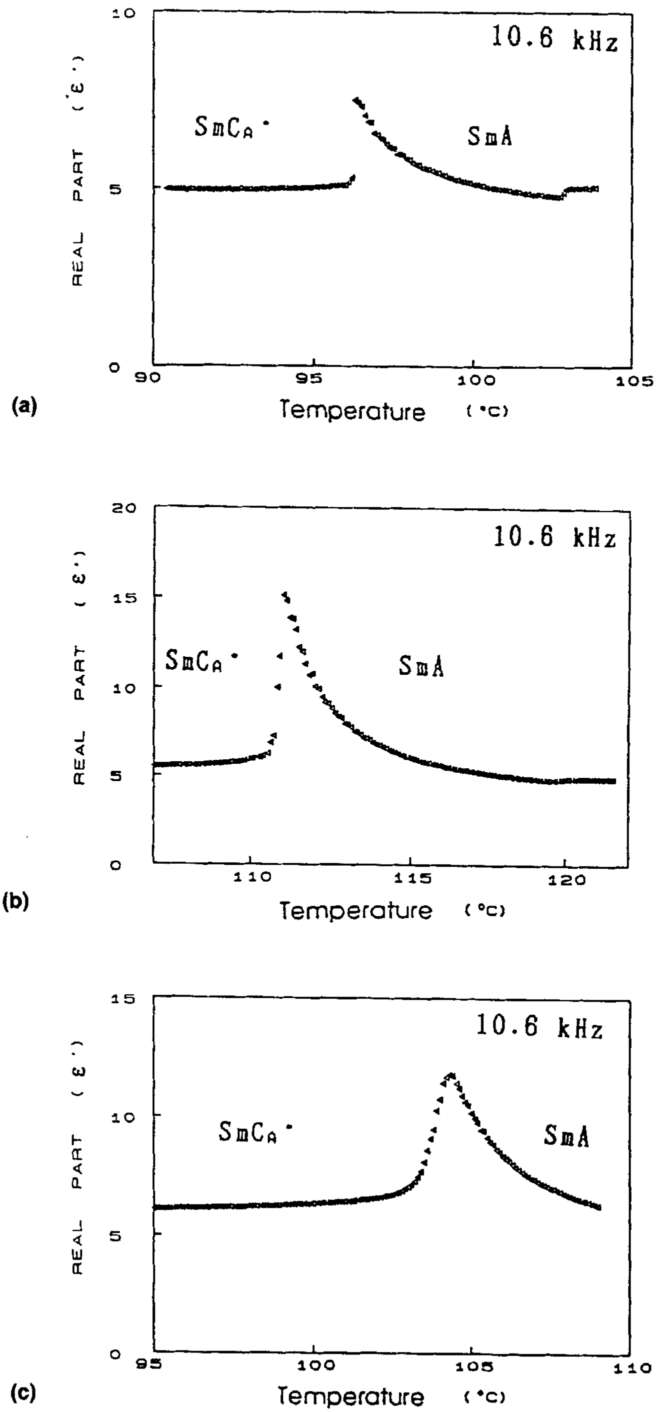


FIGURE 1 Temperature dependences of the dielectric constant ε' of (a) (S)-TFMHPDOPB, (b) (S)-TFMHPOBC and (c) (S)-TFMNPOBC, measured at 10.6 kHz.

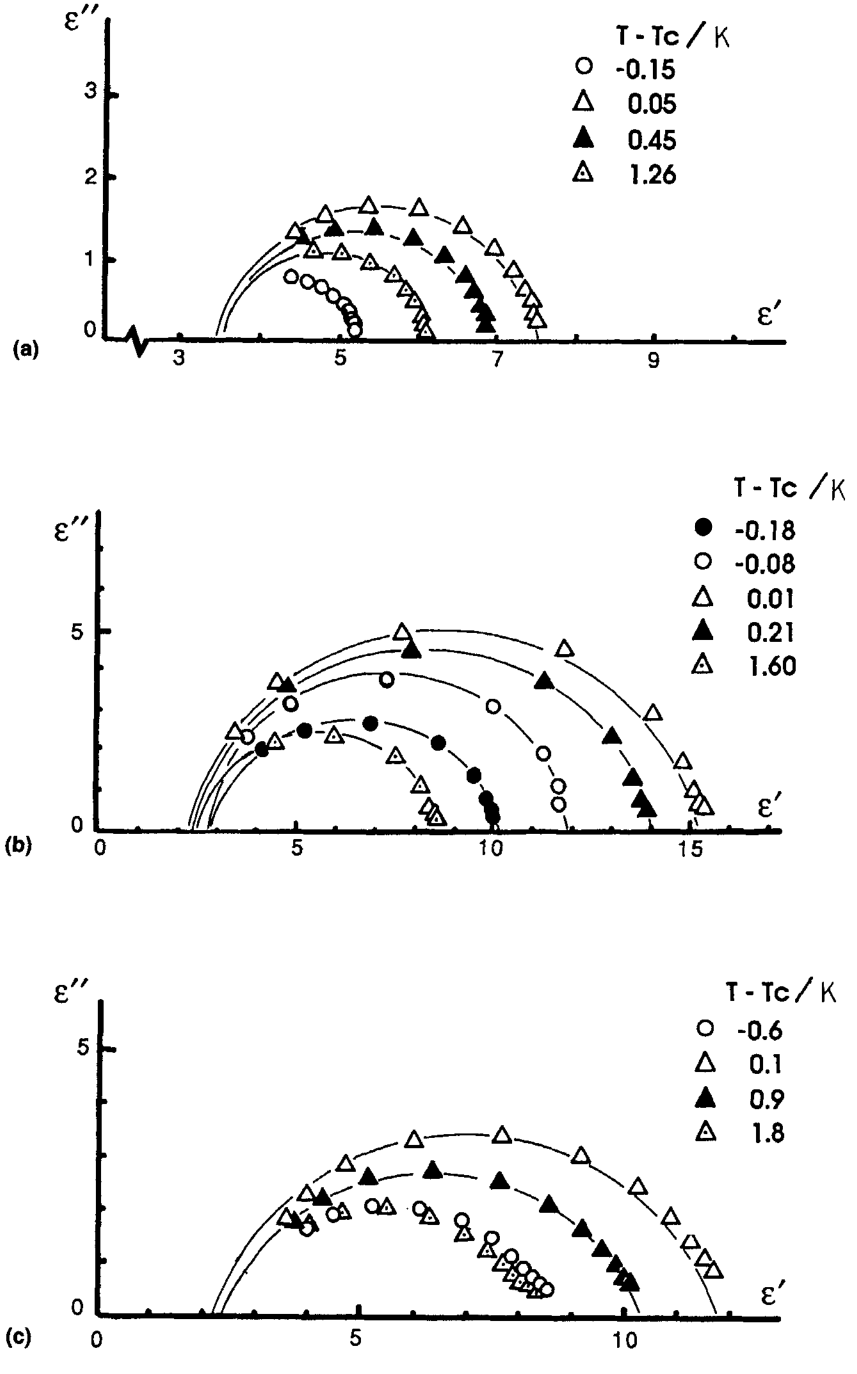


FIGURE 2 Cole-Cole diagrams of the soft mode in the SmA and SmC_A^* phases; (a) (S)-TFMHPDOPB, (b) (S)-TFMHPOBC and (c) (S)-TFMNPOBC. Tc is the SmC_A^*—SmA phase transition temperature.

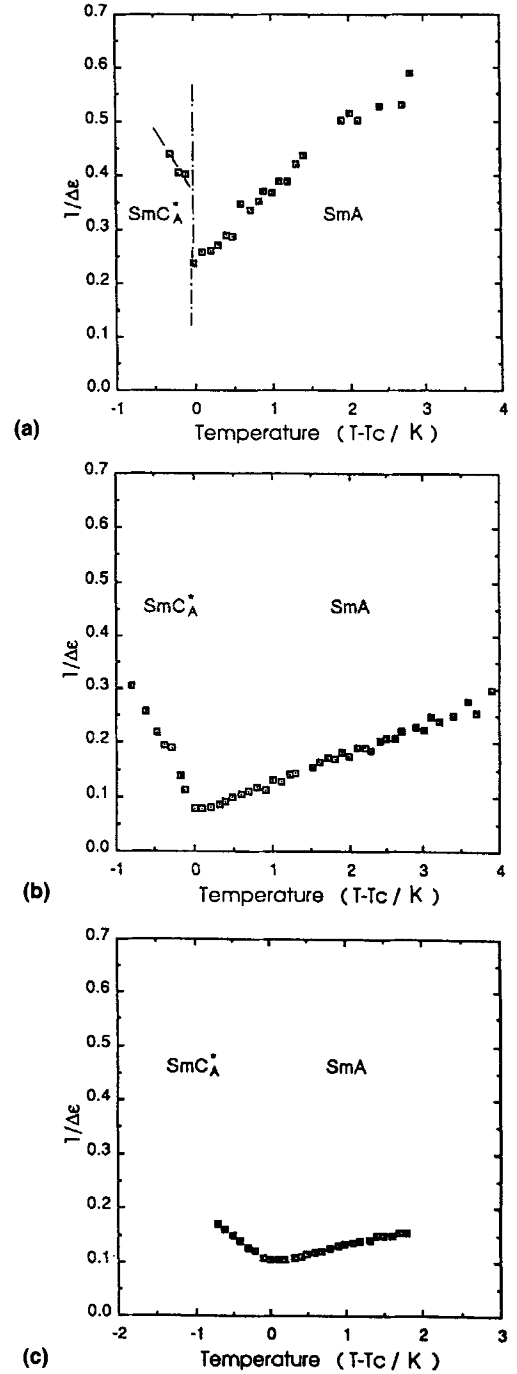
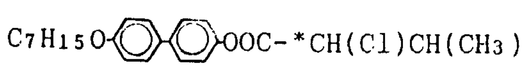


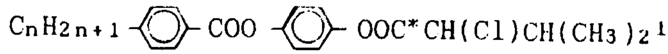
FIGURE 3 The temperature dependences of the inverse dielectric strength, $1/\Delta\varepsilon$, of (a) (S)-TFMHPDOPB, (b) (S)-TFMHPOBC and (c) (S)-TFMNPOBC. Tc is the SmC_A^*—SmA phase transition temperature.

TABLE II

List of constants obtained by the temperature dependence of $1/\Delta\varepsilon$ and the transition order

	C_P (K)	C_A (K)	$T_P - T_C$ (K)	$T_C - T_A$ (K)	order
TFMHPDOPB	7.7	1.2	1.8	1.7	1st
TFMHPOBC	19.2	2.7	1.4	0.2	Weakly 1st
TFMNPOBC	28.6	1.1	2.9	0.9	2nd

 [22]

and 17.4 K for  [19].
Thus, the Curie-Weiss constants in chiral smectics are very small compared with those of solid ferroelectrics; they are, for instance, of the order of 10^3 for the order-disorder type such as KDP[23] and $NaNO_2$[24] and of the order of 10^5 for the displacive type such as $BaTiO_3$.[25]

The large $T_c - T_A$ in TFMHPDOPB is explainable by the discontinuous jump in ε. There are no meaningful differences in C_A and $T_P - T_c$ due to the transition order, 1st and 2nd. The fairly large C_P even in the antiferroelectric transition compared with those in the ferroelectric transition may originate from large spontaneous polarization.[7] Concerning $T_P - T_c$, those for the antiferroelectric phase transition is rather large compared with those for the ferroelectric second order one, which are almost zero.[19,22]

Figure 4 shows the temperature dependences of the relaxation frequency of (a) TFMHPDOPB, (b) TFMHPOBC and (c) TFMNPOBC. It is found that the relaxation frequency in SmA also varies linearly with $(T - T_{P'})$ at least in the vicinity of the transition point. At least, TFMNPOBC clearly reveals the characteristic of the second order transition. For TFMHPOBC, the slope in the antiferroelectric phase is steep, so that it is difficult to judge the transition order by this data. However, it seems to be of the weakly first order judging from the existence of the phase boundary under an optical microscope.

4. CONCLUSIONS

The dielectric measurements were performed for three compounds in order to investigate the phase transition between the paraelectric SmA and the antiferroelectric SmC_A^* phases. One of the compounds, TFMHPDOPB, shows the first order phase transition, while the other one, TFMNPOBC, has the second order phase transition. Another compound, TFMHPOBC, seems to show the weakly first order. The Curie-Weiss law was confirmed in all compounds, and the related parameters such as the Curie-Weiss constants were discussed in relation to the other ferroelectric smectics and solid ferroelectrics. The effect of the cell thickness and the biased field may add further information to the transition behavior.

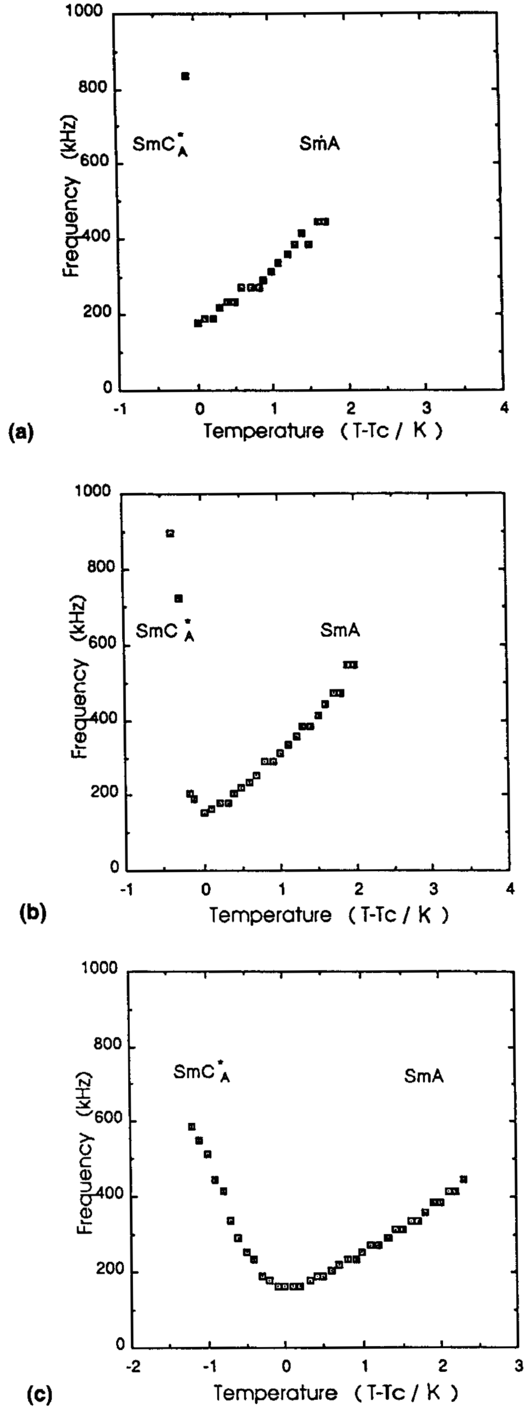


FIGURE 4 The temperature dependences of the relaxation frequency of (a) (S)-TFMHPDOPB, (b) (S)-TFMHPOBC and (c) (S)-TFMNPOBC.

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