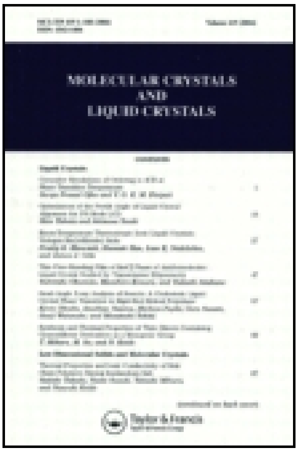

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Electrical and Optical Responses of an Antiferroelectric Liquid Crystal in SmA, SmCα* and SmC* Phases

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ELECTRICAL AND OPTICAL RESPONSES OF AN ANTIFERROELECTRIC LIQUID CRYSTAL IN SmA, SmCα* AND SmC* PHASES

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Abstract The SmA, SmCα* and SmC* phases of an antiferroelectric liquid crystal 4-(1-methylheptyloxycarbonyl) phenyl 4'-octyloxybiphenyl-4-carboxylate (MHPOBC) have been studied by means of simultaneous measurements of the dielectric constant and the electroclinic coefficient under a dc bias electric field. From the three dimensional representation of the electroclinic coefficient as a function of dc electric field and temperature, it is confirmed that there is no helix with a long pitch in the SmCα* phase and the electric field-temperature phase diagram for these phases is obtained. In the SmA phase near the phase transition temperature, the temperature dependences of the dielectric constant and the electroclinic coefficient are analyzed in terms of the phenomenological theory of Landau type and the parameters appearing in the theory are determined.

INTRODUCTION

There exist a variety of interesting phases in the antiferroelectric liquid crystal 4-(1-methylheptyloxycarbonyl) phenyl 4'-octyloxybiphenyl-4-carboxylate (MHPOBC) in an optically pure case.[1-6] Especially the intermediate SmCα* phase between the paraelectric SmA phase and the ferroelectric SmC* phase has been extensively studied because of its peculiar phenomenon called the Devil's staircase in which the stepwise change in the tilt angle is observed by changing successively the electric field or the temperature.[4,7] It is confirmed that the SmCα* phase is a tilted smectic one by the X-ray diffraction measurement[8], and the competition between the interactions in favor of either the SmC* phase or the antiferroelectric SmCA* phase is proposed to explain the Devil's staircase in the SmCα* phase.[8,9] However, the molecular orientation in this phase remains obscure and the orders of the SmA-SmCα* and the SmCα*-SmC* phase transitions have been still unknown.

In the present work, to clarify these points, we have applied to a liquid crystal sample a superposition of a sinusoidal electric field and a dc bias electric field and investigated the dependences of the dielectric constant ε and the electroclinic coefficient κ on the dc bias electric field which causes the structural change of the sample. The dielectric and optical responses to the sinusoidal electric field give us a detailed information on the softness or compliance of the material which reflects its structural change or phase transition.

In the smectic phases of the ferroelectric or antiferroelectric liquid crystals, the change of the tilt angle is induced by an applied electric field parallel to the smectic layers. This phenomenon called the electroclinic effect is due to the coupling between the polarization and the tilt angle.[10-13] In the case of MHPOBC, with decreasing temperature, the transition from the SmA phase to either the SmC* phase or the SmCα* phase occurs, depending on the magnitude of dc bias electric field. Near the transition temperature, the relation between the tilt angle and the applied electric field changes from a linear to a nonlinear one. The phenomenological theory of Landau type has been used to describe the transitional phenomena in the ferroelectric liquid crystals[14-16], but not applied to the SmA phase of the antiferroelectric liquid crystals. In the present study, we apply this theory to MHPOBC to confirm that the pre-transitional phenomenon in the SmA phase of MHPOBC can be described by the theory in which the antiferroelectric order parameters[17,18] are taken to be zero.

EXPERIMENTAL

We describe briefly the method used in this study for measuring the dielectric constant ε and the electroclinic coefficient κ. The applied electric field E is given as

$$E = E_{dc} + E_{\omega}\cos\omega t, \tag{1}$$

where E_{dc} is the dc bias electric field, E_{ω} the amplitude of the sinusoidal electric field with the angular frequency ω much lower than the relaxational angular frequency of the sample, and we assume $|E_{\omega}| \ll |E_{dc}|$. Then the electric displacement $D(E)$ induced by E is written as

$$D(E) = D(E_{dc}) + D_{\omega}(E_{dc})\cos\omega t, \tag{2}$$

where $D_{\omega}(E_{dc})$ is the amplitude of ω component of D given as

$$D_{\omega}(E_{dc}) \equiv \left.\frac{\partial D}{\partial E}\right|_{E=E_{dc}} E_{\omega} \equiv \varepsilon_0 \varepsilon(E_{dc}) E_{\omega}. \tag{3}$$

Here, ε_0 is the vacuum permittivity and $\varepsilon(E_{dc})$ is the dielectric constant under the dc bias electric field E_{dc}. By use of eq.(3), we obtain $\varepsilon(E_{dc})$ from the observed value of $D_{\omega}(E_{dc})$ as

$$\varepsilon(E_{dc}) = \frac{D_{\omega}(E_{dc})}{\varepsilon_0 E_{\omega}}. \tag{4}$$

The electroclinic coefficient κ is obtained from the ω component of the transmitted light intensity I. If the sample cell of the thickness d is placed between crossed polarizers, I is given as

$$I = I' \sin^2\left(\frac{\pi d \Delta n}{\lambda}\right) \sin^2(2\alpha), \tag{5}$$

where I' is the incident light intensity, α the angle between the director in the liquid crystal sample and one of the polarizer directions, Δn the anisotropy of the refractive index of the sample, λ the wavelength of the light in vacuum.[11] If we apply to the sample cell the electric field E given by eq.(1), the angle α is changed as

$$\alpha = \alpha_{dc} + \theta_{\omega}(E_{dc})\cos\omega t. \tag{6}$$

Here, α_{dc} is the dc component of α given as

$$\alpha_{dc} = \alpha_0 + \theta(E_{dc}), \tag{7}$$

where α_0 is the value of α with no electric field, and $\theta(E_{dc})$ the dc component of the tilt angle θ induced by the dc electric field E_{dc}. In eq.(6) $\theta_{\omega}(E_{dc})$ is the amplitude of ω component of the tilt angle θ induced by the sinusoidal electric field $E_{\omega}\cos\omega t$ and is given as

$$\theta_{\omega}(E_{dc}) \equiv \left.\frac{\partial \theta}{\partial E}\right|_{E=E_{dc}} E_{\omega} \equiv \kappa(E_{dc}) E_{\omega}. \tag{8}$$

Here, $\kappa(E_{dc})$ is the electroclinic coefficient under the dc bias electric field E_{dc} and is obtained from the observed value of $\theta_\omega(E_{dc})$ as

$$\kappa(E_{dc}) = \frac{\theta_\omega(E_{dc})}{E_\omega}. \tag{9}$$

By substituting eq.(6) into eq.(5), we have

$$I = I_{dc}(E_{dc}) + I_\omega(E_{dc})\cos\omega t, \tag{10}$$

where we have assumed $|\theta_\omega(E_{dc})| \ll |\alpha_{dc}|$. In eq.(10), I_{dc} is the dc component of I given by

$$I_{dc}(E_{dc}) = I'\sin^2\left(\frac{\pi d \Delta n}{\lambda}\right)\sin^2(2\alpha_{dc}), \tag{11}$$

and $I_\omega(E_{dc})$ is the amplitude of ω component of I given by

$$I_\omega(E_{dc}) = 2I'\sin^2\left(\frac{\pi d \Delta n}{\lambda}\right)\sin(4\alpha_{dc})\theta_\omega(E_{dc}). \tag{12}$$

If we introduce the transmitted light intensity I_0 with no electric field given by

$$I_0 = I'\sin^2\left(\frac{\pi d \Delta n}{\lambda}\right)\sin^2(2\alpha_0), \tag{13}$$

then eqs.(11) and (12) can be rewritten as

$$\frac{I_{dc}(E_{dc})}{I_0} = \frac{\sin^2(2\alpha_{dc})}{\sin^2(2\alpha_0)}, \tag{14}$$

and

$$\frac{I_\omega(E_{dc})}{I_0} = \frac{2\sin(4\alpha_{dc})}{\sin^2(2\alpha_0)}\theta_\omega(E_{dc}). \tag{15}$$

By eliminating α_{dc} from eqs.(14) and (15), we have

$$I_\omega(E_{dc}) = 4\theta_\omega(E_{dc})\sqrt{I_{dc}(E_{dc})\left(\frac{I_0}{\sin^2(2\alpha_0)} - I_{dc}(E_{dc})\right)}, \tag{16}$$

from which we obtain the electroclinic coefficient $\kappa(E_{dc})$ given by eq.(9) as

$$\kappa(E_{dc}) = \frac{I_\omega(E_{dc})}{4E_\omega\sqrt{I_{dc}(E_{dc})\left(\frac{I_0}{\sin^2(2\alpha_0)} - I_{dc}(E_{dc})\right)}}. \tag{17}$$

This indicates that $\kappa(E_{dc})$ can be calculated from the observed values of $I_\omega(E_{dc})$, $I_{dc}(E_{dc})$ and I_0.

In this study, both the dielectric constant ε and the electroclinic coefficient κ were measured as functions of the dc bias electric field E_{dc} and the temperature. The MHPOBC sample was sandwiched between two glass plates separated by 10 mm-thick spacers. The area of the ITO electrode on each of the glass plates was 25mm^2. Homogeneous alignment was obtained by coating the plates with polyimid and rubbing one of them unidirectionally. The cell was set up in a holder whose temperature was controlled within ±0.03°C by a temperature controller (CHINO DJ-11). The applied electric field E was generated by a synthesizer (Hewlett-Packard 3325A). The amplitude and frequency of a sinusoidal electric field were 3.8x10^{-2} V/μm and 120Hz much lower than the relaxational frequency of the sample. The dc bias electric field was changed up to 1.4 V/μm.

The dielectric constant ε was obtained by measuring the amplitude of the 120Hz component of the electric displacement, which was detected by a combination of charge amplifier and spectrum analyzer (Advantest TR9404).

The electroclinic coefficient κ was obtained by using eq.(17) from the measurement values of the dc components $I_{dc}(E_{dc})$ and I_0 of the transmitted light intensity I with and without the applied electric field E as well as the amplitude $I_\omega(E_{dc})$ of 120Hz component of I induced by E. The light intensity I detected by a high-speed PIN photodiode was converted into a voltage signal by an I-V converter and decomposed into the dc and 120Hz components by the same spectrum analyzer as used for the dielectric measurement. The angle α_0 between the director of the sample and one of the polarizer directions was chosen as 22.5°.

RESULTS

Electric field and temperature dependences of ε and κ

The 3D (3-dimensional) representations of ε and κ as functions of dc bias electric field and temperature are shown in Figs.1 and 2. Though these two figures give a similar information on the phase changes of MHPOBC, κ in Fig.2 is much more distinct than ε in Fig.1 and therefore we concentrate here mainly on Fig.2. We can distinguish in Fig.2 three regions which correspond to the SmA phase marked by (1), the SmCα* phase marked by (2) and the SmC* phase marked by (3), (4) and (5). In the SmA phase, κ increases gradually with decreasing temperature due to the increase of the director's fluctuation in the tilt angle direction (the soft mode). In the SmCα* phase, κ has an almost constant value higher than in the SmA phase. The SmC* phase changes its structure successively as the dc bias electric field increases. In the region of the low dc electric field (marked by (3)), κ takes a sharp peak due to the helix-unwinding process. With a further increase of dc electric field, κ shows a shoulder (marked by (4)) and then suddenly decreases to zero (marked by (5)) where the tilt angle tends to saturate. The middle state marked by (4) is peculiar to MHPOBC and has not been observed in the SmC* phases of other FLCs. In the SmCα* phase, we cannot find a sharp peak of ε or κ corresponding to a helix-unwinding process observed in the SmC* phase. This implies that there is no helix with a long pitch in the SmCα* phase.

We can obtain the electric field-temperature phase diagram among the SmA, SmCα* and SmC* phases by looking down from the top of Fig.2, where the SmCα* phase is specified as a closed region with ε and κ nearly constant. The boundary lines of the SmCα*-SmC* phases and the SmA-SmC* phases are drawn along the ridges, while the boundary line of the SmA-SmCα* phases is drawn along the edge.

The SmCα*-SmC* phase transitions induced by the dc bias electric field and by the temperature change show different features from each other. The SmCα* phase is stable under a low dc electric field, but an increase of electric field induces the transition to the SmC* phase, which accompanies a peak of κ. In the SmCα*-SmC* phase transition induced by the temperature change, there appears a sharp peak due to the helix-unwinding process in the SmC* phase. It is reported that the dielectric constant in the low temperature region of the SmCα* phase shows hysteresis in cooling and heating cycles.[19] These facts suggest that the SmCα*-SmC* phase transition is of the first order.

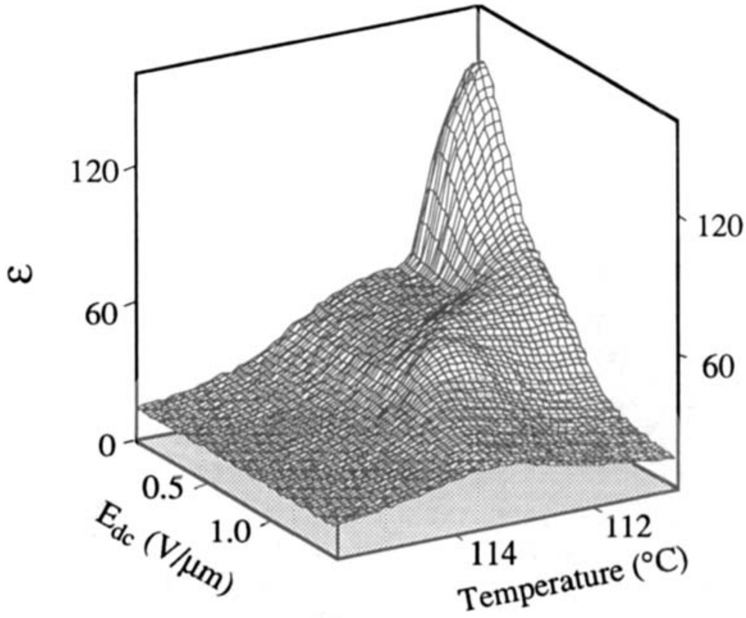

FIGURE 1 The 3-dimensional representation of ε as functions of dc bias electric field (E_{dc}) and temperature.

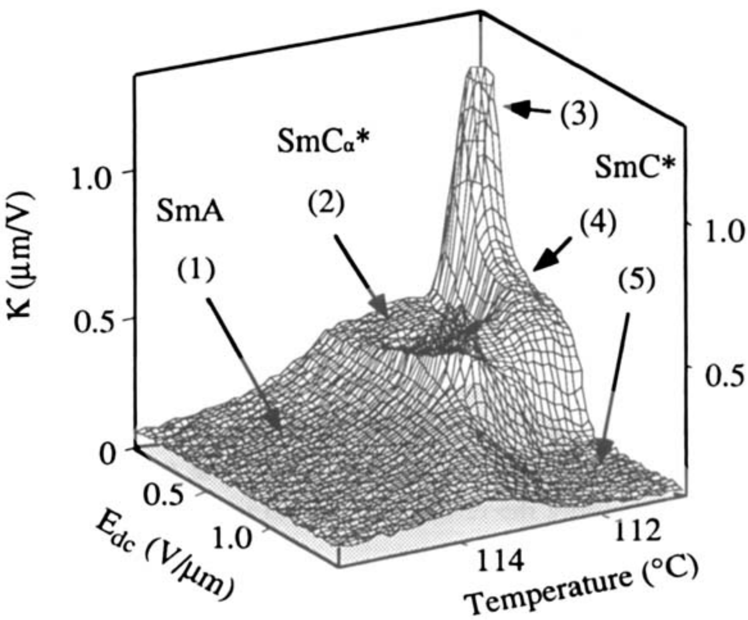

FIGURE 2 The 3-dimensional representation of κ as functions of dc bias electric field (E_{dc}) and temperature.

Under a high dc bias electric field, no SmCα* phase appears and only the SmA-SmC* phase transition takes place smoothly with decreasing temperature. The smoothness in κ or ε suggests that the SmA-SmCα* and SmA-SmC* phase transitions due to the temperature change are of the second order.

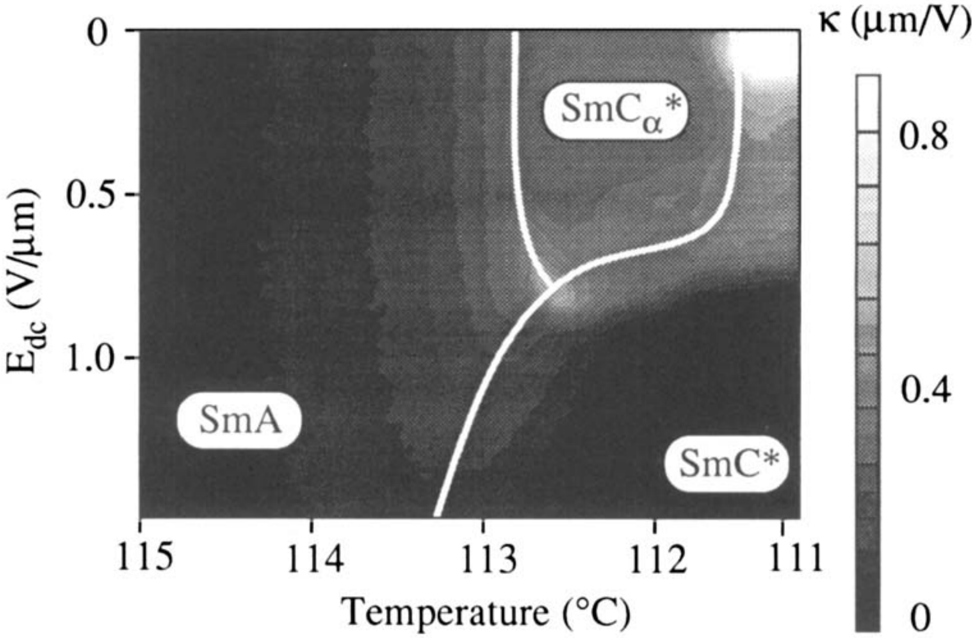

FIGURE 3 The electric field-temperature phase diagram by means of the κ measurement

Analysis of ε and κ in the SmA phase near the phase transition temperature

The critical behavior in the SmA phase near the SmA-SmCα* or SmA-SmC* transition temperature is describable by the phenomenological theory of Landau type. The antiferroelectric order parameters can be taken to be zero in the SmA phase. A simple form for the free energy density g of Landau type including the term proportional to θ^4 is given as

$$g = g_0 + \frac{1}{2}a(T - T_0)\theta^2 + \frac{1}{4}B\theta^4 + \frac{1}{2\chi}P^2 - PE - \frac{\varepsilon_0}{2}E^2 - cP\theta, \tag{18}$$

where g_0 is the density in the SmA phase without the electric field E, P the polarization parallel to E, χ the susceptibility, ε_0 the vacuum permittivity, c the coupling constant between P and θ, and T_0 the transition temperature of racemic mixture. Using the equation derived by minimizing g in eq.(18) with respect to P, we obtain a linear relation between ε in eq.(4) and κ in eq.(9) as

$$\varepsilon = \frac{\varepsilon_0 + \chi}{\varepsilon_0} + \frac{c\chi}{\varepsilon_0}\kappa. \tag{19}$$

As shown in Figs.4 and 5, we can confirm the linearity between ε and κ in both cases of changing the dc bias electric field and the temperature even in the nonlinear regime where ε and κ are dependent on the dc electric field. We can get almost the same values of c=3.5x10^7 Vm^{-1} and χ=3.7x10^{-11} Fm^{-1} in the both cases. These values are compared with c=2.9x10^8 Vm^{-1} and χ=1.4x10^{-11} Fm^{-1} for the ferroelectric liquid crystal 764E (Merck).[16] In Fig.5, the open circle shows a critical behavior near the SmA-SmCα* phase transition under the low dc electric field, while the open square shows one near the SmA-SmC* phase transition under the high dc electric field. It is to be noted that there is no difference between them.

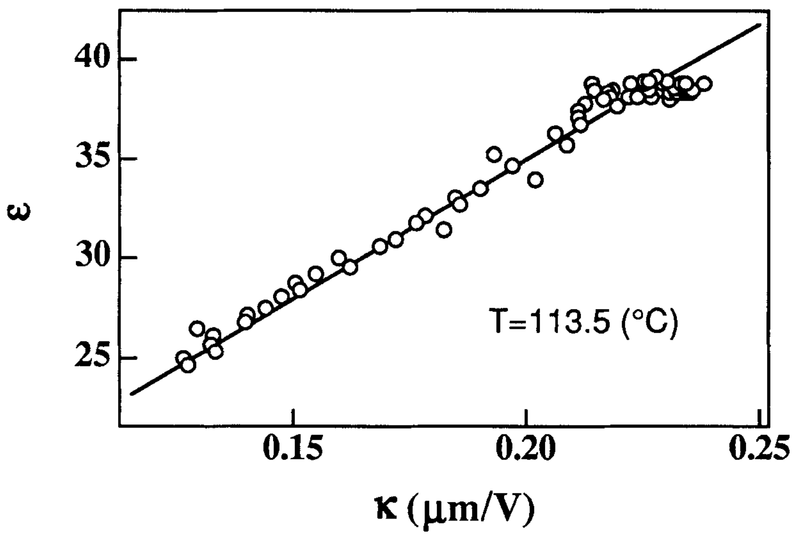

FIGURE 4 The relation between ε and κ with the temperature fixed.

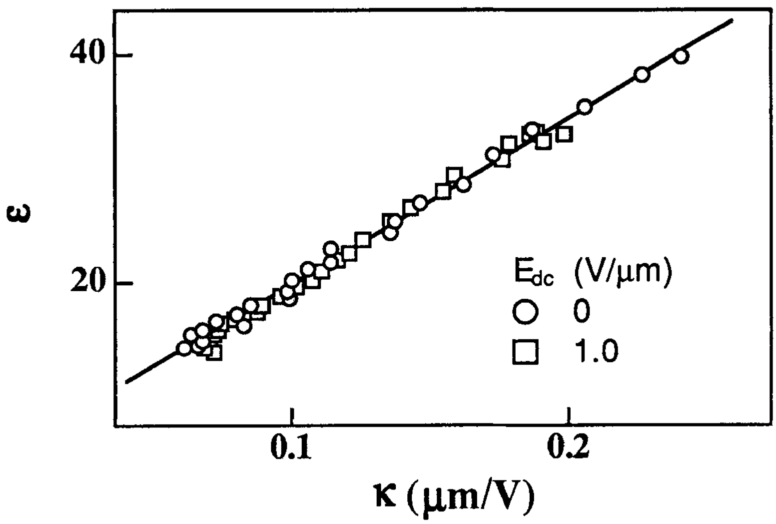

FIGURE 5 The relation between ε and κ with the dc bias electric field (E_{dc}) fixed.

From the equations for stability conditions with respect to P and θ, we obtain the equations giving the temperature dependences of ε and κ under no dc bias electric field as

$$\varepsilon = \frac{\varepsilon_0 + \chi}{\varepsilon_0} + \frac{(c\chi)^2}{\varepsilon_0 a(T - T_C)}, \tag{20}$$

and

$$\kappa = \frac{c\chi}{a(T - T_C)}, \tag{21}$$

where T_c is the transition temperature for a chiral sample given as

$$T_c = T_0 + \frac{c^2\chi}{a}. \tag{22}$$

The experimental results are fitted well by eqs.(20) and (21), as seen in Figs.6 and 7 where the solid lines are the best-fitting curves. The best-fitting value of the phenomenological parameter a is 6.0x10^3 $Jm^{-3}K^{-1}$, which is one order of magnitude less than the value of a, 6.4x10^4 $Jm^{-3}K^{-1}$, obtained for 764E (Merck).[16]

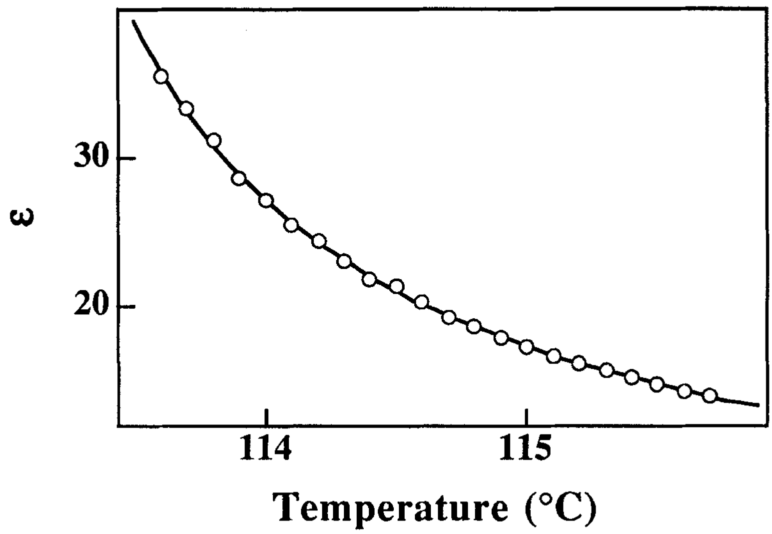

FIGURE 6 The temperature dependence of the dielectric constant ε

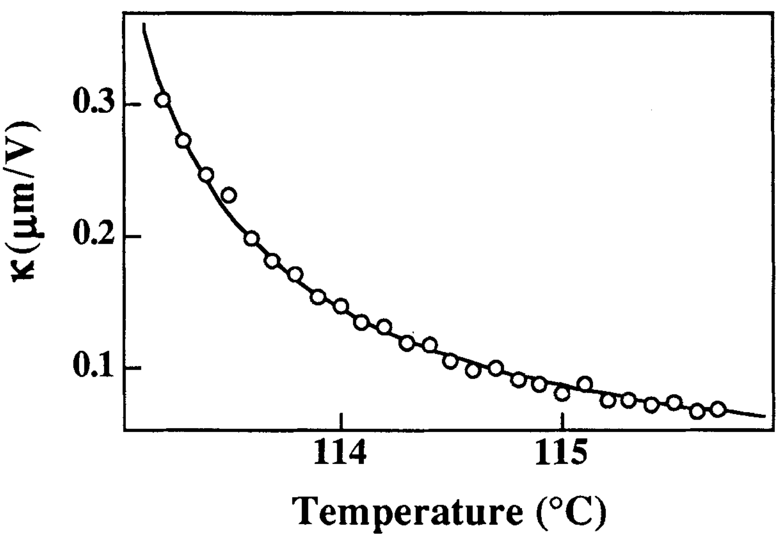

FIGURE 7 The temperature dependence of the electroclinic coefficient κ

CONCLUSION

By applying our new measuring system to MHPOBC, we have obtained a phase diagram of the SmA, SmCα* and SmC* phases. In the SmCα* phase, we cannot find a sharp peak of ε or κ corresponding to a helix-unwinding process observed in the SmC* phase, which implies that there is no helix with a long pitch in the SmCα* phase. Besides, the information on the orders of transitions between the various smectic phases is obtained.

It is also found that the phenomenological theory of Landau type explains well the critical behavior in the SmA phase, and we can evaluate the parameters appearing in the theory.

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