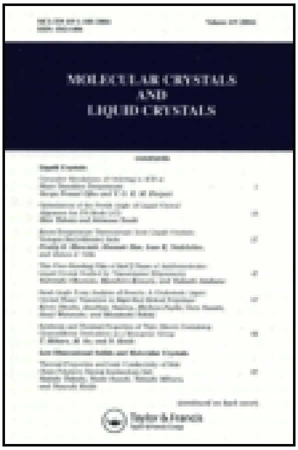

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Nonlinear Dielectric Study of Critical Behavior Near Isotropic-Nematic Phase Transition

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We studied Isotropic-Nematic (I-N) phase transition by nonlinear dielectric measurement. The third-order nonlinear permittivity ε_3 *was obtained from the third harmonic component of the electric displacement under AC electric field. The obtained* ε_3 *shows the critical behavior in I phase near I-N transition point with the critical component of one. This result agrees well with the critical behavior predicted by mean – field theory, but that of the relaxation time deviates from the theoretical prediction.*

Keywords: critical behavior; dielectric relaxation; I-N phase transition; mean-field theory; nonlinear permittivity

1. INTRODUCTION

Isotropic (I)-Nematic (N) phase transition, which is a typical phase transition in liquid crystals, is known to be weakly first order [1]. When temperature decreases in the I phase, pretransitional phenomena appear in the vicinity of the transition point (T_{IN}). Near T_{IN}, remarkable critical behavior is observed in spite of the first-order phase transition. The order parameter of this transition is the orientational order parameter S, $S \equiv (3\langle\cos^2\theta\rangle - 1)/2$, where θ is the angle between the director of the liquid crystal and the direction of each molecule, and ____ represents the spatial average.

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The I-N phase transition and the critical behavior near T_{IN} has been intensively studied by various kinds of experimental methods, for example, light scattering, NMR, electric birefringence, magnetic birefringence and flow birefringence [1]. These quantities show the pretransitional behavior near T_{IN}, and this indicates that there is strong orientational correlation between molecules near T_{IN}.

Dielectric relaxation spectroscopy is also one of the useful methods to study dynamics of liquid crystals. Owing to recent instrumental development and advances in measurement technique, it is possible to obtain the dispersion of the dielectric permittivity in a wide frequency range from μHz to near THz [2]. There is no other method covering such wide frequency range or time scale than the dielectric relaxation spectroscopy. But this method is restricted to the linear regime until recently. As the response to external field becomes easily nonlinear in soft condensed matters such as liquid crystals and polymers, nonlinear dielectric spectroscopy is useful to obtain more detailed information on the dynamics of the studied system [3–5]. Drozd-Rzoska has studied the nonlinear dielectric response of liquid crystals near I-N transition by applying: a weak AC field and a strong rectangular pulse field simultaneously [6]. In this article, we have measured the linear and nonlinear dielectric response near the I-N phase transition by a method different from the one used by Rzoska. We applied a sinusoidal electric field with an angular frequency of ω to liquid crystal. In this case, the induced electric displacement becomes the sum of the fundamental and the higher harmonic components of ω. The higher harmonic components give information on the dynamics of orientational order parameter S. Details of the experiment will be described at the experimental section.

2. THEORY OF NONLINEAR DIELECTRIC RESPONSE AT THE I-N TRANSITION

The aim of this research is to study the critical behavior of S in the isotropic phase near T_{IN} in detail by nonlinear dielectric measurements. The phenomenological mean-field theory of Landau-de Gennes [1] gives some expectations to the critical behavior of the nonlinear dielectric response near T_{IN}.

The Landau-de Gennes' free energy F for the I-N transition under an electric field E_0 is given as

$$F = F_0 + \frac{1}{2}a(T - T^*)S^2 + \frac{1}{3}BS^3 + \frac{1}{4}CS^4 + \cdots - \frac{1}{3}\varepsilon_a E_0^2 S,$$

where a, B and C are positive constants and T^* is the imaginary second-order phase transition temperature. F_0 is the non-critical part of the free energy and ϵ_a is the anisotropy of the permittivity ($\varepsilon_a = \varepsilon_{||} - \varepsilon_{\perp}$:$\varepsilon_{||}$ and $\varepsilon_{\perp}$ are the permittivities parallel and perpendicular to the directors, respectively). Although the equilibrium state in the I phase corresponds to $S = 0$, a nonzero but small value of S gives the minimum of F under electric field E_0. The induced order parameter S is proportional to E_0^2 and given as,

$$S = \frac{\varepsilon_a E_0^2}{3a(T - T^*)}.$$

A molecule which shows a liquid crystalline phase has an anisotropic shape and its physical properties are also anisotropic. Under dc electric field, the dielectric response is given by $\vec{D} = \varepsilon(E)\vec{E}_0$, and the permittivity of liquid crystal $\varepsilon(E_0)$ is given by the following dielectric tensor,

$$\varepsilon(E_0) = \varepsilon_{\text{iso}} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \frac{\varepsilon_a S}{3} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix},$$

where ϵ_{iso} is the dielectric permittivity in the isotropic phase. The equation of motion has to be considered to study the dynamics of S. For this purpose, the phenomenological equation of motion is adopted [7],

$$-\gamma \frac{\partial S}{\partial t} = \frac{\partial f}{\partial S} = a(T - T^*)S + BS^2 + CS^3 - \frac{1}{3}\varepsilon_a E_0^2.$$

If we choose the direction of the electric field as z-axis, the field-dependent permittivity is obtained as,

$$\begin{aligned} \varepsilon &= \varepsilon_{iso} + \frac{\Delta\varepsilon E_0^2}{1 + i\omega\tau} \\ &= \varepsilon_1 + \varepsilon_3 E_0^2, \end{aligned}$$

where E_0 and ω are the amplitude and the angular frequency of the applied sinusoidal electric field. We also define ε_1 and ε_3 as the linear and the third-order nonlinear permittivity. The nonlinear dielectric permittivity ϵ_3 shows the Debye-type single relaxation spectrum.

The dielectric strength $\Delta\varepsilon_3$ and the relaxation time τ_3 are respectively given as,

$$\Delta\varepsilon_3 = \frac{2\varepsilon_a^2}{9a(T - T^*)},$$

$$\tau_3 = \frac{2\gamma}{a(T - T^*)}.$$

Therefore, $\Delta\epsilon_3$ and τ_3 increase with decreasing temperature and show the critical slowing down behaviors with a critical exponent 1.

3. EXPERIMENT

The studied nematic liquid crystals are the two compounds of the 4-alkyl-4′ -cyanobiphenyl homologous series, 6 and 8CB. They were purchased from Merck Ltd. 6CB and 8CB are the typical liquid crystals with the T_{IN} at 302.0 K and 313.9 K, respectively. These compounds have a large dipole-moment but the alkyl chain lengths are different from each other. We used them without further purification.

We adopted the following method for the measurement of nonlinear dielectric permittivity. When a small sinusoidal electric field E is applied, the electric displacement D detected by a charge amplifier is measured by a vector signal analyzer HP89410. The higher-order nonlinear permittivity ε_{n} is obtained from the applied electric field E_0 dependence of the nth harmonic component of the applied frequency ω in D. We have studied the linear and the third-order nonlinear dielectric spectrum from 1 kHz–1 MHz. The fundamental and third harmonic components of electric displacement (D_1 and D_3) are respectively given as

$$D_1 = \varepsilon_1 E_0 + \frac{3}{4}\varepsilon_3 E_0^3 + \cdots,$$

$$D_3 = \frac{1}{4}\varepsilon_3 E_0^3 + \frac{5}{16}\varepsilon_5 E_0^5 + \cdots.$$

The nth harmonic component D_{n} is proportional to E_0^{n} under a small field. Therefore, we can obtain the nth order nonlinear permittivity ε_{n} defined as,

$$\varepsilon_n = \lim_{E_0 \to 0} \frac{\partial^n D}{\partial E_0^n} \cdot 2^{n-1}.$$

The sample cells used in the measurements are parallel plate ones with ITO electrodes (internal thickness of the cell was about 18 μm and electrode area was 16 mm^2). The temperature of the sample is controlled by a temperature controller LS340 with high performance (stabilization was about 10^{-3} K). The sample was cooled down from the I phase to T_{IN}.

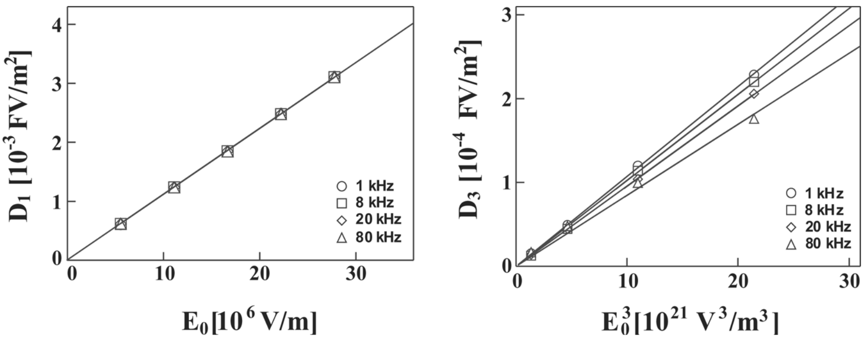
4. RESULTS AND DISCUSSION

The applied electric field E dependence of the fundamental and the third harmonic component of the electric displacement D_1 and D_3 for 6CB are shown in Figure 1(a) and (b), respectively. D_1 and D_3 are found to be proportional to E_0 and ${E_0}^3$, respectively. These suggest that D_1 and D_3 are approximately represented by $D_1 = \varepsilon_1 E_0$ and $D_3 = (1/4)\varepsilon_3 E_0^3$. We can obtain the linear ε_1 and the third-order nonlinear permittivities ε_3 from the slopes of the best-fitted lines drawn in Figure 1. Figure 1 (b) suggests that $\varepsilon_3$shows frequency dispersion in the frequency range we studied.

The nonlinear dielectric spectra $\varepsilon_3^*(\varepsilon_3^* \equiv \varepsilon_3' - i\varepsilon_3'')$ of 6CB at various temperatures are shown in Figure 2. The solid lines are the best-fitted curves of the Cole-Cole relaxation spectrum as

$$\varepsilon_3^* = \varepsilon_{3\infty} + \frac{\Delta\varepsilon_3}{1 + (i\omega\tau_3)^{\beta}},$$

where $\varepsilon_{3\infty}$ is the permittivity at high frequencies and β is the Cole-Cole parameter that represents the broadness of the distribution of relaxation times ((0 < $\beta \leq 1$)). If $\beta = 1$, this spectrum will be a Debye-type relaxation spectrum. This relaxation process corresponds to that of



(a) (b)

FIGURE 1 Applied electric field E dependence of the electric displacement D_1 and D_3 of 6CB at 302 K. The solid lines are the best-fitted ones to the data.

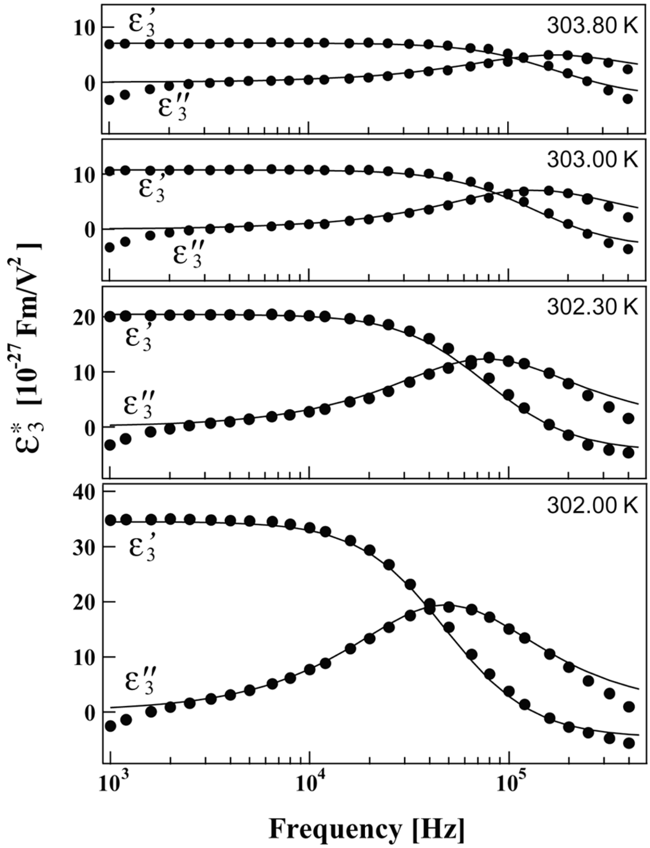
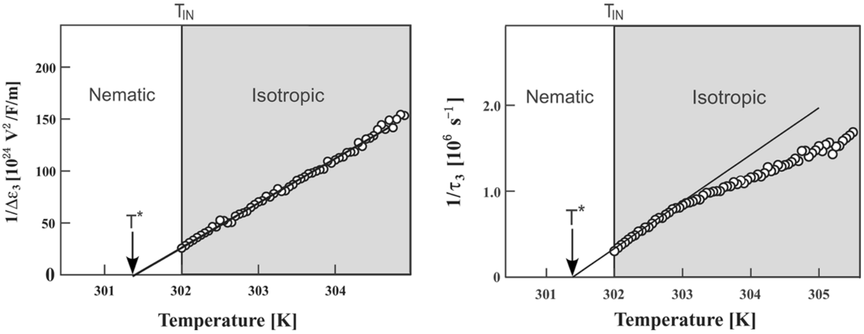


FIGURE 2 Frequency spectrum of the complex nonlinear permittivity $\varepsilon^*_3(\varepsilon^*_3 \equiv \varepsilon'_3 - i\varepsilon''_3)$ at various temperatures in the I phase (T = 303.8 K, 303.0 K, 302.3 K, and 302.0 K). The solid lines are the best fits with a Cole-Cole relaxation spectrum.

the fluctuation of *S* near I-N transition. The cooperative motion of directors of liquid crystal slows down and it cannot catch up the frequency of the applied field near T_{IN}. In the range of frequency higher than 100 kHz, another relaxation process is emerged (ε'_3 is negative) and it may correspond the rotational motion of the molecules [8]. So, we only fit the data from 1 kHz to 200 kHz to obtain the relaxation parameters of ε_3.

Figure 3(a) and (b) respectively show the temperature dependence of $1/\Delta\varepsilon_3$ and $1/\tau_3$ of 6CB. In Figure 3(a), the solid line is the bestfit to the data, and the point at which the extrapolated line intercepts



(a) (b)

FIGURE 3 Temperature dependence of the (a)$1/\Delta\varepsilon_3$ and (b)$1/\tau_3$ of 6CB in I phase. The critical point T^* is determined as a temperature where the best-fitted line crosses the temperature axis. In (b), T^* that defined as former is used to draw the best-fitted line.

the temperature axis is defined as the critical temperature T^*. We can obtain $T^* = 301.4$ K for 6CB and this result agrees with that reported by other experiment [9]. The Curie-Weiss type critical behavior also agrees the Landau-de Gennes theory.

On the contrary, the temperature dependence of $1/\tau_3$ deviates from the straight line as shown in Figure 3 (b). We use the critical temperature T^* obtained by Figure 3(a). This result differs from our expectation based on the Landau-de Gennes theory. It is probably due to temperature dependence of viscosity.

The obtained linear dielectric permittivity $\varepsilon_1{}^*$ is shown in Figure 4. Temperature dependence of ε_1 in the I phase near T_{IN} is small, but it decreases a little bit in approaching T_{IN}. Such behavior has already been reported by other authors and is considered to be due to the critical cooperative fluctuations [10].

The nonlinear permittivity ε_3 of 8CB has been also measured. Temperature dependence of ε_1 and ε_3 for 8CB near T_{IN} are similar to that of 6CB. It is known that the temperature gap between T_{IN} and T^*, ($\Delta T = T_{\mathrm{IN}} - T^*$) depends on the materials [10]. It is understood that the difference in ΔT influences the relaxation time near T_{IN}, that is, as we can approach T^* closer, the critical fluctuations increase and the relaxation frequency decreases. In this study, ΔT of 6CB and 8CB are respectively 0.6 K and 0.83 K. The slopes of $1/\Delta\varepsilon_3$ (see Fig. 3) are different for each compounds, and the slope of 8CB is larger than that of 6CB in this study. The pretransitional effect of the linear permittivity of 8CB is also larger than that of 6CB [10].

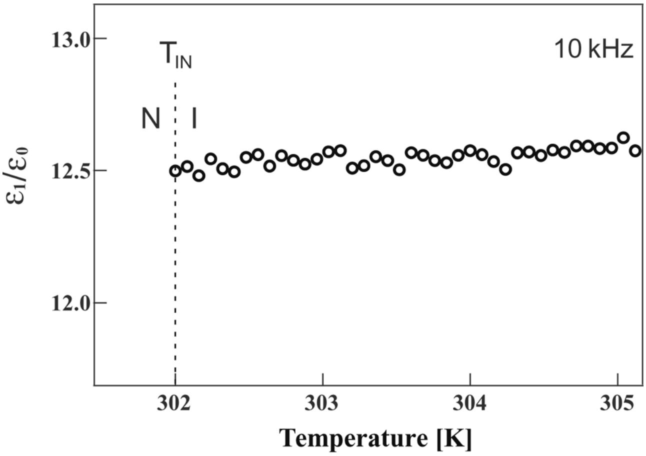


FIGURE 4 Temperature dependence of the linear permittivity ε_1 of 6CB at 10 kHz in the I phase near TIN.

5. CONCLUSION

We investigated I-N phase transition in liquid crystal, 6CB and 8CB. In I phase near T_{IN}, we measured the linear and the third-order nonlinear permittivity from the fundamental and third harmonic components of electric displacement. In the frequency region between 1 kHz and 1 MHz, the relaxation behavior that it is due to the cooperative fluctuation of director was observed in nonlinear spectrum. Temperature dependence of dielectric strength is match to the Landau- de Gennes theory well, but relaxation time dose not agree with it. One of the presumable reasons is the increase of viscosity.

The pretransitional effects of the linear and the third-order nonlinear permittivity near I-N transition are different from each liquid crystal, 6CB and 8CB. The dependence of pretransitional effect on compounds (for example other nCB series) is one of future works to study.

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