Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 29 Aug 2007.

To cite this article: Shinobu Ikeno , Masaaki Yokoyama & Hiroshi Mikawa (1976): Dielectric Behavior of Nematic Liquid Crystals under DC Electric Field, Molecular Crystals and Liquid Crystals, 36:1-2, 89-98

To link to this article: http://dx.doi.org/10.1080/00268947608084833

Mol. Cryst. Liq. Cryst., 1976, Vol. 36, pp. 89–98

Printed in Holland

Dielectric Behavior of Nematic Liquid Crystals under DC Electric Field

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(*Received January 5, 1976; in final form April 28, 1976*)

Dielectric behavior of nematic liquid crystals of *p*-methoxybenzylidene-*p*-n-butylaniline and *p*-ethoxybenzylidene-*p*-n-butylaniline have been investigated under DC electric field in relation to their optical behavior. Both dielectric permittivity and transmitted light intensity decrease at a threshold voltage of external DC electric field, and the latter reaches a constant low value at higher field, while dielectric permittivity increases via minimum to approach a constant value at higher field strength of about 2×10^4 V/cm. Such a change of dielectric permittivity under DC electric field is characteristic of nematic and supercooled states, and exhibits large dependence on both temperature and sample thickness. This dielectrical observation is discussed in terms of dielectric anisotropy of the nematic liquids oriented to the field, and the disturbance of molecular orientation due to the dynamic scattering at higher DC electric field.

INTRODUCTION

The influence of both electric and magnetic fields on nematic liquid crystals has been widely studied. The results of these studies are explained by dielectric and magnetic anisotropies of the molecules and molecular orientation of nematic liquids caused by the field. When the static electric field is applied on nematic liquid crystals, two distinctly different optical phenomena occur, i.e., the formation of domain pattern at rather low field strength,[1] and the dynamic scattering mode at higher field strength.[2] Especially, the latter phenomenon has already been utilized in well-known electro-optical display devices. Heilmeier[2] proposed that the dynamic scattering mode is caused by the disturbance of molecular orientation by hydrodynamic flow. Such a change of molecular orientation would be expected to be observed directly by the measurement of dielectric permittivity under the condition where the domain formation or dynamic scattering occurs. There has been, however, few reports on the direct observation of dielectric permittivity of nematic liquid crystals under such condition.

In the present study, we measured dielectric permittivity and transmitted light intensity under DC electric field in order to obtain information on the molecular orientation in nematic liquid crystals. An anomalous dielectric behavior was observed on *p*-methoxy-benzylidene-*p*-n-butylaniline (MBBA) and *p*-ethoxybenzylidene-*p*-n-butylaniline (EBBA) nematic liquid crystals. The dielectric observation will be discussed in terms of the molecular orientation and hydrodynamic molecular motion of the nematic liquids under DC electric field.

EXPERIMENTAL

MBBA and EBBA were synthesized according to the literature[3] and purified by vacuum distillation after being recrystallized three times at least. The nematic range of these liquid crystals were 21°C–47°C for MBBA and 36°C–80°C for EBBA, respectively. The specific resistivity of MBBA and EBBA was the order of 10^{10} $\Omega \cdot$cm. Measurements of dielectric permittivity were made in the frequency range from 30 kHz to 1 MHz with a mutual conductance bridge (Andoh Electric Co., Model TR-1C), which was modified to give DC bias up to 400 V as shown in Figure 1.[4] The output voltage from the oscillator was fixed to 3 V. Samples were held by capillary action between nickel plated electrodes (area; 2.83 cm^2) with an appropriate separation from 100 to 200 μm. The dielectric measurements were carried out in

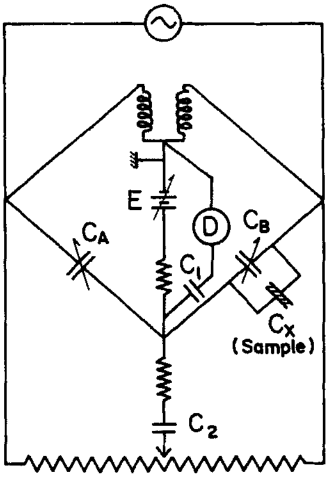

FIGURE 1 Mutual inductance bridge circuit modified to give DC electric field for dielectric measurements; C_1, C_2; condenser for cutting off DC current, E; battery for DC bias, D; detector.

stationary condition every 5 minutes after applying DC electric field. The temperature was controlled within ±0.5°C. The change of transmitted light intensity of the samples inserted between nesa coated glass electrodes was measured as a function of applied DC voltage by using Hitachi UV-Visible spectrophotometer, in a similar manner as reported by Williams.[1] The wavelength of the incident light was chosen at 650 nm, where MBBA has no absorption. The effect of applied 3 V AC voltage which was superposed on DC bias in the measurements of transmittance was examined for a 100 μm cell. The transmittance increased slightly by applying AC voltage, but the increment was as small as a few percent even at low DC field strengths.

RESULTS

Figure 2 shows the typical change of dielectric permittivity and dielectric loss tangent of MBBA as a function of external DC field. Dielectric permittivity increases slightly with increasing electric field up to around 800 V/cm, and decreases rapidly with the subsequent increase of the field up to 2–4 KV/cm, and then gradually recovers again to a steady value at higher field. Thus, dielectric permittivity of MBBA nematic liquid crystal exhibits a

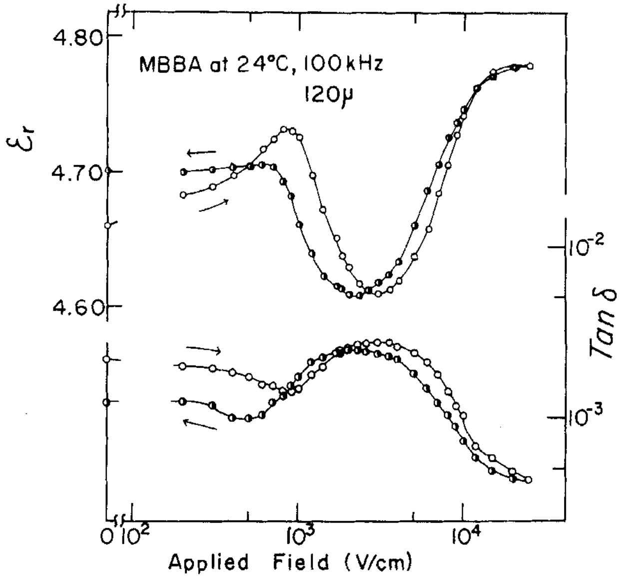

FIGURE 2 Relative permittivity and dielectric loss tangent versus applied field. Open and closed circles correspond to the measurements in the case of increasing and decreasing field, respectively.

"v-shape" curve with increasing applied field. No essential change of the "v-shape" curve could be found in the present frequency range from 30 kHz to 1 MHz. Dielectric loss tangent exhibits a maximum, corresponding to a minimum of dielectric permittivity. As shown in the figure, two slightly different "v-shape" curves were observed in the cases of increasing and decreasing field. It may be due to polarization effect changing the field distribution in the cell.[5]

In Figure 3 are compared the influence of sample thickness on the change of dielectric permittivity and transmitted light intensity of MBBA. In contrast to the "v-shape" change of dielectric permittivity, the transmitted light intensity did not show recovery even in higher field strength. The threshold voltages observed at which dielectric permittivity begins to decrease correspond well to those observed in transmitted light intensity in each different sample thickness. The threshold voltage shifts to lower field strength with increasing sample thickness in both dielectric permittivity and transmittance. This shift of the threshold voltage to lower field in transmittance with sample

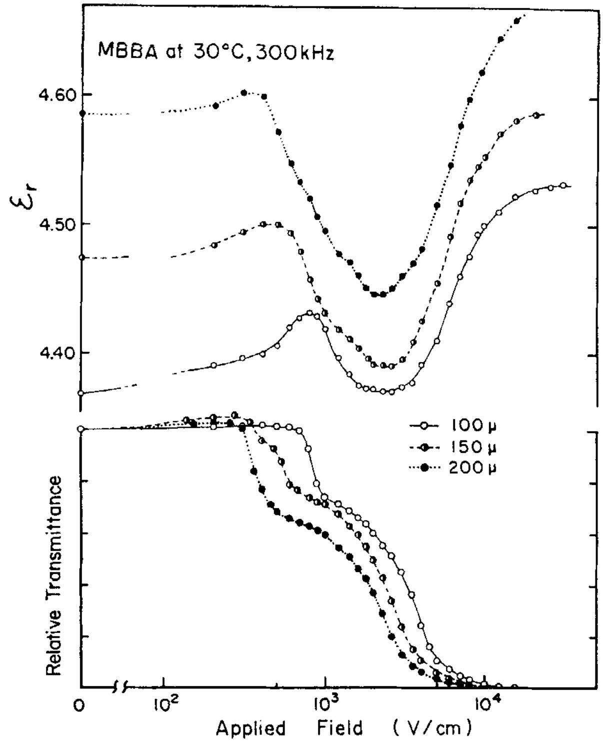

FIGURE 3 Relative permittivity and relative transmittance as a function of applied field for different sample thickness.

thickness agrees with the result reported by Williams.[1] The voltage corresponding to a minimum in the "v-shape" of dielectric permittivity seems to be less dependent on sample thickness.

In Figure 4 is illustrated the variation of dielectric permittivity of MBBA within its nematic region under DC electric field as a function of temperature. Since MBBA has narrow nematic region (21°–47°C), the effect of temperature on dielectric behavior under the field will be more clearly demonstrated in the case of EBBA, which has relatively wide nematic region (36°–80°C). Figures 5(a) and 5(b) show the variation of dielectric permittivity and dielectric loss tangent of EBBA nematic liquid, respectively.

Some characteristic features can be observed with increasing temperature; (i) Values of dielectric permittivity and dielectric loss tangent become smaller, (ii) Curves become broader and the dielectric change with the field is reduced, (iii) The "v-shape" curve is no longer observed in isotropic and crystalline states, (iv) Apparently, the threshold voltage in dielectric permittivity shifts to lower field side, and inversely the minimum point to higher field side, (v) The supercooled state gives a larger change of dielectric permittivity than nematic state.

These dielectric behavior for temperature suggests a dynamical equilibrium between molecular orientation due to DC electric field and molecular

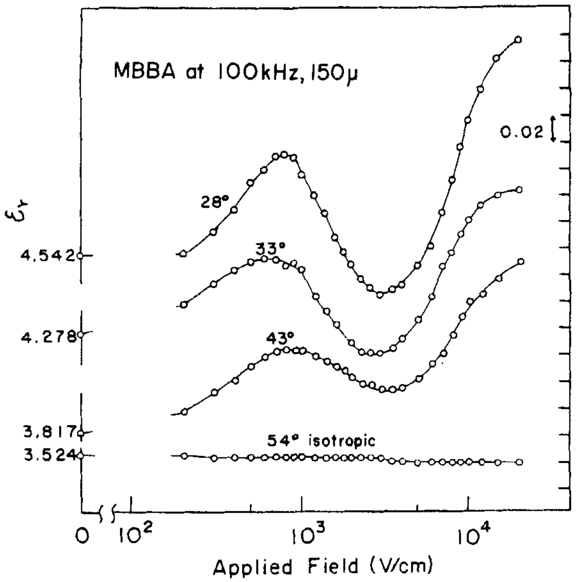

FIGURE 4 Relative permittivity for MBBA as a function of applied field for different temperatures. Each curve is drawn independently with the same ordinate scale (0.02/div.) and the figures in the left side indicate ε_r in the absence of DC bias, respectively.

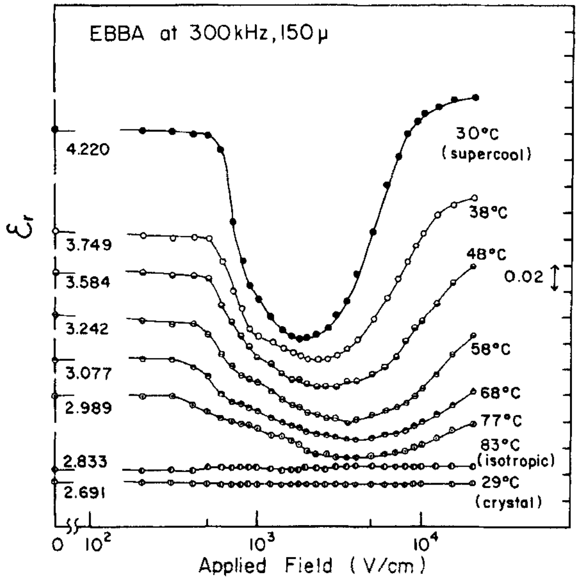

FIGURE 5(a) Relative permittivity for EBBA as a function of applied field for different temperatures.

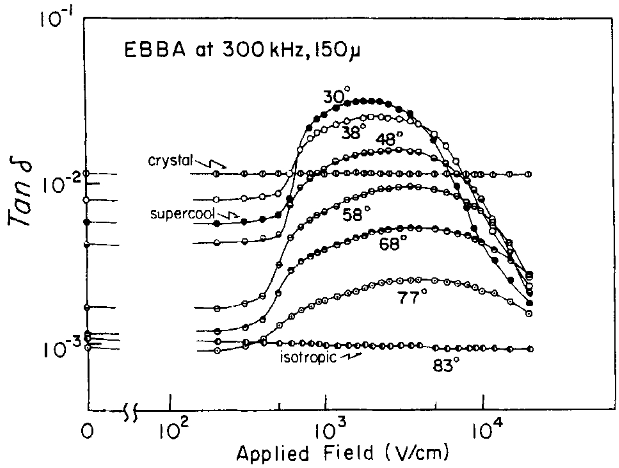

FIGURE 5(b) Dielectric loss tangent for EBBA as a function of applied field for different temperatures.

disorientation due to thermal motion, as to be discussed in the following section.

DISCUSSION

When electric or magnetic field is applied on nematic liquids, molecules are forced to orient owing to the dielectric and magnetic anisotropy of the molecules. The nematic liquid crystals used in this study have their dipoles nearly perpendicular to the molecular axis, having so-called negative dielectric anisotropy. Rondelez *et al.*[6] measured dielectric anisotropy of MBBA under magnetic field of about 10 KG, and obtained the value of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, i.e., the dielectric permittivities of the material having the long axis of molecules oriented parallel or perpendicular to the measuring electric field, respectively. They reported that $\varepsilon_{\parallel}$ is smaller than $\varepsilon_{\perp}$ and also that $\varepsilon_{\parallel}$ shows a dielectric relaxation at around 1.1 MHz, while no relaxation is observed for $\varepsilon_{\perp}$ in the frequency range of 0–10 MHz at room temperature. Therefore, the increase of the contribution of $\varepsilon_{\parallel}$ component would result in the decrease of dielectric permittivity and the increase of dielectric loss tangent, because $\varepsilon_{\parallel}$ component shows dielectric relaxation in the present frequency of 30 kHz–1 MHz.

On the basis of the present data and the above mentioned results, it is possible to set down a qualitative interpretation of the molecular orientation in nematic liquids subjected to DC electric field. The change of molecular orientation of nematic liquids under DC electric field is schematically represented in Figure 6. Since in the present study, we used comparatively thick samples and electrodes without any surface treatments, a large portion of molecules except only some in the vicinity of electrode surfaces is presumably considered to be randomly oriented under no DC electric field,[7] as illustrated in Figure 6(a).

When an external DC electric field is applied on MBBA and EBBA, negative nematic liquids, dipoles are forced to orient, and then the population of the molecules orienting perpendicular to the field direction increases gradually with increasing field strength as in Figure 6(b). The increase of the contribution of $\varepsilon_{\perp}$ component gives rise to the increase of dielectric permittivity, which can be recognized clearly in the case of MBBA under the threshold voltage, as shown in Figure 2. Over the threshold voltage, however, dielectric permittivity suddenly begins to decrease, corresponding to the change in transmitted light intensity at nearly equal threshold voltage. The latter change can be observed microscopically as the formation of domain pattern and in slightly higher field as dynamic scattering mode. Good

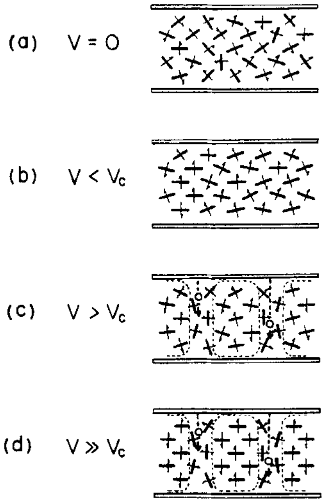

FIGURE 6 Schematic representation of molecular orientation of nematic liquid crystals under DC field V; (a) $V = 0$ (b) $V < V_c$ (c) $V > V_c$ (d) $V \gg V_c$; small open circles in (c) and (d) indicate moving ions, which give rise to hydrodynamic flow of nematic liquids.

agreement of the threshold voltages of the decrease of both dielectric permittivity and transmittance suggests that the decrease in dielectric permittivity is caused also by the disturbance of molecular orientation due to hydrodynamic flow of nematic liquid molecules.[2,8]

In still higher field strength, the total fraction of the disturbed region approaches some limiting value, which yields a constant low transmittance. Such a behavior would be illustrated in (c) and (d) in Figure 6. Since transmitted light intensity depends only on the volume fraction of the disturbed region, transmitted light intensity is almost equal in both cases (c) and (d). On the other hand, the dielectric permittivity in case of (d) is expected to give a larger value than that in the case of (c), owing to the orientation of the individual dipoles within the undisturbed region under higher electric field. This is the reason why only dielectric permittivity shows a recovery in higher field strength. The broadening of the "v-shape" curve with increasing sample thickness as shown in Figure 3 may be due to polarization effect on the oriented dipoles, which weakens the applied external field in inner layer.

The influence of external field brings about an increase of the contribution of $\varepsilon_\perp$ component, which shows no relaxation in the frequency range of 30 kHz to 1 MHz. However, the onset of hydrodynamic flow gives rise to disturbance of molecular orientation and this disturbance increases the contribution of $\varepsilon_\parallel$ component which shows dielectric dispersion in the frequency range of our measurement, resulting in an increase of dielectric loss tangent. However, in higher field, molecules in undisturbed region orient further, increasing the contribution of $\varepsilon_\perp$ component, as schematically shown in Figure 6(d). Therefore, dielectric loss tangent exhibits a maximum at the minimum point of the dielectric permittivity. Thus, the change of dielectric loss tangent with electric field is explained qualitatively by the above-mentioned mechanism.

The temperature effect on dielectric behavior is explained phenomenologically with a intuitive view of a change in molecular orientation of nematic liquids. As temperature rises, the order of molecular alignment in nematic phase decrease. Microscopically to describe the order of molecular alignment, the order parameter, S, is introduced for a system of rod-like molecules in a nematic phase,[9]

$$S = \langle \tfrac{1}{2}(3\cos^2\theta - 1)\rangle,$$

where θ is the angle between rod axis and nematic axis. Nematic phase is partly flexible, and different part even in the region undisturbed by hydrodynamic flow would give different S. The macroscopic anisotropy of dielectric constant would be related to S in the following fashion;[10,11]

$$\varepsilon_\parallel - \varepsilon_\perp = \tfrac{3}{2}\varepsilon_a S,$$

where ε_a represents the coefficient of anisotropy in dielectric constant of a rod-like molecule. The rise of temperature gives rise to the decrease in S and $S = 0$ in isotropic phase,[10] and therefore, the difference between parallel and perpendicular dielectric constants becomes smaller with increasing temperature. Consequently, the influence of hydrodynamic flow on the molecular arrangement becomes smaller in higher temperature, resulting in a shallow "v-shape" curve. Furthermore, the decrease in S requires higher field strength to attain the same degree of orientation. Thus, the minimum point in "v-shape" curve shifts to the higher field in higher temperature. In isotropic state, where $S = 0$, the external field is no longer effective to orientate dipoles. In crystalline state, molecules are frozen and dipoles are prevented to orient to the field. Thus, the variation of dielectric permittivity could not be observed under field in both isotropic and crystalline state.

In short, the dielectric behavior of nematic liquid crystals under DC bias field will be summarized as follows. Externally applied DC bias field orientates the dipoles parallel to this field (molecular axis perpendicular to the field, showing large ε value). When the bias field exceeds some threshold value, this orientation is disturbed by hydrodynamic turbulence, thus, decreasing the ε value. In high bias field, ε increases again approaching constant value, because the molecules in the region undisturbed by hydrodynamic flow continue to orient their dipoles parallel to the direction of the bias field. As $\varepsilon_\perp$ has no dispersion up to 10 MHz, and $\varepsilon_\parallel$ has dispersion at around 1.1 MHz in the room temperature, dielectric loss tangent increases at the bias field of dynamic scattering mode, due to the increase of the contribution of $\varepsilon_{\parallel}$ component.

Acknowledgement

We wish to express our appreciation to Professor Yōichi Ishida and Dr. Shinsaku Uemura of Osaka University for teaching us the circuit to measure dielectric properties under DC electric field. We also wish to express our thanks to professor Shigekazu Kusabayashi of Yamaguchi University for his encouragement in carrying out the present work.

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