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Study of Dielectric Properties of Two Mesogenic Mixtures as a Function of Temperature

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Dielectric studies as a function of temperature have been conducted on two liquid-crystalline mixtures: mixture 1, containing phenyl cyclohexane, biphenyl cyclohexane, and cyclohexane carboxylate (code name: ZLI 1701); and mixture 2, containing phenyl cyclohexane, cyano cyclohexane, and cyclohexane carboxylate (code name: ZLI 1800-000).

Each of the mixtures exhibits only the nematic phase with a similar temperature range. Both the mixtures contain phenyl cyclohexane and cyclohexane carboxylate groups. However, mixture 1 contains biphenyl cyclohexane, whereas mixture 2 contains cyano cyclohexane. Until now, no systematic study on the two mixtures have been reported. Our interest is to compare the macroscopic properties of the two mesogenic mixtures and to study the effect of replacing the biphenyl cyclohexane group in mixture 1 by a cyano cyclohexane group in mixture 2. With this aim, the variation of the dielectric permittivities $\varepsilon_{\perp}$ and $\varepsilon_{\parallel}$ with temperature has been determined for both the samples in an aligning magnetic field at frequencies of 1 kHz, 10 kHz, and 100 kHz, and the dielectric properties of the two mixtures have been compared. We have also calculated the variation of angle of inclination β of the molecular dipole moment with the director for both the samples as a function of temperature.

Keywords: angle of inclination; dielectric constant; mesogen

INTRODUCTION

The study of the dielectric and optical properties of liquid crystals is important from the theoretical point of view as well as for tailoring and optimizing material characteristics for electro-optical applications. Because the mesogenic properties of thermotropic liquid crystals are temperature dependent, the study of the thermal variation of their

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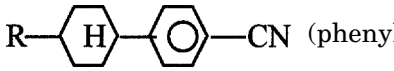
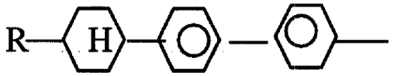
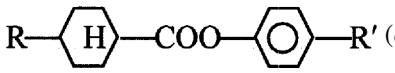
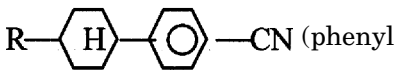
properties is of great interest and significance. Each of the mixture is in the liquid-crystalline state at very low temperature, so these mixtures are very useful in low-temperature LC devices.
Mixture 1 (code name ZLI 1701) contains

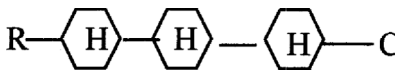

(phenyl cyclohexane or PCH),

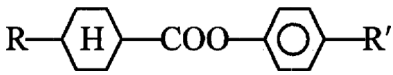

(biphenyl cyclohexane), and


(cyclohexane carboxylate).

Mixture 2 (code name ZLI 1800-000) contains


(phenyl cyclohexane or PCH),


(cyano cyclohexane or CCH), and


(cyclohexane carboxylate),

where $R=C_nH_{2n+1}$.

The transition temperatures of the two mixtures as supplied by the manufacturer (Merck Ltd.) are mixture 1, solid to nematic: $-15^{\circ}C$, and nematic to isotropic: $61^{\circ}C$; and mixture 2, solid to nematic: $-9^{\circ}C$, and nematic to isotropic: $60^{\circ}C$.

A distribution model has been proposed to determine the pretilt angle for nematic liquid crystals, and they show that mixture 2 (ZLI 1800-000), having a strongly polar cyano group, has a high pretilt angle [1]. Still, no systematic study has been made of the characteristic properties of the two mixtures. In this article, we present some experimental measurements on the dielectric studies of the two liquid-crystalline mixtures. We have also calculated the angle of inclination β of the molecular dipole moment with the director as a function of temperature for both the mixtures. We are interested to compare the macroscopic properties of the two mixtures and to study the effect of replacing the biphenyl cyclohexane group in mixture 1 with the cyano cyclohexane group in mixture 2.

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EXPERIMENTAL

Texture Studies

Prior to undertaking the dielectric studies, routine texture studies were carried out to confirm the nature of the mesophases and the phase-transition temperatures. The texture studies were conducted using a polarizing microscope (Leitz) fitted with a hot stage (Mettler FP82 HT). The powdered sample was placed on a glass slide and covered with a cover slip, and the cell thus formed was placed in the hot stage. The sample was heated at a rate of l°C/min, and the observations were performed under crossed polarizers with a magnification of 150×. Representative photographs of each of the phases were taken and the transition temperatures noted.

Dielectric Studies

A pair of indium tin oxide (ITO)-coated conducting glass plates separated by thin cover slips on three sides was used to form the sample cell (capacitor). The effective sample cell size is 4 cm by 2.5 cm by 0.05 cm, and its capacitance (air) is 21 pF (approximately). The cell was calibrated using standard liquids: benzene and p-xylene with the help of an inductance capacitance resistance (LCR) meter (6471 Forbes Tinsley). The sample was introduced into the cell as the isotropic liquid, and the open end was sealed. It was then placed in a sample holder whose temperature was controlled (±1°C). The sample was taken through a number of temperature cycles in the presence of a magnetic field of approximately 8 Kgauss to get an aligned monodomain sample. Readings for the parallel and perpendicular components of capacitance were taken at temperature intervals of 2°C during cooling (except during smectic A to nematic transition) at frequencies of 1 kHz, 10 kHz, and 100 kHz. The values of the parallel and perpendicular components of the dielectric permittivity $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ were obtained from the capacitance values by standard procedure. The bridge voltage across the sample was maintained low enough (~0.3 V) so as not to produce any electric field–induced instabilities.

RESULTS AND DISCUSSION

Texture Studies

The transition temperatures as observed from texture studies are as follows: mixture 1, nematic to isotropic: 60.4°C, and isotropic to nematic: 57.5°C; and mixure 2, nematic to isotropic: 59.5°C, and isotropic to nematic: 60.3°C.

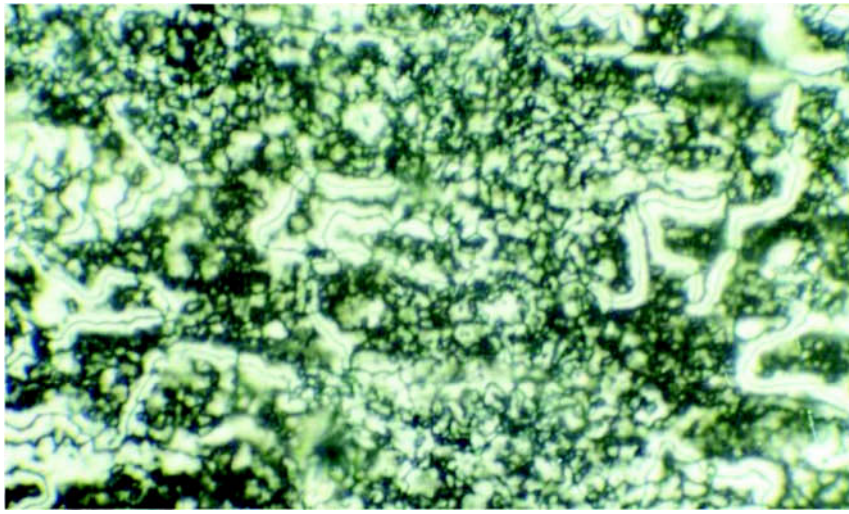

FIGURE 1 Texture photographs of mixture 1 at 55°C (cooling).

The phase-transition temperatures from nematic to isotropic for both the mixtures are in excellent agreement with the quoted values supplied by Merck Ltd. Because there is no arrangement to cool the

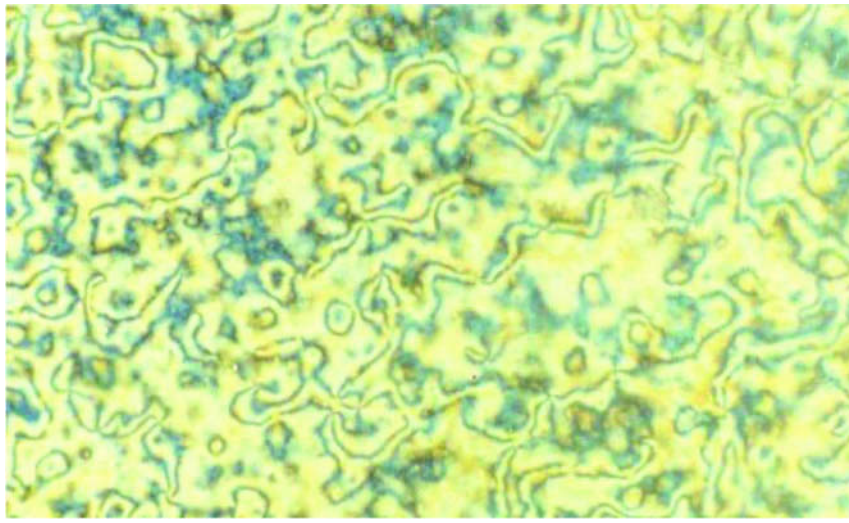

FIGURE 2 Texture photographs of mixture 2 at 55°C (cooling).

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sample below room temperature, no observations could be made below 30°C, and no photographs were taken in this temperature region. Representative texture photographs of the nematic of the two mixtures are shown in Figs. 1 and 2 respectively.

Dielectric Studies

The nature of variation of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ with temperatures for both the mixtures at frequencies of 1 kHz, 10 kHz, and 100 kHz are depicted in Figs. 3–8. The dielectric constant decreases with increasing frequency for both the mixtures. The average dielectric constant is higher for all the frequencies for mixture 2 than for mixture 1. This difference may be attributed to the presence of the highly polar CN group of cyano cyclohexane [2] in mixture 2 in place of biphenyl cyclohexane in mixture 1. The ε_{ave} curve is discontinuous with the ε_{iso} curve for mixture 2, whereas it is almost continuous for mixture 1. The ε_{ave} curve is continuous with the ε_{iso} curve for mixture 1, which is a feature exhibited by nonpolar molecules such as di-alkyl azobenzene [3]. The discontinuity in ε_{ave} at T_{NI} observed in mixture 2 is observed in nematics with strongly polar end groups and has been interpreted as a consequence of antiparallel local ordering, which produces the discontinuity [4]. Such pretransitional effects in dielectric permittivity in nematics with cyano end groups have been reported [5,6]. The reduced

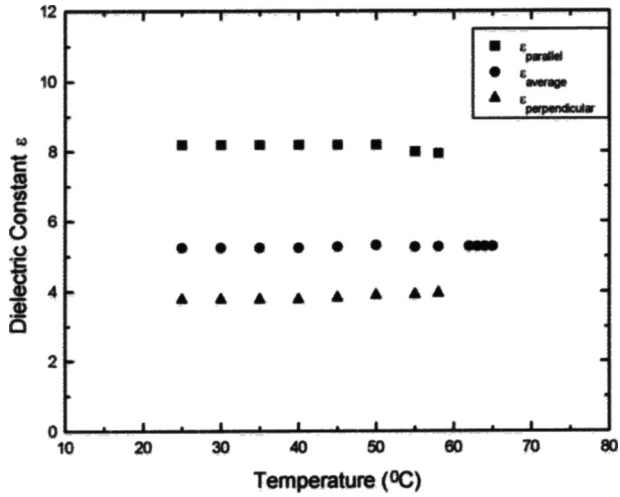

FIGURE 3 Variation of dielectric constant with temperature of mixture 1 at 1 kHz.

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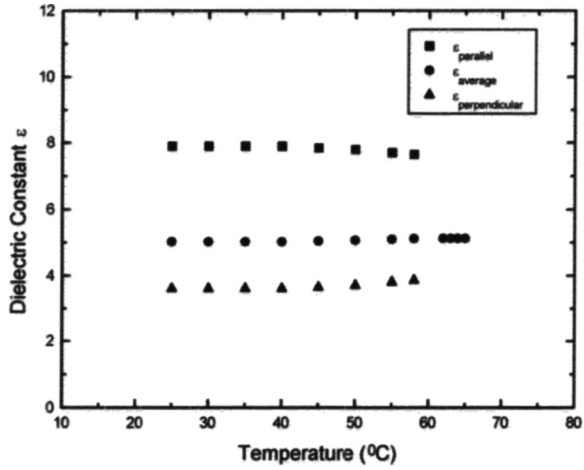

FIGURE 4 Variation of dielectric constant with temperature of mixture 1 at 10 kHz.

contribution to dielectric permittivity ε_{iso} from dipole moment μ was attributed to apparent reduction in μ values due to formation of dimers in antiparallel local ordering [7]. The pretransition in ε_{iso} near T_{NI} showing a maximum was explained as due to appreciable concentration

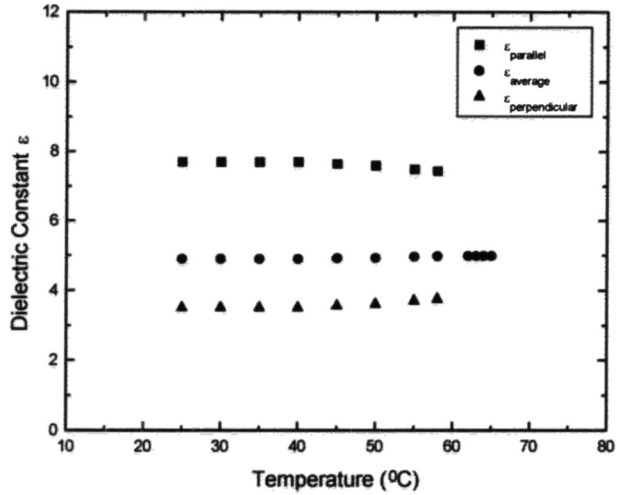

FIGURE 5 Variation of dielectric constant with temperature of mixture 1 at 100 kHz.

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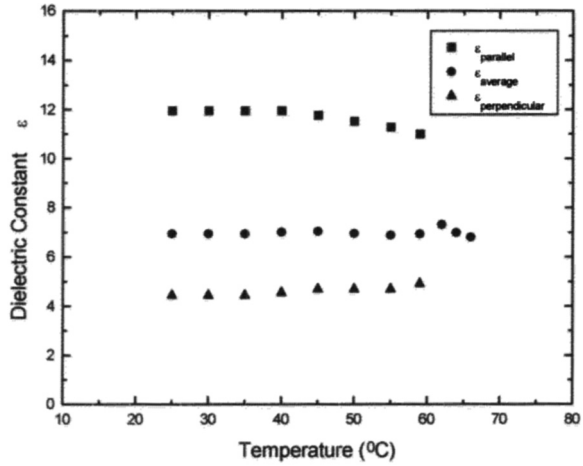

FIGURE 6 Variation of dielectric constant with temperature of mixture 2 at 1 kHz.

of dimers in a dynamic dimer–monomer equilibrium. The nature of the variation at 1 kHz has been studied, and in conjunction with the data for 10 kHz and 100 kHz, it is evident that the dielectric constant decreases with increase in frequencies for both the mixtures. The average values

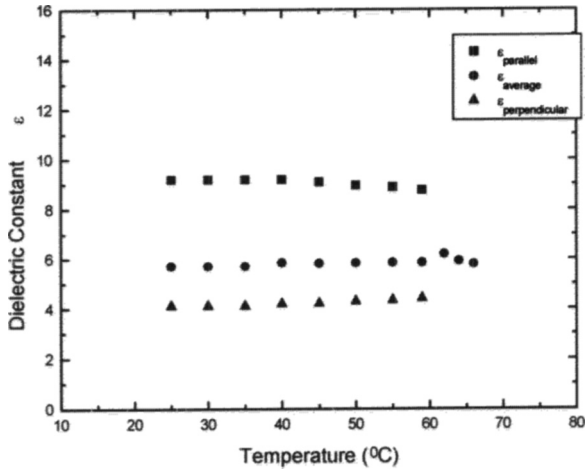

FIGURE 7 Variation of dielectric constant with temperature of mixture 2 at 10 kHz.

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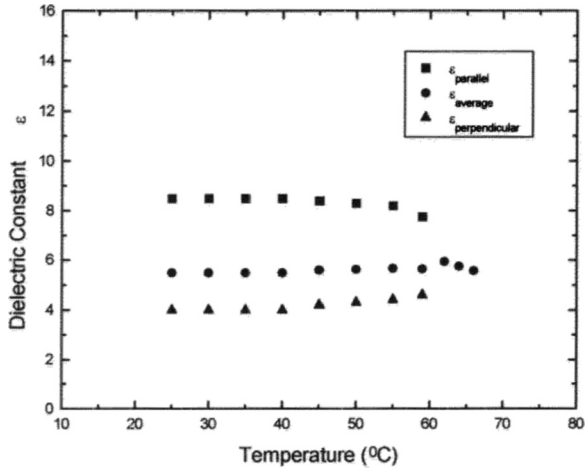

FIGURE 8 Variation of dielectric constant with temperature of mixture 2 at 100 kHz.

of dielectric permittivity ε_{ave} are 5.28, 5.05, and 4.92 at 1 kHz, 10 kHz, and 100 kHz respectively (at 45°C) for mixture 1, and the corresponding values are 7.04, 5.83, and 5.60 respectively (at 45°C) for mixture 2. This is attributed to an increase in dielectric loss with an increase in operating frequency. The effect of electrode polarization or any other parasitic phenomenon is cancelled out during the process of standardization of the sample cell using standard liquids. The effect of operating frequency on the dielectric characteristics has also been observed. With an increase in operating frequency from 1 kHz to 10 kHz and 1 kHz to l00 kHz, dielectric permittivity decreases by about 4.36% and 6.82% respectively at 45°C for mixture 1 and 1.72% and 2.05% respectively at 45°C for mixture 2.

In our optical study, refractive indices n_e and n_o have been determined as a function of temperature, and from it we have calculated polarisability α_e and α_o [since $\alpha_e = 3(n_e^2 - 1)/4\pi N(\bar{n}^2 + 2)$ and $\alpha_o = 3(n_o^2 - 1)/4\pi N(\bar{n}^2 + 2)$ where N = number of molecules per cc] in terms of molecular weight since the molecular weight was not known (the sample being a mixture). The value of order parameter $\langle P_2 \rangle$ was determined from a gradient of the Haller plot assuming a $(1 - (T_{NI}/T))$ to the power b function form. Ratio of polarisability anisotropy to average polarisability is determined from intercept of Haller [8] plot. The experimental procedure of our optical study in detail is given in Ref. [9]. Thus the values of polarisability anisotropy $\Delta\alpha$, average polarisability α_{ave}, and order parameter $\langle P_2 \rangle$ were used to calculate the angle of inclination β between the

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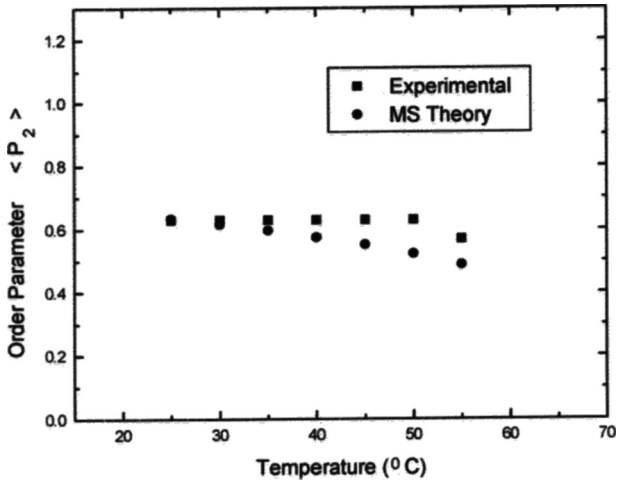

FIGURE 9 Variation of order parameter with temperature of mixture 1.

molecular dipole moment and the molecular axis by applying the following expressions [10]:

$$\varepsilon_{\text{ave}} = 1 + 4\pi \text{NhF}\left(\frac{\alpha_{\text{ave}} + \text{F}\mu^2}{3\text{kT}}\right) \tag{1}$$

and

$$\Delta\varepsilon = 4\pi \text{NhF}\left\{\frac{\Delta\alpha - \text{F}\mu^2(1 - 3\cos^2\beta)}{2\text{kT}}\right\}\langle \text{P}_2 \rangle \tag{2}$$

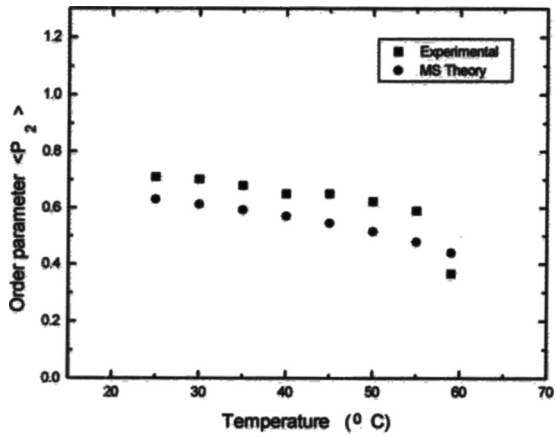

FIGURE 10 Variation of order parameter with temperature of mixture 2.

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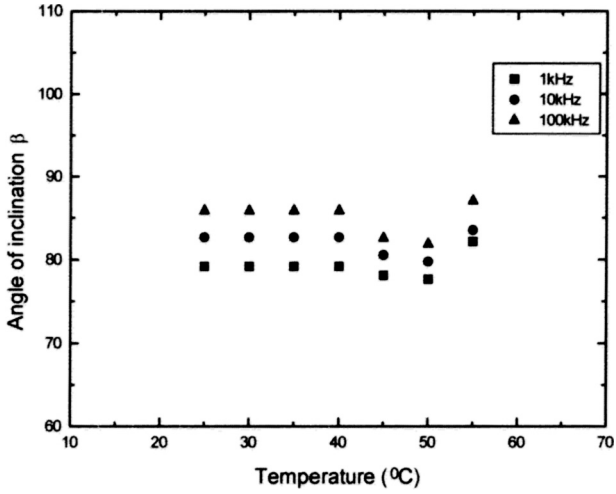

FIGURE 11 Variation of angle of inclination β with temperature of mixture 1.

where

$$\varepsilon_{ave} = \frac{\varepsilon_{\parallel} + 2\varepsilon_{\perp}}{3}, \quad \alpha_{ave} = \frac{\alpha_e + 2\alpha_o}{3}, \quad f = \frac{4\pi N(2\varepsilon_{ave} - 2)}{3(2\varepsilon_{ave} + 1)}$$

$$h = \frac{3\varepsilon_{ave}}{2\varepsilon_{ave} + 1}, \quad F = \frac{1}{1 - \alpha_{ave} f}$$

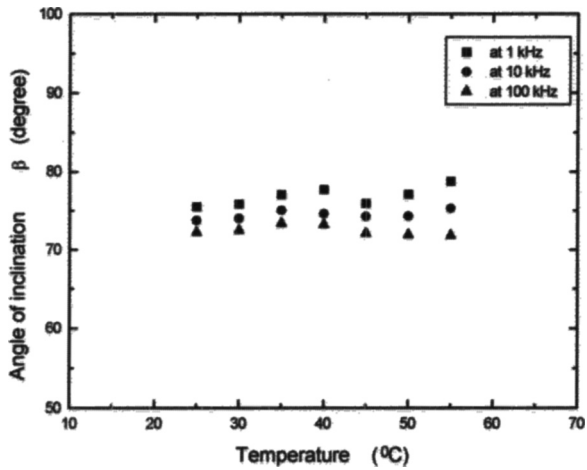

FIGURE 12 Variation of angle of inclination β with temperature of mixture 2.

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The variation of the order parameter with temperature for both the mixtures are given here (Figs. 9 and 10) for convenience. The variation of β with temperature at three frequencies of 1 kHz, 10 kHz, and 100 kHz for both the mixtures are depicted in the Figs. 11 and 12. β increases with frequency for mixture 1 whereas it decreases with frequency for mixture 2. The crystalline-to-nematic transition temperature of each of the constituent moieties is much higher (above 0°C) than that of the resulting mixtures (−9°C and −15°C). It is thus expected that the mixtures may prove to be useful in low-temperature LC devices.

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