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POLYMERS AND LIQUID CRYSTALS

Dielectric and Optical Properties of a 5-Propyl-2-(*p*-Cyanophenyl)-Pyridine Liquid Crystal

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Abstract—The temperature dependences of the dielectric and optical parameters for a 5-propyl-2-(*p*-cyanophenyl)-pyridine (3CP) liquid crystal are investigated in the vicinity of the nematic–isotropic phase transition. The dielectric spectra of the 3CP compound in the crystalline, nematic, and isotropic phases are measured in the frequency range 1–1000 MHz, and the Debye approximations of the measured spectra are obtained. Analysis of the dependence of the static permittivity on the director orientation with respect to the direction of the electric pump field demonstrates that the angle between the dipole moment and the long axis of the molecule is approximately equal to 15°. © *2003 MAIK “Nauka/Interperiodica”.*

1. INTRODUCTION

As is known, the frequency dispersion of the permittivity is one of the basic properties of liquid crystals. Elucidation of the nature of the dispersion, and, especially, the influence of different factors on this property, is an important problem in both theoretical and applied physics. At present, the region of dispersion associated with the relaxation of liquid-crystal molecules, which, as a rule, corresponds to frequencies of the meter wavelength range, has been adequately studied for many liquid-crystal systems. However, there exist a number of liquid crystals whose high-frequency dielectric properties are as yet poorly understood. This can be explained by the fact that the relaxation frequencies for this group of liquid crystals fall in the decimeter wavelength range in which precision dielectric measurements involve considerable difficulties. Among these materials is a 5-propyl-2-(*p*-cyanophenyl)-pyridine (3CP) nematic liquid crystal. The structural formula of the 5-propyl-2-(*p*-cyanophenyl)-pyridine liquid-crystal compound is presented in Fig. 1. Investigation into the optical and dielectric properties of the 3CP nematic liquid crystal is of particular interest, because this compound is similar in molecular structure to the well-known and thoroughly studied liquid crystals of the alkylcyanobiphenyl group *n*CB (n = 5–9) [1–5]. The only difference between them lies in the fact that, in the rigid core of the 3CP molecule, one carbon atom in either of the two benzene rings is replaced by a nitrogen atom. Moreover, the number of methylene fragments ($n = 3$) in the alkyl tail of the 3CP molecule is rather small for liquid crystals. The 3CP compound undergoes a phase transition from the solid crystalline state to the nematic liquid-crystal state at $T_0 = 43.5°C$ and a transition from the nematic state to the disordered isotropic liquid state at $T_c = 47.4°C$.

In this work, we experimentally investigated the temperature and frequency dependences of the permittivity, determined the refractive indices, and numerically approximated the dielectric spectra measured for the 5-propyl-2-(*p*-cyanophenyl)-pyridine compound in different phase states over a wide frequency range (f = 1–1000 MHz).

2. EXPERIMENTAL TECHNIQUE

The permittivities in the frequency range 1–30 MHz were measured on a Tesla BM560 standard *Q*-meter with the use of a measuring cell in the form of a parallel-plate capacitor. In the meter and decimeter wavelength ranges, the dielectric measurements were performed with specially devised high-sensitive sensors based on microstrip resonators of a ring type [6]. The small-step tuning of the sensors was carried out using calibrated inductors and electrically controlled capacitors (varactors), which were connected in series with the strip conductor in the antinodal region of a microwave magnetic field for the first oscillation mode of the microstrip resonator [7]. A capacitive measuring cell fabricated in the form of an interdigitation with a gap of 150 μm was placed at the antinode of a microwave electric field of the resonator. A liquid-crystal sample 200 μm thick was positioned on the interdigitation bounded by a glass border. The sample was shielded from contamination by a fluoroplastic film. The sensor

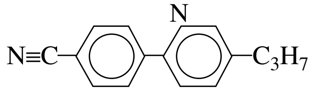

Fig. 1. Structural formula of the 5-propyl-2-(*p*-cyanophenyl)-pyridine liquid-crystal compound.

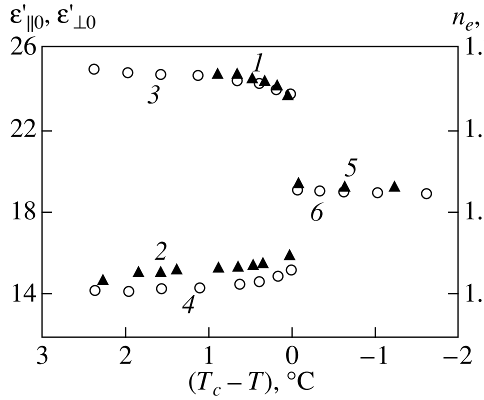

Fig. 2. Temperature dependences of the optical (closed symbols) and dielectric (open symbols) parameters for the 3CP liquid crystal in the temperature range of the transition from the nematic phase to the isotropic liquid phase.

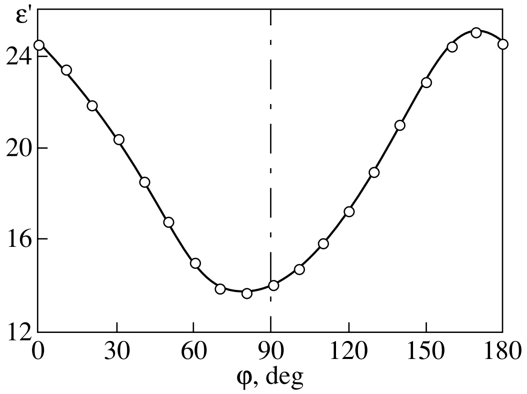

Fig. 3. Dependence of the permittivity of the 3CP liquid crystal on the angle between the director of molecules and the direction of the microwave pump field.

design made it possible to measure the dielectric spectra with a high accuracy despite the relatively small volume of the studied sample.

The real permittivities ε' were determined according to a standard technique, i.e., by measuring the difference in the resonance frequencies of the sensors with and without the sample. The imaginary permittivities ε" were calculated from the change in the loaded Q-factor of the resonator after the liquid-crystal sample was placed in it. The amplitude–frequency characteristics of the microstrip sensors were recorded on an R4-37 automated meter intended for measuring complex transmission gain factors. The absolute errors in determining the dielectric characteristics were no larger than δε' ~ 0.05 and δε" ~ 0.1. The required angle φ between the long axes of molecules in the 3CP sample and the direction of the microwave electric field in the measuring cell was specified by the appropriate direction of the static magnetic field H = 2500 Oe. The measurements were performed in a thermostat in the temperature range 0–50°C. The temperature was maintained accurate to ±0.1 K.

The temperature dependences of the ordinary (n_0) and extraordinary (n_e) refractive indices were measured at the wavelength λ = 0.589 μm with the use of an IRF-454B refractometer with a homeotropic orientation of the director in the measuring cell.

3. RESULTS AND DISCUSSION

The experimental temperature dependences of the ordinary n_0 (closed symbols *1*) and extraordinary n_e (closed symbols *2*) refractive indices are depicted in Fig. 2. This figure also shows the temperature dependences of the real parts of the longitudinal $\varepsilon'_{\parallel}$ (open symbols *3*) and transverse $\varepsilon'_{\perp}$ (open symbols *4*) permittivities, which were measured in parallel and perpendicular orientations of the liquid-crystal director with respect to the electric pump field. The heating rate of the studied sample was approximately equal to 4 K/h. The permittivities were measured at the pump frequency f = 1 MHz, at which the frequency dispersion does not manifest itself. In actual fact, the permittivities thus obtained are close to the static permittivities $\varepsilon'_{\parallel 0}$ and $\varepsilon'_{\perp 0}$. As could be expected, the optical and dielectric parameters exhibit a jump at the nematic–isotropic transition temperature ($T_c - T = 0$) of the liquid crystal. It is worth noting that the measured parameters only slightly depend on the temperature in both the nematic (curves *1*–*4*) and isotropic (curves *5*, *6*) phases.

Figure 3 shows the dependence of the real permittivity of the studied sample in the nematic phase on the angle between the direction of the static magnetic field **H** orienting the liquid-crystal molecules and the direction of the microwave electric field. This dependence was also measured at the pump frequency f = 1 MHz, which lies outside the frequency dispersion region of the sample. As is clearly seen, the dependence depicted in Fig. 3 is asymmetric about the vertical line passing through the point φ = 90°. At this angle, the long axes of the 3CP molecules are perpendicular to the pump field. Most likely, the observed asymmetry of the dependence ε'(φ) indicates that the dipole moment μ of the molecule deviates from the long molecular axis. The deviation angle can be easily calculated from the shift in the minimum of the curve ε'(φ) with respect to 90°. This angle is determined to be β ≈ 15°.

Judging from the sufficiently high values of the static permittivities ($\varepsilon'_{\parallel 0} \approx 25$ and $\varepsilon'_{\perp 0} \approx 14.4$) and the dielectric anisotropy ($\Delta\varepsilon' = \varepsilon'_{\parallel 0} - \varepsilon'_{\perp 0} = 11.4$) of the studied sample, the 3CP molecules possess a relatively large dipole moment. It is well known [1–4] that, for all homologs (n = 5–9) of the liquid crystals belonging to the alkylcyanobiphenyl group nCB, in which the dipole moment (μ = 4.3 D) is associated with the –C≡N cyano group, the dielectric parameters, as a rule, do not

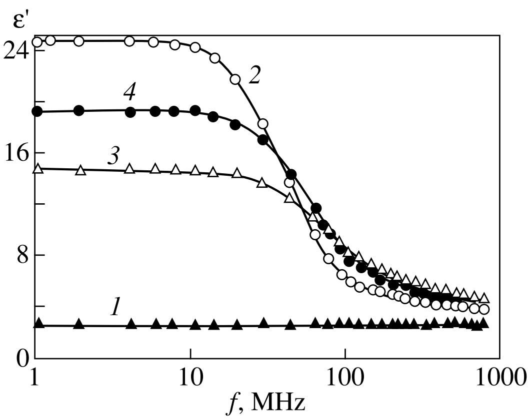

Fig. 4. Frequency dependences of the permittivity of the 3CP liquid crystal measured at different temperatures. T = (*1*) 0, (*2, 3*) 45, and (*4*) 49°C.

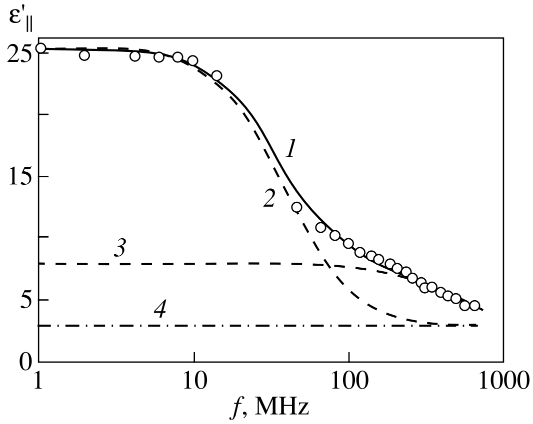

Fig. 5. Numerical approximation of the frequency dependence of the longitudinal permittivity by the sum of two Debye processes with different relaxation times.

exceed $\varepsilon'_{\parallel 0}$ = 15–17, $\varepsilon'_{\perp 0}$ = 6–8, and $\Delta\varepsilon'$ = 8–9 in the temperature range $+1 < (T_c - T) < +5$°C. From the aforesaid it follows that, owing to the presence of the pyridine ring in molecules of the 3CP liquid crystal, the dipole moment of the 3CP molecule is 40–50% larger than that of the molecules of the alkylcyanobiphenyl liquid crystals.

The frequency dependences of the real permittivity for the 3CP sample in different states of the mesophase are shown in Fig. 4. Curve *1* was measured at T = 0°C, when the sample was in the solid crystalline state. Curves *2* and *3* represent the frequency dependences of the permittivities $\varepsilon'_{\parallel}$ and $\varepsilon'_{\perp}$, respectively, which were measured for the sample at T = 45°C in the nematic liquid-crystal state. Curve *4* was recorded at T = 49°C, when the sample was in the isotropic state. It can be seen that, in the solid phase, the dispersion is virtually absent and the permittivity is estimated as $\varepsilon'_s = 2.63 \pm 0.02$. It is interesting to note that this permittivity coincides very closely with the square of the refractive index $n_{\text{is}}^2 = 2.624$ for the high-temperature isotropic liquid phase of the 3CP liquid crystal. This indicates that, in the solid crystalline phase, the orientational contribution from the rotation of the dipole moment to the permittivity is absent and the observed value of ε'_s can be associated with the quick-response processes of displacement of intramolecular electric charges.

In order to describe the frequency dispersion of the longitudinal (parallel) $\varepsilon'_{\parallel}(f)$ and transverse (perpendicular) $\varepsilon'_{\perp}(f)$ permittivities of the 3CP sample in the nematic phase, we used different approaches. The longitudinal permittivity was approximated with due regard for the fact that the dipole moment of the molecule deviates from the long molecular axis through the angle β. According to the universally accepted concepts regarding the possible mechanisms of dielectric polarization in liquid crystals [1–4, 8], the dispersion can be approximated by the sum of two Debye processes with different relaxation times [9]; that is,

$$\varepsilon'_{\parallel}(f) - n_e^2 = \frac{(\varepsilon'_{\parallel 0} - n_e^2)g_1}{1 + \omega^2\tau_{\parallel 1}^2} + \frac{(\varepsilon'_{\parallel 0} - n_e^2)g_2}{1 + \omega^2\tau_{\parallel 2}^2}, \qquad (1)$$

where n_e is the extraordinary refractive index, $\varepsilon'_{\parallel 0}$ is the static permittivity, $\omega = 2\pi f$, $\tau_{\parallel 1}$ and $\tau_{\parallel 2}$ are the relaxation times of two processes, and g_1 and g_2 are the weighting factors corresponding to these processes ($g_1 + g_2 = 1$).

The occurrence of two relaxation processes in the liquid crystal under investigation can be explained, in particular, by the misalignment of the dipole moment μ and the long axis of the liquid-crystal molecule. As a result, the longitudinal permittivity contains a contribution from the transverse component of the dipole moment μ and vice versa. Curve *1* in Fig. 5 represents the results of the numerical approximation performed for the experimental spectrum $\varepsilon'_{\parallel}(f)$ according to relationship (1). This curve is plotted for the following parameters of the liquid crystal: $\varepsilon'_{\parallel 0} = 25.2$, $\tau_{\parallel 1} = 5 \times 10^{-9}$ s, $\tau_{\parallel 2} = 3.8 \times 10^{-10}$ s, $n_e = 1.7$, $g_1 = 0.78$, and $g_2 = 0.22$.

As can be seen from Fig. 5, the frequency dependence of the longitudinal permittivity calculated within the proposed approximation is in good agreement with the experimental data over the entire frequency range covered. Dashed line *2* in Fig. 5 corresponds to the dispersion calculated at weighting factors $g_1 = 1$ and $g_2 = 0$ and fits the experimental data well only in the low-frequency dispersion region. Dashed line *3* represents the frequency dependence obtained at $g_1 = 0.78$ and $g_2 = 0.22$, which, by contrast, agrees reasonably with the experimental data only in the high-frequency dispersion region. Dot-dashed line *4* indicates the n_e^2 value to

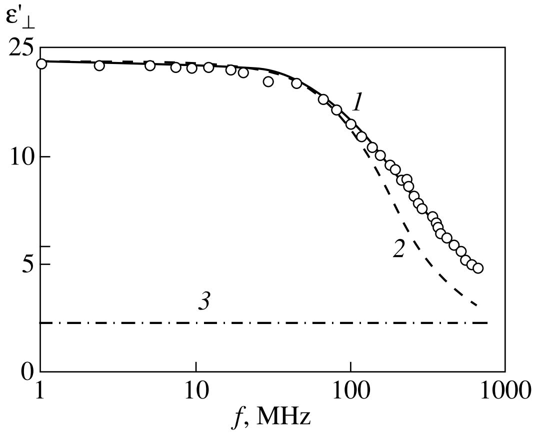

Fig. 6. Approximation of the frequency dependence of the transverse permittivity in terms of the Debye relaxation process with a continuous distribution of relaxation times.

which the longitudinal permittivity of the 3CP liquid crystal tends when $f \longrightarrow \infty$.

It should be noted that the relaxation times $\tau_{\parallel 1}$ and $\tau_{\parallel 2}$ characterize the dipole relaxation upon rotation of the molecule about the short and long axes. The ratio of the weighting factors g_2/g_1 is equal to the tangent of the angle β between the dipole moment and the long axis of the molecule. In our case, we have $\beta = 15.7°$. As can be seen, this value agrees closely with the angle $\beta \approx 15°$, which was determined from the experimental angular dependences of the permittivity (Fig. 3).

Let us now consider the transverse permittivity of liquid crystals whose relaxation frequency upon perpendicular pumping is higher than that upon parallel pumping. Under these conditions, the approximation of the transverse permittivity by one Debye relaxation process or even the sum of two Debye processes, as a rule, offers poor agreement with the experimental data. It can be seen from Fig. 6 that an increase in the frequency leads to an increase in the discrepancy between the experimental spectrum $\varepsilon'_\perp(f)$ (points in Fig. 6) and the Debye dependence with one relaxation time (dashed line *2*). This allows us to assume that small-scale vibrations of mobile alkyl groups in liquid-crystal molecules manifest themselves at high frequencies. In this situation, the dielectric relaxation times can be conveniently represented in the form of a continuous distribution in a specified time range. On this basis, the dielectric spectrum can be described by the expression [9]

$$\varepsilon'_\perp(f) - n_0^2 = (\varepsilon'_{\perp 0} - n_0^2)\int_0^\infty \frac{G(\tau)}{1 + (2\pi f\tau)^2}d\tau, \qquad (2)$$

where n_0 is the ordinary refractive index and $G(\tau)$ is the distribution function of relaxation times. In our case, the frequency dependence $\varepsilon'_\perp(f)$ was approximated by the Fröhlich distribution function [10], which is conveniently used in practical calculations; that is,

$$\begin{aligned} G(\tau) &= \frac{kT}{u_0}\frac{1}{\tau}, \quad \tau_0 \le \tau \le \tau_1 = \tau_0\exp(u_0/kT), \\ G(\tau) &= 0, \quad \tau_1 \le \tau \le \tau_0, \end{aligned} \qquad (3)$$

where u_0 is the boundary energy, which determines the range of uniform height distribution of the potential barriers of dipoles: $0 \le \delta u \le u_0$. The specific feature of the distribution function (3) is that it depends on the temperature. Since the relative width $(\tau_1 - \tau_0)/\tau_0$ of the relaxation time distribution decreases with an increase in the temperature, this dependence can be represented in the form

$$\frac{\tau_1 - \tau_0}{\tau_0} = \exp(u_0/kT) - 1. \qquad (4)$$

Next, we take the integral in expression (2) from τ_0 to τ_1 with due regard for the distribution function (3). As a result, the frequency dependence of the real part of the transverse permittivity has the form

$$\begin{aligned} \varepsilon'_\perp(f) - n_0^2 &= (\varepsilon'_{\perp 0} - n_0^2) \\ &\times \left[1 - \frac{kT}{2u_0}\ln\left(\frac{1 + \omega^2\tau_0^2\exp(2u_0/kT)}{1 + \omega^2\tau_0^2}\right)\right]. \end{aligned} \qquad (5)$$

The results of the numerical approximation carried out according to formula (5) are shown by curve *1* in Fig. 6. This curve almost coincides with the experimental points. Dot-dashed line *3* in Fig. 6 indicates the n_0^2 level to which the transverse permittivity of the liquid crystal tends when $f \longrightarrow \infty$. Curve *1* is constructed for the following parameters: $\varepsilon'_{\perp 0} = 14.4$, $T = 318$ K, $u_0 = 1.52 \times 10^{-14}$ erg, $n_0 = 1.55$, $\tau_0 = 1.85 \times 10^{-10}$ s, and $\tau_1 = 2.39 \times 10^{-9}$ s. Note that, in this case, the relative width of the continuous distribution of relaxation times appears to be comparatively small: $(\tau_1 - \tau_0)/\tau_0 \approx 10$. However, the results obtained should be treated as tentative because, in the present work, the dielectric measurements were performed in an insufficiently wide range of frequencies. In order to refine the parameters of the approximation, it is necessary to use the experimental data obtained over the entire dispersion region. Moreover, as follows from the experimental results, the dielectric spectra of liquid crystals in the high-frequency dispersion region can exhibit resonance features [11], which should also be taken into account when approximating the spectra $\varepsilon'(f)$ [12]. It should be noted that curve *2* in Fig. 6 is plotted according to the Debye equation with one relaxation time $\tau_D = 9 \times 10^{-10}$ s, which approximately corresponds to the midpoint of the range $(\tau_1 - \tau_0)$.

The frequency dependence of the permittivity for the 3CP liquid crystal in the disordered isotropic phase was also approximated on the basis of relationships (2) and (3), because it is quite reasonable that the isotropic phase is characterized by a continuous distribution of relaxation times. The excellent agreement between the calculated and experimental data was achieved with the following parameters for the liquid crystal in the isotropic phase: $\varepsilon'_{0\mathrm{is}} = 19.3$, $T = 322$ K, $u_0 = 2.28 \times 10^{-13}$ erg, $n_i = 1.6$, $\tau_0 = 2.1 \times 10^{-10}$ s, and $\tau_1 = 6.12 \times 10^{-9}$ s. A comparison of these parameters with those for the 3CP liquid-crystal compound in the nematic phase shows that the energy u_0 increases by one order of magnitude and that the upper limit of the relaxation time range changes significantly. As a result, the relative width $(\tau_1 - \tau_0)/\tau_0$ increases by a factor of more than two.

4. CONCLUSIONS

Thus, the permittivities of the 5-propyl-2-(*p*-cyanophenyl)-pyridine liquid-crystal compound in different phase states were measured over wide ranges of frequencies and temperatures. It was found that the dipole moment of the 3CP molecule significantly deviates from the long molecular axis. The deviation angle was determined to be $\beta \approx 15°$. It was demonstrated that the frequency dependence of the longitudinal permittivity $\varepsilon'_{\parallel}(f)$ for the 3CP liquid crystal in the nematic phase is adequately described by the sum of two Debye processes with different relaxation times. However, when approximating the transverse permittivity $\varepsilon'_{\perp}(f)$ in the nematic phase and the permittivity $\varepsilon'_{\mathrm{is}}(f)$ in the isotropic phase of the 3CP compound, the Debye formulas should account for the continuous distribution of relaxation times in a specified time range. It was revealed that the temperature dependences of the static permittivities are similar to those of the refractive indices in the temperature range of the phase transition from the nematic liquid crystal to the isotropic liquid.

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