
POLYMERS
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Dielectric Properties of Liquid Crystals of the Cyano Derivative Compounds with Different Fragments in the Molecular Core

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Abstract—This paper reports on the results of investigations into the influence of variations in the chemical composition of the aromatic core of cyano-containing molecules of liquid crystals on their dielectric properties in the frequency range 1–2000 MHz. It is shown that the dispersion of the longitudinal permittivity is adequately described by the sum of two Debye processes with different weighting factors and relaxation times. The frequency dependence of the transverse permittivity is well approximated by the Debye process with a continuous distribution of relaxation times in a specified range. It is established that the replacement of one benzene ring in the biphenyl core of the 5CB liquid-crystal molecule by a cyclohexane (or bicyclooctane) fragment leads to a considerable decrease in both relaxation times for the longitudinal permittivity, a change in the low-frequency limit of the relaxation time range for the transverse permittivity, and the evolution of the frequency dependence of the dielectric anisotropy. © 2004 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

Investigation into the influence of the chemical composition and structure of molecules of liquid crystals belonging to a homologous series on the dispersion of the permittivity makes it possible to elucidate the nature of relaxation processes, to explain the origin of specific features observed in the dielectric spectra, and to reveal a correlation between the physical characteristics and microscopic parameters. For example, in our earlier works [1–3], the dispersion of the longitudinal and transverse high-frequency permittivities of liquid crystals of the alkylcyanobiphenyl group n CB was studied as a function of the length of the alkyl tail ($n = 5–8$). The results of those investigations enabled us to separate the contributions of the motions of rigid and flexible molecular fragments and to assign them to the specific features observed in the dielectric spectra. In particular, it was demonstrated that, apart from the conventional Debye relaxation of molecules, the dielectric spectra of liquid crystals in the high-frequency range are characterized by the resonance dispersion regions associated with intramolecular motions of the alkyl fragments. Liquid crystals of the homologous series of alkylcyanobiphenyls n CB, alkyloxycyanobiphenyls n OCB, and cyclohexane derivatives were examined using dielectric methods in [4, 5]. Dunmur and Tomes [4] and Urban *et al.* [5] investigated how the chemical composition of the rigid core of molecules affects the dipole moment, order parameter, activation enthalpy, Debye relaxation time, and the retardation factors of molecular motion introduced in the framework of the Mayer–Meyer theory of dielectric relaxation. A number of authors (see, for example, [6, 7]) analyzed the changes in the molecular packing coefficients and rheo-

logical parameters of cyano-containing liquid crystals due to the replacement of one benzene fragment in the rigid core of the liquid-crystal molecules by other fragments.

The aim of the present work was to measure the frequency dependences of the permittivity of cyano-containing liquid crystals, to approximate these dependences numerically, and to compare the temperature dependences of the permittivities and refractive indices. For this purpose, we used the following nematic liquid crystals: 4- n -pentyl-4-cyanobiphenyl (5CB), *trans*-4-pentyl-(4-cyanophenyl)-cyclohexane (5PCH), and 4-(4'-pentyl-bicyclo[2.2.2]octane)-phenyl (5BCO). The structural formulas of the liquid-crystal molecules under investigation and the temperatures T_c of phase transitions of the liquid crystals from a nematic liquid-crystal state to an isotropic liquid state are presented in Fig. 1. These molecules differ from each other only in the chemical composition of the aromatic core. Specifically, one benzene fragment in the aromatic core of the 5PCH and 5BCO molecules is replaced by the cyclohexane and bicyclooctane fragments, respectively. However, the lengths of the alkyl tails are identical in all the molecules studied. It should be noted that, in this work, the dielectric spectra were measured for the first time over a wide frequency range ($f = 1–2000$ MHz), including the poorly studied high-frequency range of dielectric relaxation.

2. EXPERIMENTAL TECHNIQUE

The permittivities of the liquid-crystal samples in the frequency range 1–30 MHz were measured on a Tesla BM-560 standard Q-meter with the use of a mea-

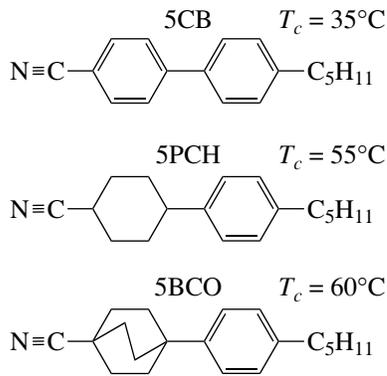


Fig. 1. Structural formulas of the liquid-crystal compound and temperatures T_c of the transition from the nematic phase to the isotropic liquid phase.

suring cell in the form of a parallel-plate capacitor. In the meter and decimeter wavelength ranges, the dielectric measurements were performed with specially devised highly sensitive frequency-tuned sensors based on ring-type microstrip resonators [2].

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 relaxation of the liquid-crystal sample placed in it. The amplitude–frequency characteristics of the microstrip sensors were recorded on R4-37 and R4-38 automated meters intended for measuring complex transmission gain factors. The absolute errors in determining the dielectric characteristics were no larger than $\delta\epsilon' \sim 0.05$ and $\delta\epsilon'' \sim 0.1$. The orientation of the long axes of molecules in the studied samples with respect to the polarization of a microwave electric pump field was provided by a static magnetic field $H = 2500$ Oe. The measurements were performed in a thermostat in the temperature range 0 – 95°C . The temperature was maintained accurate to $\pm 0.5^\circ\text{C}$.

The numerical approximation of the dielectric spectra required knowledge of the ordinary (n_o) and extraordinary (n_e) refractive indices. These data for the 5CB and 5BCO liquid crystals were taken from [8, 9]. The ordinary and extraordinary refractive indices for the 5PCH liquid crystal were measured at the wavelength $\lambda = 0.589 \mu\text{m}$ with the use of an IRF-454B standard refractometer with a homeotropic orientation of the director in the measuring cell.

3. RESULTS AND DISCUSSION

The experimental temperature dependences of the extraordinary n_e (closed symbols 1) and ordinary n_o (closed symbols 2) refractive indices of the 5PCH liquid crystal are depicted in Fig. 2. This figure also shows the temperature dependences of the real parts of the

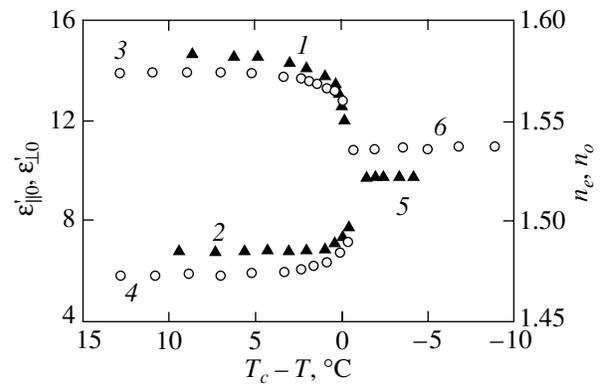


Fig. 2. Temperature dependences of the optical n_e and n_o (closed symbols) and dielectric $\epsilon'_{||0}$ and $\epsilon'_{\perp 0}$ (open symbols) parameters for the 5PCH liquid crystal in the temperature range of the transition from the nematic phase to the isotropic liquid phase (for explanation of the curves, see text).

longitudinal $\epsilon'_{||}$ (open symbols 3) and transverse ϵ'_{\perp} (open symbols 4) permittivities, which were measured in parallel and perpendicular orientations of the liquid-crystal director with respect to the polarization of the ac electric field. The temperature dependences of the refractive index and the permittivity of the 5PCH liquid crystal in the isotropic phase are shown by symbols 5 and 6, respectively. The heating rate of the studied sample was approximately equal to 5 K/h. In this experiment, the permittivities were measured at a pump frequency $f = 1$ MHz, at which the frequency dispersion does not manifest itself. Consequently, the dielectric characteristics thus obtained are close to the static permittivities $\epsilon'_{||0}$ and $\epsilon'_{\perp 0}$. It can be seen from Fig. 2 that, except for the phase transition range, the measured parameters only slightly depend on the temperature in both the nematic ($T < T_c$) and isotropic ($T > T_c$) phases of the liquid-crystal compound.

All the dielectric spectra of the liquid crystals studied were measured in the nematic phase at a temperature $T = T_c - 5^\circ\text{C}$. Figure 3 shows the frequency dependences of the real parts of the longitudinal $\epsilon'_{||}(f)$ and transverse $\epsilon'_{\perp}(f)$ permittivities and the frequency dependences of the imaginary parts of $\epsilon''_{||}(f)$ and $\epsilon''_{\perp}(f)$ for three liquid crystals. In this figure, solid lines represent the results of the numerical approximation of the experimental dependences of the real parts of the longitudinal and transverse permittivities.

The frequency dependences of the longitudinal permittivity were approximated as follows. In our previous work [2], we showed that the frequency dependence of the longitudinal permittivity $\epsilon'_{||}(f)$ over a wide range of frequencies can be correctly approximated using the

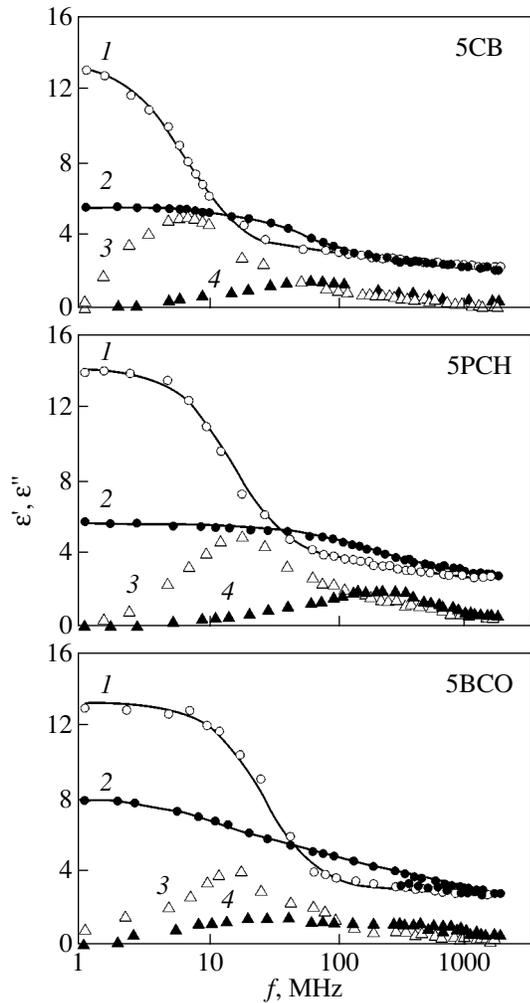


Fig. 3. Frequency dependences of the (1, 2) real and (3, 4) imaginary parts of the (1, 3) longitudinal and (2, 4) transverse permittivities of the liquid crystals. Solid lines correspond to the Debye approximations.

sum of two Debye processes with different relaxation times; that is,

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

Table 1. Main characteristics of the liquid crystals under investigation for parallel orientations of the liquid-crystal director with respect to the microwave electric pump field

Liquid crystal	$\tau_{\parallel 1}$, 10^{-9} s	$\tau_{\parallel 2}$, 10^{-10} s	ΔH , kJ/mol	$\varepsilon'_{\parallel 0}$	$\varepsilon'_{\parallel \infty}$	n_e^2
5CB	24–25	6–7	66.7	16.4	3.13	3.13
5PCH	9–9.5	3–4	71.5	14.0	2.69	2.53
5BCO	6–6.5	0.9–1.0	92	13.2	2.49	2.49

Here, 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 the two Debye processes, and g_1 and g_2 are the weighting factors corresponding to these processes ($g_1 + g_2 = 1$). It should be noted that, for all the studied samples, the best agreement between the results of the numerical approximation and the experimental points was achieved with weighting factors $g_1 \approx 0.92$ and $g_2 \approx 0.08$. Table 1 presents the relaxation times $\tau_{\parallel 1}$ and $\tau_{\parallel 2}$, which characterize the dipole relaxation upon rotation of the liquid-crystal molecules about the short and long molecular axes, respectively. This table also lists the molar activation enthalpies ΔH obtained by numerical processing of the dielectric spectra measured at three different temperatures: $T_1 = T_c - 5^\circ\text{C}$, $T_2 = T_c - 10^\circ\text{C}$, and $T_3 = T_c - 15^\circ\text{C}$. The activation enthalpy ΔH was determined from the temperature-dependent relaxation time $\tau_{\parallel 1}$ according to the Bauer equation [10]:

$$\tau_{\parallel 1} = \left(\frac{2\pi I}{k_B T}\right)^{1/2} \exp\left(\frac{-\Delta S}{R}\right) \exp\left(\frac{\Delta H}{RT}\right), \quad (2)$$

where ΔS and ΔH are the molar activation entropy and the molar activation enthalpy of the dipole reorientation, respectively; I is the moment of inertia of the molecule; R is the gas constant; k_B is the Boltzmann constant; and T is the absolute temperature. The exact value of the moment of inertia I for the liquid crystals studied is unknown. However, according to estimates [10, 11], we have $I \sim (1-3) \times 10^{-43}$ kg m² and $\Delta S \sim 100-135$ kJ/mol.

It can be seen from Table 1 that the activation enthalpy ΔH characterizing the reorientation of molecules about the short axis monotonically increases in the series 5CB–5PCH–5BCO. Our results are in good agreement with the data obtained by Urban *et al.* [5] for 5CB and 5PCH liquid crystals. The observed increase in the activation enthalpy ΔH can be explained by the increase in the molecular packing coefficient due to an increase in the size of the molecular core [11].

An analysis demonstrated that the shorter time of longitudinal relaxation $\tau_{\parallel 2}$ is virtually temperature-independent in the temperature range under investigation and proves to be shortest for the 5BCO liquid crystal (Table 1). As can be seen from Table 1, the quantities n_e^2 and $\varepsilon'_{\parallel \infty}$ determined from the frequency dependences of the permittivities are in excellent agreement.

Thus, the approximation approach proposed in our earlier work [2] offers reasonable agreement between the calculated frequency dependence of the longitudinal permittivity and the experimental data for all the liquid-crystal samples over the entire frequency range covered.

As was shown in [2], the transverse permittivity $\varepsilon'_{\perp}(f)$ should be approximated using a dispersion relation with a continuous distribution of relaxation times in a specified range. In the general case, when the relax-

ator times are distributed in the range from 0 to ∞ , the Debye dispersion relation has the form

$$\varepsilon_{\perp}'(f) - n_o^2 = (\varepsilon_{\perp 0}' - n_o^2) \int_0^{\infty} \frac{G(\tau)}{1 + (2\pi f\tau)^2} d\tau, \quad (3)$$

where n_o is the ordinary refractive index and $G(\tau)$ is the distribution function of relaxation times. The function $G(\tau)$ describes the motion of large- and small-sized molecular aggregates and individual molecules and also small-scale intramolecular motions associated, for example, with vibrations of mobile molecular fragments of the alkyl tails.

The necessity of applying the above approach to the approximation of the transverse permittivity $\varepsilon_{\perp}'(f)$ stems from the fact that, for all the liquid crystals under investigation, the frequency dependences of the transverse permittivity differ from the Debye behavior. As a consequence, the approximation of the dispersion of the transverse permittivity by the sum of two or even three Debye processes with different relaxation times, as a rule, leads to poor agreement with the experimental data. To put it differently, unlike parallel pumping, perpendicular pumping (perpendicular orientation of the polarization of the microwave electric field with respect to the director of molecules) ensures efficient excitation of various intramolecular motions with a continuous distribution of relaxation times in a specified range from $\tau_{\perp L}$ to $\tau_{\perp R}$.

For liquid crystals, the distribution function $G(\tau)$ and the range of its definition are unknown. In this work, the frequency dependence of the transverse permittivity $\varepsilon_{\perp}'(f)$ was approximated using two different functions $G(\tau)$. The first function $G(\tau)$ is a symmetric function describing the uniform distribution of relaxators in the range $\tau_{\perp L} - \tau_{\perp R}$. Upon substitution of this function into relation (3), we obtain the analytical expression [12]

$$\varepsilon'(\omega) = \frac{\varepsilon_0 - \varepsilon_{\infty}}{2 \ln a} \ln \frac{a^2 + k^2}{1 + k^2}, \quad (4)$$

where $a = \tau_{\perp L}/\tau_{\perp R}$ and $k = \omega\tau_{\perp L}$. By applying the numerical method for expression (4), it is easy to determine the limits $\tau_{\perp L}$ and $\tau_{\perp R}$ of the relaxation time range for each liquid crystal that provide the best agreement between the results of the chosen approximation and the experimental data over the entire frequency range. An analysis of the dependences $\varepsilon_{\perp}'(f)$ thus obtained (see Fig. 3, curves 2) demonstrates that this approach offers an adequate description of the relaxation processes in the studied liquid crystals for perpendicular orientations of the director of liquid-crystal molecules with respect to the polarization of the electric pump field. It should be noted that intramolecular motions can substantially affect the permittivity $\varepsilon_{\perp}'(f)$, starting from the orientational dispersion region up to frequen-

Table 2. Main characteristics of the liquid crystals for perpendicular orientations of the liquid-crystal director with respect to the microwave electric pump field

Liquid crystal	$\tau_{\perp L}$ 10 ⁻⁹ s	$\tau_{\perp R}$ 10 ⁻¹¹ s	$\tau_{\perp \varepsilon''}$ 10 ⁻¹⁰ s	p	Δn	n_o^2
5CB	9–10	2–6	3.5	0.4–0.45	0.245	2.325
5PCH	6–8	1–4	4.5	0.2–0.25	0.1	2.22
5BCO	25–30	4–9	6.4	0.05–0.1	0.08	2.25

cies in the infrared region. Hence, it is reasonable to assume that relaxators can make different contributions to the permittivity over such a wide range of frequencies. In this respect, it is of interest to compare the results of the above approximation with the data obtained for the following asymmetric distribution function of relaxation times [13]:

$$G(\tau) = \frac{1}{A} \left(\frac{1}{\tau^{1-p}} \right), \quad \tau_{\perp R} \leq \tau \leq \tau_{\perp L}, \quad (5)$$

$$G(\tau) = 0, \quad \tau_{\perp R} > \tau > \tau_{\perp L},$$

where p is the asymmetry parameter ($0 \leq p < 1$) and A is a numerically determined coefficient. The calculations demonstrate that the frequency dependences of the permittivity thus approximated almost coincide with those obtained for the symmetric uniform distribution function of relaxation times in the range $\tau_{\perp L} - \tau_{\perp R}$. Moreover, even the limits of the relaxation time range, i.e., $\tau_{\perp L}$ and $\tau_{\perp R}$, which are calculated within the above approximations also nearly coincide with each other. The numerical values of these limits for the liquid crystals under investigation are given in Table 2. This table also presents the relaxation times $\tau_{\perp \varepsilon''}$ corresponding to the transverse permittivity ε_{\perp}'' at the maximum, the asymmetry parameters p of distribution function (5), the optical anisotropies $\Delta n = n_e - n_o$, and the ordinary refractive indices squared n_o^2 .

It follows from Table 2 that, in the series 5CB–5PCH–5BCO, the limits of the relaxation time range vary insignificantly, except in the lower relaxation limit for the 5BCO liquid crystal. It is quite possible that, owing to the large molecular packing coefficient of the 5BCO liquid crystal, the rotation of molecules about the long axis is retarded as the result of stronger intermolecular interactions associated either with the aromatic cores or with the alkyl tails.

The distinctive feature of the dielectric spectrum of the 5CB liquid crystal is that the frequency dependence of the transverse permittivity in the high-frequency range significantly deviates from the Debye behavior. The dependence $\varepsilon_{\perp}'(f)$ for this liquid crystal can be satisfactorily approximated using the asymmetric distribution function (5) with a sufficiently large asymmetry parameter ($p = 0.40 - 0.45$). The dispersion of the trans-

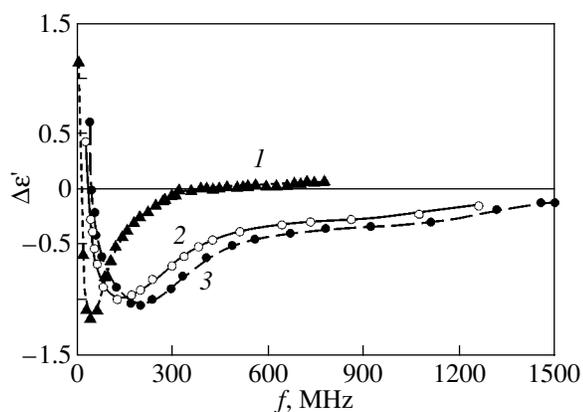


Fig. 4. Frequency dependences of the dielectric anisotropy for (1) 5CB, (2) 5PCH, and (3) 5BCO liquid crystals.

verse permittivity of the 5CB liquid crystal leads to double inversion of the sign of the dielectric anisotropy $\Delta\epsilon' = \epsilon'_{\parallel} - \epsilon'_{\perp}$ in the frequency range $\sim 350\text{--}450$ MHz. The dependences $\Delta\epsilon'(f)$ in the high-frequency relaxation region for all the liquid crystals studied are plotted in Fig. 4. As can be seen, the frequency range of negative dielectric anisotropies for the 5CB liquid crystal is considerably narrower than that for the cyclohexane and bicyclooctane homologs. As the frequency increases, the dielectric anisotropy of the 5PCH and 5BCO liquid crystals monotonically tends to zero. For these samples, zero dielectric anisotropy should be observed in the high-frequency range $f > 2000$ MHz. This behavior can be explained by the appreciable decrease in the optical anisotropy (Table 2), which the dielectric anisotropy approaches.

4. CONCLUSIONS

Thus, the permittivities of liquid crystals of the cyano derivative compounds based on alkylcyanobiphenyl (5CB), in which one benzene ring in the biphenyl core of the molecule is replaced by a cyclohexane or bicyclooctane fragment, were measured over a wide range of frequencies. It was demonstrated that the frequency dependence of the longitudinal permittivity $\epsilon'_{\parallel}(f)$ for liquid crystals in the nematic phase is well approximated by the sum of two Debye processes with different relaxation times. It was found that the activation energy determined from the temperature dependence of the longitudinal relaxation time τ_{\parallel} increases in the series 5CB–5PCH–5BCO. The assumption was made that the observed increase in the activation energy is associated with the increase in the molecular packing

coefficient. In the above series, this coefficient is maximum for the 5BCO compound.

It was established that the frequency dependence of the transverse permittivity $\epsilon'_{\perp}(f)$ for liquid crystals in the nematic phase can be well approximated by the Debye dispersion relation with either a symmetric function or an asymmetric function of the continuous distribution of relaxation times in a specified range. It was revealed that the behavior of the dielectric anisotropy of the 5CB liquid crystal in the relaxation region differs from that of the other two compounds under investigation.

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