Physics of the Solid State, Vol. 47, No. 4, 2005, pp. 765–768. Translated from Fizika Tverdogo Tela, Vol. 47, No. 4, 2005, pp. 738–741.
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POLYMERS AND LIQUID CRYSTALS

Temperature Dependence of the Dielectric Characteristics of a 5CB Liquid Crystal within the Relaxation Region

B. A. Belyaev, N. A. Drokin, and V. F. Shabanov

Kirensky Institute of Physics, Siberian Division, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia
e-mail: belyaev@iph.krasn.ru

Received July 19, 2004

Abstract—The temperature dependence of the real part of the permittivity of a 4-*n*-pentyl-4-cyanobiphenyl liquid crystal was studied within a broad frequency range of 30–5000 MHz and in the temperature interval 20–60°C in the vicinity of the nematic–isotropic-liquid phase transition. It was established that the dispersion of the longitudinal component of the permittivity can be fitted well by a sum of two Debye terms with strongly differing relaxation times. The temperature and frequency dependence of the shorter relaxation time was determined for which the best fit between calculations and experiment was achieved. *© 2005 Pleiades Publishing, Inc.*

As is well known, the frequency dispersion and anisotropy of the permittivity of nematic liquid crystals (LCs) is described by the Debye equations, from which one extracts, in particular, the relaxation times associated with molecular rotation about the short and long axes. This description, however, agrees well with experiment only up to the frequencies at which the orientational region of dispersion ends. At higher frequencies, the dielectric spectra of LCs quite frequently exhibit an additional extended interval of dispersion that is connected with various intramolecular motions of alkyl fragments and seen against the background of librations of molecules about the equilibrium position. Particularly strong dispersion at frequencies above the orientational spectral region has been observed for the perpendicular component of permittivity, $\varepsilon'_\perp(\omega)$, in LCs of the *n*-CB series [1–5]. It was shown in [1–5] that the high-frequency part of the permittivity spectrum can be fitted fairly well with a Debye equation in which a continuous distribution of relaxation times within a certain interval is assumed.

The observed frequency dependence of the parallel component of permittivity, $\varepsilon'_\parallel(\omega)$, in the same LC series implies the existence of two separated dispersion regions each of which can be approximated by a Debye equation with its own relaxation time. The resulting dielectric spectrum of the LC can be fitted well by a sum of two Debye terms with different relaxation times and different relative weighted contributions. The two observed regions of dispersion are usually assigned to rotation of molecules about the short axis and about the long axis (low- and high-frequency relaxation, respectively). Both in the nematic and in the isotropic phase, the behavior of the low-frequency relaxation time τ_1 with temperature has been studied sufficiently well and is described by an exponential relation,

$$\tau_1 = \tau_0 \exp(-\Delta H/RT), \tag{1}$$

where τ_0 is the time corresponding to the inverse of the libration frequency, ΔH is the activation enthalpy, R is the gas constant, and T is the absolute temperature. For the nematic phase of the 5CB LC, we have ΔH = 66.3–66.7 kJ/mol, and for the isotropic phase, ΔH = 33.2 kJ/mol [5, 6].

As for the temperature dependence of the high-frequency relaxation time $\tau_2(t)$, determining its character from dielectric spectra in the nematic and isotropic phases is problematic. The problems can be traced in large measure to the difficulties entailed in obtaining dielectric spectra in the microwave frequency range at an accuracy high enough to permit their subsequent approximation. The only thing known presently is that the $\tau_2(t)$ relation is substantially weaker than $\tau_1(t)$.

The present study deals with the behavior of the 5CB LC in the parallel-ordered nematic phase, as well as in the isotropic state, within a broad range of frequencies and temperatures. The resonance technique employed in our study to measure $\varepsilon'(\omega)$ made it possible to accurately determine the temperature and frequency dependences of the permittivity, which were subsequently used to derive the behavior of the relaxation time τ_2 with temperature. To do this, the temperature dependences of $\varepsilon'(\omega)$ were measured in the range 20–60°C at several fixed frequencies in the range 30–5000 MHz. This was followed by numerical approximation of each of these dependences, which permitted us not only to determine the contribution of high-frequency dispersion to the general dielectric spectrum of the LC but also to establish the temperature and frequency dependences of the τ_2 relaxation time.

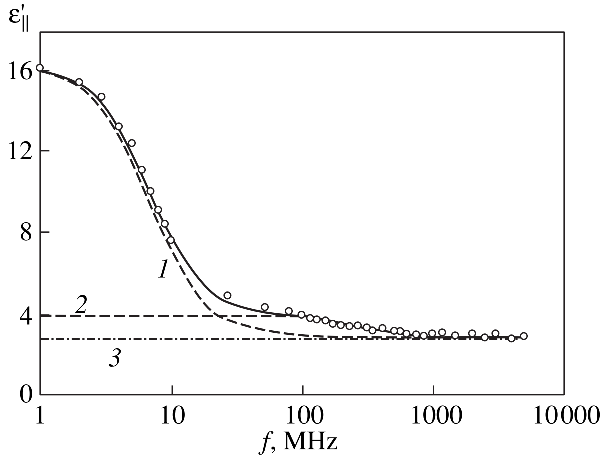

Fig. 1. Dispersion of the parallel permittivity of the 5CB LC at 30°C and its fitting (solid line) with a sum of two Debye terms differing in relaxation time. (*1*, *2*) Debye approximations with one, long or short, relaxation time, respectively, and (*3*) the n^2 level.

High-sensitivity resonance-type microstrip sensors, tuned to fixed frequencies in the above range, were fabricated. The LC was sandwiched between two metallic electrodes of a sensor in a ~100-μm-wide gap. Some design features of the sensors and the measurement technique employed are described in [7]. The absolute accuracy in determining $\varepsilon'(t, \omega)$ was not worse than ±0.02 throughout the frequency and temperature ranges covered. The sensors with LC samples were mounted in a thermostat, with the temperature varied within the range 20–60°C; in each measurement, the temperature was fixed to an accuracy of better than ±0.3°C. The director was oriented with respect to the direction of microwave electric field polarization by means of a dc magnetic field of 3 kOe.

The temperature dependences of the real part of permittivity $\varepsilon'(t)$, measured at fixed frequencies, was numerically fitted, as in [4, 5], using the relation (1)

$$\varepsilon'(t, \omega) - n^2(t) = \frac{\varepsilon'_0(t) - n^2(t)}{1 + \omega^2\tau_1^2(t)}g_1(t) + \frac{\varepsilon'_0(t) - n^2(t)}{1 + \omega^2\tau_2^2(t)}g_2(t), \qquad (2)$$

where $\omega = 2\pi f$; $n(t)$ is the optical refractive index; $\varepsilon'_0(t)$ is the static permittivity; $\tau_1(t)$ and $\tau_2(t)$ are the low- and high-frequency Debye relaxation times, respectively; and $g_1(t)$ and $g_2(t)$ are the respective weighting factors satisfying the condition $g_1 + g_2 = 1$. The temperature dependences of $n(t)$, $\varepsilon'_0(t)$, and $\tau_1(t)$ for the 5CB LC are well known; they were taken from [8, 9]. The $\varepsilon'(t)$ dependence was calculated in the following way. When fitting $\varepsilon'(t)$ in the low-frequency domain (~30–40 MHz), where $(\omega\tau_2)^2 \ll 1$, Eq. (1) was used to find the weighting coefficient $g_2(t)$, which governs the static contribution of the high-frequency permittivity to the resulting spectrum. After this, the values of $\tau_2(t)$ were adjusted numerically in the high-frequency dispersion region to obtain the best fit of the calculation to experiment at all frequencies. The value of the optical permittivity $\varepsilon_\infty = n^2$ was determined at the beginning of the experiment at the highest possible sensor frequency (5 GHz) for the nematic ($n = 1.69$) and isotropic ($n = 1.59$) phases.

To illustrate the validity of this approach in our calculations, we first consider the frequency behavior of the real part of permittivity $\varepsilon'(f)$ of the 5CB LC measured at a fixed sample temperature $t = 30$°C (points in Fig. 1). The solid line is a fit of the dispersion using Eq. (2). Dashed line *1* in Fig. 1 is a numerical fit of the dielectric spectrum for $g_1 = 1$ and $g_2 = 0$. This line is seen to fit well to experiment only in the low-frequency region of dispersion. Dashed line *2* corresponds to fitting with $g_1 = 0$ and $g_2 = 0.08$; this graph, by contrast, agrees fairly well with the experimental data only in the high-frequency region of dispersion. Finally, curve *3* corresponds to $n^2 = 1.69$. The following parameters were used to fit the spectrum of the LC under study at $t = 30$°C: $\varepsilon'_0 = 16.4$, $n = 1.69$, $\tau_1 = 24$ ns, $\tau_2 = 0.7$ ns, $g_1 = 0.92$, and $g_2 = 0.08$. We readily see that the proposed fit reflects the existence of two relaxation processes in the crystal and is fairly close to the experimental data throughout the frequency range covered.

It is important to note that the frequency range was extended to 5000 MHz in measurements of the temperature dependence of the LC dielectric characteristics because of the substantial increase in the relaxation rate that was observed to occur in $\varepsilon'(f)$ spectra with an increase in temperature. The well-known decrease in the permittivity of LCs with an increase in frequency, which gives rise to an increased relative error of ε' measurement, precludes reaching the desired accuracy in fitting the dielectric spectra, which are usually taken at fixed temperatures. As a result, this approach makes it difficult to determine $\tau_2(t)$, and this is why we resorted instead to measuring the temperature dependences of the permittivity of LC samples at fixed frequencies.

Figure 2 displays, by way of illustration, three measured $\varepsilon'(t)$ dependences and their numerical fits for frequencies of 40, 260, and 5000 MHz. The solid lines plot a temperature dependence obtained using Eq. (2), and dashed lines *1* and *2* indicate the contributions to the observed dependence from the first and second terms in Eq. (2), respectively.

First, we consider the $\varepsilon'(t)$ dependence at different frequencies. For 40 MHz, the temperature dependence of ε' is governed primarily by the first term in Eq. (2) and reflects, accordingly, the temperature dependence of $\tau_1(t)$. The second, high-frequency region of ε' dispersion is distant enough (Fig. 1) to permit us to disregard the term $(\omega\tau_2)^2 \ll 1$ in Eq. (2). As a result, using the numerical technique, it is easy to obtain the $g_2(t)$ relation, which, when substituted into Eq. (2), provides the

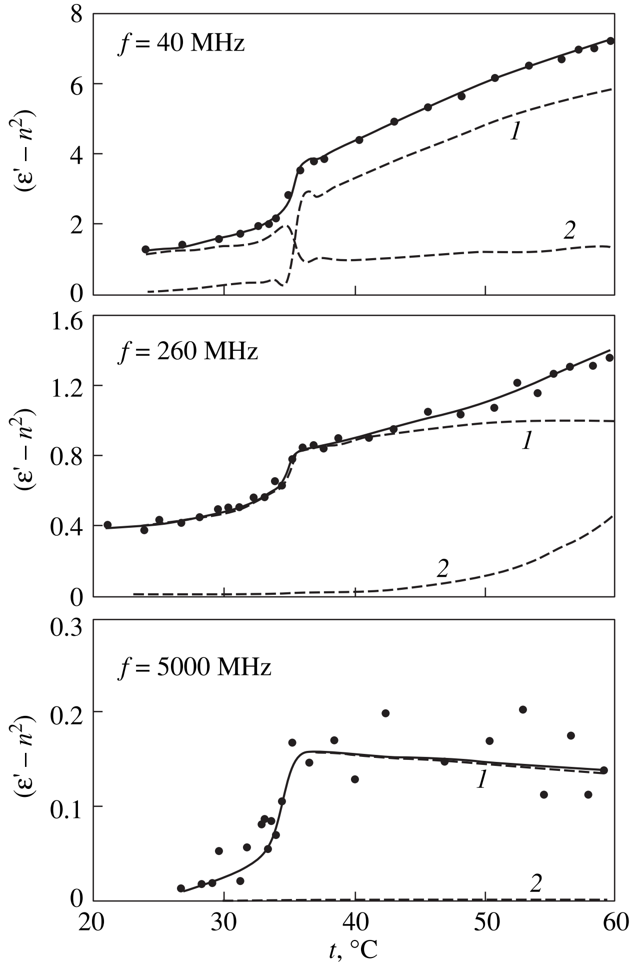

Fig. 2. Temperature dependences of the difference between the permittivity and the square of the refractive index measured at three frequencies. The solid line is a fit to a sum of two Debye terms differing in relaxation time. (*1*, *2*) Debye approximation with one, long or short, relaxation time, respectively.

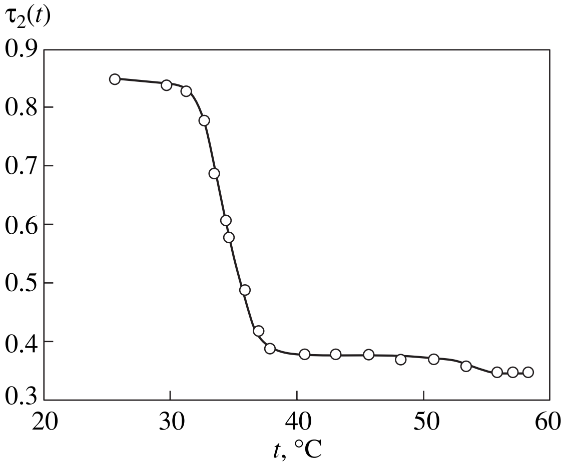

Fig. 3. Temperature dependence of the second (high-frequency) relaxation time measured at a frequency f = 260 MHz.

best fit to the experimental data. As the region of high-frequency dispersion is approached with increasing frequency (for instance, for the $\varepsilon'(t)$ relation measured at a frequency of 260 MHz), we see that the temperature dependence of $\varepsilon'(t)$ is governed primarily by the second term in Eq. (2), while the contribution from the first term becomes noticeable only at temperatures $t > 40$°C. Using the $g_2(t)$ relation thus obtained, we numerically adjust the temperature dependence of the relaxation time $\tau_2(t)$, which is plotted specifically for this case in Fig. 3. Interestingly, in both the nematic and the isotropic phase, the relaxation time is practically temperature-independent. This implies that high-frequency relaxation does not involve the overcoming of potential barriers by a molecule but rather is caused by the rotation of molecules or their fragments through small angles near the equilibrium position. However, the effect of liquid-crystal ordering of molecules on the relaxation time $\tau_2(t)$ is seen to be fairly large in the region of the transition from the nematic to an isotropic state.

When fitting the $\varepsilon'(T)$ relations with Eq. (2) at higher frequencies, it was established that the relaxation time τ_2 not only depends on temperature but is also a function of frequency, $\tau_2(t, \omega)$. For instance, at 5000 MHz, where the $\varepsilon'(t)$ dependence is determined fully by the second term in Eq. (2) (Fig. 2), the relaxation time is found to be shorter by nearly an order of magnitude than that for frequencies below 1000 MHz. Figure 4 presents the above result in a more instructive form by displaying the high-frequency relaxation time over broad ranges of temperatures and frequencies for the LC under study.

The fact that τ_2 depends on frequency indicates that high-frequency relaxation of the 5CB LC should be described by a dispersion relation with a spectrum of relaxation times lying within a certain interval. In this case, in fitting the high-frequency dispersion and the temperature dependence of $\varepsilon'(t)$ numerically, one can represent the last term in Eq. (2) in the form of the following simple empirical relation, which was proposed by Gavril'yak and Negami and is essentially a generalization of the Debye equation:

$$\varepsilon(t, \omega) = \frac{(\varepsilon_0'(t) - n^2(t))g_2(t)}{[1 + (i\omega\tau)^{1-\alpha}]^{\beta}}. \qquad (3)$$

In this expression, the coefficients α and β are numerical parameters characterizing a continuous relaxation-time distribution and τ is a time constant, which can be identified with an effective relaxation time. For $\alpha = 0$ and $\beta = 1$, the right-hand part of Eq. (3) is equivalent to the Debye equation with one relaxation time. For $\beta = 1$ and $\alpha \neq 0$, the right-hand part of Eq. (3) corresponds to the Cole–Cole model with a symmetric relaxation time

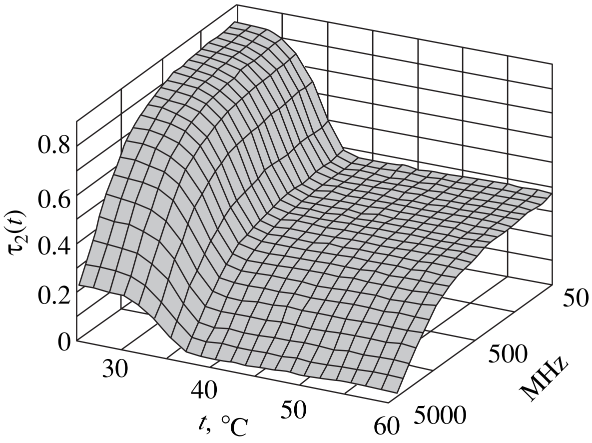

Fig. 4. Dependence of the second relaxation time on frequency and temperature.

distribution, and for $\alpha = 0$ and $\beta \neq 1$, to the Cole–Davidson model with an asymmetric distribution of relaxation times. In the latter case, by isolating the real part of Eq. (3), one can write the following equality describing the Cole–Davidson model:

$$\frac{\varepsilon'(t,\omega)}{[\varepsilon'_0(t)-n^2(t)]g_2(t)} = (\cos\theta)^{\beta}\cos\beta\theta, \qquad (4)$$

where $\tan\theta = \omega\tau$. We used this expression to fit the experimental data numerically and determined the parameter β (characterizing the extent to which the dielectric spectrum deviates from the Debye law) and the experimental temperature dependence of $\tau_2(t)$. The parameter β turned out to be ~0.5–0.7 for the nematic and isotropic LC phases. As already mentioned, the fact that β is not equal to unity is due to the asymmetric relaxation time distribution, which, in turn, should possibly be attributed to the contribution from various intramolecular motions, for example, vibrations of mobile alkyl groups of molecules, to the high-frequency permittivity of the LC under study. These motions are known to become particularly strongly manifest in the transverse component of the permittivity.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research, project no. 03-03-32470.

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Translated by G. Skrebtsov