

POLYMERS AND LIQUID CRYSTALS

Dielectric Anisotropy of 5CB Liquid Crystal in a Decimeter Wavelength Range

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Abstract—Parallel and perpendicular components of the dielectric constant for 5CB nematic liquid crystal are measured in a relaxation region. Two frequencies $f_1 \approx 30$ and $f_2 \approx 350$ MHz are determined at which the inversion of the dielectric anisotropy sign is observed. It is shown that the observed sizable high-frequency shift of f_2 with respect to the value calculated according to the Debye theory is caused by the dielectric resonance near the relaxation region. © 2000 MAIK “Nauka/Interperiodica”.

The anisotropy of the real component of the dielectric constant for nematic liquid crystals (NLC) and its dependence on the frequency $\Delta\varepsilon'(\omega) = \varepsilon'_{\parallel} - \varepsilon'_{\perp}$ is usually explained within the framework of orientation-dipole representations. In this case, ε'_{\perp} and ε'_{\parallel} correspond to the mechanisms of NLC dipole polarization connected with rotations of rigid bar-shaped molecule around the long and short axes, respectively. The anisotropy $\Delta\varepsilon'(\omega)$, as a rule, is maximum in the frequency range in which the molecular dipoles rotate through the same angle with the field. These are the frequencies at which the anisotropic properties of liquid crystals are fairly well studied and most extensively used in electrooptical and other devices.

As the pumping field frequency increases, the dispersion regions for ε'_{\perp} and ε'_{\parallel} are reached; in most cases, they are described by the Debye relaxation formula

$$\varepsilon'_D(\omega) - \varepsilon'_{\infty} = \frac{\varepsilon'_0 - \varepsilon'_{\infty}}{1 + \omega^2 \tau^2}, \quad (1)$$

where ε'_0 and ε'_{∞} are the static and high-frequency components of the dielectric constant, $\omega = 2\pi f$ is the cyclic frequency, and τ is the relaxation time of the molecule. In the dispersion region, the rotational motions of molecules are first partly, and then completely, suppressed and degenerate into librations (rotations by small angles) with a further increase in the frequency. It should be noted that, due to a difference in the relaxation times τ_{\parallel} and τ_{\perp} , the dielectric anisotropy can change its sign in the relaxation region. This effect provides additional information on the dynamic characteristics of molecules, and it is of importance for various technical devices operating at high frequencies.

The dielectric anisotropy in the relaxation region for 4-pentyl-4'-cyanobiphenyl (5CB) so far has virtually not been studied, because this frequency region lies at

the boundary between the meter and decimeter wavelength frequency ranges, which is difficult to carry out reliable measurements. As is known, the 5CB crystal is nematic up to the temperature $T = 35^{\circ}\text{C}$. It possesses a comparatively large positive magnitude of the static anisotropy $\Delta\varepsilon'_0 = 11.5$ ($\varepsilon'_{\parallel} = 18.5$ and $\varepsilon'_{\perp} = 7$) and a sufficiently large value of the dipole moment $\mu = 5.1D$; its indices of optical refraction are $n_{\perp} = 1.53$ and $n_{\parallel} = 1.71$, and the dielectric relaxation times strongly depend on temperature and fall in the range $\tau(T) \sim 27\text{--}85$ ns [1].

Figure 1 displays the frequency dependences of the real components of relative dielectric constant ε'_{\perp} (open circles) and ε'_{\parallel} (filled circles) according to the data taken from [2–5]. These data were obtained in a wide frequency range on a 5CB crystal. The experimental data were approximated with the use of formula (1) by the Debye relaxation dependences $\varepsilon'_{\parallel}(f)$ (dashed line) and $\varepsilon'_{\perp}(f)$ (solid line) by fitting of the relaxation times $\tau_{\parallel} = 24$ and $\tau_{\perp} = 40$ ns. It is important to note that the

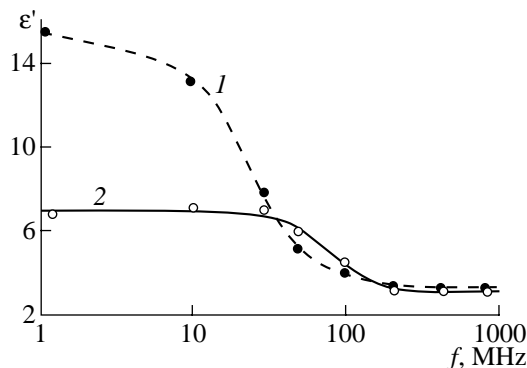


Fig. 1. Frequency dependences of (1) parallel and (2) perpendicular real components of the dielectric constant for 5CB liquid crystal. Points are experimental data, and lines indicate the approximation according to Debye.

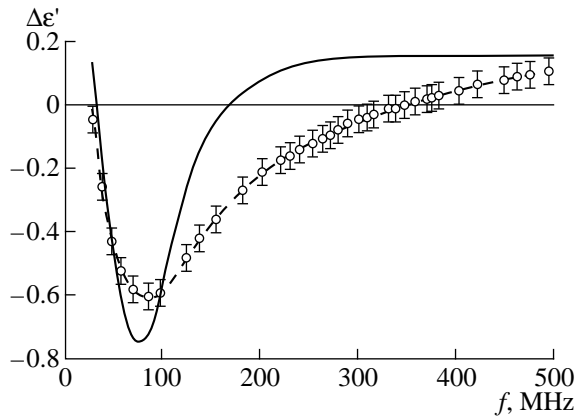


Fig. 2. Frequency dependence of the dielectric anisotropy. The solid line is the calculation according to Debye, and points are the experimental data.

experimental points fairly well fit the calculated dependences virtually over the entire frequency range; in this case, the inversion of the dielectric anisotropy sign $\Delta\epsilon' = \epsilon'_\parallel - \epsilon'_\perp$ was twice observed in the relaxation region at the frequencies $f_1 \approx 35$ MHz and $f_2 \approx 165$ MHz. This work is devoted to the experimental determination of the frequencies f_1 and f_2 , at which the anisotropy changes its sign.

The high-sensitive microstrip sensors of a circular type were used in measurements of the dielectric anisotropy in the relaxation region. These sensors were discretely tuned by close steps in the frequency range 50–1000 MHz [2]. These sensors allow the recording of the dielectric spectra with a high accuracy despite a relatively small volume of the NLC specimen under study. The NLC specimen was placed in a measuring cell between parallel metal electrodes 2.5×2.5 mm in size with the gap between them $d = 0.1$ mm. Parallel and perpendicular orientations of the long axes of crystal molecules with respect to the polarization of the high-frequency pumping field were specified by the appropriate directions of the external magnetic field $H = 2$ kOe. Measurements were carried out in a thermostat at temperature $T = 30.0 \pm 0.1^\circ\text{C}$.

The results of measurements of the dielectric anisotropy for the 5CB liquid crystal in the frequency range 50–500 MHz are presented in Fig. 2. The frequency dependence of the anisotropy $\Delta\epsilon'(f)$ obtained from the curve approximated according to Debye theory (Fig. 1) is shown by the solid line. It is seen that only the first point of the inversion of the anisotropy sign at $f_1 \approx 30$ MHz closely coincides the calculation. According to the calculations, the next change in the anisotropy sign should be observed at a frequency of 165 MHz; however, the frequency obtained experimentally is significantly higher ($f_2 \approx 350$ MHz). The disagreement observed for the second frequency of the anisotropy sign inversion should be caused by the deviation of the

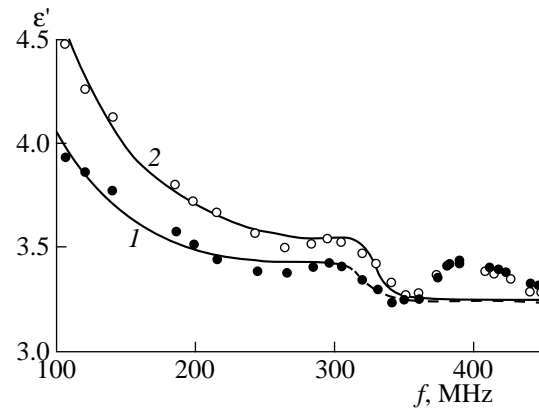


Fig. 3. Frequency dependences of (1) parallel and (2) perpendicular components of the dielectric constant for 5CB liquid crystal, calculated with account of dielectric resonance. Points are the experimental data.

dependences $\epsilon'_\parallel(f)$ and $\epsilon'_\perp(f)$ in the high-frequency relaxation range from the Debye dispersion law.

Actually, changing the frequency by small values when measuring the dielectric constant of the 5CB liquid crystal, we revealed a clearly pronounced distortion of the spectrum nearly at the very edge of the dispersion region. The results of measurements of ϵ'_\perp (open circles) and ϵ'_\parallel (filled circles) in the frequency range beginning with 100–400 MHz are shown in Fig. 3. It is seen that the characteristic feature of both spectra is the presence of a clearly distinguished minimum near the frequency of 350 MHz and a maximum near the frequency of 400 MHz.

A comparatively narrow frequency range and the shape of dispersion distortion unambiguously indicate its resonance nature, which can be associated with the intramolecular conformational vibrations caused by the mobility of molecular fragments. The frequency dependence of the real component of the dielectric constant for the material in the presence of resonance processes can be written as follows [6]

$$\epsilon'_R(\omega) - \epsilon'_\infty = \frac{1}{2} \Delta\epsilon_k \left[\frac{1 + \omega_0(\omega + \omega_0)g^2}{1 + (\omega + \omega_0)^2 g^2} + \frac{1 - \omega_0(\omega - \omega_0)g^2}{1 + (\omega - \omega_0)^2 g^2} \right], \quad (2)$$

where ω_0 is the resonance frequency, $\Delta\epsilon_k$ is its amplitude characteristic, and g is the quantity characterizing the relaxation time. It is obvious that the resulting frequency dependence of the dielectric constant for the liquid crystal under study should be described by the sum of the relaxation and resonance processes

$$\epsilon'(\omega) - \epsilon_\infty = \epsilon'_D(\omega) + \epsilon'_R(\omega). \quad (3)$$

The frequency dependences of ε'_{\parallel} and ε'_{\perp} , plotted according to formula (3) as a result of the numerical fitting of the coefficients in formula (2) are shown in Fig. 3. For $\varepsilon'_{\parallel}(f)$ (curve 1), we obtained $\omega_0/2\pi = 326$ MHz, $\Delta\varepsilon_k = 0.012$, and $g = 40$ ns; and for $\varepsilon'_{\perp}(f)$ (curve 2), the resonance frequency remained the same $\omega_0/2\pi = 326$ MHz, and the amplitude and time of the relaxation increased by $\approx 20\%$ ($\Delta\varepsilon_k = 0.014$ and $g = 50$ ns). It is seen that, in this case, there is a fairly good fit of the calculated curves to the experimental data, except a small region at about 400 MHz. Moreover, the second frequency, at which the dielectric anisotropy $\Delta\varepsilon'(f) = \varepsilon'_{\parallel} - \varepsilon'_{\perp}$ changes the sign, being calculated with account of formula (3), also agrees well with the experiment. Note that the resonance feature observed in the dielectric spectrum in the relaxation region and the related deviation of the frequency dependence of the dielectric constant from the Debye dependence is observed not only for the 5CB crystal, but also for a number of liquid-crystal homologs n CB ($n = 6, 7, 8$). In this case, upon transition from the nematic phase to the isotropic phase, the resonance persists and substantially increases in amplitude.

Thus, the experimental sizable high-frequency shift of the point of repeated inversion of the anisotropy sign for the 5CB liquid crystal with respect to the calculated frequency f_2 obtained under conditions of normal Debye relaxation is explained by the resonance feature revealed in the high-frequency part of the relaxation region. The nature of the dielectric resonance observed remains unclear. This resonance is likely connected

with the conformational vibrations of mobile molecular fragments, for example, with vibrations of the first sectors of flexible methylene groups [7], or with specific vibrations of the flexible fragments together with vibrations of the benzene rings of 5CB.

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