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Dielectric Anisotropy of Nematic 4-Pentil-4′-Cyanobiphenyl

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The dielectric anisotropy and dispersion of the real part of permittivity of 4-pentil-4′-cyanobiphenyl (5CB) were investigated in the relaxation frequency range from 10 MHz to 500 MHz. Two frequencies f_1 = 30 MHz and f_2 = 350 MHz characterizing the change of a sign of the dielectric anisotropy were obtained. The Debye relaxation fitting procedure showed that a quality of the fits was satisfactory in defining the frequency f_1, but there were discrepancies between the experimental and fitting results for the frequency f_2. It is due to the appearance of singularities on the dielectric spectrum around 300 MHz. The dielectric spectra are interpreted as a superposition of dielectric relaxation and resonance contribution. It was shown that isotropic phase and diluted solution of 5CB in benzene display the resonance dispersion region too.

Keywords: dielectric anisotropy; dielectric spectra; microwaves; nematics

INTRODUCTION

The dielectric relaxation of permittivity in nematic liquid crystals (LC) occurs in different frequency regions when electric field is parallel or perpendicular to the optical axis of mesophase. Oriented samples of LC are dielectrically anisotropic, therefore the parameter $\Delta\varepsilon'(\omega) = \varepsilon'_{\parallel} - \varepsilon'_{\perp}$ has a dielectric dispersion too. The dielectric anisotropy of LC plays an important role in applications and provide us with useful information on the material properties. Until now the dielectric anisotropy has been investigated mainly in low frequency range where the intermolecular reorientation follows immediately the electric field.

High frequency range (RF-range) is studied in a less degree. It is important to carry out experiments in the decimeter range where the intramolecular reorientation of flexible molecular fragments may occur.

It was found earlier [1,2], that in this range for the case of one or more than one relaxation times the components $\varepsilon'_{\parallel}(\omega)$ and $\varepsilon'_{\perp}(\omega)$ are described by Debye equation:

$$\varepsilon'(\omega) - \varepsilon'_{\infty} = \sum_i \frac{(\varepsilon'_0 - \varepsilon'_{\infty})_i}{1 + \omega^2 \tau_i^2}, \qquad (1)$$

where ε'_0 и ε'_{∞} are the static and high-frequency limits of the permittivity, τ_i is the mean relaxation time, *i* is the number of relaxation process and $\omega=2\pi f$.

It is very interesting to note that the dielectric anisotropy may change sign due to discrepancies between $\tau_{\parallel}$ and $\tau_{\perp}$ in relaxation region. This effect can become important for high frequency applications and it is interesting for more deeper understanding of the dynamic properties of anisotropic molecules. In the present work the frequencies, where the sign inversion of dielectric anisotropy takes place, are defined experimentally and calculated using Debye formula.

It is well known [3], that the 4–pentil -4′–cyanobiphenyl (5CB) is nematic at 22.5 C< T< 35 C, although it supercools below 22 C.

In 5CB large static dielectric positive anisotropy $\Delta\varepsilon'_0$=11.5 ($\varepsilon'_{\parallel}$=18.5, $\varepsilon'_{\perp}$=7) and large permanent dipole moment μ=5.1 D oriented along the para-axis are exist. The optical constants for 5CB are $n_{\perp}$=1.53 and $n_{\parallel}$=1.71. The times of dielectric relaxation $\tau(t)$ depend on temperature and fall into 27-85·ns interval.

EXPERIMENTAL

We investigated the dielectric permittivity and anisotropy spectra of the liquid crystal 5CB in the frequency range that is most difficult to study experimentally: from 10 to 500 MHz. The measurements were performed on ring-shaped hybrid microstrip resonators with a cell for the experimental material. The cell was fabricated in the form of vertical parallel plates at the antinodes of RF electric field. The samples were poured into the 100 μm gap between the plates and held there by surface tension forces. Discrete tuning of the frequency of the sensors with a small step was realized by miniature calibrated inductive elements, which were set into the break of microstrip resonator in the region of a current antinode [4]. The measurements were performed in a thermostatic chamber, and the temperature was maintained constant to within 0.1 C.

The real component ε' of the permittivity of the 5CB was determined according to the shift of the resonance frequency of the sensor with the sample with respect to the empty sensor. Benzene ($\varepsilon = 2.28$) was used as the reference material for calibrating the sensors. As a result, the absolute accuracy achieved in determining ε' was not worse than 0.02. To measure the anisotropy of the permittivity of the liquid crystal (the difference between $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$) a static field $H = 2500$ Oe, generated by an electromagnet, was applied. The field oriented the director of the 5CB molecules either parallel to or perpendicular to the direction of the RF pump field.

RESULTS AND DISCUSSION

In Fig.1 the frequency dependence of the real part of permittivity $\varepsilon'_{\parallel}$ and $\varepsilon'_{\perp}$ are shown in frequency range from 1 MHz to 1000 MHz for oriented methophase 5CB. Taking into account only one relaxation time for $\varepsilon'_{\parallel}$ and $\varepsilon'_{\perp}$ the

experimental points were fitted by Debay equation (1) with $\tau_{\|}$=24 ns and $\tau_{\perp}$=40 ns. It is very important to note that the experimental points hit satisfactory the fit curves, i.e. these dispersions are well described by the Debye equation. This result clearly indicates that the dielectric anisotropy $\Delta\varepsilon' = \varepsilon'_{\|} - \varepsilon'_{\perp}$ twice changes the sign at $f_1 \approx 35$ MHz and $f_2 \approx 165$ MHz.

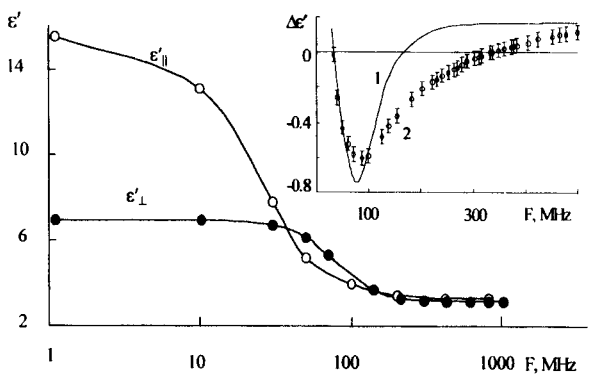

FIGURE 1. Real part of the permittivities $\varepsilon'_{\|}$ and $\varepsilon'_{\perp}$ versus frequency. Circles: experimental data. Solid lines: Debye fittings. The inset shows the dielectric anisotropy $\Delta\varepsilon'$ versus frequency from 50 to 500 MHz. Open circles: experiment. Solid curves: calculated from the Debye fitting with single relaxation time $\tau_{\|}$=24 ns and $\tau_{\perp}$=40 ns.

It is seen from the inset in Fig. 1, that the first point $f_1 \approx 30$ MHz satisfies the Debye fit. Another calculated point $f_2 \approx 165$ MHz differs considerably from the experimental point $f_2 \approx 330$ MHz. Probably this discrepancy may be connected with the deviation of $\varepsilon'_{\|}$ and $\varepsilon'_{\perp}$ from the Debye fits in high frequency range.

It has been established earlier, that the relaxation dispersion connected with reorientation motion of molecules ranges up to the frequency of 250 MHz. Above this frequency in the range from 280 MHz to 350 MHz an another resonance dispersion region has been revealed. This region had not been observed earlier.

Fig. 2 shows the spectra of real components $\varepsilon'_{\parallel}(f)$ and $\varepsilon'_{\perp}(f)$ of the permittivity of 5CB (curves 1 and 2 respectively). The spectra were measured in the ordered nematic phase at temperature t=20 C. One can see that the dispersions of $\varepsilon'_{\parallel}(f)$ и $\varepsilon'_{\perp}(f)$ have a pronounced maximum near 280 MHz (ε'_{max}) and a minimum near 350 MHz (ε'_{min}).

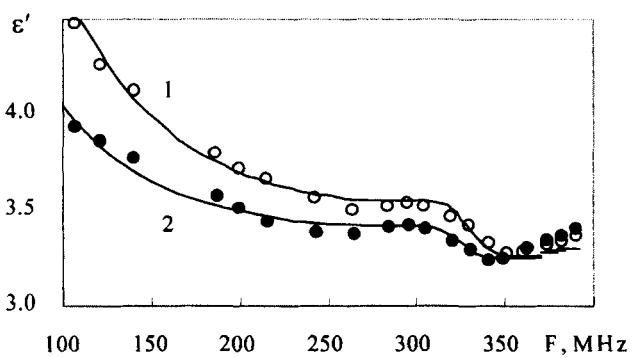

FIGURE 2. Longitudinal $\varepsilon'_{\parallel}(f)$ and transverse $\varepsilon'_{\perp}(f)$ permittivity of 5CB in nematic phase versus frequency at t=20 C. Circles: experiment. Solid lines: calculated accordingly to the equation (3).

Several studies on the dielectric relaxation have been reported elsewhere [2,3,5-7] for alkylcyanobiphenyl series at frequencies from a few Hz to a few GHz. There have been shown that the deviation from the symmetrical

Cole-Cole plots at high frequencies is a result of the presence of two or more Debye relaxation processes (see equation 1).

We suggest, that the high frequency distortion of dielectric spectra from Debye like relaxation is connected with a resonance process [8]. For the quantitative analysis of the dielectric spectra the resonance equation was used [9]:

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

where ω_0 is the resonance frequency, $\Delta\varepsilon_k$ is the dielectric strength, g is the coefficient describing the losses.

The resultant dielectric spectrum is described by a superposition of relaxation and resonance processes:

$$\varepsilon'(\omega) - \varepsilon_\infty = \varepsilon'_D(\omega) + \varepsilon'_R(\omega)\,. \qquad (3)$$

The comparison of experimental points and fitting curves in Fig. 2 shows that the quality of the fits is satisfactory excluding the region near 400 MHz. It should be noted that the second frequency, characterizing the sign change of the dielectric anisotropy, conforms to the experiment.

A characteristic feature of this dielectric resonance is stability of its frequency, whereas its amplitude depends on the temperature. It turned out the resonance dispersion region exists even in strongly diluted solution of 5CB in benzene (see Fig. 3, inset). This fact indicates that the resonance is due to intramolecular motions of the individual flexible molecular fragments.

Fig. 3 represents the relaxation dielectric spectra at t = 25 C in nematic phase (curve 1), and at t = 37 C in isotropic phase (curve 2). Curve 3 and inset show the dielectric spectra of 5CB solution in benzene. Curve 3 is the relaxation and resonance spectrum for the 90 mol % solution of 5CB in ben-

zene at t = 25 C. The inset shows the details of the resonance spectrum in strong diluted solution of 5CB (10 mol %) in benzene at t = 25 C.

It should be noted, that the high frequency singularities appeared in the dielectric relaxation spectra not only for 5CB, but for homologous series: 6CB, 7CB and 8CB.

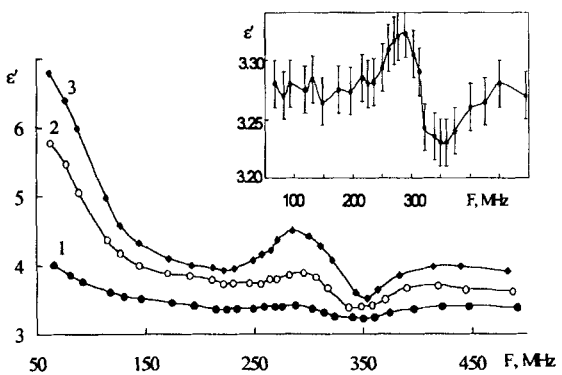

FIGURE 3. The dielectric spectra of 5CB at t = 25 C - (1), t = 37C - (2). Curve 3 shows the dielectric spectrum of 5CB (90 mol %) solution in benzene (10 mol %) at t = 25 C.
Inset: The resonance part of the dielectric spectrum of a diluted solution of 5CB (10 mol %) in benzene (90 mol %) at t = 25 C

CONCLUSION

Thus, the strong shift of the frequency f_2, at which the second inversion of a sign of the dielectric anisotropy of 5CB occurs, with respect to the frequency calculated from Debye equation is concerned with the resonance observed in high frequency relaxation region.

The nature of this dielectric resonance is not clear now. However, the obtained results show that this resonance is probably due to conformation motions of flexible molecular fragments. This assumption is also confirmed by temperature investigations of permittivity and dielectric spectra of 5CB solution. Further investigations are necessary for better understanding the nature of dielectric resonance.

Acknowledgements

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