
POLYMERS
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Permittivity of Liquid Crystals of the Alkylcyanobiphenyl Group in a Decimeter Wavelength Range

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Abstract—The high-frequency dielectric spectra of liquid crystals of the alkylcyanobiphenyl group with various length of the mobile alkyl chain C_nH_{2n+1} ($n = 5-8$) are experimentally studied. It is established that a resonance feature is observed in the frequency range of 300 MHz for all the crystals on the high-frequency branch of the orientational part of dielectric spectra. It is shown that the position of the dielectric resonance is virtually independent of the temperature and the degree of crystal dilution by benzene, but its intensity essentially depends on both factors. The nature of the dielectric resonance found is probably caused by the intramolecular motion of methylene fragments, which are strongly bound with a rigid core of molecules. © 2000 MAIK “Nauka/Interperiodica”.

For a number of mesomorphic phases of liquid crystals, the dielectric spectra often involve portions with a significant deviation from the Debye dispersion law. As a rule, the spectra are characterized by high- and low-frequency distortions depending on the molecule structure, magnitude, and type of the liquid-crystal order. The low-frequency part of the dispersion (radio-frequency range) is usually associated with the features of the orientational collective motion of molecules and mobile ionic charges [1, 2]. The high-frequency part of the spectrum is the least understood, and additional mechanisms of dielectric relaxation related to the intramolecular mobility are currently only assumed to take effect in a decimeter wavelength range [3, 4]. In our earlier detailed study [5] of the dielectric spectra of the 4-*n*-pentyl-4'-cyanobiphenyl (5CB) liquid crystal in the frequency range 50–1000 MHz, we found that, in the vicinity of 300 MHz (and at higher frequencies with an increase in the temperature), there is a rather strong deviation of the spectrum from the Debye monotonic dependence.

The present work is devoted to the study of the dielectric spectra in a decimeter wavelength range on the samples of liquid crystals from the series of 4-*n*-alkyl-4'-cyanobiphenyls with a various length of the mobile alkyl chain C_nH_{2n+1} ($n = 5-8$). As is known, the rigid core of molecules in the cyanobiphenyl compounds of liquid crystals is formed by two benzene rings, along the axis of which the strongly polar group $C\equiv N$ is situated on one side of the core (this group has a large dipole moment oriented along the long axis of the molecule) and the flexible hydrocarbon chains (“tails”), which consist of $-CH_2-$ groups, are located on the other side of the core. All the samples under study are nematic liquid crystals by type of liquid-crystal

ordering, and only for the 8CB crystal, there is also the smectic phase in the temperature range $20.9 \leq t \leq 33.5^\circ C$. The dielectric spectrum of each sample was taken twice for two states of the crystal. For measurements in the nematic phase, the temperature was set 5 K below the temperature t_{ni} of transition from the nematic state to the isotropic state, and in the case of the isotropic phase, the temperature was set 2 K above t_{ni} .

The dielectric properties of liquid-crystal mesophases were investigated in the frequency range 50–500 MHz, which corresponds to the most pronounced resonance feature in the spectrum [5]. This range of decimeter wavelengths is rather difficult to carry out reliable measurements. For this reason, we used specially devised miniature tunable microwave sensors based on the ring-shaped microstrip resonators. The sensors and techniques of resonance measurements were described in [5, 6]. A liquid crystal was placed inside an UHF measuring cell in the antinode of a high-frequency electric field between two gold-coated surfaces 2×2 mm in size with a spacing of 100 μm . The parallel orientation of long axes of the liquid crystal molecules with respect to the high-frequency field was achieved with the help of the uniform constant magnetic field $H = 2.5$ kOe. The temperature of the measuring cell was stabilized with an accuracy of 0.1°C and could be varied from 0 to 60°C.

The spectra of the real part of the permittivity for 5CB, 7CB, and 8CB liquid crystal samples, which were taken in the nematic phase under the molecular director orientation parallel to the polarization of the high-frequency field $\epsilon'_{\parallel}(f)$, are given in Fig. 1 (curves 1, 2, and 3, respectively). In order not to overload the figure, the spectrum for a 6CB liquid crystal is not shown, because it almost coincides with the spectrum of the 5CB liquid

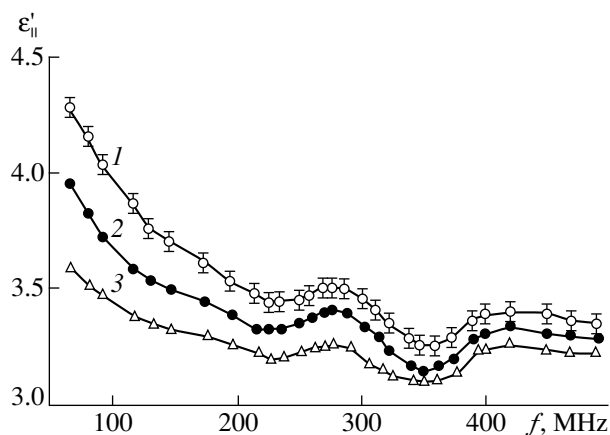


Fig. 1. Frequency dependences of the real part of the permittivity for (1) 5CB, (2) 7CB, and (3) 8CB liquid crystals in the nematic phase.

crystal sample. The absolute precision of the $\epsilon'_{\parallel}(f)$ measurements is shown in curve 1. This precision was observed in all the experimental curves and was equal to ± 0.02 . It can be seen that all the curves are qualitatively similar to each other, and the main feature of each dielectric spectrum is a clearly revealed maximum near 280 MHz (ϵ'_{\max}) and a minimum near 350 MHz (ϵ'_{\min}). The behavior of $\epsilon'_{\parallel}(f)$ in the range under consideration indicates the existence of dielectric resonance, which is observed at about the same frequency for all the samples under study.

To put it differently, the resonance location is independent on the length of the alkyl chain in cyanobiphenyls. However, as is known, this length rather strongly affects the Debye relaxation frequencies f_D . Actually, the f_D frequencies measured for 5CB, 7CB, and 8CB liquid crystals at temperatures 5 K below t_{ni} are equal 7.2, 6.2, and 5.45 MHz, respectively [7]. As the length of alkyl “tails” increases, i.e., when passing from the less “inertial” composition to the more “inertial” (Fig. 1), one can observe not only a decrease in the permittivity of the liquid crystal samples at high frequencies, but also a significant decrease in the dielectric resonance intensity, which can be evaluated from the difference ($\epsilon'_{\max} - \epsilon'_{\min}$).

Note that the intensity of the resonance observed monotonically increases with an increase in the temperature. It follows from the experiment that, upon transition from the nematic phase to the isotropic phase, the resonance intensity increases for all the samples studied more than three times. However, in this case, the characteristic frequencies corresponding to ϵ'_{\max} and ϵ'_{\min} virtually do not change, and, hence, the location of the dielectric resonance does not change as well. It is of interest to note that the resonance observed rather well manifests itself in the smectic phase, which exists in the 8CB liquid crystal. The dielectric spectra of this liquid crystal are shown in Fig. 2. These spectra were mea-

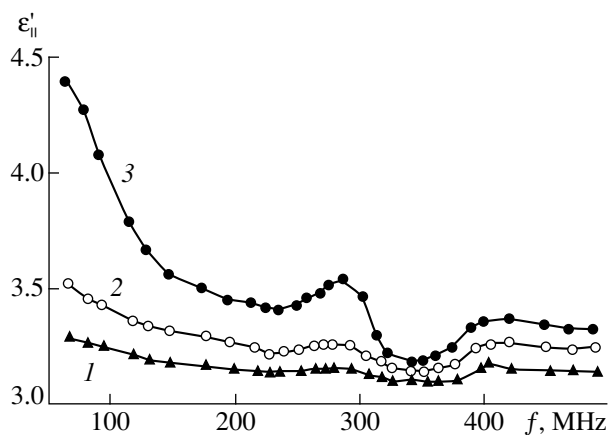


Fig. 2. Frequency dependences of the real part of the permittivity for 8CB liquid crystal in (1) smectic phase, (2) nematic phase, and (3) isotropic state.

sured for three different phases, namely, the smectic ($t = 28.5^\circ\text{C}$), nematic ($t = 35.8^\circ\text{C}$), and isotropic liquid ($t = 42.2^\circ\text{C}$) phases. It is seen that, upon transition from the nematic phase to the smectic phase, the intensity of resonance decreases approximately three times, but its location on the frequency axis remains as before.

It is known that the Debye relaxation frequency of liquid crystals increases with an increase in the temperature. As a result, the orientational part of the dielectric spectrum shifts to the right toward the high-frequency range. It is also known that, as the length of alkyl chain in a liquid crystal molecule increases, the f_D frequency, on the contrary, decreases, and, as a consequence, the orientational part of the dielectric spectrum shifts toward the low-frequency range. Therefore, taking into account the results of experiments presented in Figs. 1 and 2, we can conclude that the intensity of the dielectric resonance observed increases in any cases when the relaxation region of the spectrum (induced by the polarization of liquid crystal molecules) approaches this resonance.

The degree of deviation of the experimentally observed dielectric spectra from the Debye frequency dependences of the permittivity for liquid crystals from the series of alkylcyanobiphenyls was evaluated in [1–4] according to the Cole–Cole diagrams. The high-frequency distortions in the diagrams, as a rule, are described by a set of internal relaxation regions of the Debye type. In this case, the frequency dependence of the real part of the permittivity $\epsilon'_D(\omega)$ is represented in the form

$$\epsilon'_D(\omega) - \epsilon'_\infty = \sum_k \frac{\epsilon'_k - \epsilon'_\infty}{1 + \omega^2 \tau_k^2}, \quad (1)$$

where ϵ'_k and τ_k are the k th components of the static permittivity and relaxation time, respectively; and ϵ'_∞ is

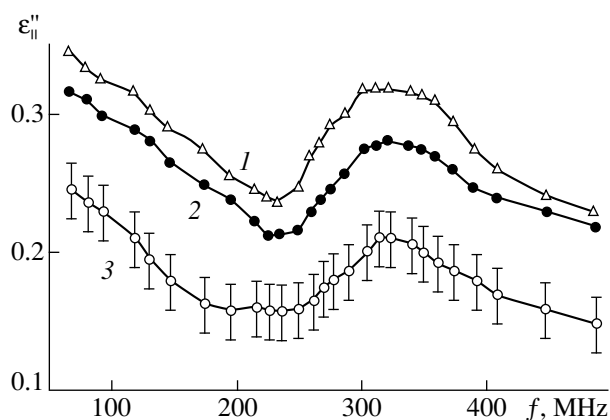


Fig. 3. Frequency dependences of the imaginary part of the permittivity for (1) 5CB, (2) 7CB, and (3) 8CB liquid crystals in the nematic phase.

the rf permittivity. Because of the limited number of experimental points presented in the papers, the spectral components of these regions and, first of all, the reasons for their appearance still remain unclear.

However, in the present work, we established that the deviation from the Debye dependence in the high-frequency part of the dielectric spectrum most likely can be connected with the resonance behavior of alkylcyanobiphenyls at high frequencies rather than with their relaxation behavior. Evidence for this conclusion is the absence of the characteristic frequency shift in the dispersion region of the dielectric spectrum with a change in the temperature of samples, which is certainly not typical of the relaxation processes. The location of a maximum in the frequency dependence of the imaginary part of the permittivity (Fig. 3) determines the resonance vibrational frequency, which turned out to be approximately identical (about 320 MHz) for all the samples studied.

The experiments performed demonstrate that the origin of the dielectric resonance found is brought about by the excitation of intramolecular vibrations. This is confirmed by the following findings. First, the resonance intensity increases with an increase in the temperature of samples, which especially clearly manifests itself in the nematic–isotropic liquid phase transition. Second, upon dilution of liquid crystals by benzene (up to 50% benzene content in the sample volume), the resonance intensity first significantly increases and then monotonically decreases, the resonance frequency being unchanged.

The vibrations of flexible alkyl groups can be the most probable intramolecular motions connected with the dielectric resonance. However, the fact that the frequency of the resonance found is virtually independent of the length of the alkyl chain suggests that only certain methylene fragments can contribute to the vibrational process. This assumption is well justified with the data obtained by the NMR method [8, 9]. According to these data [8, 9], the order parameter is strongly non-uniform along the length of alkyl chain. Its value drastically decreases toward the chain end and remains almost the same for the three first fragments in all alkylcyanobiphenyl compounds. It is quite probable that it is these vibrations of the first alkyl chain fragments strongly bound with the rigid core that manifest themselves as the dielectric resonance found at the end of the Debye dispersion region. The natural frequencies of vibrations of the next alkyl chain fragments are significantly higher, and, probably, the resonances observed at frequencies of 450–1000 MHz in the isotropic phase of a 5CB liquid crystal are caused by these fragments [15].

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