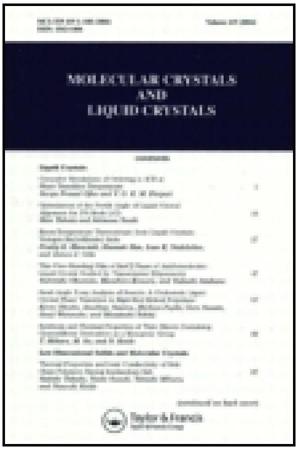

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Dielectric Relaxation in Liquid Crystals with (CH_2) Spacers in Molecules

E. I. Rjumtsev [a], A. P. Kovshik [a] & D. A. Ragimov [a]

[a] Institute of Physics of St. Petersburg University, St. Petersburg, 198904, Russia

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Dielectric Relaxation in Liquid Crystals with (CH_2) Spacers in Molecules

E.I. RJUMTSEV, A.P. KOVSHIK and D.A. RAGIMOV

Institute of Physics of St.Petersburg University, St.Petersburg, 198904, Russia

The dielectric properties of solutions of the liquid crystals with (CH_2) spacers and nitrile groups in molecules in weakly polar nematic diluent were studied. In the frequency range of a.c. electric field $(10^2\text{-}10^8)$Hz the dispersion of complex dielectric permitivities $\varepsilon_\parallel$ in nematic phase were investigated. From the dielectric spectra of $\varepsilon_\parallel$, the relaxation frequencies f_R were obtained for each of the investigated substances. It was shown that f_R increases with the (CH_2) spacers length of the central alkyl chains of molecules.

Keywords: dielectric dispersion; liquid crystals; spacers

Molecules of most of liquid crystals (LC) contain the hydrocarbon radicals (alkyl chains) as the terminal fragments. Changing length of the alkyl chains in homological LC series one can vary phase transition temperatures without any modification in the dipole structure of the molecules. The alkyl chains (spacers) can be also disposed in a centre of a mesogenic core of the strongly polar molecules, or between mesogenic part of the molecules and a terminal polar nitril group. In latter case, the LC molecule is divided into highly polar and nonpolar parts. Such a division violates a correlation between polar and nonpolar molecular parts, and it gives rise to a change in dipolar molecular structure and in macroscopic dielectric properties of LC. When the spacer separates nitril group from another part of the molecule, the changes in magnitude μ of the dipole moment and in its direction (an angle β) with respect to the long molecular axis are most significant. On the other hand[1], when the spacers are disposed in the mesogenic cores of the LC molecules, their effect on μ and β is relatively weak[2].

An investigation of macroscopic dielectric properties of LC consisting of the molecules with alkyl spacers has shown that insertion of the spacer between the strongly polar terminal group and the molecular core gives rise to decrease in a frequency of the relaxation related to a low-frequency dispersion of a longitudinal component $\varepsilon_{\parallel}$ of the dielectric permitivity[1]. This fact corresponds to a notion about that the relaxation frequency of a low frequency dispersion of $\varepsilon_{\parallel}$ decreases with increasing the molecular length. Such a low-frequency dispersion of $\varepsilon_{\parallel}$ is caused by an exclusion of an orientational contribution due to the rotation of the stick like molecules around their short axes from the dielectric polarization. On the contrary, insertion of the spacer into the central part of the molecule gives rise to an increase of the relaxation frequency related to the low-frequency dispersion of $\varepsilon_{\parallel}$. However, the LC consisted of the molecules with the spacers have a temperature intervals of existence of the nematic phase considerably different from that for LC consisted of the molecules without spacers. Since the dynamic LC characteristics are strongly dependent on the temperature, they must be compared with each other under similar conditions. A convenient method for a comparative investigation of a physical properties of LC is a mixing of compounds under investigation, or their dissolution in the same liquid crystalline solvent[4,5,6]. It should be noticed that investigation of the dielectric relaxation for the LC solutions in a nonpolar liquid crystalline solvent revealed a decrease in the relaxation frequency related to the low-frequency dispersion of $\varepsilon_{\parallel}$ with increasing length of alkyl side chain in the LC molecules[5].

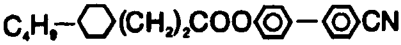
In present paper we continue to study the relaxation properties of LC with alkyl spacers, which were previously investigated in Ref.[1,6]. The compounds under investigation have been soluted in a weakly polar LC solvent. Concentrations of the solutions have been chosen such as to provide a similar clearing temperature for all mixtures.

An eutectic mixture:

$CH_3O\text{-}C_6H_6\text{-}C{\equiv}C\text{-}C_6H_6\text{-}C_7H_5$
$C_2H_5O\text{-}C_6H_6\text{-}C{\equiv}C\text{-}C_6H_6\text{-}C_8H_{17}$

which demonstrates the following phase sequence **C** 12°C **N** 64°C **I**, has been used as a solvent. The structural formulas, the phase transitions temperatures, the molecular characteristics (μ, β), the dielectric anisotropy, the concentrations (C, wt.%) and the molecular length (L, nm) of the compounds under investigation are presented in Table1. The notation of LC which are presented in the table corresponds to their mixtures in nematic solvent. The clearing point for the solutions LC1, LC2 and LC3 is 68°C.

TABLE 1 Structural forms and physical properties of the samples.

	Samples	μ,D	β°	Δε	C%	L,nm
LC1	 C 80°C N 242°C I	5,5	20	6,5	2	2,4
LC2	 C 71°C S_A 124°C N 174°C I	5,4	30	6,0	3	2,65
LC 3	 C 80 °C S_A 109°C I	5,3	30	-	8	3,03

For whole temperature interval of existence of mesophase in the mixtures under investigation, the principal dielectric permitivities $\varepsilon_{\|}'$ and the dielectric losses $\varepsilon_{\|}''$ have been measured within the frequency range 1kHz-100MHz.

For all liquid crystalline solutions under investigation, the dispersion of longitudinal component of the dielectric permitivity $\varepsilon_{\|}$, which is intrinsic to polar LCs, has been found. Since weakly polar LC has been used as a solvent, the observable dispersion is due to only dissolved strongly polar LC. This dispersion is caused by an exclusion of the orientational contribution, which is related to the rotation of the LC molecules around their short axes, from the dielectric polarization. The dependencies of $\varepsilon_{\|}$ on the frequency f of the electric field, for LC1, LC2, LC3 and for the solvent at the temperature 26,5°C are shown in Fig 1. In the same figure a circular diagram (the dependence of the dielectric losses $\varepsilon_{\|}''$ on the real part of the dielectric permitivity) is plotted for LC3. A center of the semicircle is disposed on the abscissa axis, that indicates the Debye character of the dispersion of $\varepsilon_{\|}$. The analogous diagrams have been obtained for LC1 and LC2.

From Fig.1 it is clearly seen that dispersion curves $\varepsilon_{\|}$ for the mixtures under investigation are shifted relatively to each other along the frequency scale. The maximum relaxation frequency f_R corresponds to the mixture LC3, which consists of molecules possessing a maximum spacer. At the same time, a solution of LC without spacer has a minimum relaxation frequency. Such a

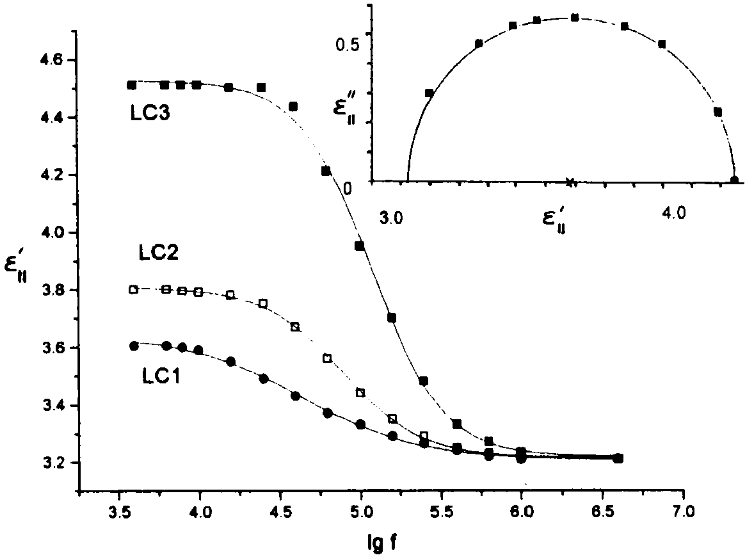


FIGURE 1 Dielectric permittivity $\varepsilon_{\parallel}'$ vs. frequency. $\varepsilon_{\parallel}''$ vs. $\varepsilon_{\parallel}'$ LC3 (50°C)

correlation between the relaxation frequency and length of the alkyl spacer in the LC1, LC2 and LC3 molecules has been observed in a whole temperature interval of existence of mesophase. This fact is illustrated by Fig.2, in which the dielectric relaxation time $\tau=1/2\pi f_R$ is plotted versus an inverse temperature 1/T for LC1, LC2 and LC3.

These results are in contradiction with a notion that an increase of length of the stick-like molecules should be accompanied by a decrease of the relaxation frequency f_R. This notion is based on the relationship[7]:

$$\tau=1/2\pi f_R=\pi\eta L^3/6kT(\ln 2p-0{,}8), \qquad (1)$$

which relates f_R to the molecular length L. Here k is Boltzman constant, η is the viscosity, p is the degree of the molecular asymmetry, and τ is the relaxation time.

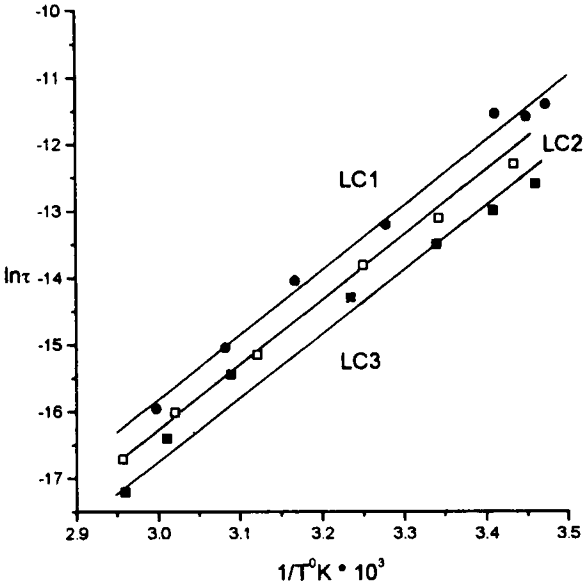


FIGURE 2 Temperature dependence of the relaxation times τ of solutions LC1 (●), LC2 (□) and LC3 (■).

For quantitative comparison between experimental and theoretical dependencies of τ on L^3, one can calculate a ratio τ/η for LC1, LC2 and LC3 by using relationship (1), magnitudes of L (Table 1), and assuming a similarity of a viscosity for all solutions.

The results of calculation and experimental data of τ (50°C) for LC1,LC2 and LC3 are shown in Fig.3. It is clearly seen that an increase of L (insertion of a spacer into molecule and it's lengthening) gives rise to a decrease of the relaxation time τ experimentally determined, whereas theoretical value of τ/η grows with increasing L. Apparently, this fact can be explained by that a presence of the alkyl spacer in a center of the LC2 and LC3 molecules can provide a partial, and even a complete freedom of a rotation of a rigid polar fragment $-COO-C_6H_6-C_6H_6-CN$ around the short molecular axis. Consequently, the dielectric polarization of LC2 and LC3 is not due to the rotation of the whole molecule around its short axis. This polarization is contributed by only reorientation of rigid polar fragment, which is separated by alkyl spacer from the nonpolar part of the molecule.

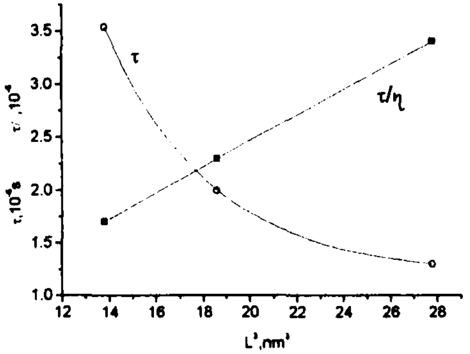


FIGURE 3 Relaxation times τ (50°C) and ratio τ/η vs. molecular length L

A similar situation is intrinsic to the polymer macromolecules, in which a chain of 5 carbon atoms (a length of the Kuhn's segment) can separate from each other the independently oriented parts of the chain. As said above, the insertion of the spacer into molecular center affects weakly the value μ and direction (the angle β) of the molecular dipolar moment (Table 1).

Thus, inserting the spacer into molecular center, one can weaken the correlation between different parts of the molecule and both molecular characteristics and the macroscopic relaxation characteristics of LCs can be determined by only the rigid polar part of the molecule.

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