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Preliminary Communication Dielectric relaxation in monotropic liquid crystals

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Preliminary Communication
Dielectric relaxation in monotropic liquid crystals

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A way of investigating dielectric relaxation phenomena occurring in the isotropic and liquid crystalline states by the use of monotropic mesogens is suggested. The application of common methods of dielectric spectroscopy in the radio frequency range (10^2–10^8 Hz) to strongly supercooled samples for the investigation of the amorphous liquid and low temperature monotropic liquid crystalline states is described. The possibility of experimental separation and investigation of the different dipole polarization mechanisms responsible for the dielectric properties of the monotropic mesogen 4-cyano-3-chlorophenyl 4-hexyl-3-chlorobiphenyl-4′-carboxylate (CChEC), whose molecules have longitudinal and normal permanent dipole moment components, is established.

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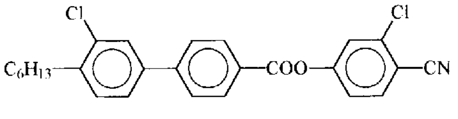
The dielectric properties of thermotropic liquid crystals exhibit a wide range of relaxation phenomena in the isotropic liquid and mesomorphous states. The investigation and comparison of dipole polarization mechanisms in the isotropic and liquid crystalline states usually require not only radio-frequency, but also microwave methods [1–4]. The latter limit the possibilities of a quantitative investigation of relaxation phenomena, especially for substances with high temperature phase transitions.

In the present paper, using radio-frequency range techniques, the first attempt is made to investigate quantitatively the molecular mechanisms governing the dispersion of the main dielectric permittivities of individual mesogens in the liquid crystalline and isotropic liquid states. The monotropic 4-cyano-3-chlorophenyl ester of 4-hexyl-3-chlorobiphenyl-4′-carboxylic acid (CChEC) was chosen for investigation. The latter is characterized by the phase transition temperatures Cr 74°C (N 33°C) I and exhibits the monotropic nematic (N) state in the temperature range 33–23°C. Measurements of the dielectric permittivities were carried out with the use of a TESLA BM507 impedance meter (5 Hz–500 kHz) and an RF impedance and transfer meter TESLA BM 538 (500 kHz–100 MHz).



CChEC

Figure 1 shows the Cole–Cole diagram obtained using experimental values of the real $\varepsilon'_{\mathrm{is}}$ and imaginary $\varepsilon''_{\mathrm{is}}$ parts of the complex dielectric permittivity $\varepsilon^*_{\mathrm{is}}$ measured for the isotropic liquid state. It is easy to see that in the frequency range $f = 10^2$–10^8 Hz the value of $\varepsilon^*_{\mathrm{is}}$ has a strong dispersion. As a result, in the high frequency range, the value of $\varepsilon'_{\mathrm{is}}$ differs negligibly from the square of the refractive index $n^2_{\mathrm{is}} = 2{\cdot}62$ at the same temperature. This means that all dipole mechanisms are excluded from the dielectric polarization during the dispersion of $\varepsilon^*_{\mathrm{is}}$. At the same time, the diagram (see figure 1) obviously indicates several molecular mechanisms governing the dispersion. That is why a further experimental analysis was carried out on the dependence of $\varepsilon'_{\mathrm{is}}$ on $\varepsilon''_{\mathrm{is}}2\pi f$. As suggested in [5], the slope of the experimental dependence of $\varepsilon'_{\mathrm{is}}$ versus $\varepsilon''_{\mathrm{is}}2\pi f$ gives the values of the relaxation times τ according to the equation

$$\varepsilon' = \varepsilon_0 - \tau(\varepsilon''2\pi f), \qquad (1)$$

where ε_0 is the static dielectric permittivity.

Figure 2 represents the plot of $\varepsilon'_{\mathrm{is}}$ versus $\varepsilon''_{\mathrm{is}}2\pi f$ according to equation (1) and the experimental data of figure 1. These results indicate that the dispersion of $\varepsilon^*_{\mathrm{is}}$ is determined by three dipole mechanisms corresponding to different (by about one order of magnitude) frequency ranges. The relaxation times $(\tau_{\mathrm{is}})_1$, $(\tau_{\mathrm{is}})_2$ and $(\tau_{\mathrm{is}})_3$ corresponding to different known dispersion mechanisms of $\varepsilon^*_{\mathrm{is}}$ are given in the table.

Analogous results were obtained by investigation of the dielectric properties of a macroscopically homogeneously

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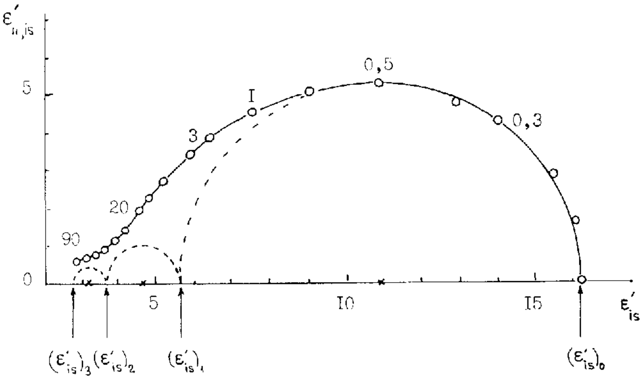

Figure 1. Cole–Cole plot of the components of ε^*_{is} for CChEC molecules in the isotropic phase at a temperature $T = 67°C$. Dashed line corresponds to the calculated data for the second and third dispersion ranges. The frequencies are given in MHz.

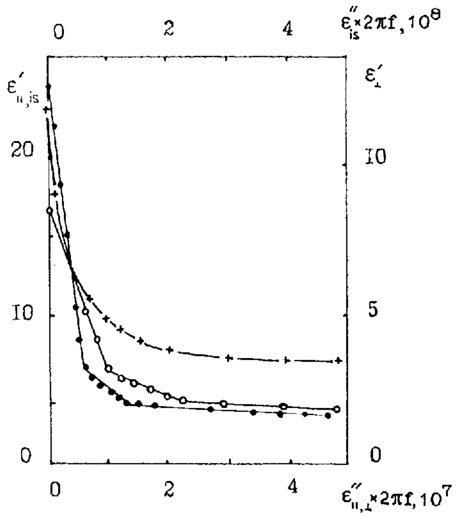

Figure 2. Values of $\varepsilon'_{\parallel}$ versus $\varepsilon''_{\parallel}2\pi f$ (●) and $\varepsilon'_{\perp}$ versus $\varepsilon''_{\perp}2\pi f$ (+) in the nematic and of ε'_{is} versus $\varepsilon''_{is}2\pi f$ (○) in the isotropic phases at temperatures 30°C, 24°C and 50°C, respectively.

oriented sample in the nematic state. The dispersions of the complex dielectric permittivities $\varepsilon^*_{\parallel}$ and $\varepsilon^*_{\perp}$ were measured in directions parallel and perpendicular to the optical axis of the sample. Figures 3 and 2 represent respectively, the Cole–Cole diagram and the corresponding plot of $\varepsilon'_{\parallel}$ versus $\varepsilon''_{\parallel}2\pi f$. Three regions of the main dielectric permittivity $\varepsilon^*_{\parallel}$ are clearly evident in the relaxation at each fixed temperature, just as was found for the isotropic phase. As to the dispersion of $\varepsilon^*_{\perp}$, it is also characterized by several dielectric relaxation mechanisms (figure 4 demonstrates this fact). However, the experimental dependence of $\varepsilon'_{\perp}$ versus $\varepsilon''_{\perp}2\pi f$ gives a smooth curve with a changing slope which does not permit us to distinguish different mechanisms of the $\varepsilon^*_{\perp}$ dispersion according to the method of [5]. Therefore, the method suggested in [6] was used for a quantitative analysis of these relaxation processes. According to the latter, the plot of the derivatives $d\varepsilon'_{\perp}/d(\varepsilon''_{\perp}f)$ and $d\varepsilon'_{\perp}/d(\varepsilon''_{\perp}/f)$ versus $\varepsilon''_{\perp}f$ and $\varepsilon''_{\perp}/f$, respectively, allows a determination of the number of relaxation processes m, and their relaxation frequencies $(f_r)_i$. The analysis of the dependence $\varepsilon'_{\perp}$ versus $\varepsilon''_{\perp}2\pi f$ using $(f_r)_i$ and m allows one to obtain the contributions of each relaxation mechanism to the $\varepsilon^*_{\perp}$ dispersion and to plot them on circle diagrams $(\varepsilon''_{\perp})_i$ versus $(\varepsilon'_{\perp})_i$. The circle diagrams obtained, together with the Cole–Cole diagram, plotted using experimental values of $\varepsilon''_{\perp}$ and $\varepsilon'_{\perp}$ at 24°C are represented in figure 4. Corresponding relaxation times $(\tau_{\perp})_{1,2,3} = 1/2\pi\,(f_r)_{1,2,3}$ are given in the table. It is easy to see, that at identical temperatures, the relaxation times $(\tau_{\parallel})_1$ and $(\tau_{\perp})_1$ differ by a factor of three, while the values of $(\tau_{\parallel})_2$ and $(\tau_{\perp})_2$ or $(\tau_{\parallel})_3$ and $(\tau_{\perp})_3$ are equal. This may be interpreted in terms of the identity of different molecular mechanisms responsible for the corresponding relaxation processes.

Apparently, for an understanding and explanation of the experimental data obtained, the molecular dipole structure of the investigated sample must be analysed

Dielectric polarization measurements using dilute solutions of CChEC in tetrachloromethane gave the value of the molecular dipole moment $\mu = 6{\cdot}6\,\mathrm{D}$. The angle β between the dipolar axis and the axis of maximum polarizability of the molecule was determined from Kerr constant measurements in dilute solutions and the equation for the molar Kerr constant

$$K_M = \frac{2}{9}\pi N_A \frac{\Delta b}{45kT}\left[2\Delta b + \frac{\mu^2}{kT}(3\cos^2\beta - 1)\right], \qquad (2)$$

where N_A is Avogadro's number and k is the Boltzmann constant.

The polarizability anisotropy Δb (we assume axial symmetry for the polarizability tensor), which is necessary for the calculation of the angle β, was obtained from refractive index measurements on the liquid crystal. The methods for experimental determination of K_M, μ and β have been previously reported; see for example, [7]. Experimental values of K_M, Δb and β are $7{\cdot}9 \times 10^{-9}\,\mathrm{cm}^5/(300\,\mathrm{V})^2$, $200 \times 10^{-25}\,\mathrm{cm}^3$, and 25°, respectively.

The value of the angle $\beta = 25°$ allows one to confirm the significant contribution to the dielectric properties of CChEC not only of the longitudinal component of the dipole moment $\mu_l = \mu\cos\beta$, but also of the normal component $\mu_2 = \mu\sin\beta$.

Taking into account the molecular dipole structure, the relaxation phenomena may now be analysed. It looks obvious that the low frequency dispersion of the main dielectric permittivities in the isotropic ε^*_{is} and in the nematic $\varepsilon^*_{\parallel}$ and $\varepsilon^*_{\perp}$ states, is related to the longitudinal dipole moment component. However, if the dispersion of

Dielectric relaxation times (s) in the nematic and isotropic phases of CChEC.

T/°C N phase	$(\tau_\parallel)_1 10^6$	$(\tau_\parallel)_2 10^7$	$(\tau_\parallel)_3 10^8$	$(\tau_\perp)_1 10^6$	$(\tau_\perp)_2 10^7$	$(\tau_\perp)_3 10^8$
24	95	80	35	30	55	23
26	65	60	30	25	55	20
28	50	45	35	15	50	19
30	30	25	25	10	50	18
T/°C I phase	$\tau_1 10^6$	$\tau_2 10^7$	$\tau_3 10^8$			
40	3	5·1	6·5			
50	1·1	1·5	2·0			
64	0·35	0·5	0·7			
67	0·3	0·4	0·5			

Error bounds are 10 per cent for relaxation times.

ε^*_{is} and $\varepsilon^*_\parallel$ is caused by the molecular rotation around the short (normal) axis, the low frequency dispersion of $\varepsilon^*_\perp$ may be governed by a precession of the longitudinal molecular axis about a conic surface. The realization of the latter is possible due to the incomplete (less than unity) orientational order in the liquid crystal [8–11]. The above marked difference between the relaxation times $(\tau_\parallel)_1$ and $(\tau_\perp)_1$ looks quite reasonable: the rotational motion of the longitudinal molecular axis around its normal requires the overcoming of potential barriers (the latter being responsible for the long-range orientational order in liquid crystals), while the precessional motion does not require that.

Evidently, for this reason, one and the same mechanism of molecular rotation around the short (normal) axis in the nematic and isotropic states may be characterized by relaxation times $(\tau_\parallel)_1$ and $(\tau_{is})_1$ differing by more than an order of magnitude—see the table. Along with the molecular mechanisms pointed out above, another one may be dielectrically active—related to rotation around the longitudinal axis. Exclusion of the latter mechanism from the dipole polarization causes the second dispersion region of ε^*_{is}, $\varepsilon^*_\parallel$ and $\varepsilon^*_\perp$ (see figures 1–4). As to the highest frequency range of the dielectric relaxation of ε^*_{is}, $\varepsilon^*_\parallel$ and $\varepsilon^*_\perp$ (the corresponding relaxation times are $(\tau_{is})_3$, $(\tau_\parallel)_3$ and $(\tau_\perp)_3$), this can probably be related to intramolecular rotations of different polar groups, for example rotation of the chlorocyanophenyl fragment around the *para*-aromatic axis of the 'crank-shaft' molecule [12]. The contribution of the latter mechanism to the dipole polarization of the sample is manifested in the highest frequency range of dispersion of ε^*_{is}, $\varepsilon^*_\parallel$ and $\varepsilon^*_\perp$.

This point of view on the different molecular mechanisms of dielectric relaxation is supported and confirmed

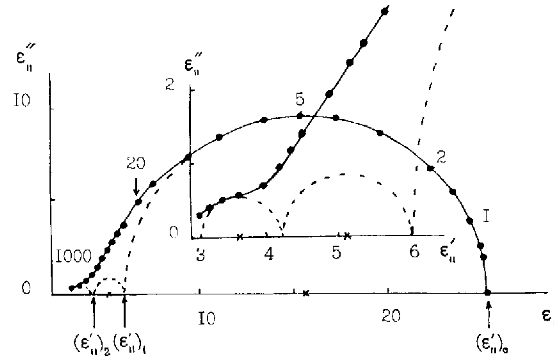

Figure 3. Cole–Cole plot of the components of $\varepsilon^*_\parallel$ in the nematic phase at temperature $T = 30$°C. Dashed line represents calculated data for the second and third dispersion ranges. The frequencies are given in kHz.

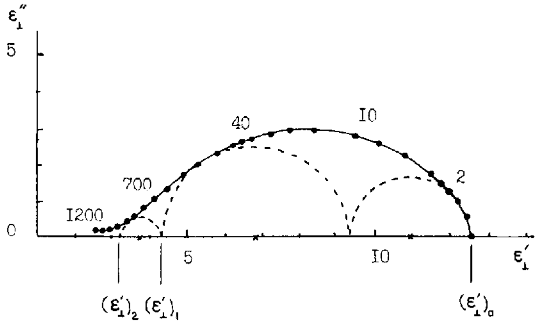

Figure 4. Cole–Cole plot of $\varepsilon^*_\perp$ in the nematic phase at a temperature $T = 24$°C. Dashed line represents calculated data for the second and third dispersion ranges. The frequencies are given in kHz.

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by the dipole structural analysis of the molecules based on the dielectric data presented above. In fact, the possibility of experimental separation of different dipole polarization mechanisms (see figures 1–4) enables one to determine the longitudinal and normal components of the molecular dipole moment. Taking the limiting values of the dielectric permittivities $\varepsilon'_{\mathrm{is}}$, corresponding to different frequency ranges, $(\varepsilon'_{\mathrm{is}})_0 = 16{\cdot}0$; $(\varepsilon'_{\mathrm{is}})_1 = 5{\cdot}7$; $(\varepsilon'_{\mathrm{is}})_2 = 3{\cdot}7$; $(\varepsilon'_{\mathrm{is}})_3 = n^2_{\mathrm{is}} = 2{\cdot}62$ (see figure 1), and using equation (2), where $i = 1, 2, 3$,

$$\mu^2_{i-1} = \frac{9(\varepsilon_i - \varepsilon_{i+1})(2\varepsilon_i + n^2_{\mathrm{is}})kT}{\varepsilon_i(n^2_{\mathrm{is}} + 2)4\pi N}, \qquad (3)$$

the values of the dipole moment components may be easily obtained as $\mu_1 = \mu \cos \beta = 5{\cdot}1\,\mathrm{D}$; $\mu_2 = \mu \sin \beta = 2{\cdot}4\,\mathrm{D}$ and $\mu_3 = 1{\cdot}9\,\mathrm{D}$. N is the number of molecules in the unit volume. Here for the limiting low and high frequency values of ε_i and ε_{i+1} for different dispersion ranges in equation (3), the experimental data presented above for $(\varepsilon'_{\mathrm{is}})_0$, $(\varepsilon'_{\mathrm{is}})_1$, $(\varepsilon'_{\mathrm{is}})_2$ may be used. The values obtained for μ_1, μ_2 and μ_3 give $\beta' = 29°$, which is quite close to the result mentioned earlier from independent measurements carried out using the sample in solution.

Results for the nematic phase could also be drawn from the dipole structure molecular analysis. For this purpose equations (4) and (5), relating the dielectric polarization $\varepsilon'_{\parallel}$ and $\varepsilon'_{\perp}$ to the longitudinal and normal components of the molecular dipole moment, can be used [8, 9]

$$\begin{aligned} (\varepsilon'_{\parallel})_0 - (\varepsilon'_{\parallel})_1 &= B\mu_1^2(1 + 2S), \\ (\varepsilon'_{\parallel})_1 - (\varepsilon'_{\parallel})_2 &= B\mu_2^2(1 - S), \end{aligned} \qquad (4)$$

$$\begin{aligned} (\varepsilon'_{\perp})_0 - (\varepsilon'_{\perp})_1 &= B\mu_1^2(1 - S), \\ (\varepsilon'_{\perp})_1 - (\varepsilon'_{\perp})_2 &= B\mu_2^2\left(1 - \frac{S}{2}\right), \end{aligned} \qquad (5)$$

where $B = 4\pi NPQ^2/3kT$, P and Q are Onsager's factors of the internal field, and S is the order parameter.

The employment of the values $(\varepsilon'_{\parallel})_0 = 28{\cdot}5$, $(\varepsilon'_{\parallel})_1 = 6{\cdot}0$, $(\varepsilon'_{\parallel})_2 = 4{\cdot}2$, $(\varepsilon'_{\perp})_0 = 12{\cdot}6$, $(\varepsilon'_{\perp})_1 = 9{\cdot}3$, $(\varepsilon'_{\perp})_2 = 4{\cdot}3$ and $S = 0{\cdot}6$ at $T = 24°\mathrm{C}$ in equations (4) and (5) leads to the following results: $\mu_1 = 5\,\mathrm{D}$, $\mu_2 = 3{\cdot}8\,\mathrm{D}$ (equation (4)) and $\mu_1 = 4{\cdot}5\,\mathrm{D}$, $\mu_2 = 3{\cdot}3\,\mathrm{D}$ (equation (5)). The value of order parameter $S = 0{\cdot}6$ was chosen by us because it is typical for the nematic phases of liquid crystalline materials at a temperature 10°C below T_{NI}. The μ values obtained differ negligibly from those obtained for the isotropic phase of CChEC. It should be mentioned that the experimental data in figures 3 and 4 illustrate the significant contribution of intramolecular polarization mechanisms to the dielectric properties of CChEC molecules, not only in the isotropic state, but also to the main dielectric permittivities $\varepsilon^*_{\parallel}$ and $\varepsilon^*_{\perp}$ in the liquid crystalline phase.

The results of the present paper show that the usage of the monotropic liquid crystalline state widely extends the possibilities of quantitative investigation of dielectric relaxation phenomena and analysis of dipole polarization molecular mechanisms in the isotropic, as well as in the liquid crystalline phases.

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