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Liquid Crystals

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Online publication date: 06 August 2010

To cite this Article Jadzyn, Jan , Legrand, Christian , Czechowski, Grzegorz and Bauman, Danuta(1998) 'Dielectric relaxation processes in the nematogen 4-cyanophenyl 4-n-heptylbenzoate', *Liquid Crystals*, 24: 5, 689 – 694

To link to this Article: DOI: 10.1080/026782998206795

URL: <http://dx.doi.org/10.1080/026782998206795>

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Dielectric relaxation processes in the nematogen 4-cyanophenyl 4-*n*-heptylbenzoate

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(Received 24 April 1997; in final form 25 October 1997; accepted 8 December 1997)

Experimental studies of the dielectric relaxation in the nematic and isotropic phases of 4-cyanophenyl 4-*n*-heptylbenzoate have been performed in the frequency range from 1 kHz to 1 GHz. In the nematic phase, measurements of the complex dielectric permittivity for two orientations of the director \mathbf{n} , parallel and perpendicular to the measuring electric field \mathbf{E} , have been carried out. It has been found that for $\mathbf{E} \parallel \mathbf{n}$, as well as in the isotropic phase, the dielectric spectra consist of two elementary domains, described by the Cole–Cole equation, whereas for $\mathbf{E} \perp \mathbf{n}$ three Cole–Cole-type domains can be distinguished. The possible molecular reorientational movements corresponding to these domains are discussed and comparison with the theoretical predictions is made.

1. Introduction

Dielectric spectroscopy yields valuable information about the molecular arrangement, intermolecular interactions and dynamics of the molecular reorientational motions in condensed matter. This method is very often used to study the molecular dynamics in various liquid crystalline phases because of its wide frequency range and its ability to follow the reorientational movements of dipolar groups or whole molecules [1]. According to the Nordio–Rigatti–Segre theory [2] as well as the theory proposed by Araki *et al.* [3] and generalized by Kozak *et al.* [4], four relaxation processes should be expected in the nematic phase of a liquid crystal. Two of them may be observed when the measuring electric field \mathbf{E} is parallel to the uniformly aligned director \mathbf{n} (ε_{\parallel}) and two for $\mathbf{E} \perp \mathbf{n}$ (ε_{\perp}). Recently, we investigated some nematic liquid crystals with the –NCS end group [5–8] and found two Debye-type relaxation processes in the nematic phase for $\mathbf{E} \parallel \mathbf{n}$: one was in the low MHz range and the second in the 0.7–1 GHz range of frequencies. We had attributed these processes to the rotation of the permanent dipole moment around the molecular short and long axes, respectively. The presence of the higher frequency relaxation in the parallel component of the dielectric spectrum gave evidence that the nematogen

molecules with the –NCS terminal group have a transverse component of the dipole moment. However, Buka *et al.* [9] had detected the high frequency relaxation in the dielectric spectrum for ε_{\parallel} of 4-heptyl- and 4-heptoxy-4'-cyanobiphenyl and explained it [10] by a combination of the rotational diffusion and flip-flop models.

Here we report the results of the dielectric relaxation study of 4-cyanophenyl 4-*n*-heptylbenzoate (1). This compound was synthesized in the laboratory of Professor R. Dąbrowski, Military Academy of Technology, Warsaw, Poland; figure 1 presents its formula and transition temperatures. We have performed dielectric measurements on the isotropic and nematic phases for both orientations of the director \mathbf{n} parallel and perpendicular to the electric field \mathbf{E} applied.

2. Experimental

Real and imaginary parts of the complex dielectric permittivity, $\varepsilon^* = \varepsilon' - j\varepsilon''$ were measured in the frequency range between 1 kHz and 1 GHz at different temperatures in the nematic and isotropic phases. The measuring cell

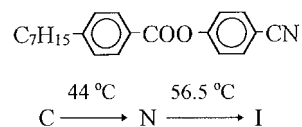


Figure 1. Structure of 4-cyanophenyl 4-*n*-heptylbenzoate (1).

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was constituted by a plane capacitor located at the end of a coaxial line [11]. Depending on the frequency region, two impedance analysers HP 4192 A (1 kHz–13 MHz) and HP 4191 A (1 MHz–1 GHz) connected with a HP 87 computer were used. In the nematic phase the molecules were oriented by means of a magnetic field of 1.2 T, and measurements were performed for $\mathbf{E} \parallel \mathbf{B}$ (ϵ_{\parallel}^*) and $\mathbf{E} \perp \mathbf{B}$ (ϵ_{\perp}^*). The accuracy of the results was better than 2% for ϵ' and 5% for ϵ'' . The temperature of the sample remained stable within $\pm 0.1^\circ\text{C}$.

3. Results

We measured the dielectric properties of compound **1** over the temperature range between 45 and 70°C . Figure 2 presents the static dielectric permittivity ϵ_s of **1** versus temperature in the nematic and isotropic phases. As can be seen, the dielectric anisotropy of the liquid crystal investigated is positive, due to the strong permanent electric dipole moment of the end $-\text{CN}$ group directed almost parallel to the molecular long axis. The average dielectric constant $\epsilon = (\epsilon_{\parallel} + 2\epsilon_{\perp})/3$ in the nematic phase is also shown in figure 2. The values of ϵ are lower than the values of ϵ_{iso} , which can be attributed to the antiparallel alignment of the molecules with their strong dipole moments in the nematic phase. Such an association of molecules with polar terminal $-\text{CN}$ groups has been manifoldly demonstrated by X-ray diffraction measurements [12], as well as by dielectric studies [13–19]. Figures 3(a) and 3(b) show the typical frequency dependence of the real (ϵ') and imaginary (ϵ'') parts of the dielectric permittivity, and figure 3(c) presents plots of ϵ'' versus ϵ' for **1** in the nematic and isotropic phases. It is seen that in the nematic phase, the most dominant dielectric relaxation process occurs in the low MHz range. In this range ($f \approx 7$ MHz) the

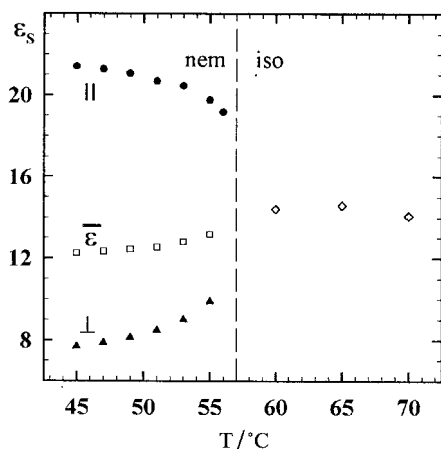


Figure 2. Static dielectric permittivity as a function of temperature in the nematic and isotropic phases for compound **1**.

dielectric anisotropy ($\Delta\epsilon = \epsilon'_{\parallel} - \epsilon'_{\perp}$) changes sign from positive to negative. In the detailed analysis of the dielectric data presented in figure 3 one must always realize that in the case of ϵ_{\perp}^* we are dealing with a relatively small amplitude of the dielectric response of the system.

In the molecule of **1**, two main polar groups, $-\text{COO}$ and $-\text{CN}$ can be distinguished. These two groups contribute to the resultant value of the permanent dipole moment and its direction does not correspond to the molecular long axis. Therefore, in the dielectric spectrum at least two dispersion regions, related to the longitudinal (μ) and transverse (μ_{\perp}) components of the dipole moment,

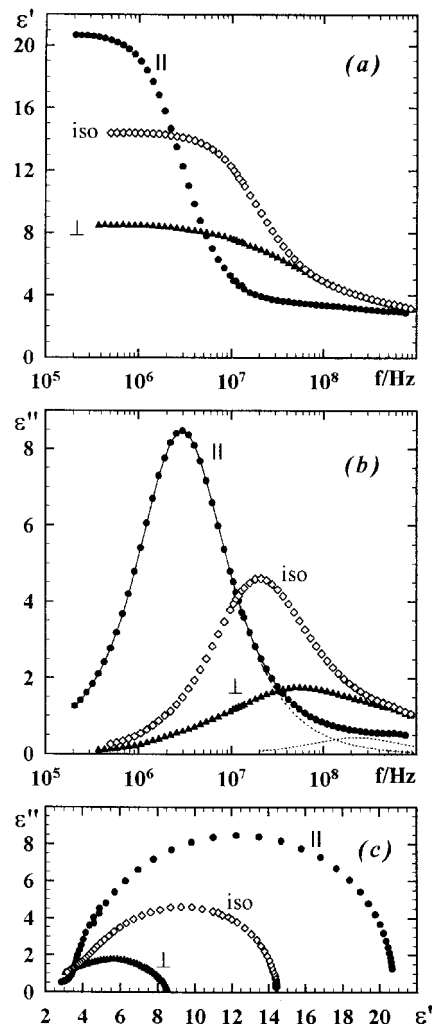


Figure 3. Experimental results of measurements of the complex dielectric permittivity as a function of frequency for compound **1** in the nematic ($T = 51^\circ\text{C}$) and isotropic ($T = 65^\circ\text{C}$) phases: (a) real part of dielectric permittivity, (b) imaginary part of dielectric permittivity, (c) ϵ'' versus ϵ' . Dashed curves in figure 3(b) (for ϵ_{\parallel}) represent resolved Cole–Cole type components, whereas the solid curve is the sum of these components.

should appear. According to theory [3,4], the auto-correlation functions of the dipole moment components can be written as follows:

$$\langle \mu_{\parallel}(0)\mu_{\parallel}(t) \rangle = \frac{1}{3} [\mu_l^2(1+2S)\phi_{00}^1(t) + \mu_t^2(1-S)\phi_{01}^1(t)] \quad (1a)$$

$$\langle \mu_{\perp}(0)\mu_{\perp}(t) \rangle = \frac{1}{3} \left[\mu_l^2(1-S)\phi_{10}^1(t) + \mu_t^2 \left(1 + \frac{S}{2} \right) \phi_{11}^1(t) \right] \quad (1b)$$

where S is the nematic order parameter and $\phi_{ij}(t)$ ($i, j = 00, 01, 10, 11$) are the functions related to the four relaxation modes, which involve the motions of the molecular axes in Euler space [4, 20].

Based on these theoretical calculations and taking into account our previous results [5–8], we have tried to separate the dielectric spectra experimentally obtained into two components. However, here we have assumed a more general case, where these components are described by the Cole–Cole equation [21]:

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \sum_{i=1}^n \frac{A_i}{1 + (j\omega\tau_i)^{1-k_i}} \quad (2)$$

Parameter k characterizes the distribution of the relaxation times, and when it is equal to zero equation (2) reduces to the Debye equation. A_i and τ_i denote the dielectric strength and the relaxation time, respectively. The strength A_i is a difference between the static and high frequency values of the permittivity, $\varepsilon'_{0i} - \varepsilon'_{\infty i}$, related to a given relaxation process. A_i , τ_i and k_i are adjustable parameters in the fitting procedure, which has been made using the least-squares method.

Figure 4 presents the numerical decomposition of the experimentally obtained ε'' versus ε' into components described by the Cole–Cole equation. In the isotropic phase and for the parallel component of the permittivity in the nematic phase, the experimental data can be fitted very well with two Cole–Cole plots. It was found that for the case $\mathbf{E} \parallel \mathbf{n}$, over the whole range of temperature studied, the k_1 parameter is almost equal to zero (≤ 0.01), and the k_2 parameter is of the order 0.1, but the error in the estimation of the latter value is about 50% because of the very small amplitude A_2 . However, the existence of the second relaxation process in $\varepsilon_{\parallel}^*$ seems to be clear, as shown in figure 3(b).

In the isotropic phase the need for decomposition of the dielectric spectrum into two components is not in question. From our fits, it follows that with rise of temperature the distribution of the relaxation times in the first component increases ($k_1 = 0.02, 0.04$ and 0.06 for $60^\circ, 65^\circ$ and 70° , respectively), whereas the opposite situation is observed for the second component

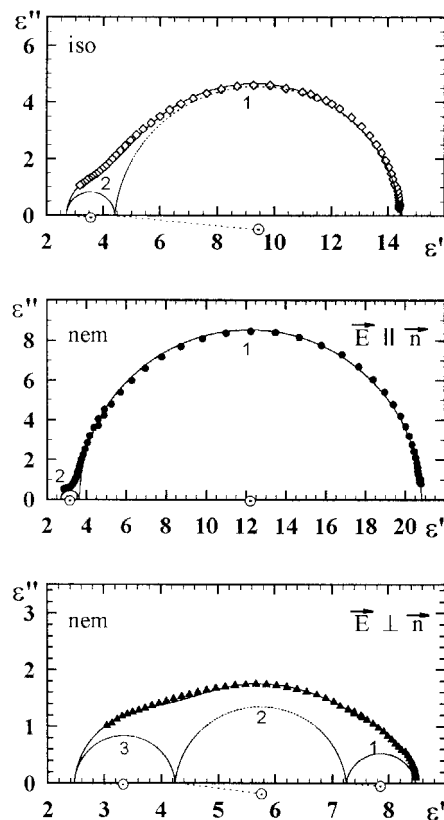


Figure 4. Cole–Cole diagrams for the isotropic phase ($T = 65^\circ\text{C}$) and two orientations in the nematic phase ($T = 51^\circ\text{C}$).

($k_2 = 0.06, 0.04$ and 0.02 for $60^\circ, 65^\circ$ and 70° , respectively). Attempts to resolve the curve of $\varepsilon(\omega)$ for $\mathbf{E} \perp \mathbf{n}$ into two Cole–Cole regions did not give a satisfactory fit to the experimental data. It was found that good fitting is possible only when the existence of three relaxation regions is assumed. We have obtained the following values of the k parameters: $k_1 = k_2 = 0.08 \pm 0.02$, $k_3 = 0.04 \pm 0.02$ (independent of temperature). Our results are in good agreement with those obtained by Lippens *et al.* [13], Druon and Wacrenier [22] and Nozaki *et al.* [23], who had also resolved the perpendicular component of the dielectric permittivity of some nematics into three domains.

The values of A_i and τ_i resulting from our fits are presented in table 1 and in figures 5 and 6. Using the Arrhenius equation and the data given in figure 6, the activation energies corresponding to the particular domains were calculated and the results are gathered in table 2.

4. Discussion

For the molecule of compound **1**, the longitudinal component of the dipole moment μ_l is significantly higher than the transverse component μ_t , and therefore

Table 1. Dielectric strength (A_i) and relaxation times (τ_i) corresponding to the various modes of molecular movements for compound 1.

$T/^\circ\text{C}$	A_1	τ_1/ns	A_2	τ_2/ns	A_3	τ_3/ns
Nematic, $\mathbf{E}\parallel\mathbf{n}$						
45	17.91	94.35	0.88	0.78	—	—
47	18.00	80.39	0.86	0.46	—	—
49	17.44	65.08	1.05	0.60	—	—
51	17.18	53.42	0.95	0.70	—	—
53	16.97	42.44	1.15	0.61	—	—
55	16.10	33.02	1.11	0.57	—	—
56	15.25	27.69	1.23	0.66	—	—

Nematic, $\mathbf{E}\perp\mathbf{n}$						
45	0.82	33.86	2.47	3.51	1.96	0.40
47	0.86	29.19	2.89	3.15	1.67	0.34
49	0.93	24.77	3.03	3.12	1.69	0.34
51	1.22	19.57	3.00	2.98	1.78	0.33
53	1.36	17.88	3.36	3.05	1.80	0.31
55	1.85	15.53	3.53	3.27	2.02	0.32

Isotropic						
60	10.04	7.74	1.72	0.40	—	—
65	10.14	5.96	1.80	0.35	—	—
70	8.80	4.78	1.74	0.32	—	—

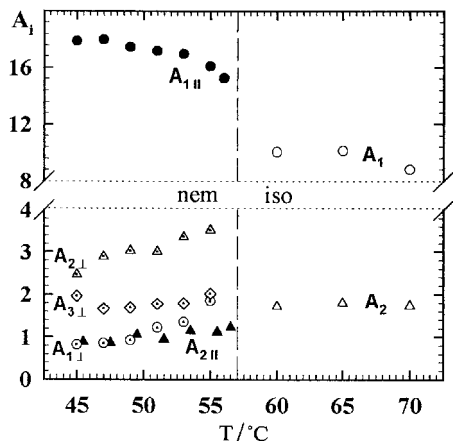


Figure 5. Dielectric strengths versus temperature for compound 1 in the nematic and isotropic phases.

the relaxation process with the highest strength observed in the dielectric spectrum for the case $\mathbf{E}\parallel\mathbf{n}$ (domain 1) must be connected with the rotation of the permanent dipole moment around the molecular short axis. This rotation is strongly affected by the nematic potential, and therefore is characterized by the longest relaxation time, in agreement with theory [2–4] (mode 00). As the temperature rises, the orientational order decreases and as a result τ_1 and A_1 grow smaller. At the nematic–isotropic phase transition, a jump in both these values, as well as a significant change in the activation energy, is observed. The parameter k for this process is very

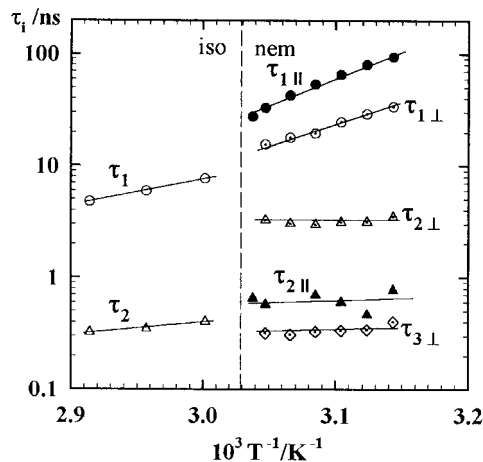


Figure 6. Relaxation times τ_i versus temperature for compound 1 in the nematic and isotropic phases.

Table 2. Activation energy E_A^a (kJ mol^{-1}) for particular domains in the nematic and isotropic phases for compound 1.

Phase	Domain		
	1	2	3
Nematic, $\mathbf{E}\parallel\mathbf{n}$	91	~ 0	—
Nematic, $\mathbf{E}\perp\mathbf{n}$	70	~ 0	0
Isotropic	46	21	—

^aThe accuracy of E_A determination is about $\pm 2 \text{ kJ mol}^{-1}$.

small, suggesting that in the first approximation it can be described by the Debye function, as has been found previously for other liquid crystal materials [5–9, 13, 22]. The process corresponding to domain 2 in the parallel component of the permittivity is most probably related to the pure reorientational movements of the molecule around the long axis (mode 01). This process is characterized by the shortest relaxation time and is revealed in the dielectric spectrum of ε_{\parallel} only because $\mu_{\perp} \neq 0$ and the relaxation strength A_2 is very small in comparison with A_1 . The rotation around the long axis is not influenced by the nematic order and τ_2 remains constant within experimental uncertainty over the whole temperature range of the nematic phase. The activation energy is about zero, suggesting that the rotation around the molecular long axis is quite free.

In the perpendicular component of the permittivity, the high frequency relaxation process (domain 3) has a very similar relaxation time to τ_2 for $\mathbf{E}\parallel\mathbf{n}$ and its activation energy is also equal to zero. In theory [2–4], this process is defined as mode 11 and because it is connected with the transverse component of the dipole moment, it must be dominated by molecular rotation around the long axis. However, the contribution

from other movements (precession about the director, librational motions) cannot be excluded. The relaxation strength of domain 3 in ε_{\perp} as well as the relaxation time τ_3 do not change with temperature in the nematic phase, which means that the influence of the nematic order on this kind of motion is negligible.

According to theory [2–4], the mode 10, which should be observed in ε_{\perp} is associated with stochastic precessional movements and/or fluctuations of the molecular long axis with respect to the director and is, to some extent, influenced by the long range orientation [12]. Therefore, it is possible that in the experimentally obtained dielectric spectrum, the relaxation time corresponding to this mode will be longer than that connected with the 11 and 01 modes. The domain 2 appearing in ε_{\perp} for **1** is characterized by a resultant relaxation time which is about one decade longer than the time for domain 3. We suppose that this domain could be related to the mode 10. Its relaxation strength increases with rise in temperature in the nematic phase and the characteristic relaxation time remains almost constant. The activation energy is about 0, similar to that for domain 3.

The relaxation processes corresponding to domain 1 in ε_{\perp} are not predicted by theory [2–4]. It is true, that the relaxation time corresponding to domain 1 observed in $\mathbf{E}_{\perp}\mathbf{n}$ is of the same order of magnitude as τ_1 in the case of $\mathbf{E}\parallel\mathbf{n}$. Therefore, it could be connected with the rotation around the molecular short axis and revealed in the dielectric spectrum because of imperfect orientation of the sample. However, in this case both τ_1 times (for ε_{\parallel} and ε_{\perp}) should be exactly equal. Meanwhile, τ_1 for $\mathbf{E}_{\perp}\mathbf{n}$ is about two to three times shorter than that for $\mathbf{E}\parallel\mathbf{n}$ and a difference in the activation energy occurs. Similar observations have been made by other authors [13, 22]. One possible way to explain the results obtained at low frequency is by assuming that there exists an orientation defect which is not permanent. Druon and Wacrenier [22] had supposed that this defect is related to the existence of small groups of associated molecules with a life time of the same order of magnitude as τ_1 for $\mathbf{E}\parallel\mathbf{n}$, these groups containing 100–200 molecules [12, 22]. In the simplest model, which describes the molecular association due to dipole–dipole interaction, the existence of only a pair of associated molecules is considered, which means the occurrence in the liquid crystal sample of both monomers and dimers. Steric interactions can then lead to tilting of the long axis of the dimer and a neighbouring monomer, and as a result the mean direction of the molecular axes in the group of associated molecules can create an angle with the director, \mathbf{n} . Assuming such interactions Dalmolen *et al.* [17] tried to explain the significant broadening of the molecular distribution function for some 4-alkyl-4'-cyanobiphenyls with respect to this function as predicted

by mean-field theories of nematics [24, 25]. Wacrenier *et al.* [26] introduced the hypothesis about the existence of an orientation defect with a short correlation time into the Nordio, Rigatti and Segre theory [2] and obtained very good agreement between theoretical predictions and experimental results. It seems that the occurrence of domain 1 in the perpendicular component of the dielectric spectrum of the liquid crystal investigated in this work can also be interpreted in this way, because the ability of this compound to undergo molecular association is confirmed by the results presented in figure 2.

In the isotropic phase the dielectric spectrum is a weighted sum of all relaxation processes, although we are also able to distinguish in ε_{iso} 2 domains with very different relaxation times, relaxation strengths and activation energies. The dominant process (domain 1) is very probably related to the rotation of the dipole moment around the molecular short axis, but contributions from other relaxation processes cannot be excluded. The second domain of the critical frequency is similar to the frequency of domain 2 for $\mathbf{E}\parallel\mathbf{n}$, and domain 3 for $\mathbf{E}_{\perp}\mathbf{n}$ in the nematic phase is probably connected with some sort of stochastic precessions, fluctuations and reorientations of molecules around their long axes. The activation energy is now different from zero in contrast with the nematic phase. This indicates that the nematic packing is able to improve the conditions for rotation of molecules around the long axes in comparison with the rotation of randomly distributed molecules in the isotropic phase. The relaxation times corresponding to both domains in the isotropic phase decrease with increasing temperature because of diminishing viscosity.

This work was supported by Polish Research Project No. 2P 03B 160 09, coordinated by KBN.

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