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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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To cite this Article Kresse, H. , Hartmann, P. , Schäfer, W. and Szulzewsky, I.(1991) 'Dielectric relaxation of a nematic eutectic mixture with a high glass temperature', *Liquid Crystals*, 10: 1, 127 – 133

To link to this Article: DOI: 10.1080/02678299108028236

URL: <http://dx.doi.org/10.1080/02678299108028236>

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Dielectric relaxation of a nematic eutectic mixture with a high glass temperature

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(Received 12 November 1990; accepted 16 February 1991)

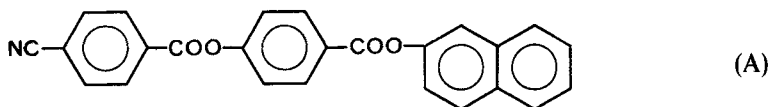
Dielectric relaxation measurements in the frequency range from 2 Hz to 100 kHz have been carried out on an oriented binary nematic mixture of low molecular liquid crystals with a glass temperature of 307 K. For both relaxation frequencies, $f_{R\parallel}$ and $f_{R\perp}$, a glass behaviour according to the Vogel-Fulcher law could be detected. The Cole-Cole distribution parameter for reorientation around the long molecular axis increases strongly with decreasing temperature. This effect is discussed with regard to the optical biaxiality of the mixture.

1. Introduction

Recently low molecular liquid crystals with relatively high glass transition temperatures have been synthesized [1-3]. The disadvantage of these new substances is the high melting temperature of about 440 K in relation to the glass temperature of about 300 K. It was shown by Wedler *et al.* [3] that in multicomponent eutectic mixtures the crystallization can be avoided at moderate cooling rates of 5 K min^{-1} . By calorimetric measurements, the samples have been found to be fairly stable in time when maintained at a temperature of about 20 K above the glass transition. A tendency toward crystallization is found to increase with increasing temperature. Dielectric relaxation measurements on oriented samples proved that both reorientation processes, the rotation around the short and long axes of the molecules follow the Vogel-Fulcher law. In the glass state all of these processes are frozen, however, a separate absorption peak has been detected and attributed to an intramolecular motion [4]. The aim of this article is to present a systematic dielectric investigation of a sample with a higher glass temperature and a lower tendency to crystallization than the sample investigated before [4] in order to obtain quantitative data on the intensity of the respective relaxation processes.

2. Substances and experiments

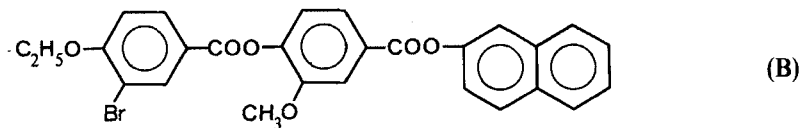
The substances, 4-(4'-cyanobenzoyloxy)-(2-naphthyl)-benzoate



C 447.5 K (g 290.0 K) N 581.2 K I, $x_A = 0.20$

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and 3-methoxy-4-(3-bromo-4-ethoxybenzoyloxy)-[2-naphthyl]-benzoate



CI 407 K CII 422 K (g 300 K N 382 K)I, $x_B = 0.80$

were mixed in the isotropic phase with the mole fractions given. For the eutectic mixture the following transition temperatures, have been found by microscopic and calorimetric investigations: C 409 K (g 307 K) N 412 K I.

The measuring cell consists of two silver plates ($d = 200 \mu\text{m}$, $A \sim 2 \text{ cm}^2$), and was calibrated with cyclohexane. Dielectric measurements were made using a modified Sawyer-Tower bridge [5] in the frequency range 1 Hz to 100 kHz. The bridge was limited to a resistance of $R < 2 \text{ G}\Omega$.

The sample was cooled from a high temperature in the isotropic phase (435 K) at a rate of 3 K min^{-1} in a magnetic field of 0.7 T which was applied in the direction perpendicular to the measuring electric field thus mainly permitting the study of the rotation of the transversal dipoles. The dielectric absorption curves shown in figure 1

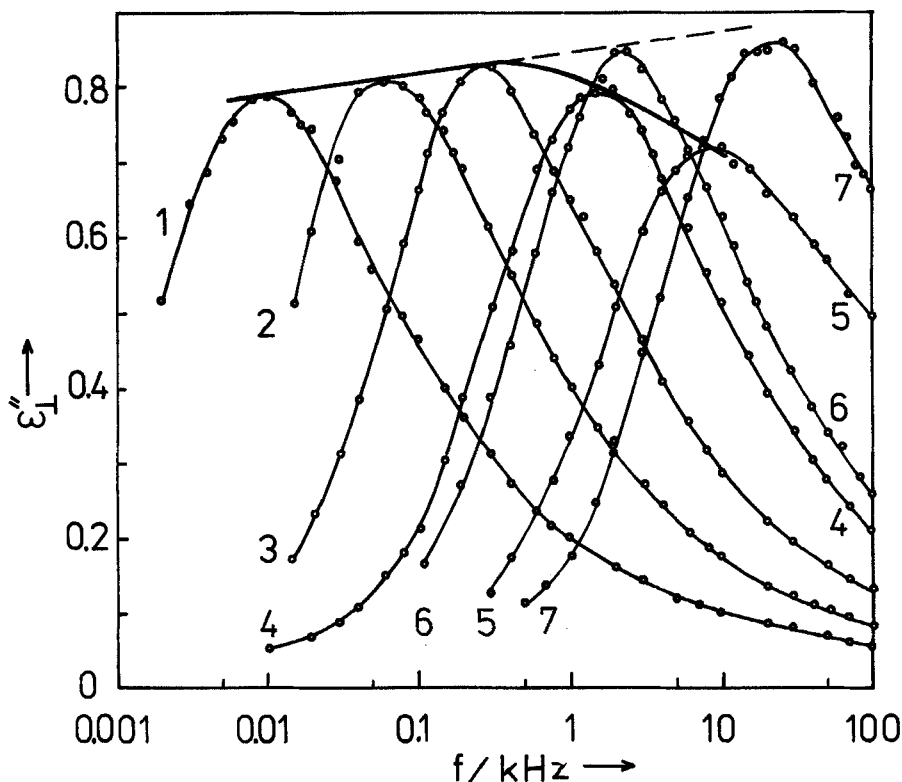


Figure 1. The dielectric loss as a function of frequency measured for the configuration in which the electric and magnetic fields are perpendicular. $T(1) = 316.9 \text{ K}$, $T(2) = 322.2 \text{ K}$, $T(3) = 326.5 \text{ K}$, $T(4) = 331.2 \text{ K}$, $T(5) = 336.9 \text{ K}$, $T(6) = 332.7 \text{ K}$ and $T(7) = 342.7 \text{ K}$. The maxima from $T(1)$ to $T(5)$ are connected by a line; the expected maximum intensity is indicated by a broken line.

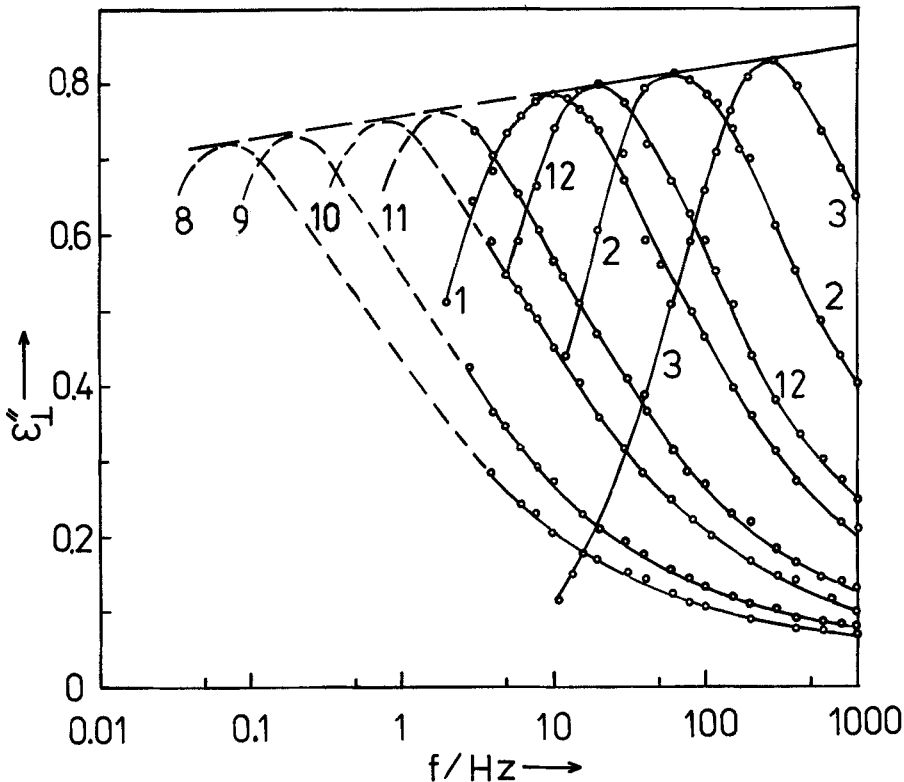


Figure 2. ϵ''_T -Values at lower temperatures $T(8)=308.5$ K, $T(9)=309.7$ K, $T(10)=312.2$ K, $T(11)=313.9$ K, $T(12)=319.2$ K and at $T(1)$, $T(2)$, $T(3)$ of figure 1. The broken line at the top indicates the expected intensity at the maximum. The broken lines at different temperatures are extrapolated absorption curves. The absorption curves of $T(13)$ – $T(17)$ are not shown in figures 1 and 2.

were obtained in the following thermal sequence. The sample was cooled to 316.9 K where we measured the absorption curve 1. Curves 2, 3, 4 and 5 we measured on heating. In order to diminish the effect of crystallization on the absorption intensity which can be seen in curves 4 and 5, we heated the sample to the isotropic phase and then cooled to 332.7 K, measurements performed at this temperature are presented by curve 6. Again the sample was heated to the isotropic phase and cooled to 342.7 K; the result is given by curve 7.

Figure 2 shows a set of absorption curves measured after cooling the sample from the isotropic phase to 308.5 K (see curve 8). Curves 9, 10, 11 and 12 were obtained by heating. The absorption maximum value of curve 12 is found to fit well on the extrapolated line from curves 1–3 obtained from figure 1. It is worth mentioning that during this heating run there was no indication of crystallization. Due to the low frequency limitations of our bridge the absorption maximum of curves 8–11 has been estimated by linear extrapolation obtained from the absorption maxima of curves 1, 2, 3 and 12. As an approximation the same shape (Cole–Cole distribution parameter) for the absorption curves 8–11 as for curve 1 has been used. This extrapolation method has enabled us to determine approximate values of relaxation frequency for the measurements at lower temperatures. The error bars are given in figure 5.

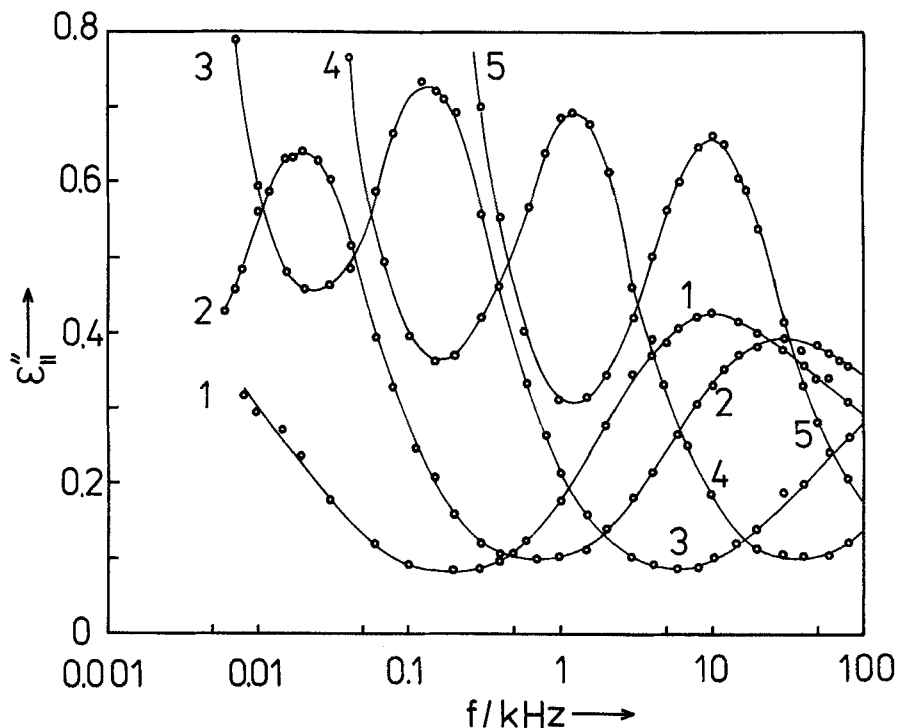


Figure 3. Dielectric absorption curves of $\epsilon''_{||}$ at $T(1)=336.7$ K, $T(2)=341.9$ K, $T(3)=350.2$ K, $T(4)=360.9$ K and $T(5)=373.2$ K. Data of $T(6)$ – $T(13)$ are not given.

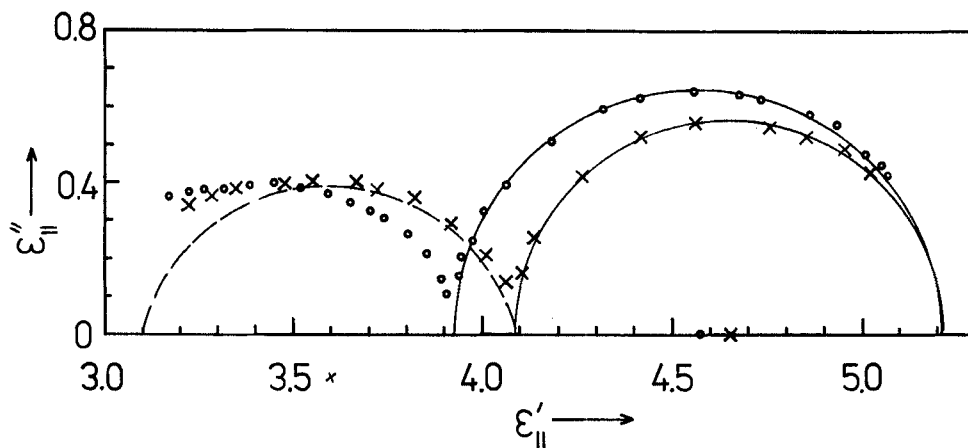


Figure 4. The Cole-Cole plot of $\epsilon''_{||}$ at $T=340.2$ K (\times) and $T=341.9$ K (\circ).

In order to study the reorientation of the longitudinal electric dipole, the sample was heated for every measurement into the isotropic state and cooled down to the respective temperature in a magnetic field which was parallel to the electric measuring field. At 341.9 K (see curve 2 in figure 3) we can see that there are two absorption maxima, one at about 20 Hz and the other at 30 kHz. At the lower temperature $T(1)$ of 336.7 K only the high frequency absorption peak could be detected whereas at the

higher temperatures of curves 3–5 only the low frequency peak is observed and at low frequencies the contribution of the conductivity to ϵ''_{\parallel} was measured. In relation to the former experiments we have to take into account a small degree of crystallization because of the relatively high temperatures necessary to detect the low frequency absorption of ϵ''_{\parallel} .

The Cole–Cole plot at 341.9 K in figure 4 demonstrates that the low frequency absorption can be described by a Debye relaxation. The corresponding high frequency process was approximated at low frequencies by a Cole–Cole equation.

3. Discussion

Two interesting results can be deduced from the experiments. The first is shown in the Arrhenius plot in figure 5. The Debye relaxation process for the molecular reorientation around the short axis, indicated by $f_{R\parallel}$, is the slowest detected relaxation. The high frequency absorption found in the parallel direction (see figure 3) has the same relaxation frequency as the reorientation around the long molecular axis given in figures 1 and 2. Therefore, we can assume that this process is also related to the reorientation around the long molecular axis and can be observed due to fluctuations of the directions of the molecular long axis [6, 7] and perhaps this effect arises in part from the destruction of the nematic order due to the beginning of crystallization.

Generally both relaxation processes can be fitted to the Vogel–Fulcher law [8]

$$f_R = f_{R0} \exp[-A/(T - T_0)],$$

where f_{R0} and A are constants and T_0 is the temperature at which $f_R \rightarrow 0$. Due to the lack of experimental points at low frequencies of $f_{R\parallel}$ and the extrapolation of $f_{R\perp}$ of the last five points, the T_0 values for the parallel and the perpendicular values of f_R given in the table are not in agreement with each other. Generally there is no reason why T_0 for each process should be the same.

However, we have to consider that by calorimetric investigations only one step in C_p at 307 K could be detected. This means there are no separate freezing-in processes for $f_{R\parallel}$ and $f_{R\perp}$. Probably both reorientation processes are coupled with each other and restricted to the same glass transition.

A second result can be deduced from the Cole–Cole plot given in figure 6. The interesting point is that the maximum of ϵ''_{\perp} decreases with decreasing temperature which is quite unusual. On the other hand the perpendicular component of the static dielectric constant increases at lower temperatures. From a phenomenological point of view this effect can be described by a strong increase of the distribution parameter if we neglect deviations on the high frequency side. One possible explanation for this behaviour is an increasing tendency for the decoupling of different molecular motions from each other. If we assume a stronger hindrance of the rotation of the relatively board-like naphthyl part in both compounds of the mixture it may result in a slowing down of the relaxation frequency of the COO group coupled to the naphthyl group. On

Fitting parameters according to equation (1).

Process	Number of points	f_{R0}/Hz	A/K	T_0/K
$f_{R\perp}$	13	4.85×10^{13}	3258	228
$f_{R\parallel}$	17	2.56×10^{11}	1277	264

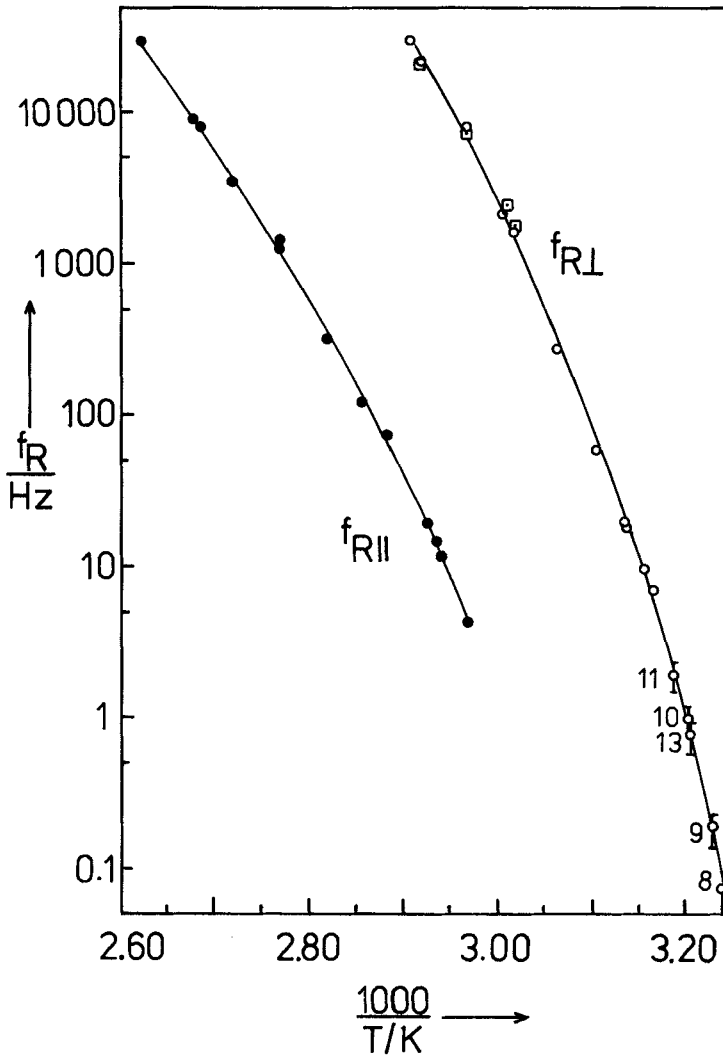


Figure 5. The Arrhenius plot of the relaxation frequencies $f_{R||}$ and $f_{R\perp}$. The low frequency absorption of $\epsilon''_{||}$ is indicated by ● whereas the high frequency is shown by □. The data of □ agree well with the points of $f_{R\perp}$ (○). The lines are related to the fitted curves according to equation (1). The extrapolated relaxation frequencies according to figure 2 (curves 8–11) and an additional one (13) are indicated.

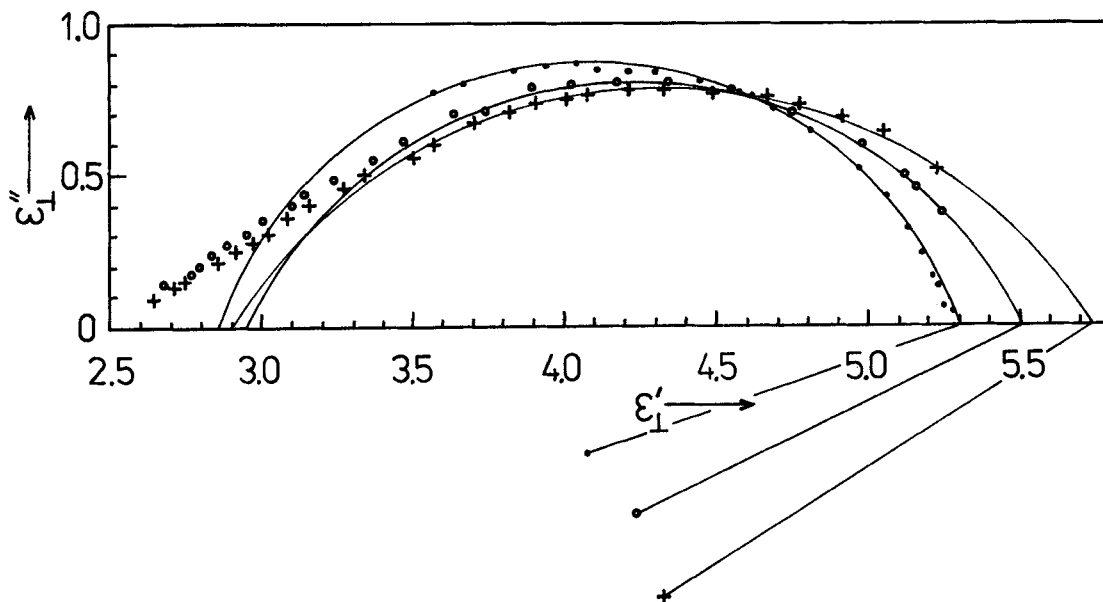


Figure 6. The Cole-Cole representation of ϵ''_{\perp} . The high frequency part was neglected from $\epsilon'_{\perp} < 0.5$. $T = 342.2$ K (●), 322.2 K (○) and 316.9 K (+).

the other hand the naphthyl groups can show a tendency for an orientation perpendicular to the nematic director like a stack of boards if the free volume is reduced. Therefore, the hindrance of the naphthyl group rotation may manifest itself in an optical biaxiality, a result which has been confirmed by means of optical conoscopy [9].

The authors wish to thank Professor Dr Demus, Dr sc. G. Pelzl and Dr W. Wedler for helpful discussions and Dipl. Chem. U. Bakowski for the conoscopic investigations.

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