MOLECULAR DYNAMICS OF
n-p-(ETHOXYBENZYLIDENE) p'-PROPYLANILINE
IN NEMATIC AND SOLID PHASES AS STUDIED
BY DIELECTRIC RELAXATION SPECTROSCOPY

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The complex dielectric permittivity $\varepsilon^*(\nu, T) = \varepsilon'(\nu, T) - i\varepsilon''(\nu, T)$ of n-p-(ethoxybenzylidene) p'-propylaniline has been measured in the frequency range from 1 Hz to 13 MHz and temperature range from 360 K to 180 K on heating and on cooling the sample. Dielectric relaxations have been found in nematic and solid phases. A detailed analysis of the observed processes has been performed and the parameters describing molecular dynamics have been evaluated. The comparison of results with those obtained for the other Schiff bases is discussed.
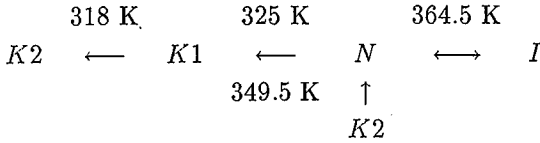
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1. Introduction

Dielectric relaxation spectroscopy (DRS) is a very efficient method used for investigation of the dynamics of dipolar molecules. Due to the wide frequency range available the detection of molecular reorientations can be performed in liquids, glasses, and solids [1]. In the paper we used the DRS to study the ethoxybenzylidene propylaniline (EBPA) liquid crystalline material revealing the polymorphism of solid state [2]. Our aim was to understand the complexity of the dielectric permittivity data observed for all phases as a composition of the single-particle relaxation processes. In addition our goal was to check whether the temperature dependence of evaluated parameters reflects the phase transitions found in our differential scanning calorimetry and polarising microscopy studies [2, 3].

2. Experimental

The chemical structure of EBPA is shown below. The phase diagram found for the typical cooling and heating rates of about 5 K/min [2] is the following:

$$
\begin{array}{ccccc}
318\text{ K} & & 325\text{ K} & & 364.5\text{ K} \\
K2 & \longleftarrow & K1 & \longleftarrow & N & \longleftrightarrow & I \\
& & 349.5\text{ K} & \uparrow & \\
& & & K2 &
\end{array}
$$

For dielectric studies the sample in the liquid state was introduced into the parallel-plate rectangular capacitor with brass electrodes separated by a distance of 50 μm. The capacity of the empty cell was 103 pF. The complex dielectric permittivity $\varepsilon^*(\nu, T) = \varepsilon'(\nu, T) - i\varepsilon''(\nu, T)$ has been measured using the Hewlett Packard 4192A LF impedance analyzer in the frequency range from 1 Hz to 13 MHz. Measurements have been performed in the range from 360 K to 180 K on heating and on cooling the sample in 10 K steps. The heating rates have been changed from 0.5 K/min to 20 K/min. A usual cooling rate was 2 K/min. However, in some cases the sample was cooled with the rate of 200 K/min before the heating runs. In the nematic phase of EBPA $\varepsilon_\parallel^*(\nu, T)$ and $\varepsilon_\perp^*(\nu, T)$ measurements have been performed for the samples oriented by the magnetic field $B = 0.7$ T, respectively parallel and perpendicular to the measuring electric field. Dielectric anisotropy of the EBPA sample was equal to –0.12.

3. Results

The temperature dependence of the real permittivity ε' observed at a frequency of 1 kHz for several cooling and heating runs is presented in Fig. 1. On slow cooling (o, □) first a small drop of ε' corresponding to the $I \rightarrow N$ transition and then an abrupt jump of ε' ascribed to the $N \rightarrow K1$ transition were detected. During further lowering the temperature to 180 K, $\varepsilon'(T)$ was decreasing slowly to $\varepsilon' = 2.45$ which seems to be caused by a gradual transformation from $K1$ to $K2$. On heating the sample that was cooled fast (200 K/min), the $\varepsilon'(T)$ dependence (x) reflects a transformation unobserved in other runs. The sample melts at 349 K which points to the $K2 \rightarrow N$ transition, no matter how fast the sample was cooled before (x, ■). So, the observed temperature dependence of the electric permittivity conforms with the monotropic scheme of phase transitions found earlier [2]. The ranges of transition temperatures found then are shown near the upper (for cooling) and lower (for heating) temperature axes in Fig. 1.

Figure 2 presents $\varepsilon_\parallel''(\nu)$ and $\varepsilon_{\parallel,\perp}''(\nu)$ for several temperatures of the nematic phase. The relaxation process observed in the MHz range for the sample oriented parallel is presented by the Cole–Cole ($\varepsilon''(T)$ vs. $\varepsilon'(T)$) plots in Fig. 3. The situation observed at $T = 331.8$ K needs separate comments. For the parallel orientation a vanishing of the relaxation process is observed (Fig. 2b). At the same time, for the perpendicular orientation another process with a distinctly smaller amplitude and a considerably higher critical frequency appears. It might be due to the freezing of the nematic phase. A corresponding motion is then observed at lower temperatures which is illustrated in Fig. 4a and b.
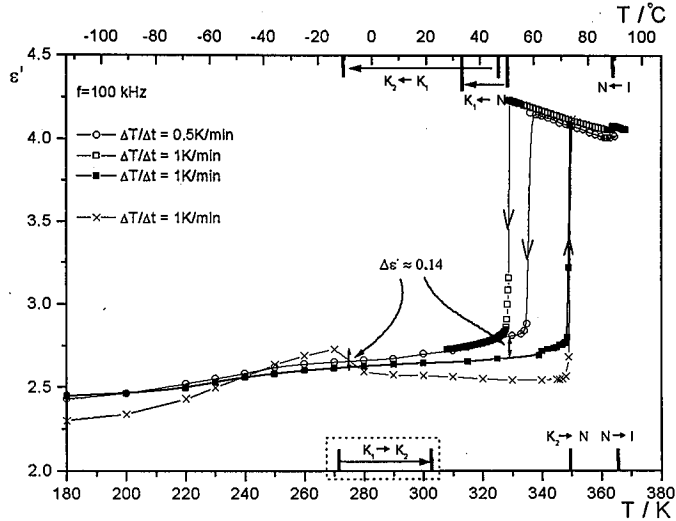
Fig. 1. ε' as a function of temperature for EBPA measured at 1 kHz on slow cooling ($\square$, o), subsequent heating ($\blacksquare$) of the sample and on heating (x) of the sample cooled very fast before.

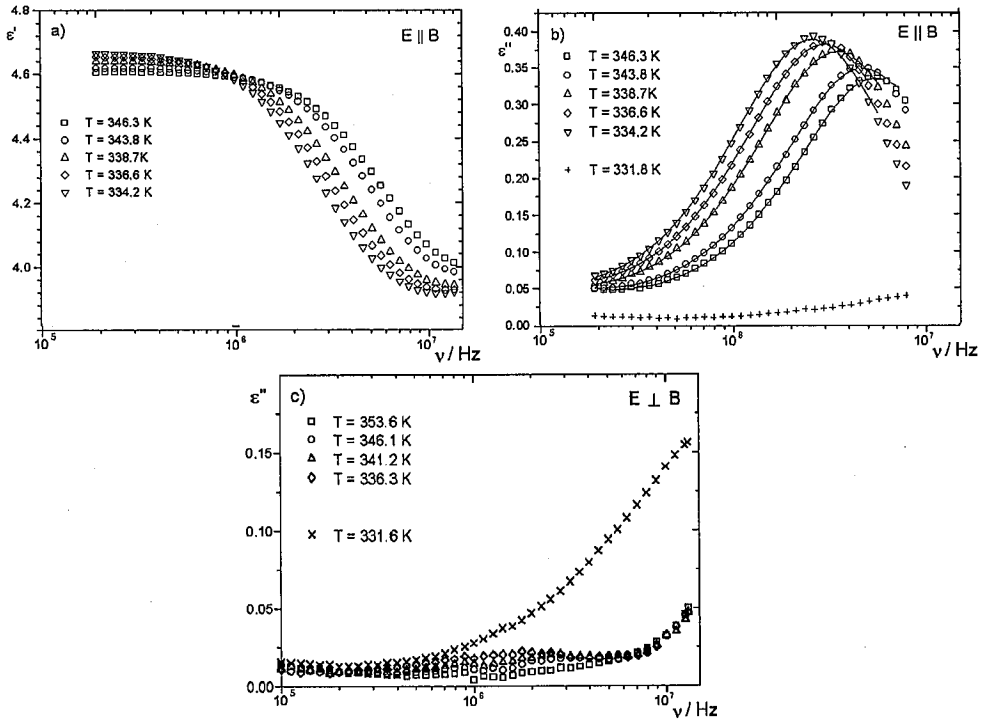Fig. 2. Frequency dependence of dielectric permittivity during cooling of the nematic phase of EBPA; (a) ε' vs. ν for $\boldsymbol{E} \parallel \boldsymbol{B}$, (b) ε'' vs. ν for $\boldsymbol{E} \parallel \boldsymbol{B}$ and (c) ε'' vs. ν for $\boldsymbol{E} \perp \boldsymbol{B}$ at different temperatures.

4. Discussion

4.1. Nematic phase

As for the nematic phases of other materials, the dielectric relaxation observed in EBPA of parallel geometry is connected with the reorientations of molecules around the short axes. The Cole–Cole formula [4] can be used for the analysis of the spectra

$$(\varepsilon^* - \varepsilon_\infty)/(\varepsilon_0 - \varepsilon_\infty) = 1/\left[1 + (\mathrm{i}2\pi\nu\tau)^{1-\beta}\right], \tag{1}$$

where β describes the distribution of the relaxation times around the most probable value $\tau = 1/2\pi\nu_{max}$ and ε_0 and ε_∞ mean the low and the high frequency limits
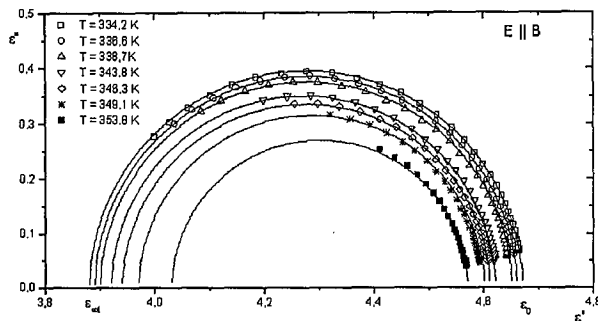
Fig. 3. ε'' vs. ε' plots for several temperatures of the nematic phase of EBPA for $\boldsymbol{E} \parallel \boldsymbol{B}$. The semicircles correspond to the Cole–Cole Eq. (1) with $\beta = 0$.

of dielectric permittivity. Figure 3 shows that Eq. (1) fits well the data giving the Debye type of relaxation with $\beta = 0$. The Arrhenius activation energy estimated from the $\nu_{max}(T)$ dependence is (64.3 ± 3) kJ/mole. This value is similar to those characterising the reorientations around the short axis in the nematic phase of the other compounds [5].

4.2. Solid phases

The dielectric relaxation processes have been observed in both solid phases of EBPA, i.e. in the metastable solid phase $K1$ obtained in a fast cooling of the sample (Fig. 4a) and in the stable solid phase $K2$ obtained in the course of a slow cooling of nematic and then of the $K1$ phase [3] (Fig. 4b). In both phases the shapes of the absorptions $\varepsilon''(\nu)$ are complex for all temperatures and cannot be described successfully by Eq. (1). A consistent description of the spectra could be achieved assuming a superposition of two relaxation processes. The fits of two Cole–Cole functions are displayed in Fig. 4a and b. However, the fitting procedure was not easy as the considered absorption regions occurred to be very near to each other. Moreover, an increase in temperature results in shifting the maximum of absorption towards frequencies above the limit of the experimental range available. Thus the fitting parameters, i.e. dielectric increments $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$, β_1 and β_2, τ_1 and τ_2 are characterised by relatively large errors. The β distribution parameters
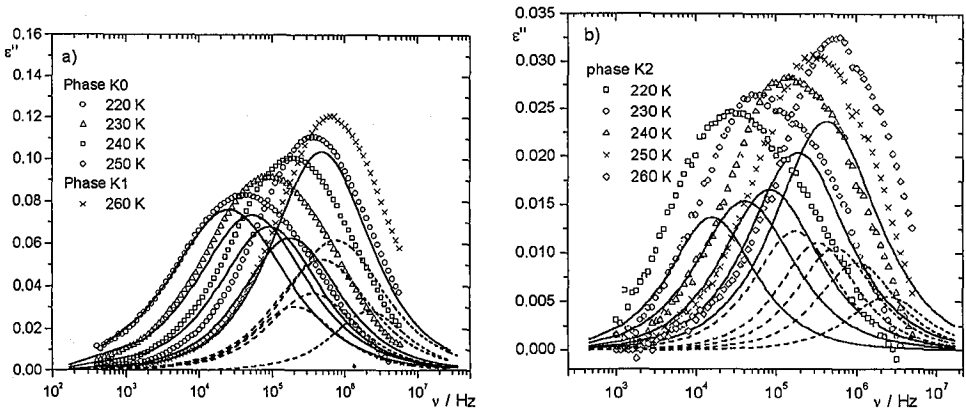
Fig. 4. Frequency dependence of imaginary part of permittivity during heating the phase $K1$ (a) (later interpreted as $K0$ and $K1$ phases) and the phase $K2$ (b). Solid and dashed lines show the absorption curves for two relaxation processes obtained by fitting two Cole–Cole contributions.
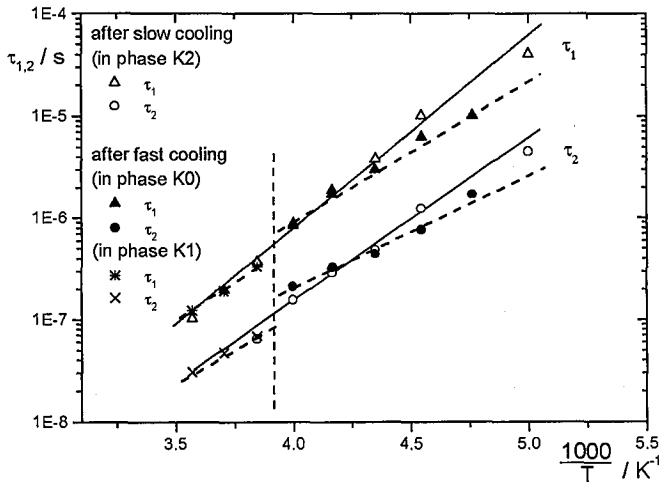

Fig. 5. Arrhenius plots of $\log \tau$ vs. $1/T$ for two rotational motions observed in the phases $K0$, $K1$, and $K2$ of EBPA.

are as follows: for the phase $K2$ $\beta_2 = 0$ and $\beta_1 = 0.15$ whereas for the phase $K1$ the β_1 and β_2 vary in the range of 0.2 ± 0.05. While analysing the results one can find that the temperature behaviour of two extracted relaxation processes in the phase $K1$ is different than in the phase $K2$. In Fig. 4b one can see the regular temperature shift of fitted curves for both processes while in Fig. 4a the irregular temperature behaviour of the $\varepsilon_1''(\nu)$ and $\varepsilon_2''(\nu)$ fitting curves needs an explanation. It seems that on a fast cooling of the sample (200 K/min) a new phase, called further $K0$, is created. Thus, on heating $K0$ transforms into $K1$ at about 250 K which causes a jump of $\varepsilon_1''(\nu)$ and a drop of $\varepsilon_2''(\nu)$ (Fig. 4a). Further the $K1 \rightarrow K2$

transition takes place at about 270 K which was detected in $\varepsilon'(T)$ dependence (Fig. 1). In temperatures up to 250 K the $\varepsilon'(T)$ dependence marked by (x) can be now identified with the new phase $K0$. This completes the above interpretation of temperature behaviour of real permittivity as it explains why that part of curve (x) does coincide with $\varepsilon'(T)$ curves marked by (o) and (■) as they correspond to the phase $K2$.

In Fig. 5 $\log \tau$ vs. $1/T$ is shown for τ_1 and τ_2 obtained in the analysis of $\tan \delta(\nu) = \varepsilon''(\nu)/\varepsilon'(\nu)$ for which the fittings were the most truthful. For the case when the sample was cooled first very fast (full points and dashed lines) the phase transition between $K0$ and $K1$ is evidenced as jumps at about 260 K for both sets of points (vertical dashed line) which corresponds well with the $\varepsilon''_{1max}(T)$ and $\varepsilon''_{2max}(T)$ behaviour. For both relaxation processes the Arrhenius activation energies in the phase $K0$ ($\Delta H_1 = (27 \pm 4)$ kJ/mole and $\Delta H_2 = (22 \pm 4)$ kJ/mole) are slightly smaller than those in the phase $K1$ ($\Delta H_1 = (30 \pm 4)$ kJ/mole and $\Delta H_2 = (25 \pm 4)$ kJ/mole). In the phase $K2$ (open points and solid lines) the relaxation processes are characterised by the similar relaxation times and the energy barriers ($\Delta H_1 = (36 \pm 2)$ kJ/mole and $\Delta H_2 = (30 \pm 2)$ kJ/mole).

In order to ascribe the observed relaxation processes to the molecular motions one has to specify the dipolar groups in the EBPA molecule:
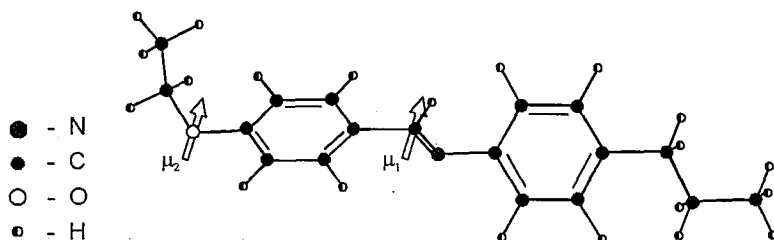
The dipole moments of the ethoxy group around C–O ($\mu_{CO} \approx 1.3$ D) and the bridging azomethine group ($\mu_{CHN} \approx 1.6$ D) have non-vanishing projections on the short molecular axis. Thus, in our kHz–MHz observations a rotation of the terminal group around the C–O bond as well as a reorientation of the molecule as a whole around the long axis should be detected. The strength of the absorption observed in the phase $K2$ is much smaller than that in the phases $K0$ and $K1$. Thus, it seems clear that $\varepsilon''_{1max}(T)$ and $\varepsilon''_{2max}(T)$ are not only functions of μ_1^2/T and μ_2^2/T, respectively, but rather of $N_1(T) \, \mu_1^2/T$ and $N_2(T) \, \mu_2^2/T$ which makes the identification of the motions not so obvious. The numbers of rotating dipoles N_1 and N_2 must be lower in $K2$ than in $K0$ and $K1$, no matter of their temperature dependences. One can presume that in the phase $K2$ obtained in a slow cooling in a small part of the solid sample the nematic order of molecules was preserved and only there the MHz reorientations of the whole molecules around the long axes were possible. If so, one can suggest this process to be identified as a relaxation "2" and to decay with an increase in temperature as shown in Fig. 4b by dashed $\varepsilon''(\nu)$ curves. At the same time the increase in temperature enables one to rotate a larger number of OC_2H_5 terminal groups which can be regarded as a process "1". It is difficult to decide whether the rotational dynamics of dipoles in $K0$ obtained in effect of a fast cooling and then in $K1$ is the same as in $K2$. Both motions have

the relaxation rates close to each other. The fact that $\tau_1(T)$ and $\tau_2(T)$ in $K2$ are similar to $\tau_1(T)$ and $\tau_2(T)$ in the phase $K0$ and identical with those in $K1$ can be regarded as a hint for similarity of dynamics in all three phases. The internal rotation is suggested to be a bit slower than the reorientation of the whole molecule which can be explained by the sterical factor (see Scheme). A different temperature dependence of ε''_{max} in those phases, i.e. various $N_i(T)$ must be caused by different structural arrangements of the molecules leading to differences in their rotational freedom. For the phases $K0$ and $K1$ regarded as the metastable ones an increase in temperature can accelerate the changes of N_i towards the values close to those observed at the stable solid phase $K2$ [7].

Generally there is no contradiction between the interpretation of the EBPA dynamics and the results observed for other molecules of Schiff bases family like *n-p*-methoxybenzylidene *p'*-butylaniline (MBBA), 2-hydroxy-4-methoxybenzylidene 4'-butylaniline (OHMBBA), and 4-ethoxybenzylidene 4'-butylaniline (EBBA) [8, 9]. For the members of that homologous series a complicated phase diagram has been established with several metastable solid phases depending on the cooling rates. It suggests that the phase $K0$ found in a fast cooling of EBPA can be regarded as another metastable phase with a different molecular packing and molecular mobility. In all materials two relaxation regions corresponding to alkyloxy groups rotations and to reorientations of the whole molecules around the long axes were detected in metastable solid phases. For MBBA [8] even the temperature dependence of two absorptions observed in the metastable solid phase reveals features similar to those found for the stable solid phase $K2$ of EBPA which support our interpretation of the results. In view of the above discussion the expectation of an additional true crystalline phase of EBPA seems to be justified.

5. Conclusions

It was found that the molecular rotation of EBPA around the short axis behaves similar as in other nematics. The phase situation and the molecular dynamics below the nematic–solid transitions strongly depend on the cooling rates. An analysis of dielectric data allows us to find three solid phases. They are characterized by two relaxation processes which can be attributed to the intra and overall molecular rotations.

Acknowledgments

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