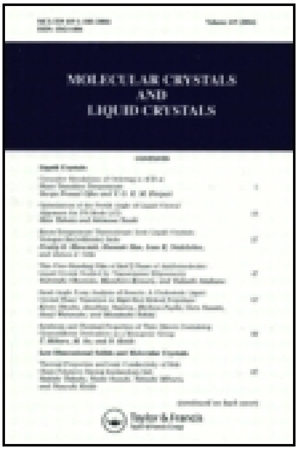

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Dielectric Relaxation of N-P-(Ethoxybenzylidene) P′-Propylaniline (EBPA) in Nematic Phase

Andrzej Bak [a] , Antoni Kocot [b] & Maria Massalska-Arodź [c]

[a] Chair of Physics, Technical University of Rzeszów, Rzeszów, Pola, 2, Poland

[b] Institute of Physics, Silesian University, Katowice, Uniwersytecka, 4, Poland

[c] Henryk Niewodniczanski Institute of Nuclear Physics, Kraków, Poland

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Dielectric Relaxation of N-P-(Ethoxybenzylidene) P'-Propylaniline (EBPA) in Nematic Phase

ANDRZEJ BĄK[a], ANTONI KOCOT[b] and
MARIA MASSALSKA-ARODŹ[c]

[a]*Chair of Physics, Technical University of Rzeszów, Rzeszów, Pola 2, Poland,*
[b]*Institute of Physics, Silesian University, Katowice, Uniwersytecka 4, Poland and*
[c]*Henryk Niewodniczanski Institute of Nuclear Physics, Kraków, Poland*

The complex dielectric permittivity $\varepsilon^*(\nu,T) = \varepsilon'(\nu,T) - i\varepsilon''(\nu,T)$ of EBPA has been measured in the frequency range from 10 Hz to 10 MHz in temperatures from 360 K to 200 K on heating and on cooling the sample. Dielectric relaxation observed in the nematic phase is presented and interpreted.

Keywords: dielectric relaxation; liquid crystals; molecular dynamics

INTRODUCTION

Apart of the PAA the MBBA compound is the most thoroughly studied liquid crystalline material[1]. However investigations of properties of the members of the MBBA homologous series known as Schiff basis were not so popular[2]. Studies of ethoxybenzylidene propylaniline (EBPA) of molecules with summary chemical formula the same as the MBBA molecules have been undertaken only recently[3, 4]. The phase diagram of EBPA found for the typical cooling and heating rates of about 5K/min[3] is the following

$$\begin{tikzcd} K2 & K1 \arrow[l, "318K"'] & N \arrow[l, "325K"'] \arrow[r, leftrightarrow, "364.5K"] & I \\ & & K2 \arrow[u, "349.5K"] \end{tikzcd}$$

This monotropic scheme of phase transitions shows polymorphism of solid state, i.e. the metastable solid phase K1 and the stable one K2. The aim of the present paper is to describe the molecular dynamics of EBPA molecules in the nematic and supercooled nematic phase.

EXPERIMENTAL

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 10 Hz to 10 MHz. Observations of the permittivity changes have been performed each 10 K in the range from 360 K to 200 K on heating and on cooling the sample. Measurements have been performed for sample without external orientation as the dielectric anisotropy was checked to have small negative value of 0.12.

RESULTS AND DISCUSSION

In Figure1 the temperature dependence of the real permittivity ε' observed at frequency of 100 kHz is presented. On slow cooling (o, □) first a small drop of ε' corresponding to the I → N transition was detected as observed by DSC and polarizing microscopy changes[3]. On further cooling an abrupt jump of ε' with Δε ~ 1.4 was found which has been ascribed to the N → K1 transition. For cooling rate of 0.5 K/min (o) the transition temperature $T_{N \to K1}$ is a bit higher than that reported earlier[3] but for ΔT/Δt = 1 K/min (□) $T_{N \to K1}$ shifts to the temperature range where that transition was found previously.

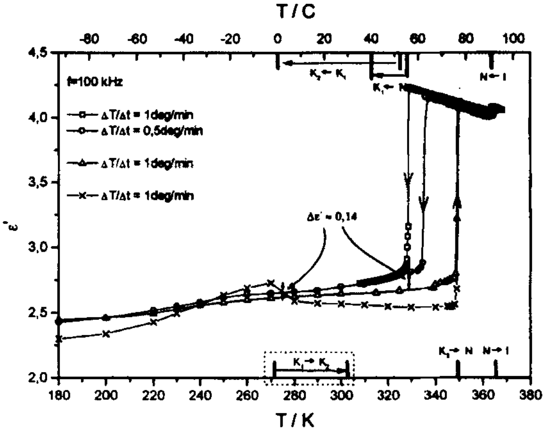

FIGURE 1 ε' for EBPA measured at 100 kHz as a function of temperature on slow cooling (□, o), subsequent heating (Δ) of the sample and on heating (x) of the sample cooled very fast earlier.

On cooling the sample to 180 K the ε'(T) decreases slowly with temperature to ε' = 2.45. On further heating (Δ) with ΔT/Δt = 1 K/min the ε'(T) seems to increase gradually up to 290 K along nearly the same ε'(T) curve as on cooling while at the higher temperatures the experimental points have smaller values than those observed on cooling. An abrupt jump of ε'(T) with Δ ε = 1.57 back to values corresponding to the nematic phase has been observed at temperature equal to that of K2 → N transition. Comparison of heating ε'(T) curve marked by (Δ) with the ε'(T) curve (x) observed on slow heating the sample that was previously cooled rather fast shows essential differences. Generally ε' data in solid phases are measured with the larger experimental error than in liquid phases. However, in the case of EBPA one can explain the difference by the fact that on fast cooling the sample the metastable phase K1 was formed which transformed on heating to the stable phase K2 and only then to the nematic. Contrary to that on slow cooling the transition N → K1 is followed by continuous transformation to K2 so on heating only K2 → N transition has been observed. Different thermal history of each K2 phase reveals in the difference between results (Δ) and (x) above 290 K. According to that identification of phases the difference between ε'(T) curves marked by (o) and (Δ) above 290 K is due to the fact that in range 290 – 330 K one ε'(T) curve was observed for the metastable solid phase K1 (o) on cooling while the other for the stable solid phase K2 (Δ) on heating. That difference reaches the same value of $\Delta\varepsilon = 0.14$ as that caused by the abrupt K1 → K2 transition. It was found[5] that the difference of the static permittivities between K1 and K2 is not only caused by a different arrangement of molecules in each phase but also by the fact that restricted reorientations of ethoxy groups observed there are correlated in a different way to the motions of the propyl chains. There is no contradiction of the above understanding of $\varepsilon'(T)$ and the phase diagram observed by DSC and polarizing microscopy methods earlier[3].

Figure 2 presents $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$ for several temperatures of the supercooled nematic phase. The evidence of N→K1 transition is shown in Figure 2b where one can see that cooling of the sample from 336 K (nematic) to 334 K (phase K1) causes disappearence of the absorption with maximum at about 10^6 Hz. At 334 K the new absorption of magnitude the same as raported earlier[4] arrives at about 10^7 Hz. The effect is too large to be consider as a result of the resonance of the bridge even for large drop of 1.6 of the dielectric constant in this transition.

The dielectric dispersion and absorption have been observed at MHz frequencies which suggests that the corresponding relaxation process is connected with reorientations of EBPA molecules around the short axes. The Arrhenius activation energy estimated from the $\nu_{max}(T)$ dependence is of about (77.5 ± 4) kJ/mole. In order to find the value of the dielectric increment $\Delta\varepsilon$ connected with the relaxation observed the $\varepsilon''(\varepsilon')$ Argand diagram is presented in Figure 3 for several temperatures.

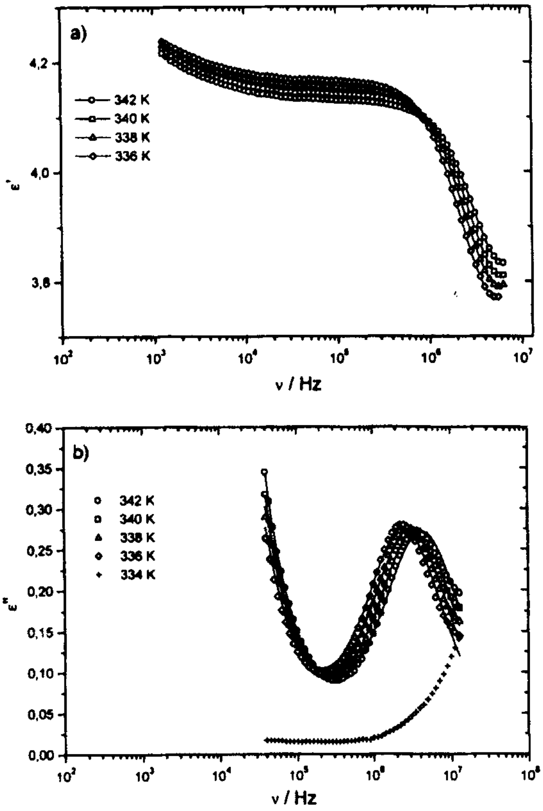

FIGURE 2 Frequency dependence of dielectric properties during cooling of the nematic phase of EBPA ; (a) ε'-vs.-ν and (b) ε''-vs.- ν at different temperatures.

The solid lines show the fitting of the Cole-Cole formula[6] in the following form for chosen temperature

$$\varepsilon'' = [(\Delta\varepsilon/2)^2 + (\Delta\varepsilon/2\,\tan(\pi\beta/2))^2 - (\varepsilon' - \varepsilon_0 + \Delta\varepsilon/2)^2]^{1/2} - \Delta\varepsilon/2\,\tan(\pi\beta/2) \qquad (1)$$

where β describes the distribution of the relaxation times around the most probable τ value. In the Table 1 the $\Delta\varepsilon$ and β parameters calculated with help of the fitting procedure are collected together with the values of $\tau = 1/2\pi\nu_{max}$. The values of β occur to be very small which means that the relaxation connected with reorientations of the EBPA molecules around the short axes is the Debye process.

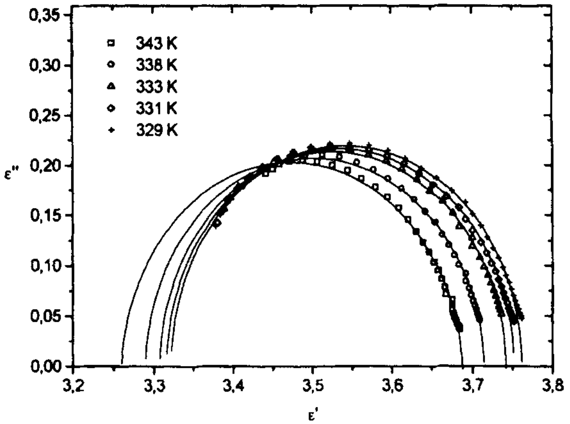

FIGURE 3 ε''-vs.-ε' Argand diagram for several temperatures of nematic phase of EBPA.

The high frequency limit of electric permittivity is equal to ε' ~ 3.3, i.e. it is much higher than a dielectric constant for the solid state (ε' ~ 2.5). It means that there should be expected a second relaxation process connected with fast reorientations around the long molecular axes as in nematic phases of the other liquid crystals. This motion „survives" the N → K1 transition as is shown by (+) in Figure 2b.

Let us consider now the $\Delta\varepsilon(T)$ changes obtained in the fitting procedure. Theoretical description of dielectric increments observed in anisotropic phases[7] gives the following formula

$$\Delta\varepsilon_\lambda(T) = g_\lambda(T)\, S(T)\, \mu_\lambda^2 / 3kT, \qquad \lambda = \parallel \text{ and } \perp \tag{2}$$

where g(T) is the so-called Kirkwood correlation factor and S(T) is the parameter characterizing the long range orientational ordering of elongated molecules of liquid crystalline phases.

TABLE 1 The $\Delta\varepsilon$ and β parameters together with the relaxation time τ in 10^{-8} s for nematic phase of EBPA.

T [K]	$\Delta\varepsilon$'	β	τ [s]
343	0,427 ± 0,020	0,04 ± 0,01	3,5903E-8 ± 0,06E-8
338	0,423 ± 0,007	0,01 ± 0,01	5,5179E-8 ± 0,07E-8
333	0,428 ± 0,006	0 ± 0,009	8,324E-8 ± 0,1E-8
331	0,433 ± 0,005	0 ± 0,009	9,7972E-8 ± 0,12E-8
329	0,440 ± 0,001	0	11,487E-8 ± 0,13E-8

It can be seen from the Table 1 and the Figure 3 that the change of the temperature from 338 K to 329 K causes increase of $\Delta\varepsilon$ from 0.423 to 0.440, i.e. of about 4%. There is no detailed knowledge about the temperature and time evolution of the orientation of molecules and/or domains in the sample of EBPA. Assumption that in temperatures far below the clearing point $S(T) \approx$ const. allows to conclude that correlations between parallel components of the reorienting dipolar moments are small because $g_{\|} \equiv 1$ in formula (2) gives nearly the same growth of calculated $\Delta\varepsilon = \Delta\varepsilon_{\|}$.

CONCLUSIONS

Dielectric relaxation spectroscopy results have confirmed the phase diagram of the EBPA compound found earlier in the DSC and polarizing microscopy measurements[3] with the polymorphism of solid state. In the nematic phase the Debye relaxation detected in the MHz range is connected with reorientations of the EBPA molecules around the short axes hindered by the activation energy barrier of $\Delta H = 77.5$ kJ/mole.

Acknowledgments

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