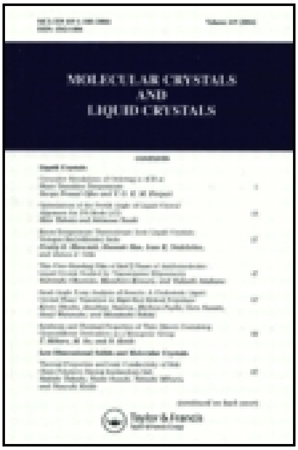

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Dielectric Relaxation Studies of 4-N-Butyl-4′-Thiocyanobiphenyl (4TCB)

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Complex dielectric permittivity of 4-n-butyl-4′-thiocyanobiphenyl has been investigated in the frequency range from 0.1 Hz to 10^6 Hz in the smectic E and isotropic liquid phases. In the smectic E phase dispersion with unexpectedly low relaxation frequency has been observed. It was related to the reorientation of the molecules about the short molecular axes and could be described by Arrhenius process. No evidence of preparation to a glass transformation till 246 K has been detected.

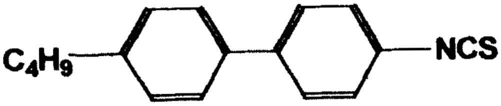
Keywords: liquid crystals; dielectric relaxation

INTRODUCTION

4-n-butyl-4'-thiocyanobiphenyl (4TCB) belongs to the well known liquid crystalline homologous series of molecules with a strong longitudinal dipole moment of thiocyano group [1]. Nevertheless its phase behavior is known only from the preliminary results [2]: On heating of the sample a small anomaly was found on DSC curve at 218 K with a shape which was not typical for crystal-liquid transition but rather for a glass-liquid transformation. Further at 356 K the large peak was observed corresponding to the transition into isotropic liquid phase. No melting has been found. In polarizing microscopy observations on heating to 360 K and on cooling to nitrogen temperatures only the transition between isotropic and anisotropic liquid was found. Fig.1 presents the texture of the anisotropic phase of 4TCB observed at 340 K. According to the known textures [3] it is identified with the smectic E phase of molecules ordered nearly as well as in the crystal. In the other members of this homologous series the smectic E phase was also identified [4]. The true crystalline ordering of 4TCB molecules was found in our pressure DTA studies [5] only above 88.7 MPa at about 360 K. For lower pressures no crystallization but also no evidence of a glass transition was found. Elevation of pressure leads to increase of the smectic E-crystal transition temperature. The aim of the paper was to investigate the molecular dynamics of 4TCB molecules in the smectic E phase with help of the dielectric relaxation spectroscopy. Due to the longitudinal dipole moment of 4TCB molecules one observes their reorientations about short axes mainly [6]. Our intention was also to clarify the fact of existence of a glass at low temperatures suggested by DSC observations.

EXPERIMENTAL

The 4TCB sample of 99.5 % purity has been synthesized at the Military Academy of Technology, Warsaw. The schematic chemical structure of the molecule is shown below.



Dielectric relaxation spectroscopy measurements of the complex dielectric permittivity $\varepsilon^*(\nu,T) = \varepsilon'(\nu,T) - i\,\varepsilon''(\nu,T)$ have been performed on the programmed Solartron Schlumberger in combination with the Chelsea Interface in the frequency range from 0.1 Hz to 10 MHz. ε' has been measured with 3% and ε'' with 7% accuracy. The sample in the isotropic liquid phase has been introduced into a gold cell-capacitor with the distance of 50 μm between the electrodes. Measurements have been performed each 5 K on cooling and on heating the sample in the temperatures from 230 K to 373K. Due to the lack of the nematic phase the sample could not be oriented in an external magnetic field of 0.6T. As dynamics of molecules do not depend on their orientations information about sample alignment was not crucial in our investigations.

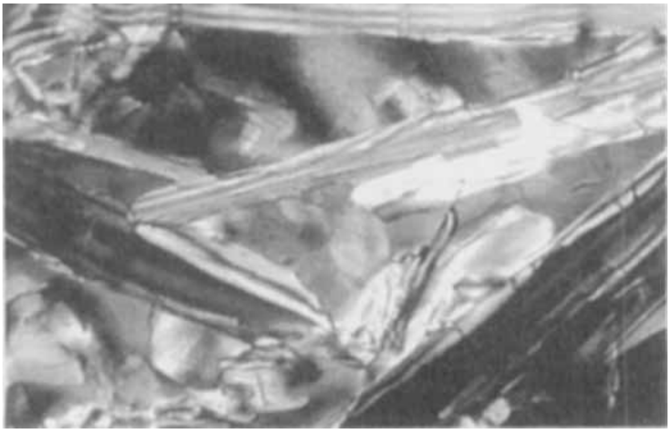


FIGURE 1 Texture of the smectic phase of 4TCB observed at 340 K
See Color Plate IV at the back of this issue.

RESULTS AND DISCUSSION

Dielectric relaxation phenomenon has been observed only in the smectic E phase (see Figs.2 and 3). Up to 10^7 Hz no relaxation was detected in the isotropic phase. At the highest frequency shown in Fig.2b one can see that the transition from the isotropic (solid symbols) to S_E phase causes a large drop of the electric permittivity from 6 to 3. That decrease arises from the fact that above 10 kHz the data in the isotropic phase are related to a static electric permittivity ε_0 while in S_E phase to the relaxed value ε_∞, i.e. the high frequency limit of ε'.

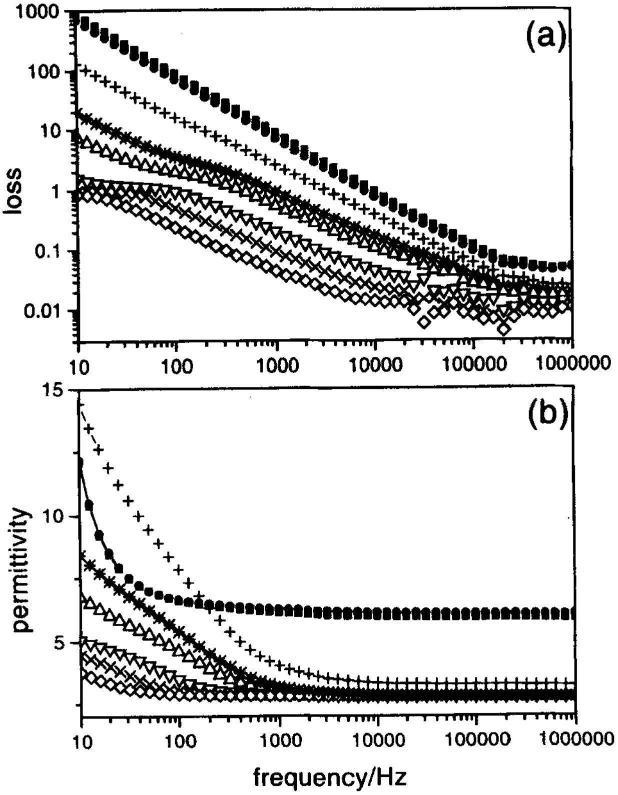


FIGURE 2 Dielectric loss (a) and dispersion (b) curves observed on cooling for several temperatures: ■ - 373 K, ● - 355 K of the isotropic phase and + - 352 K, * - 349 K, Δ - 346 K, ∇ - 337 K, x - 328 K and ◊ - 319 K of smectic E phase.

To fit $\varepsilon^*(\nu)$ data observed in S_E the Cole-Cole formula

$$\varepsilon^*(\nu) = (\varepsilon_0 - \varepsilon_\infty) / (1 - (2\pi i\nu\tau)^{1-\alpha}) + i A\nu^{-B} + Q\nu^{-q} \qquad (1)$$

was used with the parts $iA\nu^{-B}$ and $Q\nu^{-q}$ describing the contributions from the electric conductivity and the double layer effect, respectively [6]. α describes

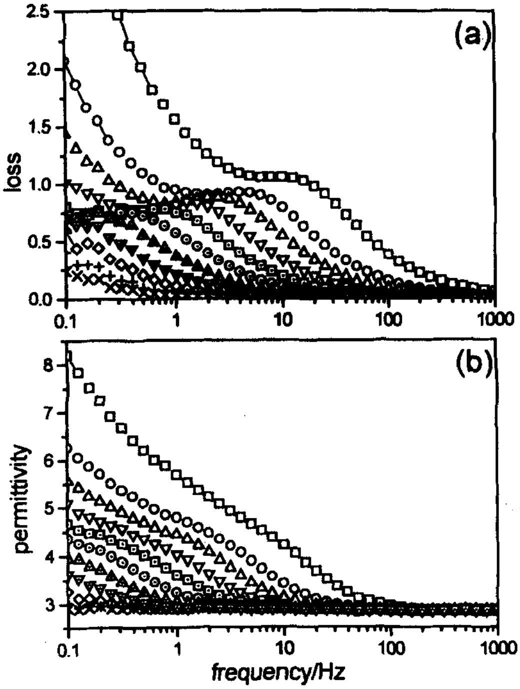


FIGURE 3 Dielectric loss (a) and dispersion (b) curves observed for the temperatures of the smectic E phase: □ - 323 K, o - 313 K, Δ - 307 K, ∇ - 301K, ⊡ - 295 K, ⊚ - 289 K, ▲ -283 K, ▼ - 277 K, ◊ - 271 K, + -271 K, x - 259 K.

the distribution of the relaxation times around the $\tau = 1/\ 2\pi\nu_{max}$. In our observations the relaxation frequencies ν_{max} (T) are unexpectedly low. The influence of the electric conductivity on the data at frequencies lower than 10 Hz is strong which did not allow to introduce an additional asymmetry parameter for description of the relaxation. The experimental points $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$ for 308 K and curve fitted to them using the eq.(1) are presented in Fig. 4. Fig.5 presents the temperature dependence of ε_0 and ε_∞ values fitted for data observed on cooling and on heating. As the alignment of the smectic E sample is only occasional the $\varepsilon_0(T)$ cannot be treated as the material parameter. It describes the properties of the examined sample. For selected data of $\varepsilon_0(T)$ the error bars related to the standard deviation are given. Relatively large errors of ε_0 are caused by the fluctuation of the Cole-Cole distribution parameters $\alpha(T)$ in the range from 0.04 to 0.12. One can see that in whole temperature range $\varepsilon_\infty \approx 2.8$ was found. The fact that (it is the) value of dielectric constant expected for the solid state indicates that

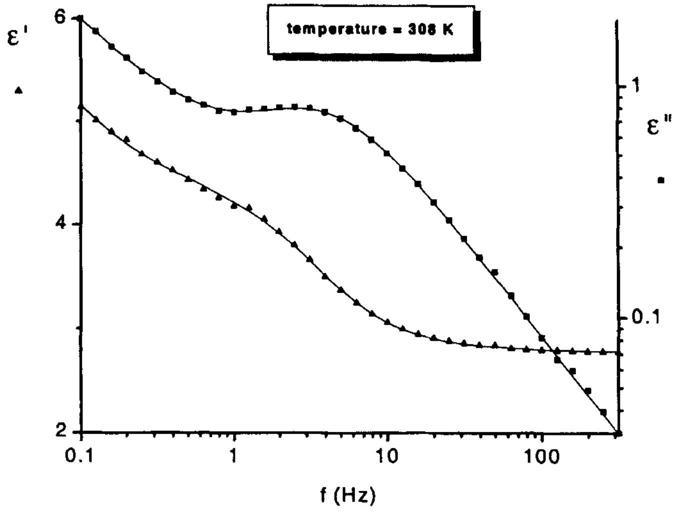


FIGURE 4. Experimental data and curves $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$ fitted using eq. (1). Fitted parameters are the following: $\varepsilon_0 = 4.06 \pm 0.04$, $\varepsilon_\infty = 2.77 \pm 0.01$, $\nu_{max} = (3.75 \pm 0.06)$ Hz, $\alpha = 0.07 \pm 0.02$, $A = 0.44 \pm 0.02$, $B = 0.63 \pm 0.02$, $Q = 0.29 \pm 0.03$, $q = 0,58 \pm 0.03$.

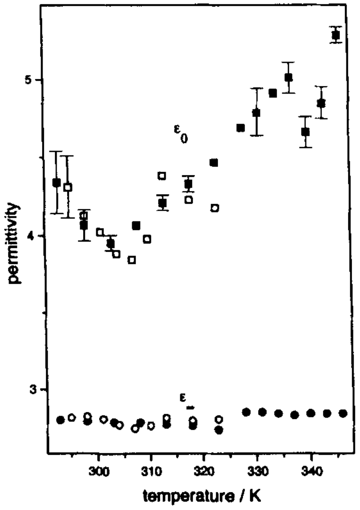


FIGURE 5. Temperature dependence of ε_∞ and ε_0 obtained on fitting the equation (1) for cooling (open symbols) and heating (solid symbols).

practically no high frequency relaxation should be observed by dielectric spectroscopy. Therefore the detected dispersion must be related to the reorientations of the longitudinal dipole moments of molecules. The observed decrease of $\varepsilon_0(T)$ with decreasing temperature seems to indicate a spontaneous growth of planar orientation of molecules on cooling.

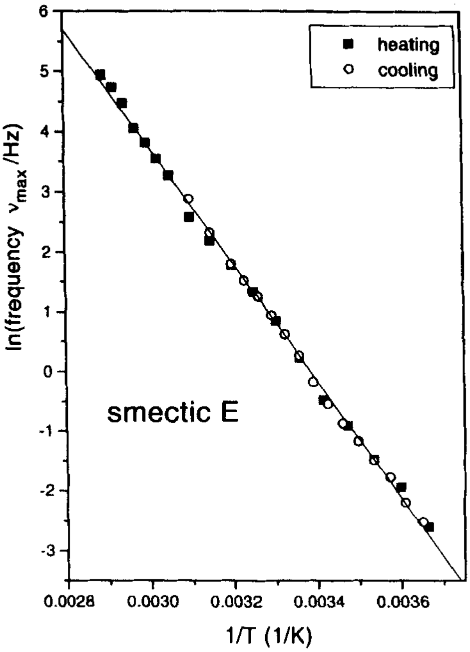


FIGURE 6. Temperature dependence of relaxation time log ν_{max} vs. 1/T evaluated in the temperature range from 246 K to 373K. The solid line represents the fit of the Arrhenius formula.

The temperature dependence of ν_{max} is presented in Fig.6. The ln (ν_{max}) vs. 1/T is well fitted by the straight line. The process of reorientations is activational and the activation energy hindering the motions in the smectic E phase is equal $\Delta H = (81 \pm 5)$ kJ/mole. The extrapolation of ν_{max} to 356 K, i.e. the temperature of S_E / I transition gives the value of 500Hz. It means that in the smectic E phase the reorientations are of about 5 decades slower than in the isotropic phase where ν_{max} must be higher than $5 * 10^7$ Hz (Fig.2b). The extremely large step in the rate of motions reflects a dramatic change of orientational order at this transition [5].

In the range of temperatures analyzed there is no evidence of the Vogel-Fulcher [7] type of relaxation which on low temperatures accompanies the approaching to the liquid-glass transformation. Neither preparation to vitrify nor to crystallization of the smectic E phase can be traced down to 246 K. Probably the influence of the glass transition on the data should be observed at much lower temperatures and frequencies.

SUMMARY

In the smectic E phase of 4-n-butyl-4'-thiocyanobiphenyl the Debye dielectric relaxation has been observed with ν_{max} below 130 Hz. The process has occurred to be activational and ascribed to be connected with molecular reorientations about the short molecular axes. In the smectic E - isotropic transition a strong jump of the rate of motions of about 5 decades has been found indicating a significant change of the molecular arrangement. No traces of crystallization or transformation to glass have been observed down to 246 K.

Acknowledgements

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