Linear and Non-linear Dielectric Pretransitional Behavior Near the Isotropic-nematic Phase Transition for 4-cyano-4-*n*-pentylbiphenyl (5CB)

G. Czechowski, J. Jadżyn, J. Zioło, S. J. Rzoska[a], and M. Paluch[a]

Institute of Molecular Physics, Polish Academy of Sciences, ul. A. Smoluchowskiego 17, 60-179 Poznań, Poland
[a] Institute of Physics, Silesian University, Uniwersytecka 4, 40-007 Katowice, Poland

Reprint requests to Prof. J. Z.; E-mail: ziolo@us.edu.pl

Linear and non-linear dielectric permittivity measurements for *n*-pentylcyanobiphenyl 5CB are presented. By two different experimental methods the same value of the temperature discontinuity for the isotropic-nematic transition was obtained. Broadband dielectric relaxation tests showed a significant influence of the pretransitional behavior on the dynamic properties above and below the nematic clearing temperature (T_{I-N}). The form of the loss curves is clearly non-Debye'an and can be portrayed within the Cole–Davidson approximation (CD). In the isotropic and nematic phases the CD parameter β_{CD} drops on approaching the clearing temperature. This is connected with the broadening of the dielectric absorption width.

Introduction

Dielectric relaxation is one of the basic tools for studying dynamics in complex liquids [1–4]. Regarding the isotropic phase, the vast majority of dielectric relaxation studies suggest the validity of the Arrhenius temperature dependence and the quasi-Debye spectrum of relaxation times, which agrees with the mean-field description for the I–N transition. Druon et al. [5] and Lippens et al. [6] tested nematic *n*-cyanobiphenyls (7CB, 8CB) and compared Cole–Cole plots in the nematic and in the isotropic phase. For the latter they reported a strong asymmetric deformation. In 1985 Buka et al. [7] suggested that for rod-like molecules like *n*-cyanobiphenyls this behavior may be the result of two single relaxation time Debye-processes. For 8CB and 7CB Bose et al. [8] pointed to possible validity of the Martin-Maier-Saupe meanfield model. Recently, Jadżyn et al. [9] summarized the molecular interpretation of dielectric relaxation of nematic liquid crystals basing on measurements in 4-(trans-4-*n*-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT). A resolution into elementary spectral contributions to the Cole–Cole plot was performed with the use of the formula [9]

$$\varepsilon^* = \varepsilon_\infty + \sum_i \frac{\Delta\varepsilon_i}{1+(i\omega\tau_i)^{1-k_i}}. \qquad (1)$$

On approaching the nematic clearing temperature T_{I-N}, a series of physical properties exhibit a strong pretransitional increase, proportional to $T-T^*$, where $T > T_{I-N}$ and $T^* = T_{I-N} - \Delta T$. The temperature T^* denotes the extrapolated hypothetical continuous phase transition, and ΔT is the measure of the discontinuity of the transition. The properties mentioned above include among others: the Cotton-Mouton effect, the optical and electrooptic Kerr effects and the non-linear dielectric effect (*NDE*) [1]. The short-range order effect also influences the linear dielectric properties. The static dielectric permittivity in the isotropic phase exhibits the simple power-law dependence

$$\varepsilon_{\mathrm{iso}}(T) = \varepsilon^* + a(T - T^*) + A(T - T^*)^{1-\alpha}, \qquad (2)$$

where α denotes the specific heat exponent. For the non-linear and linear dielectric permittivity the experimental temperature dependencies agree well with the fluidlike hypothesis, which assumes that $\alpha = 0.5$ [10, 11]. The experimental values were: $\varepsilon^* = 10.74$, $a = -0.028$, $A = 0.144$, $\alpha = 0.5 \pm 0.04$.

In the present paper we report a quantitative analysis of the dielectric relaxation in the isotropic and nematic phase of 5CB close to the clearing temperature. It is shown that the mentioned relaxation processes indicate a new kind or pretransitional behavior.

Experimental

The tested compound *n*-alkylpentylcyanobiphenyl (5CB) was synthesized and purified at the Institute of Chemistry, Military Technical University, Warsaw. The purity of the compound, checked by chromatography, was 99.9%, and the phase transitions were: crystal- (24 °C) -nematic- (34.9 °C) -isotropic. The dielectric relaxation spectra were recorded with an HP 4194A im-
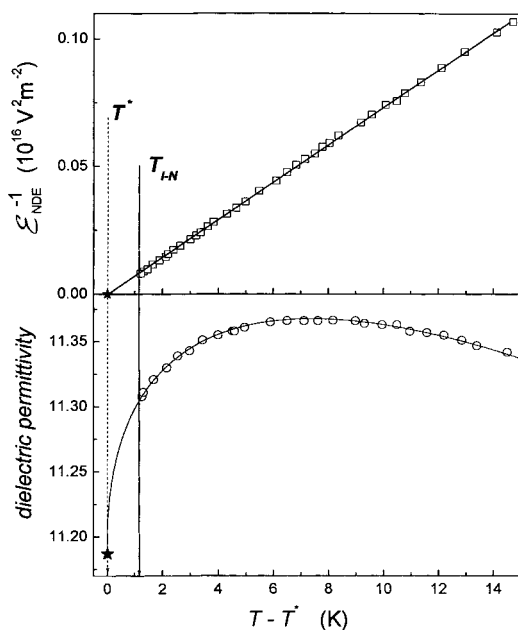

Fig. 1. The static dielectric permittivity and the nonlinear dielectric effect in the isotropic phase of 5CB. Equations (2) and (3) parameterize solid lines, respectively. The solid vertical line shows the nematic clearing temperature, and the dashed line indicates the position of the extrapolated point of a continuous phase transition, shown by a star.

pedance-gain-phase analyzer in the frequency range 100 kHz to 100 MHz. A three-electrode plane capacitor was used, and an external biasing D.C. electric field (5 V/0.5 mm) was applied for the nematic ordering. In such a case, the $\varepsilon_{\mathrm{II}}(\omega)$ dielectric spectrum can be recorded only. The strength of the probing a.c. electric field was 500 mV/0.5 mm). The temperature of the sample was stabilized within ±0.01 °C. The measurements of the non-linear dielectric permittivity were taken using a Modulation Domain Analyzer HP 53310A [12].

Results and Discussion

Figure 1 shows the inverse of the *NDE* and dielectric permittivity as a function of temperature in 5CB. In case of non-linear dielectric measurements the relation

$$\varepsilon_{\mathrm{NDE}} = \frac{A_{\mathrm{NDE}}}{T - T^*} \qquad (3)$$

is satisfied, where $\varepsilon_{\mathrm{NDE}} = (\varepsilon_{\mathrm{HIGH\ ELECTRIC\ FIELD}} - \varepsilon_{\mathrm{LOW\ ELECTRIC\ FIELD}})/E^2$ is a measure of the nonlinear dielectric effect, and A_{NDE} = amplitude ($A_{\mathrm{NDE}} = 165 \cdot 10^{-16}$ V^2 m^{-2}).
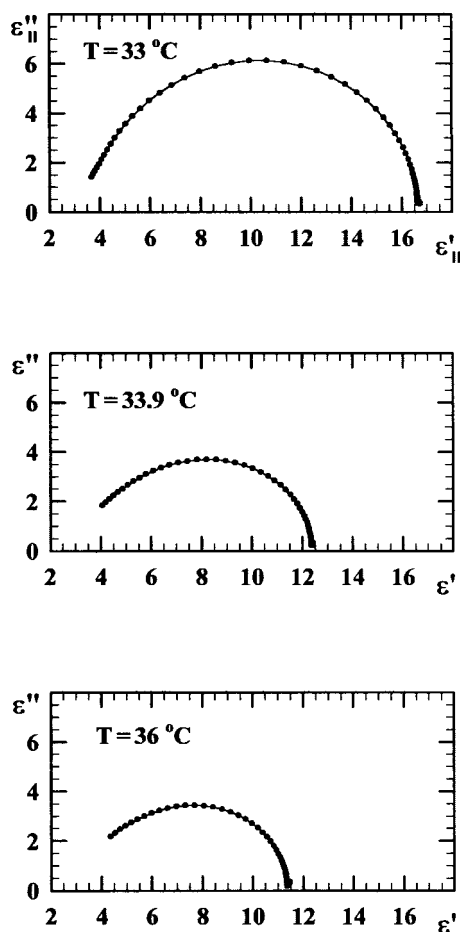

Fig. 2. The Cole–Cole plot by of dielectric relaxation in the isotropic and nematic phase of 5CB. The fit follows the Cole–Davidson relation (4) with the following parameters: $\beta_{\mathrm{CD}} = 0.87$ and $\tau_{\mathrm{CD}} = 23$ ns for 33 °C, $\beta_{\mathrm{CD}} = 0.59$ and $\tau_{\mathrm{CD}} = 17.4$ ns for 34.9 °C, $\beta_{\mathrm{CD}} = 0.63$ and $\tau_{\mathrm{CD}} = 9.7$ ns for 36 °C.
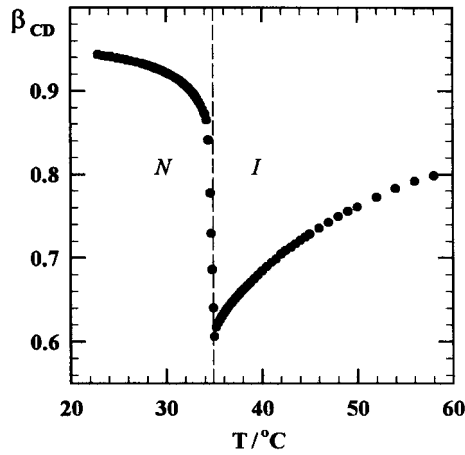
Fig. 3. The temperature evolution of the width of loss curves characterized by the Cole–Davidson power parameter, β_{CD}, (relation (4)).

The static dielectric permittivity data can be described by (2). It is worth stressing that for the linear and non-linear methods the same value of ΔT was obtained.

Results for the complex permittivity in the nematic and isotropic phase are shown in Figure 2. The Cole–Davidson relation describes the experimental data obtained:

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_S - \varepsilon} = \frac{1}{(1 + i\,\omega\,\tau_{CD})^{\beta_{CD}}} , \tag{4}$$

where β_{CD} is the empirical width parameter. This parameter can be conveniently transformed [13] into the corresponding stretching exponent β_{KWW} defined by the Kohlrausch-Williams-Watts law [14]:

$$\Phi(t) = \exp\left[-\left(\frac{t}{\tau_{KWW}}\right)^{\beta_{KWW}}\right]. \tag{5}$$

Regardless of the theory, the microscopic interpretation of the stretching parameter β_{KWW} is always associated with the distribution of the relaxation time. As shown in Fig. 3, the temperature dependence of the parameter β_{CD} gives clear evidence of pretransitional behavior both in the nematic and isotropic phase.

Recently, Massalska-Arodz et al. [15] and Urban et al. [16] studied the dielectric permittivity of isopentyl-cyanobiphenyl (5*CB), a compound resembling the structure of 5CB, which can be supercooled down into the isotropic phase. They observed a strong broadening of the loss curves on cooling in the supercooled state. In our case such boradening takes only in the isotropic phase. In the nematic phase a narrowing of the loss curves on cooling takes place. However, in both phases the parameter β_{CD} drops on approaching the clearing temperature, which is connected with the broadening of the dielectric absorption width. It is the result of the quasi-critical enhancement of the distribution of the relaxation time [17].

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