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Linear and nonlinear dielectric studies in the isotropic and smectic E phases in 4,4-alkyl-4'-isothiocyanatobiphenyl

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Abstract. Results are presented of studies of linear and nonlinear dielectric measurements in the isotropic, smectic E phase in 4,4-alkyl-4'-isothiocyanatobiphenyls (4BT). The mean-field behaviour was valid up to the smectic E phase transition. In the smectic E phase the Vogel–Fulcher law describes temperature and pressure dependences of the relaxation time. An analysis of the higher temperature relaxation time data led to predictions of the mode coupling theory with the power law universal function $\tau = A(T - T_C)^\gamma$, where $\gamma = -3.3$, $T_C = 288 \pm 15$ K. Increase of pressure brings the ε'' curve closer to the Debye shape.

1. Introduction

In recent years a great deal of effort has gone into the study of pretransitional properties close to the isotropic liquid–liquid crystal transition [1, 2]. The most interesting behaviour of this kind of phase transition is exhibited by the fluidlike anomalies:

- (i) the anomaly of dielectric permittivity described by

$$\varepsilon - \varepsilon^* + a_1(T - T^*) + a_2(T - T^*)^\varphi \quad T > T_C \quad (1)$$

where T^* is the temperature of the supercooled isotropic phase, $\varphi = 1 - \alpha$ [3, 4], a_1 , a_2 are coefficients, α the critical exponent and ε^* is the value of ε at $T = T^*$, and

- (ii) the anomaly of the nonlinear dielectric effect (NDE) given by the following equation:

$$\mathcal{E} = \frac{A_{NDE}}{(T - T^*)^\psi} \quad (2)$$

where $\mathcal{E}_{NDE} = (\varepsilon_E - \varepsilon_0)/E^2$ is the measure of NDE and ε_E and ε_0 the dielectric permittivity in a strong and a weak electric field (E), respectively. The exponent $\psi = 1$ [5, 6]. Applying the Landau–de Gennes model [7] one can obtain: $A_{NDE} = (2/3a)\varepsilon_0\Delta\varepsilon^f\Delta\varepsilon^0$, where a is the amplitude of the susceptibility and $\Delta\varepsilon^0$, $\Delta\varepsilon^f$ denote the molecular anisotropy of dielectric permittivity in the zero-frequency limit and for the measurement frequency, respectively. One of the basic parameters describing the phase transition from the isotropic liquid to liquid crystalline mesophases is the discontinuity of the transition, defined as $\Delta T = T_{cl} - T^*$, where T_{cl} is the nematic or smectic clearing temperature. The most frequently studied case for which both the above equations are fulfilled is the isotropic–nematic (I–N) transition. NDE measurements for the n-alkylcyanobiphenyl (nCB) series show that also for the isotropic–smectic A (I–S_A)

transition equations (1) and (2) [8] can be applied. The mentioned results show that the simple mean-field description may be valid on approaching both the I–N and I–S_A phase transitions.

Measurements of the complex dielectric permittivity $\varepsilon^* = \varepsilon'(f) - i\varepsilon''(f)$ provide information about dynamical properties of molecules (f is the frequency of the electric field). To describe the increase of relaxation time upon cooling the normal liquid into the moderately supercooled state, power law fits have been discussed. For instance one can write e.g.

$$\tau = A^*(T - T_C)^\gamma. \quad (3)$$

For the lower temperature in the glass phase, the relaxation can be described by the Vogel–Fulcher formula

$$\tau = \tau_0 \exp(DT_{VF}/(T - T_{VF})). \quad (4)$$

In the present work we tested the pretransitional properties of 4,4-alkyl-4'-isothiocyanatobiphenyls (4BT) revealing only the smectic E phase with a high tendency to supercooling [9]. The smectic E phase can be considered as being a 'soft' crystal. It is worth noting that the results presented below are probably the first obtained by the nonlinear method for this kind of complex liquid.

2. Experiment

Measurements of NDE were performed using an apparatus described in [10]. The linear dielectric measurement covered the frequency range from 10^{-2} to 10^7 Hz. Two different measurement systems were used: a frequency response analyser (Solartron SI 1260), and a Hewlett–Packard impedance analyser (4192A). A pressure system with a specially designed measurement capacitor is described in detail elsewhere [11].

The 4BT sample was synthesized at the Institute of Chemistry, Military Academy of Technology (WAT) in Warsaw.

In figure 1 the inverse of NDE versus temperature for 4BT is presented. The picture is similar to the isotropic–smectic A transition. From equation (2) we can calculate the discontinuity of the transition which in this case is equal to $\Delta T = 22$ K. This value is the highest obtained for the isotropic–liquid crystal transition so far. Such a large value of ΔT is the reason why one cannot observe the bending down [3, 12] in the course of the temperature dependence of dielectric permittivity ($\varepsilon(T)$) shown in the inset in figure 1.

Two dielectric loss spectra for 4BT measured under isobaric (ambient pressures) and isothermal conditions are shown in figures 2 and 3 as master curves after normalization to $\varepsilon''/\varepsilon''_{max}$ versus f/f_P . After this normalization and rescaling of the abscissa, all data fall on one master spectrum within reasonable error margins independent of temperature (figure 2). The half width at half height of the shown peaks is broader than the width of the Debye peak. For isobaric measurements the half width is 1.4 decades (figure 2) and for isothermal loss curves it seems to decrease with pressure from 1.6 to 1.2 in the studied region. The inset in figure 2 shows the temperature dependence of the relaxation time in the supercooling smectic E phase of the 4BT compound. To describe the high temperature behaviour the power law fit (3) is applied: $\tau = A(T - T_C)^\gamma$, where $\gamma = -3.3$, $T_C = 288 \pm 15$ K and for the lower temperature range, according to the Vogel–Fulcher formula: $\tau = \tau_0 \exp(DT_{VF}/(T - T_{VF}))$ where $\tau_0 = 15 \pm 6$ ns. The Vogel–Fulcher temperature $T_{VF} = 128.5 \pm 20$ K, and the strength parameter $D = 23 \pm 6$ were obtained. Hence the smectic E phase in 4BT can be classified as a strong glass former [13].

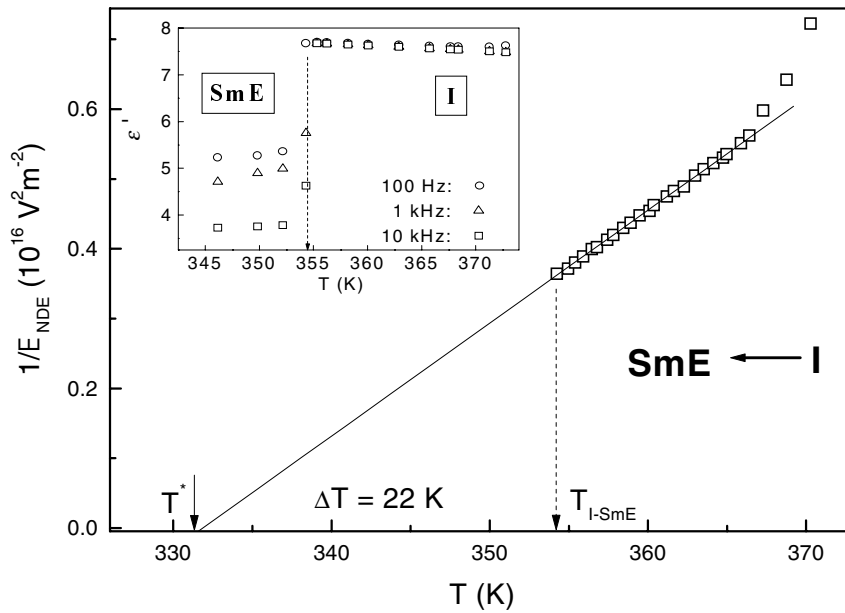


Figure 1. Reciprocal of NDE versus temperature interval above isotropic–smectic E transition (T_{I-SmE}) in 4BT. The inset presents dielectric permittivity for three frequencies around T_{I-SmE} .

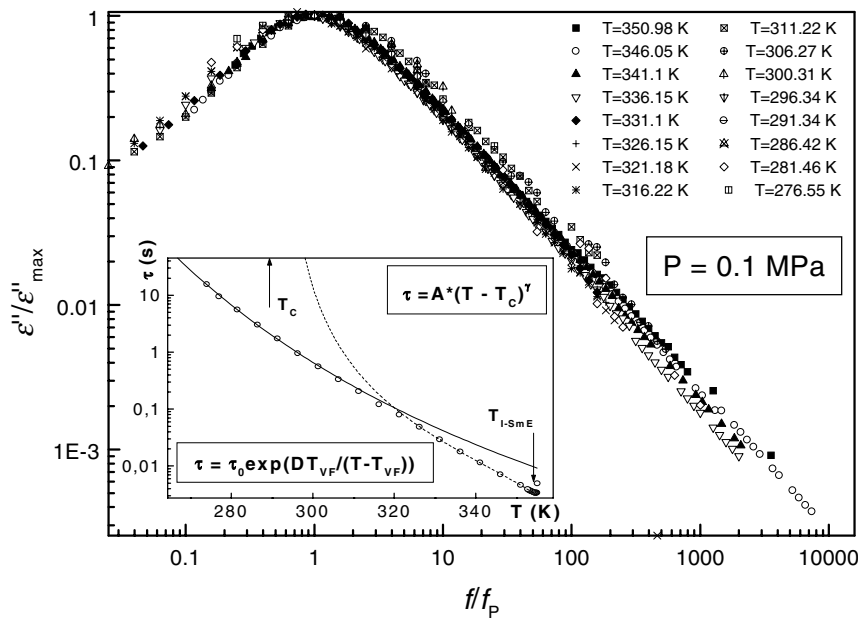


Figure 2. Master plot for several temperatures, below the isotropic–smectic E transition at ambient pressure for 4BT. The inset shows the evolution of relaxation times as a function of temperature. The dashed line describes the power law and the solid one the Vogel–Fulcher equation (see text).

For isothermal measurements we applied the pressure analogue of the Vogel–Fulcher equation: $\tau = \tau_{0P} \exp(D_P P / (P_{VF} - P))$ [14], where for the isotherm $T = 345$ K: $D_P = 37$,

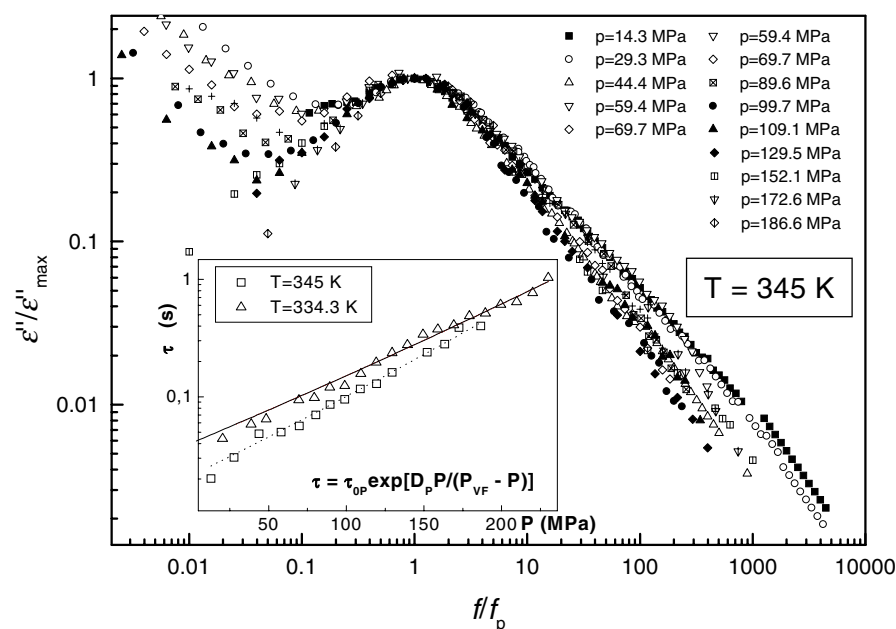


Figure 3. Master plot for experimental points obtained from pressure measurements at $T = 345$ K. The half width of absorption peaks seems to decrease with pressure. The inset shows the approximation pressure dependence of the relaxation time according to the Vogel–Fulcher equation.

$P_{VF} = 3000$ and for the isotherm $T = 334.3$ K: $D_P = 41$ and $P_{VF} = 2754$. Results of these approximations for the two isotherms mentioned above are plotted in the inset of figure 3.

3. Conclusions

Results presented above show that in studying a compound which exhibits a smectic E phase, an extremely large discontinuity ΔT exists, which make it impossible to observe fluid-like anomalies described by (1). The temperature dependences of the relaxation time in the smectic E phase are demonstrated in the crossover from liquid-like behaviour described by a power law (3) to glass-like behaviour according to the Vogel–Fulcher law (4). Increase of pressure brings the half width of the ε'' curve closer to Debye's value. This is due to the fact that pressure shifts the molecules along the local director. This facilitates ordering of the intermolecular structure. In consequence the neighbourhoods of all molecules become similar and hence only a single value of the relaxation time is observed.

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