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Dynamics of the nonlinear dielectric properties of a nematogenic compound dissolved in a nonpolar medium

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The nonlinear dielectric spectra of 4-(*trans*-4′-*n*-hexylcyclohexyl)isothiocyanatobenzene (C_6H_{13}CyHx Ph NCS, 6CHBT) in benzene solutions were recorded in the whole concentration range up to an appearance of the two-phase isotropic and nematic region (0.82 mole fraction of 6CHBT, at 25 °C). Two electric fields: (i) the field of high strength (110 kV/m) and low frequency (85 Hz) causing the dielectric nonlinearity, and (ii) the probing field of low strength and high frequency (100 kHz–3 GHz), were used. At about of 0.2 mole fraction of 6CHBT the nonlinear dielectric increment becomes positive. With increasing of 6CHBT concentration the dynamics of the increment shows a critical-like behavior, which can be interpreted in terms of the reorientation of the growing pseudonematic domains in the solutions studied.

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I. INTRODUCTION

In principle, there are two ways for reaching the nematic state in a system composed of the nematogenic molecules. The first one, the "natural" for thermotropic liquid crystals, consists in temperature decrease of the pure liquid being in the isotropic state. At some temperature T_{NI} the liquid becomes turbid in the whole volume or becomes birefringent in the polarizing microscope observation. So, the determination of the isotropic to nematic *phase transition temperature* does not afford any difficulties.

The nematic state can also be reached in another way: by increasing, at constant temperature, the number of mesogenic molecules in the unit volume. The increase can be realized by applying high pressure to pure isotropic liquid or by growing the concentration of mesogenic molecules dissolved in nonmesogenic solvent. The pressure-induced nematic phase is not a subject of the paper, but we will focus the attention to the increasing concentration method only.

The increase of the mesogenic molecules concentration in solution leads finally to the appearance of the nematic phase, provided that the temperature of the solution is not higher than the clearing temperature of the dissolved compound. Still, in case of solutions, the designation of the isotropic to nematic phase transition is not so simple as in case of pure compounds (T_{NI}) because the transition goes through the two-phase region, as proper to the first-order phase transition. So, one determines *two concentrations of nematogenic compound* which correspond, respectively, to the appearance of the first drop of the nematic phase and the disappearance of the last drop of the isotropic phase in the mixture. The determination of these two boundary concentrations, or, more general, of the phase diagram for a nematogenic compound and solvent mixture, can be performed with the polarizing microscope, for example.

The transition from the isotropic to nematic phase, classified as a weakly first order or close to second order, is still a subject of numerous papers [1–13]. Pretransitional phenomena observed in the pure isotropic mesogenic liquids in vicinity to the nematic phase are mostly interpreted in the frame of the Landau–de Gennes theory [14]. Due to the existence of a short-range orientational order of the mesogenic molecules, the pseudonematic domains are formed in the isotropic phase, and their size increases as the temperature of the liquid approaches to the transition to the nematic phase. The Landau–de Gennes theory shows that the intermolecular correlation length ξ depends on temperature in the following way:

$$\xi(T)=\xi_0\left[\frac{T^*}{T-T^*}\right]^{1/2}, \tag{1}$$

where ξ_0 is of the order of the molecular length, and T^* denotes the temperature of virtual transition of the second order. Usually the value of T^* is of a few degrees below the nematic to isotropic phase transition temperature ($T_{\rm NI}$). Equation (1) shows that the correlation length becomes infinite at T^*.

The Landau–de Gennes theory was successfully used for interpretation of the experimental results obtained with the static methods (magnetic [1] and electric [2] birefringence, light scattering [3], nonlinear dielectric effect [4]) as well as the dynamic methods (molecular spin-lattice relaxation [5,6], dynamic light scattering [7], and optical Kerr effect [8–13]). In particular, predicted by the theory temperature dependence of the relaxation time τ for the reorientation of the prenematic domains in the medium of the viscosity η,

$$\tau(T)=\frac{V_{eff}^*\eta(T)}{k(T-T^*)^{\gamma}}, \tag{2}$$

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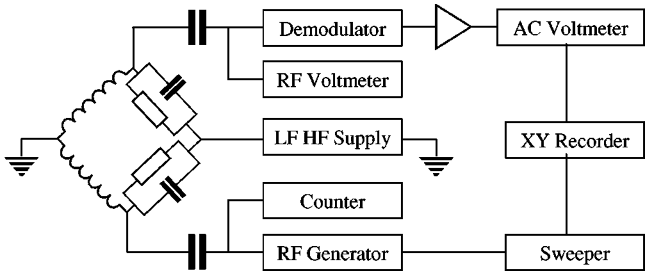

FIG. 1. Block diagram of the apparatus used.

reproduces the experimental data in a very good manner, with the critical exponent γ value close to the unity [14]. V_{eff}^{*} denotes the constant connected with the effective volume of the rotating entity [15,16], and k is the Boltzmann constant.

In our recent paper [17] we presented the pretransitional behavior of the nonlinear dielectric relaxation measured for pure nematogenic 4-(*trans*-4′-*n*-hexylcyclohexyl) isothiocyanatobenzene, C_6H_{13}CyHx Ph NCS, 6CHBT. The results were interpreted in the frame of Landau–de Gennes theory and the conclusions were convergent with that obtained with other dynamic studies of the prenematic effects [7–12]. A subject of the studies presented in this paper are the pretransitional effects occurring in solutions of nematogenic compound (6CHBT) in nonpolar medium (benzene). At constant temperature, the nonlinear dielectric relaxation spectra were recorded for increasing concentration of the mesogenic compound.

II. EXPERIMENT

6CHBT (melting point = 12.5 °C, the transition from the nematic to isotropic phase at T_{NI} = 43.1 °C) was synthesized and purified at the Institute of Chemistry, Military University of Technology, Warsaw. The purity of the compound, checked by the chromatography, was 99.5%. Benzene was distilled and stored over the metallic sodium.

The measurements of the nonlinear dielectric effect in the frequency domain were performed with the precise equipment designed at the University of Leuven, Belgium [18]. The block diagram of the apparatus is shown in Fig. 1 and the basic operation of the method is illustrated in Fig. 2.

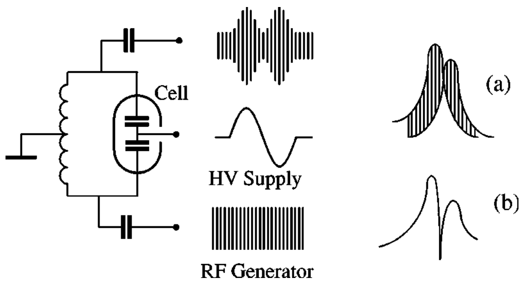

FIG. 2. Diagram of the resonance circuit, excited by the high frequency generator sweeper and modulated by high voltage at 85 Hz. Both cell capacitors contain the sample. The inductor is exchangeable. The hatched area of inset (a) corresponds to the modulation depth at any point of the sweep and provides the signal (b) upon demodulation.

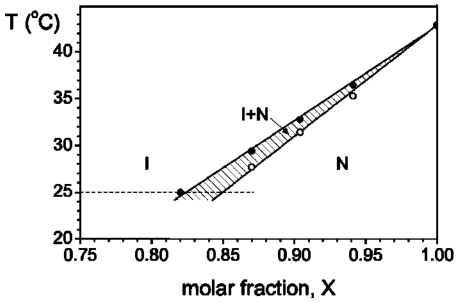

FIG. 3. Phase diagram for 6CHBT and benzene mixtures. X denotes the molar fraction of 6CHBT. The nonlinear dielectric spectra were recorded at 25 °C. The hatched area denotes the isotropic and nematic ($I+N$) two-phase region.

A high electric field of low frequency (85 Hz) is applied to the sample contained in two identical capacitors. The resonant circuit, which consists of the sample cell and an inductor connected in parallel, is excited at the appropriate frequency by an rf generator. By exchanging the inductors, the frequency range from 0.1 MHz to 100 MHz can be covered. The sample is subjected to the resultant of two fields: one static of high amplitude, the other of low amplitude at selected high frequency. As soon as the impedance of the liquid is modified by the action of the periodic high field, the amplitude modulation of the high frequency resonant voltage occurs. The modulation depth reflects the difference between the resonance curves at peak field strength and at zero field. Demodulation and consecutive amplification provide the signals that are recorded as function of the swept frequency. The signals reveal a shift of the resonant frequency together with changes of bandwidth and resonant voltage. A fit of the data to the derivative of the expression relating the voltage to the resonance parameters yields the field-induced changes of the complex impedance [18]. In the radiowave to microwave frequency range, a partial coaxial resonant cavity is used. It mainly consists of a closed (partially coaxial) cylinder in which a standing electromagnetic wave can be set up. The solution under study is the field-sensitive element included in a high-voltage capacitor terminating the coaxial line that influences the resonance properties of the circuit. The frequency is selected by changing the length of the cavity which can be altered between 0 and 55 cm by means of an adjustable short circuit. The dimension of the cavity gives an operational frequency domain from about 100 MHz up to 500 MHz; by striking higher harmonic frequencies, the frequency window can be extended to 3 GHz [19,20].

The viscosity was measured with a Haake RV20 rotational viscometer. The details were described in paper [21].

III. RESULTS AND DISCUSSION

Figure 3 presents the phase diagram for the mixture of 6CHBT and benzene, determined with the use of the polarizing microscope. The boundaries of the isotropic and nematic coexistence region are, in the limits of experimental errors, the straight lines.

The frequency dependence of the nonlinear dielectric increment, defined as a difference between the permittivity measured in the presence of strong electric field (E_0) and in the absence of the field,

$$\Delta\varepsilon = \varepsilon_{E_0} - \varepsilon, \tag{3}$$

was measured for 6CHBT solutions at constant temperature of 25 °C.

In our recent papers [22,23] we have shown the nonlinear dielectric spectra recorded for diluted solutions of 6CHBT in benzene. In the solutions the intermolecular dipolar interactions are so reduced that one is able to investigate the nonlinear relaxation of the individual dipolar molecules. In such a case the increment (3) is negative due to the Langevin saturation of the orientation of the dipoles forced by the strong electric field, leading to a decrease of the permittivity of the studied liquid. The relaxation of the increment occurs in the frequency range of several hundreds of megahertz, similar to that observed in the linear dielectric spectroscopy, and the position of the dielectric absorption maximum is only weakly dependent on 6CHBT concentration. The results obtained for diluted dipolar solutions can be well reproduced by the theory of Coffey and Paranjape [24], Kasprowicz-Kielich and Kielich [25], Alexiewicz [26], and Dejardin and Kalmykov [27–29], which describes the nonlinear orientational relaxation processes in *noninteracting dipolar systems*.

The positive nonlinear dielectric increment can be observed in a system in which the intermolecular aggregates, susceptible to the strong electric field, exist. A classical example of such a system are solutions of carboxylic acids or *cis*-lactams in nonpolar solvents, where the hydrogen bonded cyclic dimers of considerable compensated dipole moment are in equilibrium with polar monomers. A strong electric field shifts the equilibrium towards the more polar species (monomers). It gives an increase of the permittivity of solution. The nonlinear dielectric increment of such systems, measured with the ac electric field of low strength shows the relaxation in the frequency range corresponding to the kinetics of the dimerization process [20]. In case of dipolar mesogenic molecules dissolved in nonpolar medium, the positive nonlinear increment of permittivity can be related to the orientational effects, forced by the strong electric field upon the molecular aggregates—the pseudonematic domains—existing in the isotropic solutions.

As shows Fig. 4, the relaxation of the positive nonlinear dielectric increment appears in the frequency range at least one order of magnitude lower than that corresponding to the relaxation of the negative dielectric increment [22,23]. Besides, both the strength and the position of the nonlinear dielectric absorption strongly depend on 6CHBT concentration. For 6CHBT concentrations higher than 20% mole fraction, i.e., when the positive nonlinear effect rises, the Langevin dielectric absorption becomes so significant, that our experimental setup was no longer able to detect the nonlinear dielectric effects with a reasonable precision for the frequencies $\geqslant 50$ MHz.

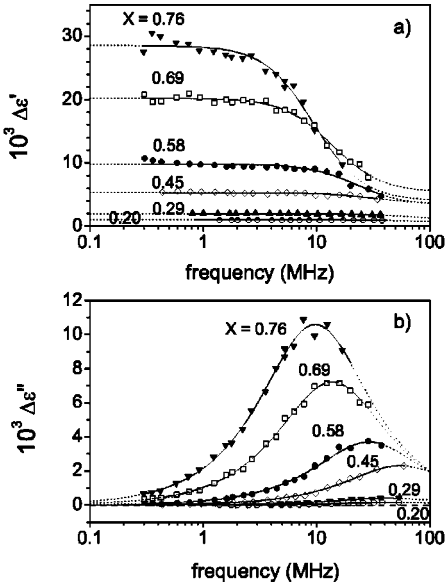

FIG. 4. Relaxation of the nonlinear real (a) and imaginary (b) parts of the positive dielectric increment measured for different molar fractions of 6CHBT in benzene, at 25 °C. The solid lines represent the best fit of the Debye-type Eq. (4) to the experimental data.

The experimental nonlinear dielectric spectra presented in Fig. 4 can be reproduced in a very good manner by the Debye-type function with a single relaxation time (τ),

$$\Delta\varepsilon^* = \Delta\varepsilon' - i\Delta\varepsilon'' = \frac{\Delta\varepsilon^\circ}{1+i\omega\tau}, \tag{4}$$

where $\Delta\varepsilon^\circ$ is the strength of the positive nonlinear dielectric effect and ω denotes the angular frequency of the measuring electric field of low intensity. So, from a formal point of view, the relaxation of the positive nonlinear dielectric increment measured both in pure mesogenic compound at different temperatures and in solutions of the compound in nonpolar solvent at constant temperature but for different concentrations, can be described in the same way. In both cases, the nonlinear dielectric relaxation proceeds according to a simple exponential law.

The data presented in Fig. 5 show that both the static value of the dielectric increment and the nonlinear relaxation time exhibit the critical-like behavior for increasing concentration of 6CHBT. Taking into account the similarities mentioned above in temperature and concentration behavior of the dynamic nonlinear dielectric properties measured, respectively, in pure mesogenic compound [17] and in solutions, we propose the following modification of the Eq. (2) for description of critical dependence of the relaxation time on concentration of mesogenic compound:

$$\tau(X) = \frac{V^*_{eff}\,\eta(X)}{kT(X^*-X)^\alpha}, \tag{5}$$

where X stands for the molar fraction of the solute. X^* denotes, in analogy to T^*, the concentration of virtual transition of the second order, and α is the critical exponent.

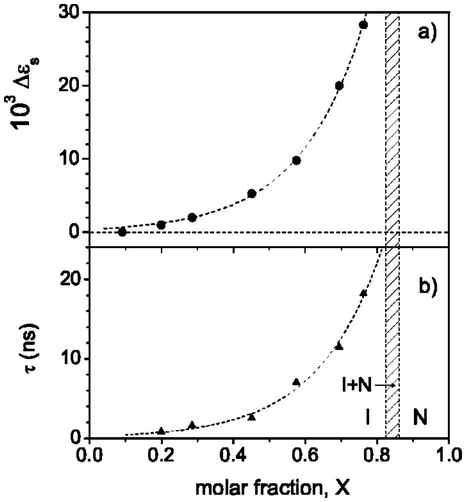

FIG. 5. 6CHBT in benzene molar fraction dependence of the static nonlinear dielectric increment (a) and the nonlinear relaxation time (b) at 25 °C.

According to Eq. (5), for the virtual concentration X^*, the viscosity to the relaxation time ratio is equal to zero. Figure 6 shows that the extrapolation of η/τ to zero points out, within the experimental errors, the 6CHBT concentration equal to the limit of the isotropic and nematic coexistence region. That means, the second-order phase transition in studied 6CHBT in benzene solutions occurs together with an appearance of homogeneous nematic phase in the mixture.

Figure 7 shows that the linear relation of $\ln(\eta/\tau)$ vs $\ln(X^*-X)$ predicted by Eq. (5) is fulfilled in quite good manner in our experiment. The slope of the line gives for the exponent α the value 0.92 ± 0.13, which within the experimental errors, equals to the value of the exponent γ resulting from the temperature dependence of the nonlinear relaxation time measured in pure 6CHBT [17].

The correlation length ξ, corresponding to our experiment, depends on the number of mesogenic molecules in the unit volume of solution. Two experimental facts are crucial for the formulation of the concentrational dependence of ξ: (i) in the transition to nematic phase, occurring for 6CHBT molar fraction $X^*=0.86$ (which corresponds to the molar concentration $N^*=3.14\ \text{mol/dm}^3$), the domain size becomes infinite, and (ii) in the transition to the two-phases region ($X=0.82$, $N=3.06\ \text{mol/dm}^3$) the domains become macroscopic, observed with the polarizing microscope, i.e., the domain's dimension is greater than ~ 500 nm.

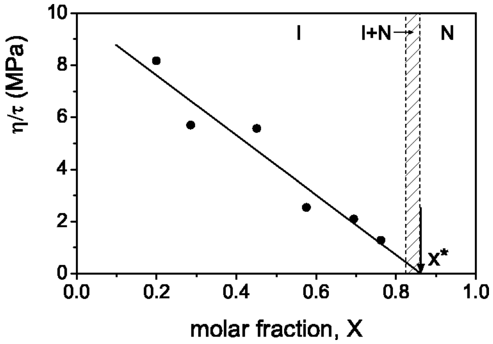

FIG. 6. An extrapolation procedure for the determination of the virtual concentration X^* of nematogenic 6CHBT in benzene.

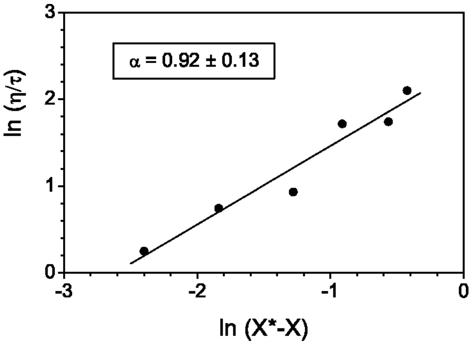

FIG. 7. According to Eq. (5) dependence of $\ln(\eta/\tau)$ vs $\ln(X^*-X)$ should be linear; the slope of the line gives the value of the critical exponent α.

A rough estimation shows that the following dependence of the correlation length on mesogenic molecules molar concentration (N),

$$\xi(N)=\xi_0\left[\frac{N^*}{N^*-N}\right]^2, \tag{6}$$

fulfills the above two conditions. For $N=3.06\ \text{mol/dm}^3$, i.e., at the transition from the isotropic phase to the two-phase region, the correlation length $\xi\approx1.5\cdot10^3\xi_0$. The effective length ξ_0 of 6CHBT molecule estimated from the molar volume at 25 °C ($V\cong296\ \text{cm}^3/\text{mol}$) is equal to about 8 Å, so an average "diameter" of the domains is of order 1000 nm, observed as macroscopic droplets. On the other side, the smallest 6CHBT concentration in CCl_4, for which the positive nonlinear increment can be detected, is about 0.20 mole fraction ($N\cong1.5\ \text{mol/dm}^3$). Then, the correlation length, estimated with Eq. (6), is about $\xi\cong5\xi_0$, the value convergent with that resulting from the Kerr studies [10,12].

IV. CONCLUSIONS

We have presented the studies of the pretransitional behavior of the dynamic nonlinear dielectric properties in solutions of mesogenic compound (6CHBT) in nonpolar solvent (benzene). For the molar fractions of 6CHBT higher than about 20%, the positive dielectric increment appears, and it shows the relaxation in the frequency region of tens of megahertz. For increasing 6CHBT concentration, at constant temperature, the static value of the dielectric nonlinear effect and the relaxation time show a critical-like behavior.

We have shown a compatibility in description (in the frame of the Landau–de Gennes theory) of the critical behavior of the nonlinear relaxation time measured in the pure mesogenic compound as a function of temperature and measured in the mixtures as a function of concentration of the mesogenic compound. In particular, the critical exponents determined in the both experiments have the same value, close to the unity, in accordance to the mean field theory prediction.

In analogy to the studies of the pretransitional effects in pure mesogenic compounds, where the virtual temperature T^* of the second-order phase transition is determined, the effects studied in the solutions (at constant temperature) can be characterized by the virtual concentration X^*. It was found that for the system studied, the value of X^* is very close to 6CHBT concentration for which the transition to homogeneous nematic phase occurs.

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