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Dynamics of the Self-Assembling of Mesogenic Molecules in the Prenematic Region of Isotropic Liquid

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The linear and nonlinear dielectric relaxation spectra, recorded in the isotropic phase of mesogenic 4-(*trans*-4′-*n*-hexylcyclohexyl)isothiocyanatobenzene (6CHBT), reveal an equilibrium between the molecules that are involved and non-involved in the pseudo-nematic domains, which are spontaneously formed in the prenematic region. A perturbation of the equilibrium by a static electric field of high strength ($E_0 \approx 10^7$ V/m) is followed by a nonlinear dielectric relaxation process that, measured with the probing electric field $E(\omega)$ of small amplitude and variable high frequency (up to 100 MHz), reflects the rate of the domains formation. The fraction of the mesogenic molecules involved in the prenematic domains at different temperatures is estimated.

Introduction

The Fröhlich relations[1] between the static dielectric permittivity (ϵ_s), or its derivative ($d\epsilon_s/dT$), and the electric field-induced increments of the basic thermodynamic quantities—the Helmholtz free energy (ΔF) and the entropy (ΔS):

$$\frac{\Delta F}{E^2} \equiv \frac{F(T,E) - F_0(T)}{E^2} = \left(\frac{\epsilon_0}{2}\right)\epsilon_s \qquad (1)$$

$$\frac{\Delta S}{E^2} \equiv \frac{S(T,E) - S_0(T)}{E^2} = \frac{\epsilon_0}{2}\frac{\partial\epsilon_s}{\partial T} \qquad (2)$$

give us the possibility to have a new examination of the molecular interpretation of the experimental results obtained with the dielectric methods. In the above equations, E denotes the strength of the probing electric field; U_0, S_0, and F_0 are the values of the thermodynamic quantities (per unit volume) in the absence of the electric field; T is the absolute temperature; and ϵ_0 is the permittivity of free space ($\epsilon_0 = 8.85$ pF/m). Although Fröhlich published his equations about 50 years ago[1] and the significance of his thermodynamic approach was emphasized by other founders of the physics of dielectrics,[2−4] to the best of our knowledge, until now, the experimental physicist has not interpreted the static dielectric data in the way proposed by eqs 1 and 2, and our recent papers[5−7] seem to be the first in that field.

The static permittivity of a dielectric material reflects not only an increase of the capacity of the cell filled with that material but, as it results from the Fröhlich relations, also corresponds to the Helmholtz free energy increment (i.e., represents a maximum of the energy that can be yielded during the isothermal discharge of the capacitor). The derivative of the permittivity, in turn, represents the entropy change caused by the application of the electric field to the dielectric material. As shown recently,[5−7] the idea implied in eqs 1 and 2 can lead to quite nontrivial conclusions about the molecular aspects of the pretransitional phenomena observed in liquid crystalline materials.

The conclusions resulting from the analysis of the temperature behavior of the permittivity derivative $\partial\epsilon_s/\partial T$ seem to be especially interesting and important. A very slow increase of the derivative (of a negative value) is observed for the nonmesogenic dipolar liquids when their temperature decreases. No pretransitional effects are observed up to the first-order transition to the crystalline phase.[8] In the case of mesogenic liquids, the permittivity derivative shows an anomalous increase in the vicinity of the weakly first-order transition from the isotropic (I) phase to the nematic (N) phase.[9−11] For highly polar mesogenic liquids, such as *n*-alkylcyanobiphenyls (molecular dipole moment of $\mu \approx 5D$[11]), the increase in the permittivity derivative is so strong that several degrees before the transition to the nematic phase, the derivative changes its sign and becomes positive;[5] thus, according to eq 2, the entropy increment ΔS also becomes positive. This observation seems to be important, as $\Delta S > 0$ means that the application of the probing electric field leads to an *increase of the molecular disorder* in mesogenic liquid instead of an *increase of the molecular order* (normally observed in dipolar liquids). Such an anomaly is possible only when, before the application of the electric field, the molecular dipoles are not randomly distributed, as in "normal" liquids, but some spontaneous molecular self-organization process occurs. In the case of nematogenic liquids, that process leads to the formation of pseudo-nematic domains in the isotropic liquid. The experimental observation on the permittivity derivative temperature behavior undoubtedly highlights that, within the prenematic domains, the dipolar molecules are self-organized

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preferably in the antiparallel manner; therefore, the external electric field, by forcing a parallel arrangement of molecular dipoles, destroys the local molecular order in the prenematic region. Such a field effect must lead to the increase in entropy.

The pseudo-nematic domains (the existence of which manifests itself strongly in the prenematic anomalous behavior of the specific heat capacity)[11] are surely dynamic entities, and, as such, they should be in equilibrium with the free mesogenic molecules. Because the antiparallel molecular arrangement results in some reduction of the polarity of the domains (in comparison to the set of the randomly oriented dipolar molecules), the equilibrium should be perturbed by the strong electric field,[12,13] and the nonlinear dielectric spectroscopy,[14,15] as well as the Kerr effect,[16,17] can then be used to study the dynamics of this self-organization process. This paper presents the experimental results obtained with the linear and nonlinear dielectric spectroscopy in the vicinity of the isotropic-to-nematic (I−N) phase transition of a mesogenic compound from the homologous series $C_nH_{2n+1}C_yH_xPhN=C=S$ (for $n = 6$, 4-(*trans*-4′-*n*-hexylcyclohexyl)isothiocyanatobenzene (6CHBT)), which is composed of molecules with an intermediate polarity ($\mu \approx 2.5$ D).[11]

Experimental Section

The compound studied (6CHBT) was synthesized and purified at the Institute of Chemistry at the Military University of Technology in Warsaw, Poland. The purity of the compound, as checked by chromatography, was >99.5%. The temperature of the phase transition from the isotropic liquid to the nematic liquid crystal is $T_{NI} = 43.5$ °C, and the enthalpy of the transition is given as $\Delta H_{NI} = 1.6$ kJ/mol.[18]

The linear dielectric characteristics were measured with a Hewlett−Packard model HP 4194A impedance/gain phase analyzer in the frequency region from 50 kHz to 100 MHz. The static values of the permittivity were taken as a low-frequency plateau of the real part of the complex dielectric permittivity. The measuring cell consisted of three plane electrodes (composed of gold-plated brass): one central and two grounded on each side, with the distance between the electrodes being ~0.5 mm. The sample volume necessary for the measurements is ~0.15 mL. The measuring voltage was 1 V (rms). High-performance electrical heating, using a Scientific Instruments model 9700 temperature controller, ensured very good temperature stabilization (at the millikelvin level), with the possibility of varying the temperature in steps of 10^{-2} K. Such equipment allows one to determine the permittivity with a relative accuracy of >0.5%.

The nonlinear dielectric spectra were recorded with the experimental setup that has been described in detail in ref 13. A high electric field E_0 (up to 10^7 V/m) of low frequency (85 Hz) is applied to the sample contained in two identical capacitors placed in the two arms of the bridge system. One of the cells is a reference cell, and the second cell is connected in parallel to an inductor and such a resonant circuit is excited at the appropriate frequency by a radio frequency (rf) generator. By exchanging the inductors, the frequency range from 0.1 MHz to 100 MHz can be covered. Therefore, the sample is subjected to the resultant of two fields: one static of high amplitude E_0, the other of low amplitude (~10^2 V/m) at selected high frequency $E(\omega)$. The nonlinear dielectric data are obtained by monitoring the modulation of the parameters of the resonant circuit induced by the application of a high field to the capacitor of the circuit.
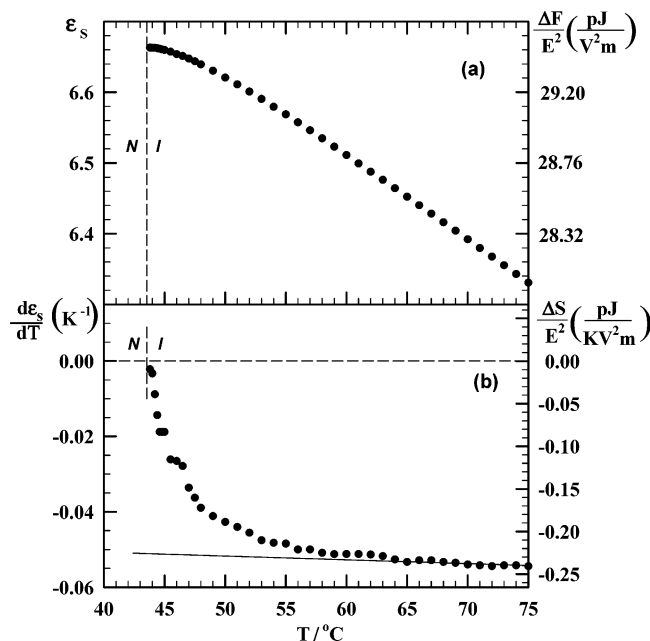

Figure 1. Temperature dependence of (a) the static dielectric permittivity and (b) its derivative, and the corresponding Helmholtz free energy (ΔF) and the entropy (ΔS) increments induced by the probing electric field in the isotropic phase of 6CHBT. The solid line represents a "normal" entropy behavior in dipolar liquids.

Results and Discussion

Figure 1 presents the temperature dependence of the static dielectric permittivity (Figure 1a) and its derivative (Figure 1b) and, correspondingly, the field-induced increments of the Helmholtz free energy ΔF and the entropy ΔS (per unit volume and unit electric field strength), calculated from eqs 1 and 2. An anomalous increase of the entropy increment is observed in the isotropic phase of 6CHBT by as much as ~15 degrees before the transition to the nematic phase. Very close to the transition, two contributions to the resulting entropy increment—namely, the negative one (due to the field ordering of the molecular dipoles in bulk liquid) and the positive one (due to the field disordering of the spontaneously self-organized molecules in the prenematic domains)—balance each other. Therefore, in the temperature region very close to the I−N phase transition, the application of the probing electric field apparently does not lead to any orientational effect in the liquid studied. Therefore, the temperature dependence of the static dielectric permittivity of the polar liquid studied behaves here in a manner quite similar to that observed for nonpolar liquids.

The pseudo-nematic domains, which are the precursors of the approaching nematic phase, are an essential factor; they have a strong influence on the physical properties of mesogenic liquids. Therefore, the important question concerns the extent of the pretransitional spontaneous molecular self-organization (i.e., the proportion of the mesogenic molecules involved in the domains, with respect to the total number of molecules in the unit volume), at a given temperature. Some quantitative information on that problem can be found from the analysis of the temperature behavior of the dielectric absorption spectra ϵ''-(ω) recorded for isotropic 6CHBT and is shown in Figure 2. One can notice that the value of the imaginary part of the permittivity at the maximum of the absorption band (ϵ''_{max}) shows a nonmonotonic temperature dependence. Far from the I−N transition, as the temperature decreases, the intensity of the band increases, attains its maximum, and then begins to decrease (see Figure 3). In the case of the first-order phase
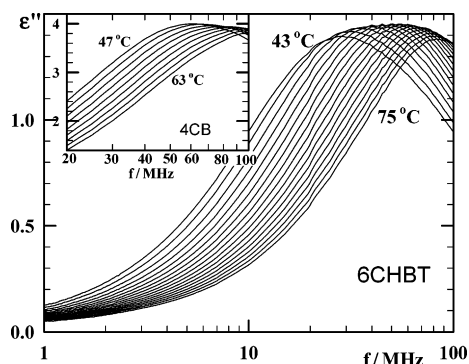
Figure 2. Anomalous temperature dependence of the intensity of the dielectric absorption in the vicinity of the weakly first-order isotropic−nematic (I−N) phase transition of 6CHBT. Inset shows the dependence of the nonmesogenic compound in the vicinity of the first-order I−Cr phase transition in *n*-butylcyanobiphenyl.[8]
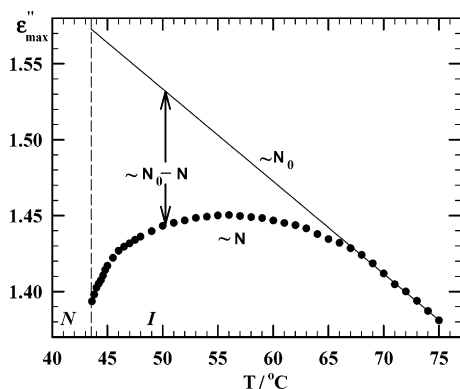

Figure 3. Temperature dependence of the maximum of the dielectric absorption bands of 6CHBT, and a sketch for evaluating the fraction of molecules involved in the pseudo-nematic domains.

transition, as shows the inset in Figure 2 for the I−Cr transition in the nonmesogenic compound *n*-butylcyanobiphenyl (denoted as 4CB),[8] the ϵ''_{max} (T) dependence shows an increase going up to the temperature of the phase transition.

The anomalous dependence of ϵ''_{max} (T) observed for mesogenic 6CHBT certainly reflects the molecular rearrangement that occurs in the prenematic region. Because the value of ϵ''_{max} is proportional to the number of relaxing dipoles in the unit volume ($\mathscr{N}$), the aforementioned spectroscopic observation undoubtedly shows that, in the prenematic region, a certain number of molecules "disappears". Of course, the molecules that have "disappeared" are involved in the prenematic domains, where the molecular dynamics proceeds under conditions that are rather similar to those which exist in the bulk nematic liquid crystal, rather than to those which exist in the isotropic liquid. Hence, based on the temperature dependence of ϵ''_{max}, the fraction of the molecules self-organized in the prenematic domains can be estimated by the following reasoning. If one assumes that, far from the transition to the nematic phase, the experimental dependence ϵ''_{max} (T) reflects the dielectric absorption of the entire number of molecules contained in the unit volume ($\mathscr{N}_0$) (such as that for nonmesogenic polar liquids), rather than in the prenematic region, at a given temperature, the difference between the measured value of ϵ''_{max} and the value extrapolated (represented by the solid line in Figure 3) is proportional to the difference between the real number of relaxing molecular dipoles $\mathscr{N}$ and the total number of molecules $\mathscr{N}_0$. Therefore, the ratio $(\mathscr{N}_0 - \mathscr{N})/\mathscr{N}_0$ represents the fraction x of the mesogenic molecules that "disappeared" in the dielectric spectrum (i.e., the fraction of the molecules involved in the
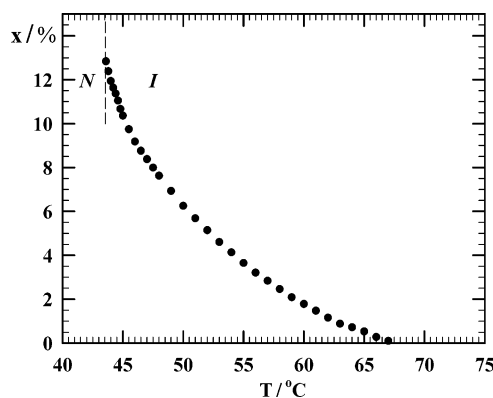

Figure 4. Fraction of mesogenic 6CHBT molecules involved in the precursors of the nematic phase, as a function of the temperature.

pseudo-nematic domains). As presented in Figure 4, this fraction attains a value of ∼12% at the temperature just before the transition to the nematic phase. Of course, the empirical procedure that we have proposed allows one to get only a rough estimation of the value of *x*, but, nevertheless, it gives us some idea of the extent of the prenematic molecular self-organization process.

Finding the relaxation band (or bands), because of the dynamics of the molecules involved in the prenematic domains, is rather a difficult task (and probably hopeless). In principle, the corresponding dielectric absorption band should appear in a frequency region (by ∼1 order of magnitude, as in the bulk nematic phase) that is lower than that recorded for "free" molecules (see Figure 2). However, to record this new dielectric absorption band, it is necessary here that the directors **n** (representing the molecular local order in the domains) are more or less uniformly oriented in the direction of the probing electric field. Such an orientation, which can be quite easily achieved in the bulk nematic liquid crystals, in the case of randomly distributed directors **n** of the pseudo-nematic domains of *microscopic size* (even close to the I−N transition, the liquid is transparent), is rather impossible.

Still, the molecules involved in the pseudo-nematic domains can manifest their existence in the dielectric spectrum but only if the biasing dc electric field of a very high strength E_0 is applied to the liquid (i.e., in the condition of the nonlinear dielectric response of the system).

In the nonlinear dielectric experiment, one detects the permittivity increment $\Delta\epsilon$ as a difference between the permittivity values measured in the presence (ϵ_{E_0}) and the absence (ϵ) of the dc biasing field of high intensity ($\Delta\epsilon = \epsilon_{E_0} - \epsilon$). The increment $\Delta\epsilon$ is measured with a probing dc field of low amplitude and high (variably) frequency. Both the sign and the frequency behavior of $\Delta\epsilon$ are dependent on the type of the intermolecular interactions and the molecular ability for the self-organization to occur in the liquid studied. In the simplest case of non-interacting dipolar systems, the nonlinear permittivity increment is negative ($\Delta\epsilon < 0$), which reflects the Langevin saturation of the dipoles orientation in liquids. The frequency dependence of the nonlinear dielectric effect then can be described quite well with the Coffey−Kielich[19−21] and Déjardin−Kalmykov[22−24] theories. In such a case, the frequency that corresponds to the maximum of the nonlinear dielectric absorption band only slightly differs from that observed in the linear dielectric spectrum. It means that the relaxation time for the rotational Brownian diffusion of dipolar molecules in liquids is only slightly influenced by the strong dc electric field. This problem is competently presented in ref 25. However, in

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practice, the non-interacting dipolar systems can be realized exclusively as very diluted solutions of the dipolar compound in the nonpolar medium and they play some reference role.

In concentrated dipolar systems, the intermolecular interactions generally lead to the formation of such a diversity of multimolecular entities that the nonlinear dielectric response of high complexity cannot be analyzed in terms of the usual spectroscopic quantities. The complex nonlinear dielectric response ($\Delta\epsilon^*(\omega) = \Delta\epsilon'(\omega) - i\Delta\epsilon''(\omega)$), measured with a weak electric field $E(\omega)$, reveals itself as the nonlinear dielectric spectrum with well-shaped nonlinear dispersion (real part) $\Delta\epsilon'$-(ω) and absorption (imaginary part) $\Delta\epsilon''(\omega)$ only in a very special case. That special case requires the following two conditions to be fulfilled simultaneously: (1) a reversible molecular aggregation process of one type must be strongly dominant in the liquid studied (the reversibility of the process denotes the existence of an equilibrium between the reaction partners), and (2) the polarity of the partners from both sides of the equilibrium must be different and the greater the difference, the higher the strength of the nonlinear dielectric response. As the strong static electric field E_0 shifts such an equilibrium toward the more-polar side, here, the nonlinear dielectric increment takes positive values. This increment, which is measured with a weak probing electric field $E(\omega)$, shows the relaxation in the frequency domain corresponding to the rate of the intermolecular process studied.

In a previous paper,[26] it was shown that the nonlinear dielectric spectra, which have been recorded for a system in which one type of the intermolecular equilibrium occurs (or rather strongly predominate), can be formally described by the Debye-type relaxation equations, with a single relaxation time. Such a type of equilibrium can be found, for example, in hydrogen-bonded systems where the dimerization of *cis*-lactams[27] or carboxylic acids[28] leads to the formation of weakly polar cyclic dimers that are in equilibrium with the polar monomers.

The nonlinear dielectric spectra, recorded in the prenematic region of 6CHBT,[29] reveal the features of a system in which one type of equilibrium between the entities of different polarity occurs and all the experimental data highlight the equilibrium between the molecules spontaneously self-organized in the pseudo-nematic domains (of markedly reduced polarity) and the free mesogenic molecules. First of all, one can detect the nonlinear dielectric spectra only for temperatures lower than ~60 °C (i.e. when the first prenematic symptoms are also appearing in the linear static (see Figure 1b) and in the linear dynamic dielectric studies of 6CHBT (see Figure 3)). Next, the nonlinear dielectric increment is positive[29] and the nonlinear absorption bands $\Delta\epsilon''(\omega)$ are of the Debye-type form (see the solid lines in Figure 5). Finally, the strengths of the nonlinear dielectric absorption spectra increase as the temperature approaches the I−N transition, whereas, at the same time, the strengths of the linear absorption band are decreasing (see Figure 5).

Figure 6 allows one to make a comparison of the temperature dependence of the relaxation times determined from the linear and nonlinear dielectric studies of 6CHBT. The molecular self-assembling process, the kinetics of which is studied with the nonlinear dielectric spectroscopy, is characterized by the relaxation time being essentially longer than that corresponding to the Brownian rotational diffusion of individual molecules observed in the linear dielectric spectra. The difference between these two relaxation times increases as one approaches the transition to the nematic phase (i.e., as the size of the domains
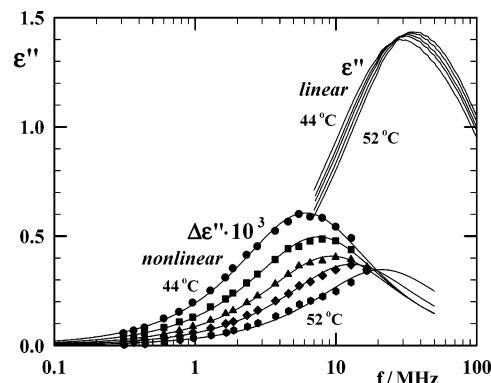

Figure 5. Linear and nonlinear dielectric spectra recorded in the pre-nematic region of isotropic 6CHBT. The solid lines represent the Debye-type frequency dependence of the dielectric absorption bands (in both the linear and nonlinear cases).
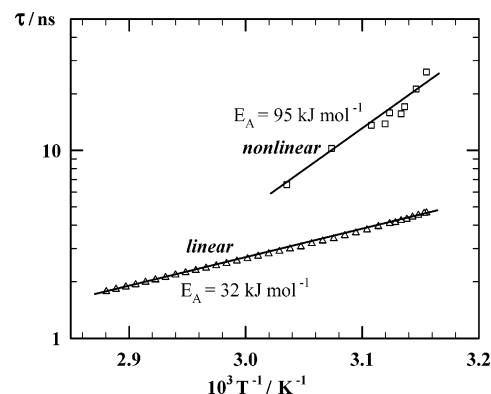

Figure 6. Arrhenius plots for the linear and nonlinear dielectric relaxation times determined in the pre-nematic region of isotropic 6CHBT.

are increasing) and close to the transition, the difference is ~1 order of magnitude. In terms of the activation energy, the data presented in Figure 6 show that the energy corresponding to the formation of the pseudo-nematic domains is ~3 times higher than that of the diffusional rotation of single molecules.

Conclusion

In conclusion, the presented results of the studies of mesogenic liquid in its isotropic phase, using linear and nonlinear dielectric relaxation spectroscopy, allow one to better understand the nature and dynamics of the spontaneous self-organization of the mesogenic molecules in a region close to the isotropic−nematic (I−N) phase transition. In particular, spectroscopic evidence is given for the existence of an equilibrium between the pseudo-nematic domains and the freely moving mesogenic molecules. An original method for estimation of the fraction of the mesogenic molecules involved in the pseudo-nematic domains is proposed, thus giving important information on the temperature evolution of the pre-nematic self-assembling process.

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