

# Pretransitional critical-like behavior of dielectric permittivity in mixtures of mesomorphic and nonmesomorphic compounds

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Static dielectric measurements are performed in the temperature range of the isotropic-nematic phase transition of binary mixtures of mesomorphic *n*-heptylcyanobiphenyl (7CB) and nonmesomorphic: (a) *n*-heptylcyanophenyl (7CP) and (b) carbon tetrachloride (CCl<sub>4</sub>), the solutes of different molecular shape and polarity. In the whole studied range of the solutes mole fraction ( $x$ ) ( $x_{max} \approx 0.17$ ), the critical-like temperature behavior of the permittivity in the vicinity of the transition from the isotropic phase to the two-phase (nematic+isotropic) region can be well described with a critical exponent close to 0.5, as in a pure 7CB, indicating the tricritical nature of the transitions. It seems to be important that the fitting-determined temperatures of the virtual second-order transition in the solutions,  $T^*$ , i.e., the temperature limit of the thermodynamic stability of supercooled isotropic phase, correspond well to the experimentally observed low-temperature limits of the two-phase isotropic+nematic region.

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## I. INTRODUCTION

Most of the phase transitions occurring in liquid crystalline materials are termed weakly first order in nature because the enthalpy and the volume changes at the transitions are small in comparison to those observed at the melting point. As a consequence, large pretransitional effects, reminiscent of second-order behavior, are usually observed in the region of the transition point. The most spectacular pretransitional phenomena, observed in the vicinity of the isotropic (*I*) to nematic (*N*) phase transition, are due to the existence of a short-range orientational order of the mesogenic molecules, leading to the formation of pseudonematic domains in the isotropic liquid. The size of the domains increases as the temperature of the liquid approaches the nematic phase transition. The phenomenon can be quantitatively described by an intermolecular correlation length  $\xi$  in the manner developed by Landau in his theory of the second-order phase transition, and then applied by de Gennes to the isotropic to nematic transition, thus yielding to the following temperature dependence of the correlation length [1]:

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

where the constant  $\xi_0$  is of the order of the molecular length and  $T^*$  denotes the temperature of the virtual second-order transition. As can be seen from Eq. (1), for  $T \rightarrow T^*$  the correlation length tends to infinity.

It is worth mentioning a peculiarity of the isotropic to nematic phase transition, namely, the fact that the region closest to the critical point ( $T^*$ ) is inaccessible to experiment

because the transition of the first order occurs at a temperature  $T_{NI}$  somewhat higher than  $T^*$ . As a consequence, the determination of the critical exponents must be performed by using extrapolations, which, as a rule, lead inevitably to diversity in the final results obtained by different authors. This is one of the reasons that can explain why, despite numerous papers devoted to the *I-N* phase transition, the nature of the critical behavior in the vicinity of the transition is not properly understood yet.

The pretransitional effects in the vicinity of the *I-N* transition can be detected mainly in nonlinear studies of mesogenic liquids subjected to an external stimulus of sufficiently strong amplitude. The experimental data on the subject are numerous and, among them, one can quote the static measurements of birefringence due to the magnetic [2] or electric [3] field, light scattering [4], and nonlinear dielectric effect [5,6], as well as dynamic studies on molecular spin-lattice relaxation [7,8], dynamic light scattering [9], transient grating optical Kerr effect [10,11], nonlinear dielectric relaxation [12–14], etc. The Landau-de Gennes theory was successfully used for interpreting the experimental data obtained with the nonlinear techniques.

The linear dielectric properties reveal themselves in the prenematic effects mainly in the case of strongly polar mesomorphic liquids. The effects, for example, a peculiar temperature dependence of the static permittivity [15–18] and the activation energy for molecular rotation derived from the dielectric relaxation time [17–21] or an anomalously slow rotational diffusion [20,21] (broadening of the absorption spectra) in the vicinity of *I-N* transition, are still without a convenient theoretical description.

This paper concerns the transition from the isotropic to nematic phase going through the two-phase (*I+N*) region. We present the experimental results on temperature pretransitional behavior of the linear static permittivity of strongly

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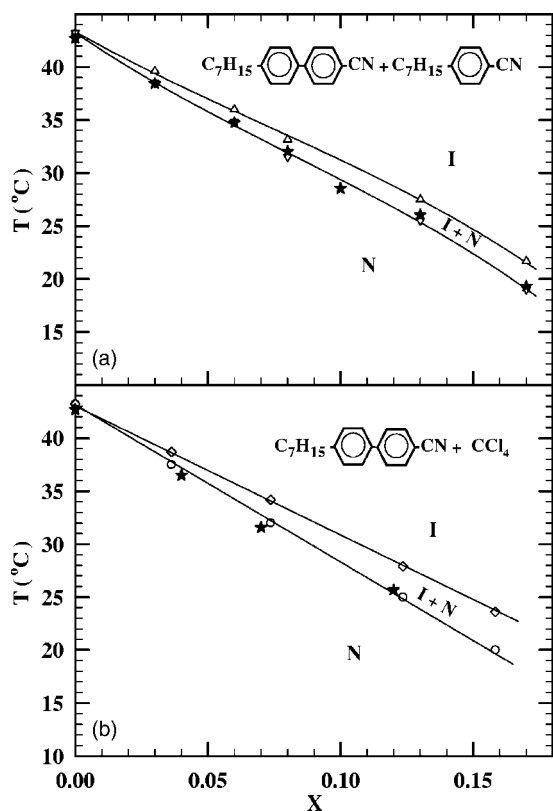


FIG. 1. Phase diagrams for mixtures of mesogenic 7CB and nonmesogenic 7CP (a) and  $\text{CCl}_4$  (b).  $X$  is the mole fraction of nonmesogenic solute. Open points are the temperatures of the transitions determined with the optical method. The symbol ( $\star$ ) denotes the temperature  $T^*$  of the virtual second-order transition (see the text).

polar mesomorphic *n*-heptylcyanobiphenyl (7CB) in two-component mixtures with two kinds of nonmesomorphic molecules: (a) *n*-heptylcyanophenyl (7CP)—of a quite similar structure and polarity as the mesomorphic solvent (7CB) and (b) carbon tetrachloride ( $\text{CCl}_4$ )—the solute composed of the spherical, nonpolar molecules.

## II. EXPERIMENT

*n*-heptylcyanobiphenyl,  $\text{C}_7\text{H}_{15}\text{PhPhCN}$ , 7CB ( $T_{NI} = 43.3^\circ\text{C}$ ), and *n*-heptylcyanophenyl  $\text{C}_7\text{H}_{15}\text{PhPhCN}$ , 7CP, were synthesized and purified at the Institute of Chemistry, Military University of Technology, Warsaw. The purity of the compounds, checked by chromatography, was better than 99.5%. Carbon tetrachloride of the spectroscopic grade was purchased by Fluka. The temperature of the phase transitions in a pure 7CB and in the solutions was determined with the use of the polarizing microscope. The static values of the permittivity were taken as the low-frequency plateau of the real part of the complex electric permittivity measured with a HP 4194A impedance and gain phase analyzer in the frequency region of 50 kHz–1 MHz. The permittivity was determined with an accuracy better than 0.5%. The measuring capacitor consisted of three plane electrodes: one central and two grounded on each side. A dc biasing electric field was

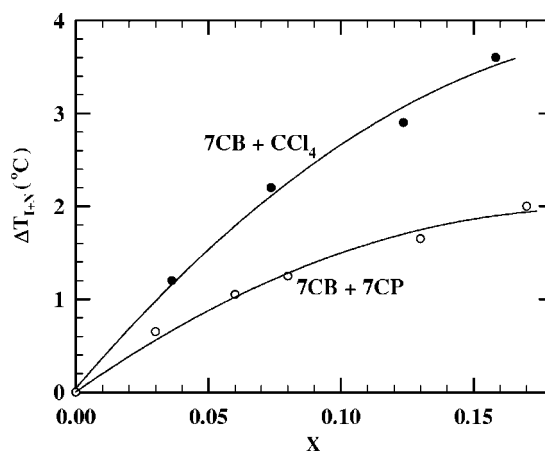


FIG. 2. Temperature extent of the two-phase ( $I+N$ ) region in 7CB+nonmesogenic solute mixtures as a function of the mole fraction of the solute.

applied to the capacitor for the measurements of  $\epsilon_{\parallel}$  in the nematic and two-phase region in solutions. A highly performing electrical heating of the capacitor made with a Unipan 650H controller assured a temperature stabilization better than  $10^{-3}$  K and the possibility of varying the temperature by  $10^{-2}$  K steps.

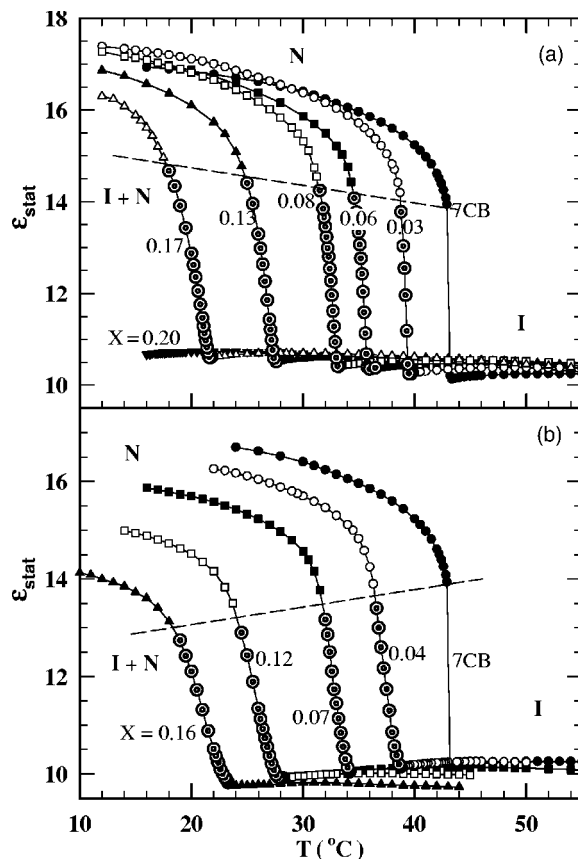


FIG. 3. Temperature dependence of the static dielectric permittivity measured in the isotropic phase, the two-phase ( $I+N$ ) region ( $\odot$ ) and the nematic phase of 7CB+7CP (a) and 7CB+ $\text{CCl}_4$  (b) mixtures for different mole fractions of the solute.

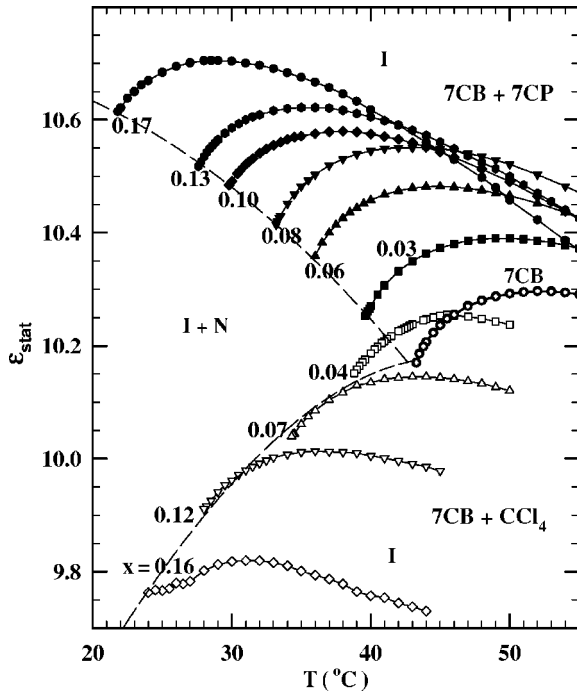


FIG. 4. Temperature behavior of the static permittivity measured in the isotropic phase of 7CB+7CP and 7CB+CCl<sub>4</sub> mixtures for different contents of the solute.

### III. RESULTS AND DISCUSSION

Figure 1 presents the phase diagrams for the mixtures studied. As appropriate for transitions of the first order, the two-phase (isotropic+nematic,  $I+N$ ) region is observed and the temperature extent of the region essentially depends on the nature of the solute [22–28]. As shown in Fig. 2, for a given concentration of the solute, the region of coexistence of the isotropic and nematic phases in the mixtures 7CB+CCl<sub>4</sub> is about twice as large as that observed in the mixtures 7CB+7CP, where, as we mentioned above, both the shape and the polarity of mesogenic solvent and nonmesogenic solute molecules are highly similar. However, despite the differences in the phase diagrams, the nematic phase in both mixtures disappears at a quite similar value of the mole fraction of the solutes (somewhat less than 0.20 mole fraction).

Figure 3 presents the temperature dependence of the static dielectric permittivity measured in the isotropic and nematic phases of the mixtures studied. The permittivities corresponding to the two-phase region are distinguished in the figure. It is worth mentioning that the transitions from the isotropic phase to the  $I+N$  region, and next from the  $I+N$  region to the nematic phase, manifest themselves quite differently in the static permittivity behavior. The permittivity changes drastically at the beginning of the two-phase region, whereas at the end of the region it merges smoothly with the permittivity of the nematic phase. So, as a result, the temperature of the transition from  $I+N$  region to  $N$  phase cannot be determined precisely on the basis of the static permittivity measurements, contrary to the case of transition from the isotropic phase to the two-phase region.

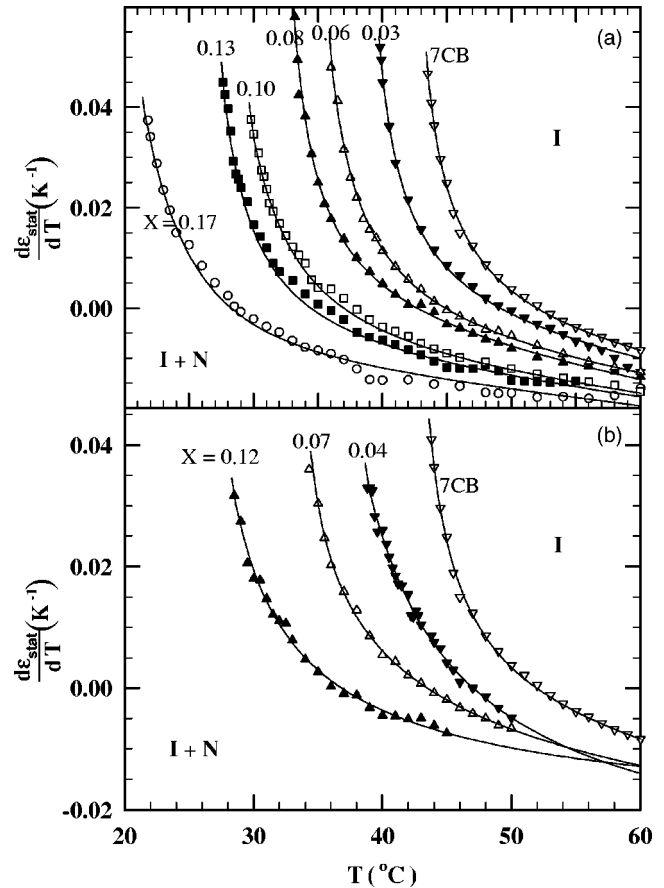


FIG. 5. Pretransitional critical-like behavior of the static permittivity derivative in the vicinity of the transition from the isotropic phase of 7CB+7CP (a) and 7CB+CCl<sub>4</sub> (b) mixtures to the two-phase ( $I+N$ ) region. The solid lines represent the best fit of Eq. (2) to the experimental data obtained for  $\sigma=0.5$  and  $T^*$  values shown in Fig. 1.

The prenematic temperature behavior of the static permittivity measured in the isotropic phase of the two mixtures studied is shown in Fig. 4. The nature of the solute added to mesogenic 7CB clearly reflects itself in the concentrational evolution of the permittivity of the mixtures: (i) as a decrease of permittivity—in the case of the nonpolar solute and (ii) as a permittivity increase—in the case of the polar one (but only when the dipole's density of the solute is higher than that of the solvent—just the case of 7CB+7CP mixtures). Nevertheless, for both mixtures studied, about 10 deg before the transition from the isotropic phase to the two-phase region, the permittivity exhibits a maximum, similarly to that observed for *pure* 7CB [21]. The permittivity derivative shows a critical-like behavior as the temperature approaches the transition to the  $I+N$  region (Fig. 5). The solid lines in Fig. 5 represent the best fit of the equation [17]

$$\frac{d\epsilon}{dT} \propto A(T-T^*)^{-\sigma}, \quad (2)$$

to the experimental data. In Eq. (2)  $A$  is a constant,  $\sigma$  is a critical exponent, and together with  $T^*$  they are three-fitting parameters. For both 7CB+7CP and 7CB+CCl<sub>4</sub> mixtures,

the experimental critical-like temperature dependences of the permittivity derivative presented in Fig. 5 can be quite well reproduced by Eq. (2) with the same value of the exponent  $\sigma=0.5$  and  $T^*$  values as depicted in Fig. 1.

The exponent value obtained for the mixtures studied is very close to that observed for pure mesogenic solvent (7CB) [21] and, as it was shown in many papers [29–32], it corresponds to the tricritical hypothesis of the  $I$ - $N$  phase transition. Our results show that transitions from the isotropic liquid to the two-phase  $I+N$  region in mixtures also belong to that class of phase transitions.

The main result of the presented studies is shown in Fig. 1: the temperature line of the transitions from the  $I+N$  region to the nematic phase in the mixtures of mesogenic + nonmesogenic compounds is convergent with the temperature  $T^*$  of the virtual second-order transition to the nematic phase of the mixtures, determined by fitting Eq. (2) to the data points in Fig. 5. The finding seems not very surprising, as the temperature  $T^*$  denotes the limit of the thermodynamic

stability of supercooled isotropic phase of the mixtures, but the result is probably not trivial and merits being theoretically grounded. It gives, for example, a new look on those experimental results, obtained for “pure” mesogenic compounds, where the difference between the temperature of the  $I$ - $N$  transition ( $T_{NI}$ ) and the virtual transition ( $T^*$ ) was important (about 1 K and greater). The results presented in this paper suggest that the most probable reason for these incomprehensible results is the impurities of the mesogenic compound, leading to the formation of the two-phase region of a noticeable extension.

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