

DIELECTRIC RELAXATION OF 4-CYANOPHENYL 4'-*n*-DECYLOXYBENZOATE IN THE ISOTROPIC, NEMATIC, AND SMECTIC A PHASES

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The paper presents the results of the dielectric relaxation study performed for the isotropic, nematic, and smectic A phases of 4-cyanophenyl 4'-*n*-decyloxybenzoate (C₁₀H₂₁O-Ph-COO-Ph-C≡N, CP10DB) in the frequency range from 100 kHz to 100 MHz. In the nematic and smectic A phases the permittivity was measured with the probing electric field E parallel to the macroscopic molecular orientation (the director n). The recorded dielectric spectra correspond to the rotation of CP10DB molecules around the short axis and can be quite well described in the framework of the Debye model. It was found that the values of the activation energy for the molecular reorientations in the isotropic and smectic A phases of CP10DB are quite close to each other, whereas in the nematic phase the energy is remarkably higher.

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1. Introduction

Application of an electric field to dielectric materials brings about the response, which contains many valuable data on dynamic properties of the materials at a microscopic level. It concerns mainly liquids or liquid crystals where the rotating entities are well defined and often a particular type of molecular movement can be quite easily recognized [1-4]. It refers mainly to the elongated and rigid molecules where the rotations around the two principal axes, corresponding to the maximum (short axis) and to the minimum (long axis) of the momentum of inertia, are sufficiently differentiated to give in the dielectric spectrum two separated absorption bands. Of course, the dielectric absorption occurs when the rotation

is followed by a change of the projection of the molecular dipole moment on the direction of the probing electric field.

In oriented liquid crystalline phase, a new axis of symmetry — the director n — appears. As a result of competition between the nematic potential and the thermal energy, an angle between the long molecular axes and the director n is, on average, different from zero and the order parameter is smaller than one. Therefore, the molecules can rotate on the cone around the director n and, as shown in [5], a new absorption band can be recorded in dielectric spectrum.

In this paper we analyze the behavior of the dielectric absorption band corresponding to the rotation of the mesogenic CP10DB molecules around the short axis in three phases: isotropic, nematic, and smectic A. Study of this type of molecular movement yields the most important information about the molecular dynamics in the presence of the liquid crystalline potential.

2. Experimental

The compound studied 4-cyanophenyl 4'-*n*-decyloxybenzoate (CP10DB) was synthesized and purified at the Institute of Chemistry, Military University of Technology, Warsaw. It has the following sequence of phase transitions:

crystal—55.5°C—smectic A—76°C—nematic—84.8°C—*isotropic*.

The dielectric relaxation spectra were recorded with a HP 4194A Impedance/Gain-Phase Analyzer in the frequency range from 100 kHz to 100 MHz. The concentric output (via HP4194A impedance probe), used for the measurements up to 100 MHz, requires a capacitor of a special design. The capacitor we used consists of three plane electrodes: one central electrode and two grounded electrodes on each side. Because the impedance probe is very sensitive to the magnetic field, a biasing d.c. electric field was used for the ordering the sample in liquid crystalline phases.

3. Results and discussion

Figure 1 presents the experimental frequency dependence of the real ϵ' and imaginary ϵ'' parts of the electric permittivity of CP10DB measured in the isotropic (I), nematic (N), and smectic A (S_A) phases. Because the permittivity in the liquid crystalline phases was measured for the samples oriented with biasing d.c. electric field, the $\epsilon_{ij}^*(\omega)$ component of the permittivity tensor was recorded.

The analysis of the dielectric relaxation spectra of CP10DB in the studied frequency region can be carried out with the use of Cole–Cole empirical equation [6]:

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{A}{1 + (i\omega\tau)^{1-k}} + i \frac{\sigma}{\epsilon_0\omega}, \quad (1)$$

where ϵ_∞ denotes the value of the permittivity measured at high frequency and often is taken as a square of the refractive index, A is the dielectric strength, ω — the angular frequency, and τ — the relaxation time. Equation (1) takes into

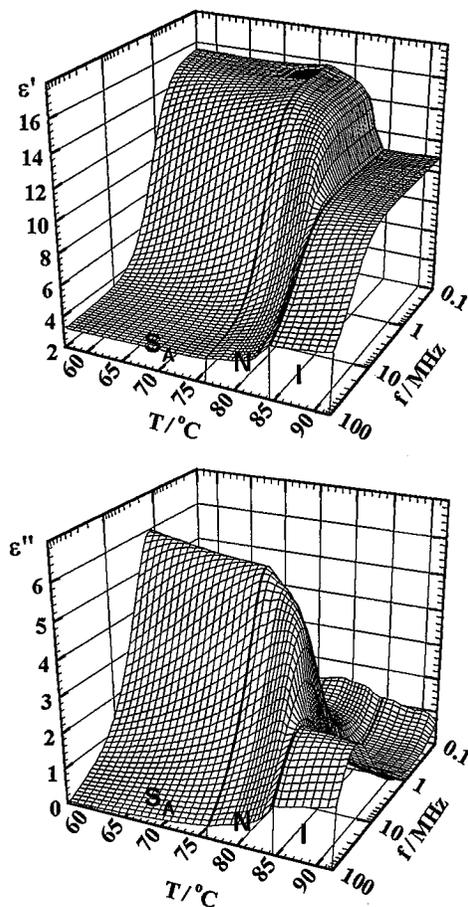


Fig. 1. Real ϵ' and imaginary ϵ'' parts of the electric permittivity of CP10DB in the isotropic (I), nematic (N) and smectic A (S_A) phases as a function of frequency f of measuring electric field \mathbf{E} and temperature T . In N and S_A phases the permittivity was measured for $n \parallel \mathbf{E}$.

account a distribution of relaxation times. For the limiting value of the distribution parameter $k = 0$, the relaxation process is described by a single relaxation time. It is just the case of studied CP10DB: the fitting of Eq. (1) to the experimental data gives for the parameter k values of about 10^{-2} in the all three phases of the substance. Thus, the relaxation process studied can be considered with a good approximation as the Debye-type one [7].

Because in the low frequency range the dielectric losses due to conductivity of the CP10DB cannot be neglected, in Eq. (1) an appropriate term was added. σ denotes the conductivity (in S/m) of the sample and ϵ_0 is the permittivity of free space ($\epsilon_0 = 8.85 \text{ pF/m}$).

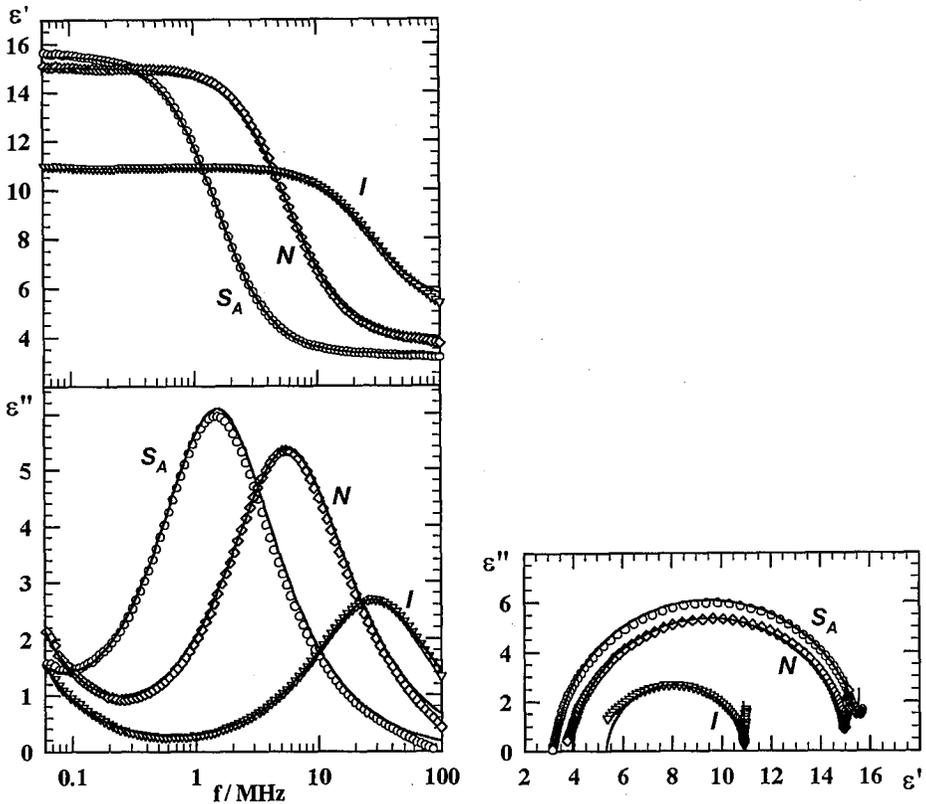


Fig. 2. Experimental dielectric characteristics (points) for isotropic (I, 90°C), nematic (N, 80°C) and smectic A (S_A , 60°C) phases of CP10DB are well described in the framework of the Debye model (Eq. (1), solid lines).

Figure 2 presents, as an example, the best fitting of Eq. (1) (solid lines) to the experimental data (points) at three temperatures corresponding to the three different phases of CP10DB. The data are very well reproduced in the framework of the Debye model ($k \ll 1$) with a single relaxation time. Figure 3 shows the temperature dependence of the dielectric strength A and the relaxation time τ resulting from the fitting. In Fig. 4 the dependence for the relaxation time is presented in a form of Arrhenius plot.

The analysis of the presented results leads to the conclusion that the dielectric relaxation spectra of CP10DB, recorded in the frequency range between 100 kHz and 100 MHz, correspond to the molecular rotation around the short axis. Both the values of the dielectric strength and the relaxation time and their temperature dependences reflect the features of this type of molecular movement [2-5].

The phase transition from the isotropic to nematic phase of CP10DB manifests itself with a strong increase in the dielectric strength and the relaxation time. The activation energy derived from the temperature dependence of the re-

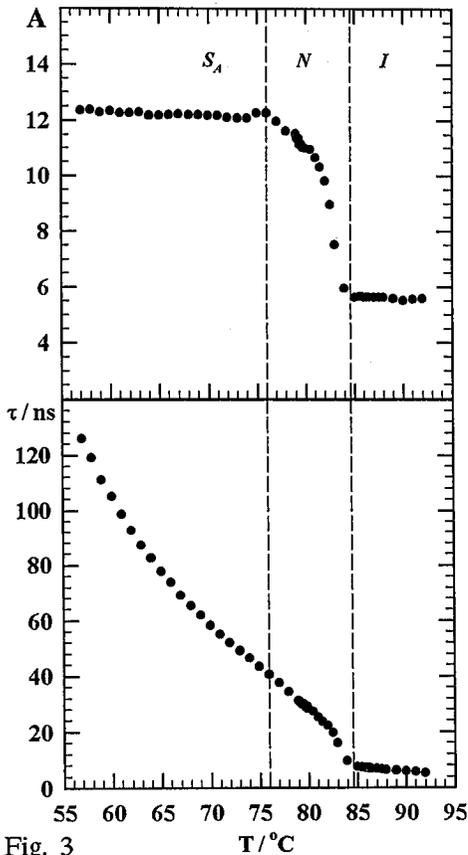


Fig. 3

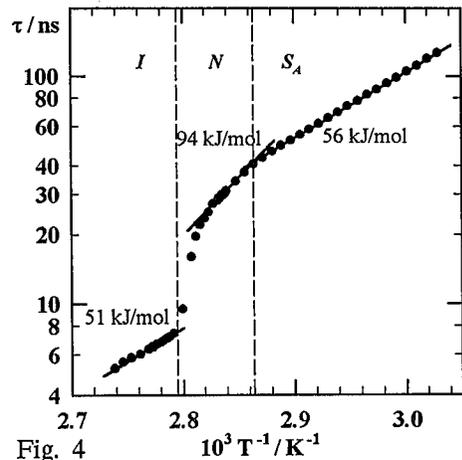


Fig. 4

Fig. 3. Temperature dependence of dielectric strength A and relaxation time τ corresponding to rotation of CP10DB molecules around the short axis in different phases.

Fig. 4. Arrhenius plot for the dielectric relaxation time of CP10DB in isotropic, nematic, and smectic A phases. Values of the activation energy are given in the figure.

laxation time also strongly increases in the nematic phase, as compared to the isotropic one. As seen in Fig. 4, the isotropic to nematic transition in CP10DB is not very sharp (as usual for nematogen molecules with the long hydrocarbon chains) and the choice of the temperature range where the Arrhenius dependence (linear dependence of $\log \tau$ vs. T^{-1}) fulfills, is somewhat arbitrary. Nevertheless, the mentioned above strong increase in the activation energy corresponding to the molecular rotation around the short axis in the nematic phase is doubtless.

The nematic to smectic A phase transition brings about not so spectacular changes in the molecular dynamics of CP10DB molecules as observed for isotropic to nematic transition (see Figs. 3 and 4). The molecular ordering in the smectic A layers, which leads to the dramatic changes in many physical properties of a substance such as viscosity, elastic constants, or transport phenomena, manifests

itself in dielectric relaxation only as a change of the slope in the Arrhenius dependence of the relaxation time (Fig. 4). However, it is interesting and important to notice that the value of the activation energy related to the rotation around the short molecular axis determined for the relatively high ordered smectic A phase of CP10DB is quite close to the value found in the isotropic phase of the compound.

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