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Dielectric and viscous properties of mesogenic *n*-nonylcyanobiphenyl (9CB)

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Abstract

Static and dynamic linear dielectric properties and shear viscosity of freely flowing 9CB in the isotropic (I), nematic (N) and smectic A (S_A) phases were investigated. Pretransitional effects observed in the vicinity of the I to N phase transition manifest themselves as anomalies in the temperature dependence of the static permittivity, the rotational diffusion exponent and the activation energy of molecules rotating around their short axis. As a presmectic effect, a jump in the temperature dependence of the shear viscosity of freely flowing nematic 9CB is observed at about 0.5 °C before the transition to the S_A phase.

1. Introduction

Weakly first order phase transitions in liquid crystalline materials are accompanied by pretransitional effects which are still a subject debated in numerous papers. The pretransitional phenomena are due to the existence of a short range order of molecules in mesogenic liquids either in the isotropic phase, or in the nematic phase, leading to the formation of pseudo-nematic domains or pseudo-smectic layers, respectively. The size of the entities so formed increases as the temperature approaches the phase transition. Especially rich pretransitional phenomena are observed in the vicinity of the isotropic to nematic phase transition and they concern both the linear [1–7] and nonlinear physical properties [8–20] of isotropic mesogenic liquids. In the case of the nematic to smectic A transition, the most spectacular pretransitional effects concern the viscous [21–24] and elastic properties [25–29] of nematic liquid crystals.

In this paper, we present the dielectric and viscous properties of mesogenic compound (9CB) with a relatively narrow temperature range of the existence of the nematic phase.

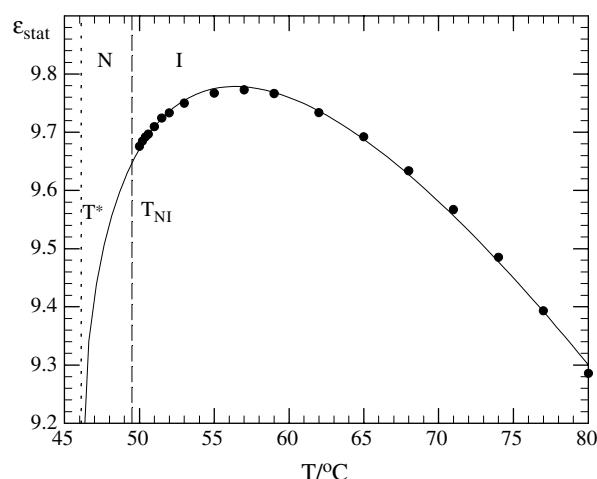


Figure 1. Evolution of the static dielectric permittivity of 9CB as a function of the temperature in the vicinity of the isotropic to nematic phase transition. The solid line represents the best fit of equation (1) to the experimental data (full circles).

2. Experimental section

n-nonylcyanobiphenyl ($C_9H_{19}PhPhCN$, 9CB), with the sequence of phase transitions (Cr) 41 °C (S_A) 47.5 °C (N) 49.5 °C (I), was synthesized and purified at the Institute of Chemistry, Military University of Technology, Warsaw. Dielectric characteristics of the compound were measured with an HP 4194A impedance/gain phase analyser 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 capacitor consisted of three plane electrodes: one central and two grounded on each side. A dc biasing electric field applied to the capacitor allowed the measurements of the parallel component of the permittivity $\epsilon_{\parallel}(\mathbf{n} \parallel \mathbf{E})$ in the nematic and smectic A phases. The high performance electrical heating, obtained by using a Unipan 650 controller, assured an excellent stabilization of the temperature (better than 10^{-3} K) with the possibility of varying the temperature by steps as small as 10^{-2} K. Such equipment allows us to determine the permittivity with a relative accuracy better than 0.5%.

The viscosity was measured with a Haake viscometer Rotovisco RV 20 with the measuring system CV 100. The system consists of a rotary beaker filled with the studied liquid and a cylindrical sensor of Mooney-Ewart type (ME15) placed in the centre of the beaker. The liquid gap was 0.5 mm. The accuracy of the viscosity measurements was 0.5%. The temperature of the sample was controlled with an accuracy of 0.1 °C.

3. Results and discussion

3.1. Static dielectric permittivity

Figure 1 presents the temperature dependence of the static permittivity $\epsilon_{\text{stat}}(T)$ measured in the isotropic phase of 9CB. Several degrees before the transition to the nematic phase, the dependence presents a maximum, as usually observed for strongly polar mesogenic liquids [30, 31]. This pretransitional effect reflects a significant enhancement of the antiparallel

dipolar aggregation in the isotropic liquid when the transition to the liquid crystalline nematic phase approaches. It is worth mentioning that the effect is not observed in the case of the first order phase transition from the isotropic liquid to the solid crystalline phase [2].

For mesogenic *n*-alkylcyanobiphenyls like 9CB, assimilated to symmetric-top molecules with a permanent dipole moment directed about the long molecular axis, the temperature evolution of the static permittivity in the isotropic phase is given by [31]

$$\varepsilon_{\text{stat}}(T) = \varepsilon_{\text{extr}} + A(T - T^*) + B(T - T^*)^{1-\sigma}, \quad (1)$$

where T^* is the extrapolated temperature of a virtual continuous phase transition, $\varepsilon_{\text{extr}}$ is the extrapolated value of the dielectric permittivity at T^* , A and B are amplitudes, and σ is the fractional exponent associated with a prenematic behaviour. The result of the best fit of equation (1) to the experimental data is represented by a solid line in figure 1, with the following explicit values of the parameters: $\varepsilon_{\text{extr}} = 8.8147$, $A = -0.07789$, $B = 0.55496$, $T^* = 46.1^\circ\text{C}$, $\sigma = 0.505$. The clearing temperature for 9CB is $T_{\text{NI}} = 49.5^\circ\text{C}$, so that $\Delta T = T_{\text{NI}} - T^* = 3.4^\circ\text{C}$, a value resulting from the weakly discontinuous character of the I–N transition for this compound. The σ value of the critical exponent obtained corresponds to the tricritical hypothesis of the I–N transition [32, 33].

3.2. Dielectric relaxation

Figure 2 presents the dielectric relaxation spectra (dispersion $\varepsilon'(\omega)$ and absorption $\varepsilon''(\omega)$) recorded in the isotropic, nematic and smectic A phases of 9CB. As mentioned above, for the nematic and smectic phases, the dielectric spectrum $\varepsilon_{\parallel}^*(\omega, T)$ was recorded. The spectra were resolved into two elementary contributions of the Cole–Cole type [34]:

$$\varepsilon^*(\omega, T) = \varepsilon'(\omega, T) - i\varepsilon''(\omega, T) = \varepsilon_{\infty}(T) + \sum_{k=1}^2 \frac{A_k(T)}{1 + [i\omega\tau_k(T)]^\alpha}, \quad (2)$$

corresponding to molecular rotations around the short and long axes. In equation (2) ω denotes the angular frequency, ε_{∞} is the permittivity measured at a sufficiently high frequency to prevent dipolar reorientation, A_k is the dielectric strength, and τ_k is the relaxation time of the k th relaxational process.

As the strength of the dielectric absorption band corresponding to the rotation of 9CB molecules around their long axes is much less than that due to the rotation around the short axes, and as its sensibility to the phase transitions is very weak, we will not discuss this contribution here.

Figure 3 presents, in the form of an Arrhenius plot, the temperature dependence of the dielectric relaxation time (τ) corresponding to 9CB molecule rotation around their short axes. According to the Arrhenius equation

$$\tau(T) = C \exp\left(\frac{E_A}{RT}\right), \quad (3)$$

the value of the relaxation time is determined by the ratio of the activation (E_A) and the thermal (RT) energies. C is the constant.

Figure 4 presents the temperature dependence of the activation energy obtained, as proposed in [2], from the differentiation of the dependence shown in figure 3. As shown in figure 4(a), far from the phase transitions the activation energy behaves ‘normally’, i.e. E_A appears to be temperature independent, which customarily is taken as a criterion for the ‘Arrhenius behaviour’ of the system. However, as presented in figure 4(b), the detailed analysis shows a relatively weak, but beyond the experimental errors, temperature dependence of the activation energy for 9CB molecule rotational diffusion around their short axes. The sharp and

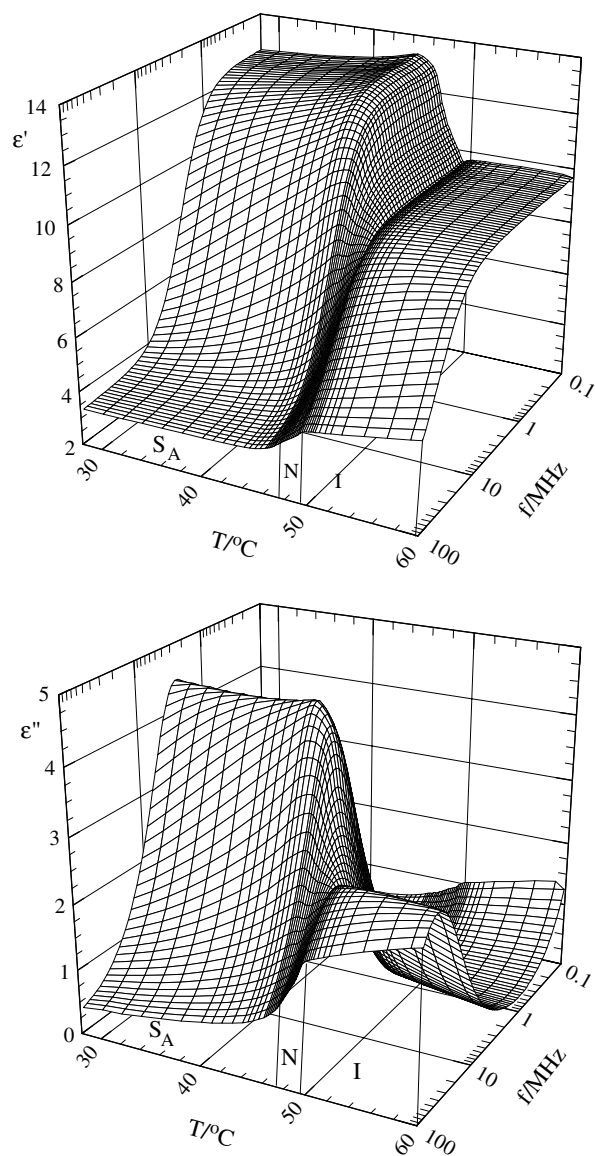


Figure 2. Dielectric relaxation spectra of 9CB in the isotropic (I), nematic (N) and smectic A (S_A) phases.

abrupt variations of E_A with respect to T are observed in the temperature interval of about 5°C where the phase transitions occur. Resulting from the dynamic dielectric experiment, the activation energy E_A reflects the frequency of the collisions between the molecules undergoing a rotational Brownian motion. That frequency, being a function of the liquid temperature and density, determines the length of the mean square angular displacement (MSAD) of a given molecular axis. As shown in figure 4, strong fluctuation effects occurring in the vicinity of the weakly first order phase transitions essentially influence molecular dynamics, leading to unexpectedly high values of E_A .

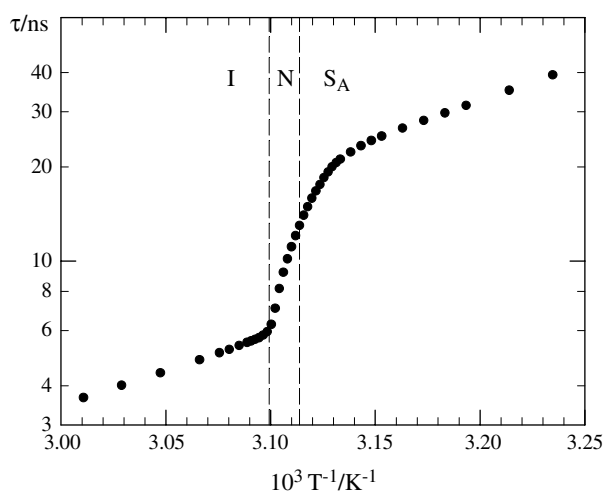


Figure 3. Arrhenius plot for the relaxation time corresponding to the rotation of 9CB molecules around their short axes.

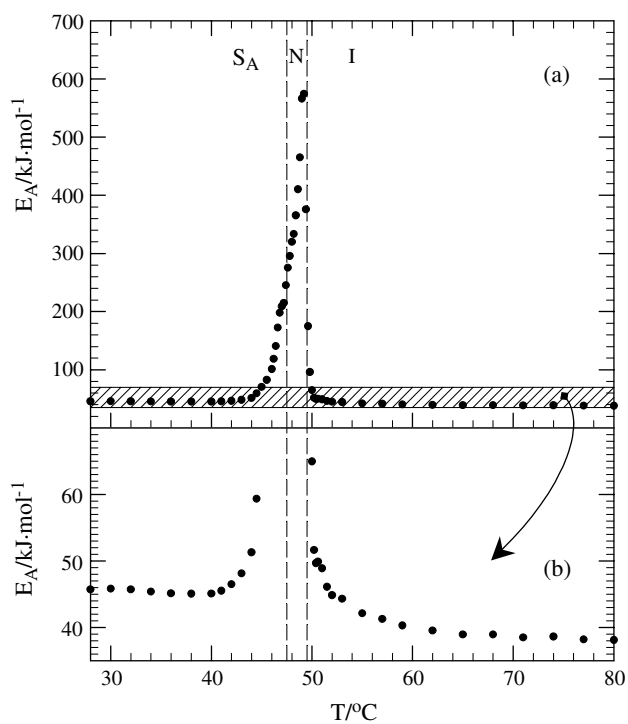


Figure 4. Plot of the activation energy of 9CB molecules in diffusional rotation around their short axes in different phases as a function of the temperature.

In the case when the MSAD depends linearly on the time, we are dealing with the normal Brownian rotational diffusion. Then, the relaxation process follows a simple exponential decay and the dielectric response in the frequency domain fulfils the Debye equation. In other

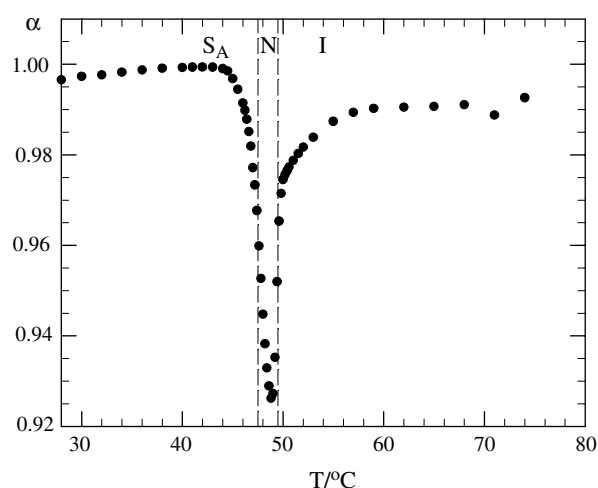


Figure 5. Temperature behaviour of the anomalous rotational diffusion exponent α obtained from the best fit of the Cole–Cole equation (2) to the experimental dielectric spectra of 9CB.

cases, we can deal with an enhanced diffusion (superdiffusion) or slowing down diffusion (subdiffusion), depending on the value of the exponent α in the power-law dependence of the MSAD on the time. The superdiffusion is characterized by $\alpha > 1$ and subdiffusion is described by the fractional value of the exponent, $\alpha < 1$. The normal Brownian diffusion ($\alpha = 1$) is located on the limit threshold between super- and subdiffusion.

In the dielectric relaxation spectrum anomalous diffusion leads to some changes in the shape of the absorption band. The subdiffusion, in the simplest case, causes a symmetric broadening of the band, in comparison to that predicted by the Debye equation. Such types of experimental results are well described by the Cole–Cole equation (2), which quite recently was considered as an empirical one and nowadays has received a strong physical background. As shown in many theoretical papers [35–44], the Cole–Cole relaxational behaviour is a direct consequence of the anomalously slow molecular rotational diffusion in the system under investigation. So, the dielectric relaxation spectroscopy becomes a quite simple and reliable experimental method for determining the value of the exponent α , a fundamental quantity representing the extension of the anomalously slow rotational diffusion in a complex polar liquid.

Figure 5 presents the temperature dependence of the anomalous rotational diffusion exponent α resulting from the best fit of the Cole–Cole equation (2) to the experimental dielectric spectra. Both in the isotropic and smectic A phases of 9CB, the value of the exponent α is close to unity, indicating a normal Brownian rotational diffusion of the molecules. The effect is more pronounced in the smectic phase, where the dielectric absorption bands show a quite perfect Debye’s shape ($\alpha \approx 1$). A similar behaviour was observed in the case of *n*-octylcyanobiphenyl (8CB) [45]. However, in 9CB, due to a relatively narrow temperature range of the nematic phase (2 °C), an anomalous decrease of the exponent α is observed not only in the vicinity of the phase transitions, but it extends in the whole range of the nematic phase existence in the compound. This strong decrease of α observed at the temperature of the I–N transition in 9CB has no correspondence in the temperature behaviour of the same fractional exponent in the case of 8CB, where the temperature range of existence of the nematic phase is more than three times larger (about 7.5 °C). Still, in the temperature dependence of the

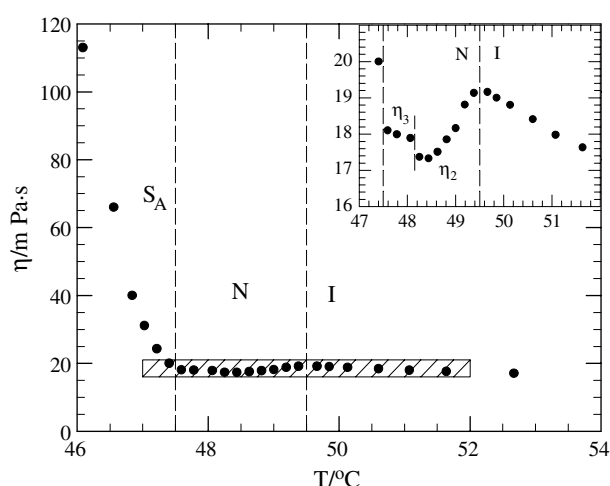


Figure 6. Temperature dependence of the shear viscosity measured for freely flowing 9CB in different mesophases. The inset shows a jump of the shear viscosity near the N–S_A transition.

exponent α nothing particular happens at the transition N–S_A of both compounds: the exponent behaves continuously.

It seems important to compare the temperature behaviour of the activation energy E_A with respect to that of the exponent α . As can be seen in figures 4(a) and 5, both dependences show some similarities, which probably are not a happy coincidence: in the temperature ranges where the Arrhenius dependence holds (i.e. the activation energy E_A is roughly constant), the exponent α is also weakly temperature dependent and its value remains close to unity. However, the conclusion on a strict *connection between the Arrhenius behaviour of the dielectric relaxation time and the normal Brownian diffusion*, though tempting, requires to be confirmed by other experimental and theoretical studies.

3.3. The shear viscosity

In recent papers [22, 24], we have presented the results of measurements of the shear viscosity of freely flowing nematic liquid crystals. The main conclusion was the following: the nematic liquid crystal, in its free flow, adopts such a manner of flow which corresponds to the minimum of its viscosity at given conditions. One of the most spectacular effects is observed in the vicinity of the N–S_A phase transition: not far from the transition to the smectic phase, one observes a spontaneous change of the molecular alignment (the director \mathbf{n}) going from that corresponding to the η_2 Mięsowicz viscosity coefficient ($\mathbf{n} \parallel \mathbf{v}$) to that corresponding to the η_3 coefficient ($\mathbf{n} \perp \mathbf{v}$). The change is due to the formation of precursors of smectic layers where the molecular mobility, as proper to the η_2 viscosity, is restricted. As the temperature approaches the N–S_A transition η_2 goes to infinity, and as η_3 is practically unaffected by the transition η_2 and η_3 viscosities intersect, and from there η_3 is the lowest possible viscosity of the nematic liquid crystal. In previously studied compounds, where the temperature range of the nematic state was much more extended than that in 9CB, the intersection point between the viscosities took place a few degrees before the N–S_A transition. As shown in figure 6, in the case of 9CB, due to a relatively narrow temperature range of the nematic phase, the presmectic increase of η_2 viscosity is so dramatic that in experiment one observes a jump of the shear viscosity (see the inset of figure 6) measured for a free flowing nematic liquid crystal.

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