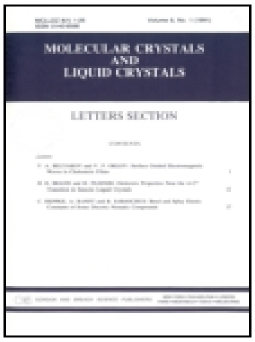

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Change of the Prenematic Order in the Isotropic Phase Close to the Isotropic–Nematic Phase Transition with Increasing Aerosil Nanoparticles Density

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*The influence of the hydrophilic and hydrophobic aerosil nanoparticles density on the formation of the prenematic order close to the isotropic – nematic (I–N) phase transition is presented. The lowering of the activation energy, with the increase of aerosil nanoparticles density, suggests a change of the prenematic order in the isotropic phase. The temperature dependence of the static dielectric permittivity for 4–*n*–pentyl–4′–cyanobiphenyl (5CB) exhibits an anomaly near the I–N phase transition. With the increase of aerosil density, a substantial modification in the anomaly of the static permittivity was observed in the isotropic phase. Indicated changes are different for hydrophilic and hydrophobic aerosil as a result of different surface interaction between nematic molecules and aerosil nanoparticles.*

Keywords: liquid crystals; dielectric spectroscopy; activation energy; prenematic order; aerosil nanoparticles; static electric permittivity anomaly

Introduction

The molecular dynamics of nematic liquid crystals, forming dispersions with solid nanoparticles, have currently received great attention [1–3]. The nematogen can be dispersed with different types of aerosil nanoparticles, which vary in size and surface treatment. In this case, the nanometer length scale of aerosil particles acts as molecular additives, which change the properties of the liquid crystal host. By changing the aerosil density in the dispersion, a controlled disorder can be introduced into the soft matter. This opportunity opens a new area for the exploration of the influence of structural effects, surface interactions and finite size effects on the molecular dynamics and thermal properties of liquid crystals (LCs) [4–6].

Broadband dielectric spectroscopy (BDS) is particularly useful for the examination of molecular dynamics of polar molecules under geometrical restrictions. The changes in the relaxation rate, dielectric strength and the broadening or asymmetry of the relaxation processes, provide important information about molecular dynamics in confinement. Extensive studies were particularly devoted to the investigation of the influence of the aerosil nanoparticles density on the molecular dynamics in 4–*alkyl*–4′–cyanobiphenyls (*n*CB) near

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*Address correspondence to Stanisław Andrzej Różański, Stanisław Staszic University of Applied Sciences in Piła, Podchorazych 10, 64–920 Piła, Poland. E-mail: srozansk@asta–net.com.pl the isotropic-nematic (I–N) phase transition [1–3]. Also, in the last years, the growing interest has been dedicated to investigate the origins of the pretransitional anomaly of the static dielectric permittivity in the isotropic phase of nematic liquid crystals near the I–N phase transition [7–10]. This anomaly of the static dielectric permittivity shows the following characteristic features: (i) strong bending down in the isotropic phase of *n*CB near the I–N phase transition, (ii) temperature dependence of the static dielectric permittivity with and without pronounced maximum in the isotropic phase near the I–N phase transition. The observed anomalies were related to the decrease of the effective dipole moment, caused by the antiparallel association of the molecules and the formation of the prenematic domains [10, 11]. Moreover, the position (parallel or perpendicular to the long axis of the molecule) and values of the dipole moments play crucial role in the observed pretransitional anomalies [7, 9, 10].

In the present work, the influence of hydrophilic and hydrophobic aerosil nanoparticles on the pretransitional anomaly of the static dielectric permittivity will be investigated. The temperature dependence of the activation energies of the observed relaxation processes was evaluated using the first derivative method.

Experimental

The well known nematic liquid crystal 4–*n*–pentyl–4′–cyanobiphenyl (5CB) with sequence of phase transition temperatures Cr – 295 K – N – 308 K – I was used to probe the influence of aerosil nanoparticles concentration on the origin of the isotropic to nematic phase transition (I–N). The nematic phase of 5CB can be easily supercooled to about 270 K. The dipole moment of about 4 D determined by the cyano group is directed parallel to the long axis of the 5CB molecule. The size of the 5CB molecule is about 0.7 nm in diameter and 1.9 nm in length [12]. The nematogenic material obtained from Merck was used without any special purification.

The hydrophilic and hydrophobic aerosil nanoparticles, with the average diameter of about 7 nm, were delivered by Degussa. The surface of hydrophilic aerosil 300, with a specific area of 300 m^2/g, is covered by hydroxyl groups and in solution can form a hydrogen bonded network. Aerosil 300 was used to prepare 5CB mixtures with the density of 0.01, 0.05, 0.10 and 0.15 g/cm^3. The treatment of the surface of the hydrophobic aerosil R812 with a specific area 280 m^2/g prevents the formation of H-bonded agglomerates in the mixture. Two mixtures of aerosil R812 with 5CB were prepared: 0.05 and 0.10 g/cm^3. The aerosil was dried before mixing with 5CB in a vacuum oven at a temperature of about 473 K to remove water and other impurities. The procedure of liquid crystal–aerosil samples preparation was previously described in detail [1].

The dielectric measurements were performed using a HP 4291B RF impedance analyzer and home–made sample holder in the frequency range of 10^6–10^9 Hz. The electrodes of the measuring capacitor were spin–coated with polyimide SE1211 to promote homeotropic orientation of the liquid crystal molecules with respect to the electrode surface (parallel to the measuring electric field). The system used for stabilization and control of the temperature was nearly the same as described in [13].

The dielectric data were evaluated using the superposition of several Havriliak–Negami formulas:

$$\varepsilon^*(\omega, T) = \varepsilon_\infty + \frac{\Delta\varepsilon}{\left[1 + (i\omega\tau_{\mathrm{HN}})^{1-\alpha}\right]^{\beta}}, \tag{1}$$

where the parameters characterizing the relaxation processes are the relaxation time τ_{HN} and dielectric strength$\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$. ε_s denotes the static electric permittivity and ε_∞ is the high frequency limit of the permittivity. The exponent α describes the broadening and β the asymmetry of the relaxation process. The relaxation time $\tau_{\max}$ in the maximum of the relaxation process is related with α, β and τ_{HN} by the following equation:

$$\tau_{\max} = \tau_{\mathrm{HN}} \sin^{-1/\alpha}\left[\alpha\pi/(2+2\beta)\right] \sin^{1/\alpha}\left[\alpha\beta\pi/(2+2\beta)\right]. \tag{2}$$

Results and Discussion

Activation energy of the relaxation process can be obtained from fitting the temperature dependence of the relaxation frequency using the Arrhenius law:

$$f = f_0 \exp\left(-\frac{E_A}{k_B T}\right), \tag{3}$$

where E_A denotes the activation energy,f_0 is the pre–exponential constant, $k_{\mathrm{B}} = 1.381\cdot10^{-23}$ J·K^{-1} is Boltzmann's constant, and T is the temperature. By taking the logarithm of the Equation 3, the experimental data can be fitted by the linear formula:

$$\ln f = \ln f_0 - \frac{E_A}{k_B T}. \tag{4}$$

The temperature dependence of the activation energy can be derived from Equation 4 by applying the first derivative method to obtain the value of the activation energy at every temperature:

$$\frac{d(\ln f)}{d(1/T)} = -\frac{E_A}{k_B}. \tag{5}$$

The above described procedure shows, that the temperature dependence of the activation energy in the isotropic phase of 5CB exhibits the critical anomaly near the isotropic to nematic phase transition [1]. Figure 1 shows the temperature dependence of the activation energy in the isotropic phase, near the isotropic to nematic phase transition, for bulk 5CB and for the chosen densities of aerosil nanoparticles. Additionally, the temperature dependence of the activation energy was fitted using the following power–law formula:

$$E_A = A(T - T^*)^{-\gamma}, \tag{6}$$

where A denotes a constant, T^* is a virtual temperature, and γ a critical exponent. The solid lines in Figure 1 present the best fit of Equation 6 to the experimental data. Table 1 summarizes all obtained values of fitting parameters for bulk 5CB and for different densities of hydrophilic and hydrophobic aerosil nanoparticles.

In the range of the experimental uncertainty, the values of critical exponent γ oscillate around 0.21, which differs from the predicted value of 0.5 by the simple mean field model. The difference between the values of the virtual temperature T^* and the nominal phase transition temperature $T_c = 308$ K change from 1 to 4 degrees. The values of constant A are higher for bulk 5CB and LC composites with hydrophilic aerosil (with exception of 0.01 g/cm^3 sample) in comparison with hydrophobic samples.

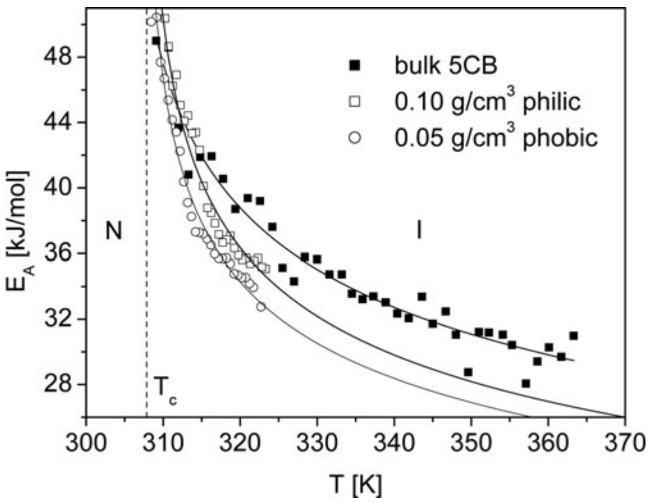

Figure 1. Temperature dependence of the activation energy for bulk 5CB and chosen densities of hydrophilic and hydrophobic aerosil. The solid lines show the best fits to Equation 6 to the experimental data.

Figure 2 shows the temperature dependence of the activation energy, after linearization of the Equation 6 to the form:

$$\ln E_A = -\gamma \ln(T - T^*) + \ln A. \tag{7}$$

It is evident from Figure 2 that additions of the proper amount of aerosil nanoparticles to the liquid crystal causes changes in the values of activation energy, in the isotropic phase, near the I–N phase transition. It is interesting, that the level of decrease in activation energy depends on the type of aerosil nanoparticles dispersed in the liquid crystal. The decrease in activation energy is more pronounced for hydrophobic than for hydrophilic aerosil. This behavior can suggest the significant influence of nanoparticles on the formation of prenematic order near the I–N phase transition. The presence of nanoparticles in liquid crystals destroys and prevents the creation of the prenematic order. The difference in influence of hydrophobic and hydrophilic aerosil arises from different treatment of the surface of nanoparticles. The hydrophilic aerosil with hydroxyl groups on the surface have tendency to orient nematic molecules perpendicularly to the surface and form hydrogen

Table 1. Fitting parameters obtained from Equation 6

	A [kJ·K$^\gamma$/mol]	T^* [K]	γ	δT [K]
bulk 5CB	69 ± 5	304 ± 1	0.21 ± 0.02	8
0.01 g/cm^3 philic	53 ± 2	307.8 ± 0.3	0.14 ± 0.02	0
0.05 g/cm^3 philic	50 ± 10	308 ± 1	0.35	4
0.10 g/cm^3 philic	62 ± 7	307.3 ± 0.5	0.21 ± 0.04	5
0.15 g/cm^3 philic	61 ± 9	307.2 ± 0.7	0.19 ± 0.06	4
0.05 g/cm^3 phobic	57 ± 3	307.3 ± 0.2	0.20 ± 0.02	0
0.10 g/cm^3 phobic	56 ± 9	306 ± 2	0.15 ± 0.06	0

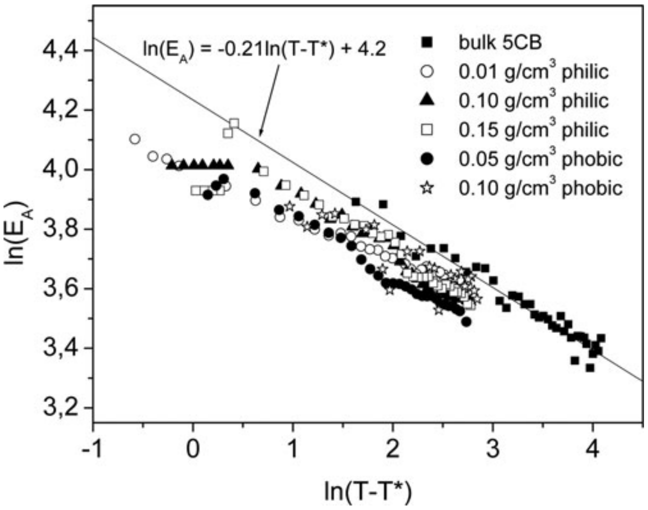

Figure 2. Temperature dependence of the activation energy in the double logarithmic scale for bulk 5CB and composite samples in the isotropic phase.

bonded structure in the mixture. The surface treatment of hydrophobic aerosil prevents the formation of hydrogen bonds and only sterically interacts on the structure of LC.

Figure 3 shows the influence of aerosil nanoparticles concentration on the pretransitional anomaly of the static electric permittivity near the I–N phase transition. The static electric permittivity values ε_s were extracted from the dielectric data as the low frequency plateau of the real part of the permittivity. Similarly, the static electric permittivity values ε_c in the clearing temperature T_c were taken from the static permittivity in the isotropic phase. The observed static permittivity anomalies can be divided to the two types with

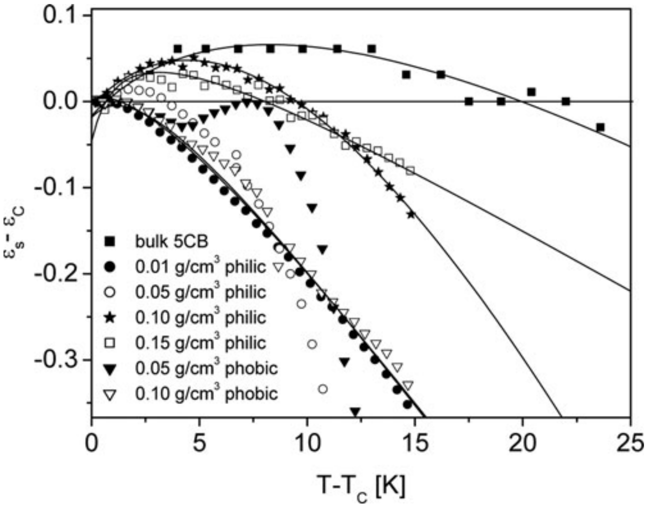

Figure 3. The normalized temperature dependence of the static electric permittivity, near the isotropic to nematic phase transition, for different concentrations of the aerosil nanoparticles.

Table 2. Fitting parameters obtained from Equation 8

	ε_v	T_v [K]	a	A	ε_c
bulk 5CB	10.36	298	−0.018	−2.80	9.307
0.01 g/cm^3 philic	6.35	303.8	−0.035	−0.65	5.880
0.10 g/cm^3 philic	16.35	289	−0.069	−15.68	11.446
0.15 g/cm^3 philic	9.19	307	−0.015	−0.25	8.971
0.10 g/cm^3 phobic	4.11	305.6	−0.035	−0.47	3.742

and without evident maximum. The anomalous behavior of the static permittivity, near the I–N phase transition, can be explained as a result of the decrease of the permanent dipole moment caused by an antiparallel association of the molecules and the formation of the prenematic domains in the isotropic phase near the I–N phase transition [10]. The magnitude of the anomaly of the static permittivity can be characterized by the temperature shift δT between the temperature T_{max} in the maximum of the permittivity (if possible to define this maximum) and clearing temperature T_c. In Table 1, the values of the temperature shifts δT are presented for different types and concentrations of the aerosil nanoparticles.

The solid lines presented in Figure 3 were obtained by fitting the experimental data by the following rescaled formula proposed in [14]:

$$\varepsilon_s - \varepsilon_c = \Delta\varepsilon + a(T - T_c - \Delta T) + A(T - T_c - \Delta T)^{-1/2}, \tag{8}$$

where $\Delta\varepsilon = \varepsilon_v - \varepsilon_c$ and $\Delta T = T_v - T_c$. ε_v and T_v describe the hypothetical coordinates of the phase transition. The fitting parameters a, A, ε_v and T_v estimated from the formula 8 are collected in Table 2. However, the quality of the experimental data for hydrophilic and hydrophobic aerosil concentration of 0.05 g/cm^3 precludes obtaining of the correct fitting parameters from Equation 8.

The magnitude of the static permittivity anomaly δT is about two times lower for hydrophilic aerosil concentrations in comparison to the bulk 5CB, besides the 0.01 g/cm^3 concentration, which is close to zero. Surprisingly, δT is also close to zero for all hydrophobic aerosil nanoparticles concentrations. The presence of the nanoparticles in the liquid crystal prevents the formation of the prenematic domains and disturbs the formation of the antiparallel orientation of the dipole moments of the molecules. The effect is less pronounced for hydrophilic aerosil because the liquid crystal molecules additionally orient on the hydroxyl group covered nanoparticles surfaces. However, the hydrophobic nanoparticles destroy the prenematic domains and remove nearly totally the permittivity anomaly.

Conclusions

The observed decrease of the activation energy near the I–N phase transition with the increasing aerosil nanoparticles concentration can be related to the influence of the disorder on the formation of the prenematic domains. The first derivative method allows one to distinguish the changes in the temperature dependence of the activation energy. The temperature dependence of the static dielectric permittivity of 5CB exhibits an anomaly in the isotropic phase near the I–N phase transition. With the increasing hydrophilic aerosil density the permittivity anomaly decreases, which suggest the reduction and the decay of prenematic domains in the isotropic phase. The presence of the hydrophobic aerosil removes the dielectric anomaly in the isotropic phase of 5CB and prevents the creation of the prenematic domains. Moreover, the presence of nanoparticles in the liquid crystal host disturbs the antiparallel associations of the dipole moments of the molecules near the I–N phase transition. The different influence of hydrophilic and hydrophobic aerosil on the pretransitional anomaly in static dielectric permittivity arises mainly from the different surface treatment of the nanoparticles. Comparable to the hydrophobic nanoparticles the hydrophilic one imposes not only steric forces on the liquid crystal phase but also an important role plays the surface interaction of the liquid crystal molecules with nanoparticles. This competition between steric forces and surface interactions results in a not complete disappearance of the static dielectric permittivity anomaly. Moreover, for low concentration of hydrophilic aerosil (< 0.05 g/cm^3) the effects related with surface interactions play a minor role in modification of prenematic domains in the isotropic phase near the I–N phase transition.

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