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Pretransitional Behavior and Dynamics in Liquid Crystal–Based Nanocolloids

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Abstract

The impact of nanoparticles on phase transitions in liquid crystal (LC)—nanoparticle nanocolloids is still little known. This contribution results for dodecylcyanobiphenyl (12CB), pentylcyanobiphenyl (5CB), and hexyl isothiocyanatobiphenyl (6BT) as the LC host with the addition of BaTiO₃ barium titanate barium titanate nanoparticles. The latter has a strong impact on the value of dielectric constant, relaxation time, and the discontinuity of the isotropic–mesophase transitions. The first-ever high-pressure studies in such systems are also presented.

Keywords: liquid crystals, nanocolloids, dielectric constant

1. Introduction

Nanocolloids exhibit unique fundamental properties, important for a variety of innovative applications. They are obtained by adding to a liquid even a small amount of solid nanoparticles (NPs) [1, 2]. Liquid crystals (LC) have attracted particular attention as dispersing medium for nanoparticles due to the richness of phase transitions associated with the emergence of subsequent elements of symmetry, dominant importance of mesoscale structures, and the enormous sensitivity to exogenic impacts, such as pressure or electric field [3]. Consequently, one can expect that adding of nanoparticles can enable qualitative tailoring of properties of liquid crystals, yielding novel features without new chemical synthesis. It is expected that nanoparticles, with the length scale below 100 nm, can act as the specific additive moderator of molecular properties of the liquid crystalline host. The impact on the local field or geometrical

hindrances associated with NPs can influence the local symmetry of the host, leading to the shift of phase transition temperatures or the decrease of the switching voltage [4]. The addition of NPs to a liquid host can also strongly change electric and heat conductivities [1, 2, 4]. All these are associated with a variety of topological defects (TD) introduced by NPs within mesomorphic fluid phases with different forms of ordering. Regarding application, the perspective type of LCs + NPs nanocolloids is related to highly birefringent nematics host with either positive or negative dielectric permittivity on increasing frequency from the kHz domain. This leads to so-called “Dual Frequency Functionality (DFN) materials” [4]. The last decade of study, still preliminary, clearly showed that there are clear links between material engineering-related issues for LCs + NPs hybrid composites with such challenging and seemingly distant areas as the physics of glass forming systems, quantum physics, superconductors physics, and even the cosmology. Consequently, nanocolloidal LCs + NPs soft hybrid composite systems can be considered as a unique *fundamental laboratory on the desk* [4].

All these led to the growth of theoretical and experimental interests in LC-based nanocolloids [1, 2, 4]. For the LC host materials, a particularly important issue constitute the impact of subsequent phase transitions on properties of subsequent mesophases. This is associated with the range of pretransitional effects, the way of their characterization, and the discontinuity measure of predominantly weak discontinuous phase transitions. In fact, these phenomena constituted the background for the Landau-de Gennes model, one of the most basic and successful theoretical approaches for the physics of liquid crystals and more generally the soft matter [4, 5]. Regarding experimental insight, the broadband dielectric spectroscopy (BDS) plays the unique role in soft matter systems [4–7]. First, it can directly detect the pretransitional behavior associated with the emergence of mesomorphic fluctuations related to approaching subsequent mesophases. Second, BDS enables a study of the complex dynamics.

Surprisingly, these fundamentals for the physics of liquid crystal issues are still (very) weakly addressed for LCs + NPs nanocomposites [8]. In fact, the first clear evidence has only recently appeared [8]. This contribution presents the resume of this result with some new insights. Subsequently, new authors' results in other LC materials are communicated. The latter also includes results of the first-ever high-pressure studies for LCs + NPs nanocolloids.

2. Experimental

The tested samples of dodecylcyanobiphenyl (12CB), pentacyanobiphenyl (5CB), and hexylisothiocyanatobiphenyl (6BT) were synthesized and deeply purified to reach the minimal electric conductivity at Military University of Technology in Warsaw, Poland. They exhibit the following mesomorphisms: *Isotropic-Smectic-A-Solid* for 12CB, *Isotropic-Nematic-Solid* for 5CB, and *Isotropic-Smectic-E-Solid* for 6BT [3, 9]. The samples of 12CB and 5CB belongs to one of the most “classical” liquid crystalline homologous series: of n-cyanobiphenyls (nCB), regarding both fundamentals and practical implementations. All nCBs molecules have approximately a rod-like form, with a permanent dipole moment parallel to the long axis. Its approximate value

is equal to $\mu \approx 5D$ [9]. All these lead to a large anisotropy of dielectric permittivity for the perfectly ordered sample, namely, $\varepsilon_{\perp} = 4$ and $\varepsilon_{\parallel} = 19$. BaTiO₃ nanoparticles (NPs) ($d = 50$ nm) were purchased from Research Nanomaterials (USA). All BaTiO₃ phases exhibit ferroelectricity except the cubic phase, which is associated with applied in this research nanoparticles. Mixtures of 12CB and BaTiO₃ NPs were sonicated with ultrasound frequency $f = 42$ kHz for a few hours in the isotropic phase (60°C) until obtaining the homogenous mixture for study. No sedimentation for at least 24 h was observed; hence, the tested nanocolloid did not contain additional stabilizing agents. The impedance analyzer (Solartron SI 1260) enabling high-resolution determination of dielectric constant with permanent five digits resolution was used. For the static domain between 1 kHz and 1 MHz, changes of real part of dielectric permittivity $\varepsilon'(f)$ were below 1%; so measurement of dielectric constant $\varepsilon = \varepsilon'(f)$ were carried out for $f = 50$ kHz. The temperature was controlled by Julabo thermostat (with external circulation, 20 L volume). The temperature stability of samples was better than 0.02 K. Samples were placed in the measurement capacitor made from Invar, with $d = 0.2$ mm gap and diameter $2r = 20$ mm. Its design is given in references [3, 6]. The quartz ring was used as the spacer. This enable observation of the interior of the capacitor. The latter and the macroscopic gap of the capacitor made it possible to avoid bubbles, distorting results. For each concentration of nanoparticles, at least three series of measurements were carried out. Additionally, properties of samples were controlled after measurements (phase transition temperatures, sedimentation).

3. Results and discussion

The broadband dielectric spectroscopy (BDS) offers the possibility of the insight into processes: (i) coupled to leading intermolecular interactions and (ii) dynamics. The first issue can be

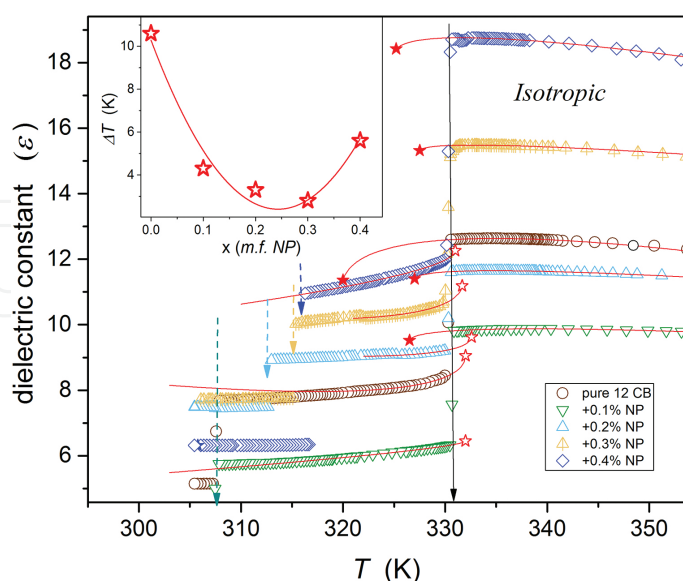


Figure 1. The behavior of dielectric constant ($f = 10$ KHz) in 12CB + BaTiO₃ nanocolloids in 12CB, covering the isotropic liquid, SmA, and solid mesophases. Solid red curves are described via Eq. (1) [8]. The inset shows the impact of nanoparticles concentration on the discontinuity of the I-SmA transition.

detected analyzing the evolution of dielectric constant. The second issue is related, for instance, to dielectric relaxation time. The first-ever study focusing on phase transitions *universal* properties in LCs + NPs nanocolloid are recalled in **Figure 1** [8]. They were conducted in dodecyl cyanobiphenyl (12CB) with the isotropic-smectic-A—solid mesomorphism. The rod-like structure, with the permanent dipole moment, located along the main molecular axis causes that studies of dielectric constant, i.e., the real (primary) component of dielectric permittivity in the low-frequency region, where $\varepsilon = \varepsilon'(f) \approx \text{const}$ allows to distinguish between parallel and antiparallel ordering dominated in the system. This fact and the appearance of premesomorphic fluctuation cause the notable pretransitional anomaly in the isotropic phase [8–11]:

$$\varepsilon(T) = \varepsilon^* + a^*(T - T^*) + A^*(T - T^*)^\phi, \quad T > T^C \quad (1)$$

where (ε^*, T^*) describe the loci of the hypothetical continuous phase transition, $T > T^C = T^* + \Delta T^*$, ΔT^* is the temperature metric of the discontinuity of the isotropic–meso phase transition, and T^C is for the isotropic–mesophase transition “clearing” temperature. The power exponent $\phi = 1 - \alpha$, where α is related to the specific heat “critical” anomaly. A^*, a^* are constant amplitudes.

Experiments for I-N, I-N*, I-SmA, and I-SmE phase transitions showed that for all cases the exponent $\phi \approx 0.5$ and then $\alpha \approx 0.5$. The exponent α is related to the pretransitional anomaly of the specific heat: $d\varepsilon/dT \propto c_p \propto (T - T^*)^{-\alpha}$ [10, 11]. Such behavior is shown in **Figure 1** via solid, red curves terminated with stars indicating the hypothetical continuous phase transition. As shown in Ref. [8], the addition of BaTiO₃ nanoparticles did not change the value of the exponent $\alpha \approx 0.5$. However, the value of dielectric constant can be decreased or increased even by 50% in comparison to pure 12CB. The presence of NPs has a notable impact on the smectic-A mesophase, or rather SmA modified by NPs mesophase, but the very weak influence on the clearing temperature. These features are well visible in **Figure 1**, where additionally the inset presents the very strong influence of NPs amount on the value of the discontinuity ΔT^* , being one of the most important characteristics of the isotropic–mesophase transition.

Subsequently, new results regarding LCs + NPs nanocolloids are preliminary discussed. 12CB belongs to the n-cyanobiphenyls (nCB), one of the most classical liquid crystalline series regarding both fundamentals and applications. Its key and the most known representative is pentylcyanobiphenyl (5CB) with isotropic–nematic–crystal mesomorphism. On compressing, the clearing temperature usually increases and such an evolution for 5CB is shown in **Figure 2**, which includes also the extension into the negative pressures domain. Consequently, one can approach the I-N transition as the function of temperature or of pressure. The behavior of dielectric constant for both paths in 5CB and 5CB + BaTiO₃ nanocolloids is presented in **Figures 3** and **4**.

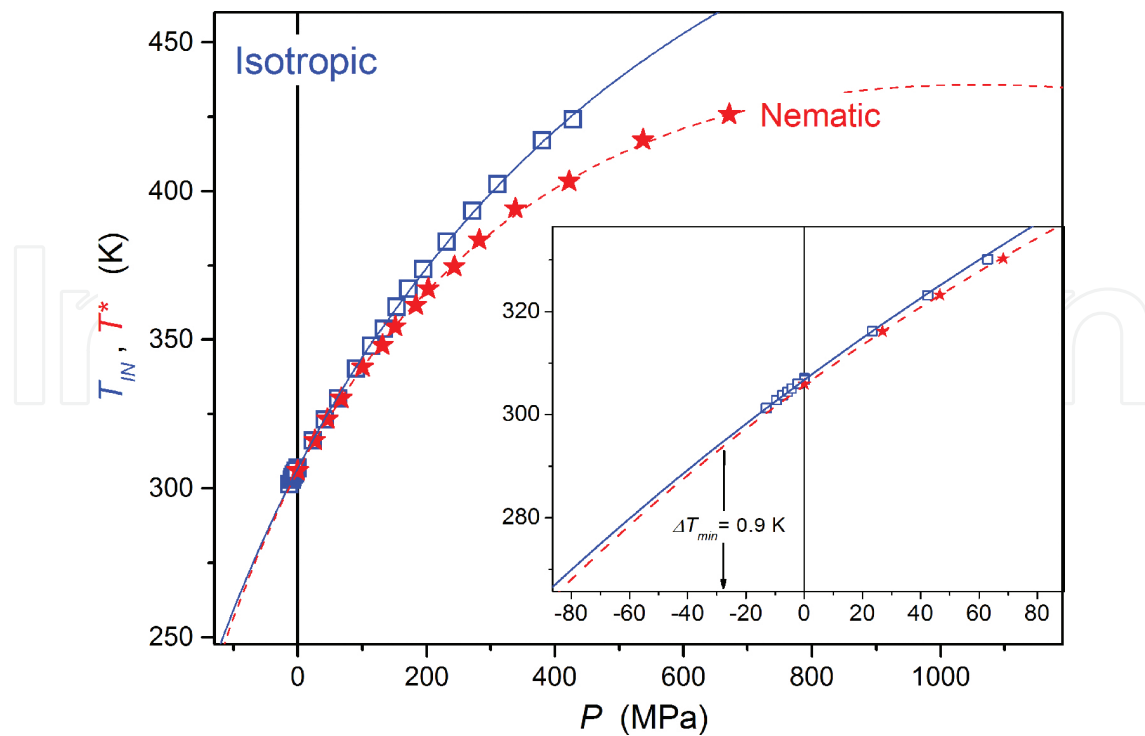


Figure 2. The pressure dependence of the isotropic–nematic (I–N) “clearing” temperature in 5CB [12]. The stars and the dotted curve are for the hypothetical continuous phase transition.

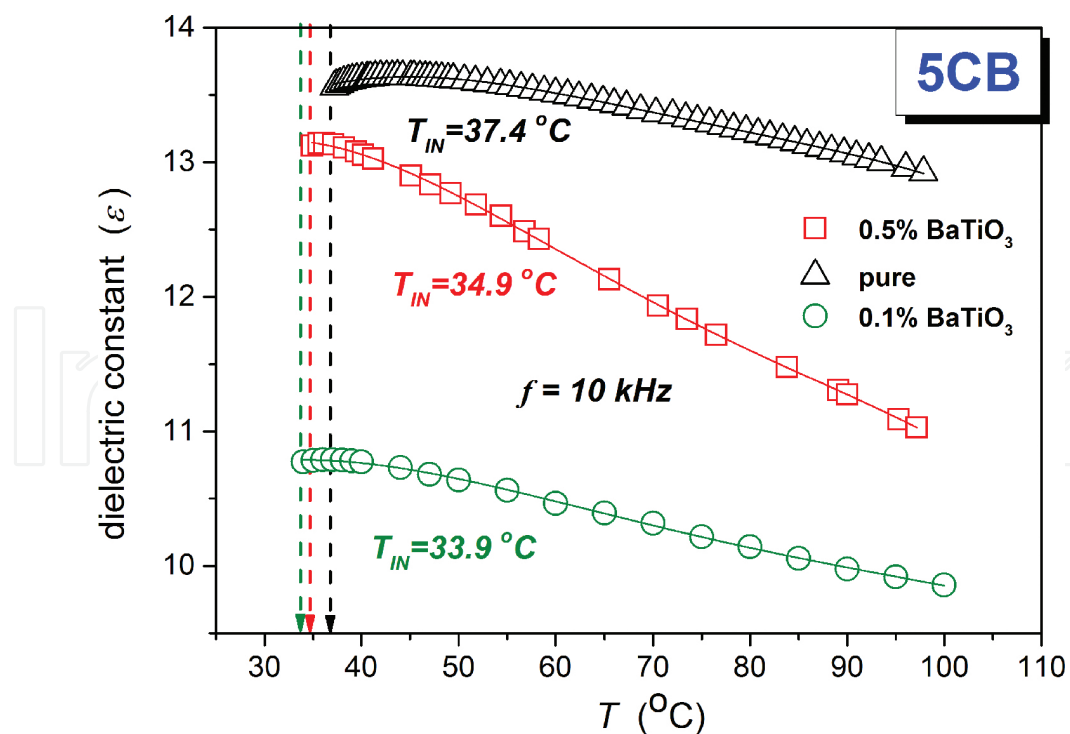


Figure 3. The pretransitional behavior of dielectric constant in 5CB + BaTiO₃ nanocolloids. The solid curves are related to Eq. (1).

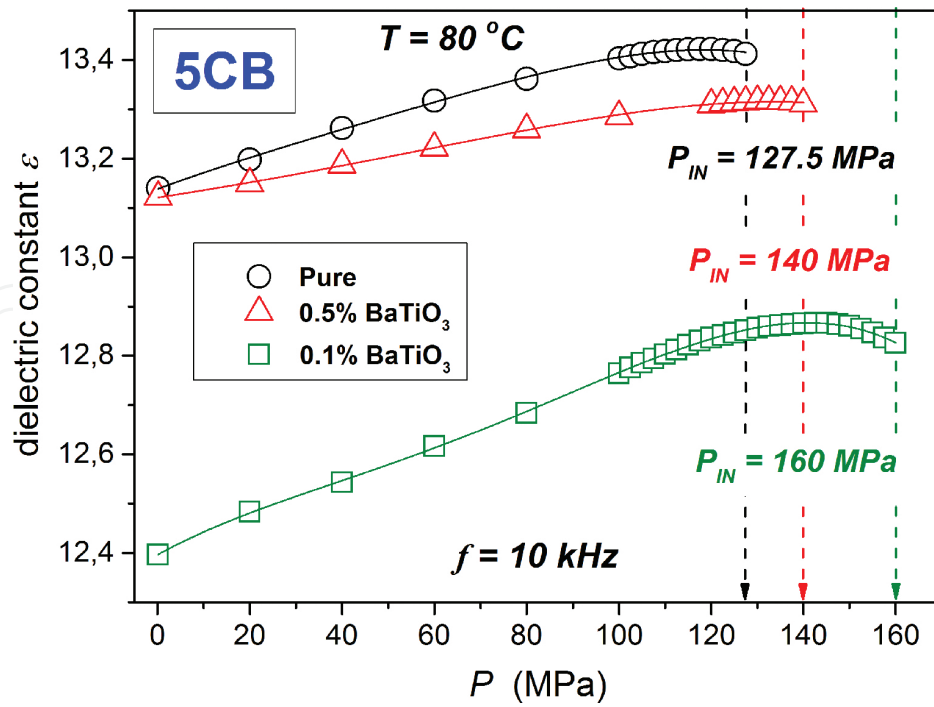


Figure 4. The pretranslational behavior of dielectric constant in 5CB + BaTiO₃ nanocolloids for the isothermal path of approaching the clearing point. The solid curves are related to Eq. (2).

The pretranslational behavior dominates the behavior of dielectric constant in the whole tested temperature range, up to $T_{10} + 70K$. It is associated with an increasing impact of prenematic fluctuations characterized by \vec{n} and $-\vec{n}$ equivalence for the director indicating the orientational ordering [3]. This causes the ordering of permanent dipole moments in the antiparallel way, and consequently, the dielectric permittivity within prenematic fluctuations is governed by its perpendicular component ($\varepsilon_{\perp} \approx 4$ for 5CB). On approaching the clearing temperature, the volume occupied by prenematic fluctuations increases leading to the crossover $d\varepsilon/dT < 0 \rightarrow d\varepsilon/dT > 0$. One can estimate that for the crossover at $d\varepsilon/dT = 0$:

$$N_{fluct} \cdot \varepsilon_{fluct} = N_{bckg} \cdot \varepsilon_{bckg} \rightarrow N_{fluct} \cdot \varepsilon_{\perp} + N_{bckg} \cdot \left[(1/3) \varepsilon_{\parallel} + (2/3) \varepsilon_{\perp} \right]$$

where N is for the number of molecules, ε_{\perp} and ε_{\parallel} are for the perpendicular and parallel components of dielectric constant, indexes *fluct* and *bckg* denote fluctuations, and the fluid-like background with chaotically arranged rod-like molecules. For 5CB one can approximate, $\varepsilon_{\perp} \approx 4$ and $\varepsilon_{\parallel} \approx 19$, and the substitution of these values lead to the estimation $N_{fluct}/N_{bckg} \approx 0.3$, i.e., 23% of the molecules are contained within prenematic fluctuations. It is visible that in 5CB doped with BaTiO₃, the number of molecules within fluctuations is reached closer to the I-N transition than in the “native” material what can be linked to steric distortions introduced by nanoparticles within prenematic fluctuations.

It is visible in **Figure 3** that the addition of nanoparticles has a weak impact on the clearing temperature but notably changes the discontinuity ΔT^* . **Figure 4** presents the pretranslational

effect in 5CB + BaTiO₃ nanocolloids for the isothermal compression. In this case, the addition of NPs has a strong impact on the loci of the clearing point, the discontinuity of the phase transition ΔP^* , the loci of $d\varepsilon/dT$ crossover, and the value of the isotropic–nematic transition P_{IN} . In this case, the pretransitional anomaly is described by the pressure counterpart of Eq. (1) [12, 13]:

$$\varepsilon(P) = \varepsilon^* + a_P^* \left(|P^* - P| \right) + A_P^* \left(|P^* - P| \right)^\phi, P < P^C \text{ and } T = \text{const} \quad (2)$$

where $(\varepsilon^*, T^*, P^*)$ describe the loci of the hypothetical continuous phase transition, $P < P^C = P^* - \Delta P^*$, ΔP^* is the temperature metric of the discontinuity of the isotropic–mesophase transition, and P^C is for the isotropic–mesophase transition “clearing” temperature. The power exponent $\phi = 1 - \alpha$, where α is related to the specific heat “critical” anomaly. A_P^*, a_P^* are constant amplitudes.

When comparing the isothermal and the isobaric behavior, it is worth recalling that the shift of temperature influences mainly the activation energy, whereas the compression changes the free volume. The impact of nanoparticles on more complex mesophases is shown in **Figures 5–7**, which focuses on the Smectic E phase in hexyl-isothiocyanatobiphenyl (6BT). The SmE phase belongs to the group of the most complex mesophases which in some classification is located even beyond the family of liquid crystals. The SmE phase is characterized by both the complete orientational and translational ordering, but the specific of the latter causes the viscoelasticity of SmE to be close to the “liquid-type” border [3, 9].

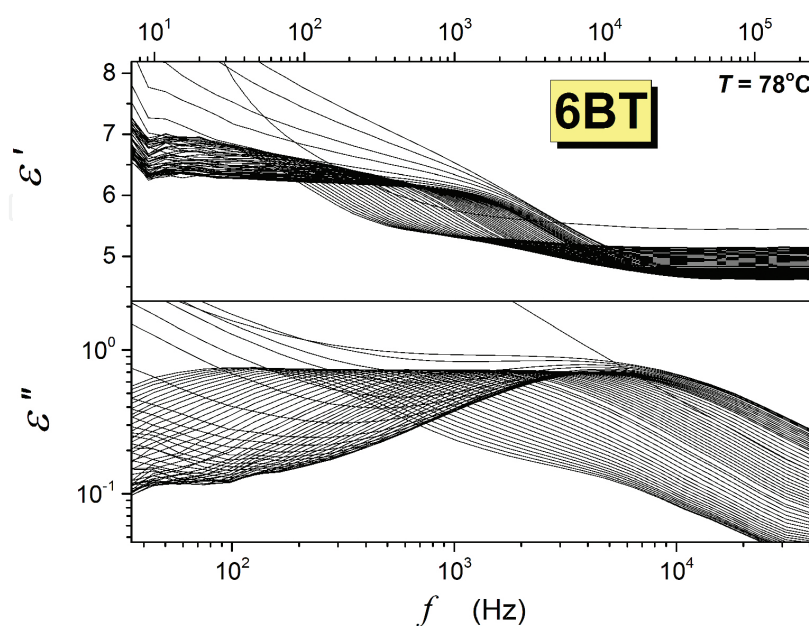


Figure 5. Dielectric spectra showing the real and imaginary parts of dielectric permittivity in the SmE phase of 6BT.

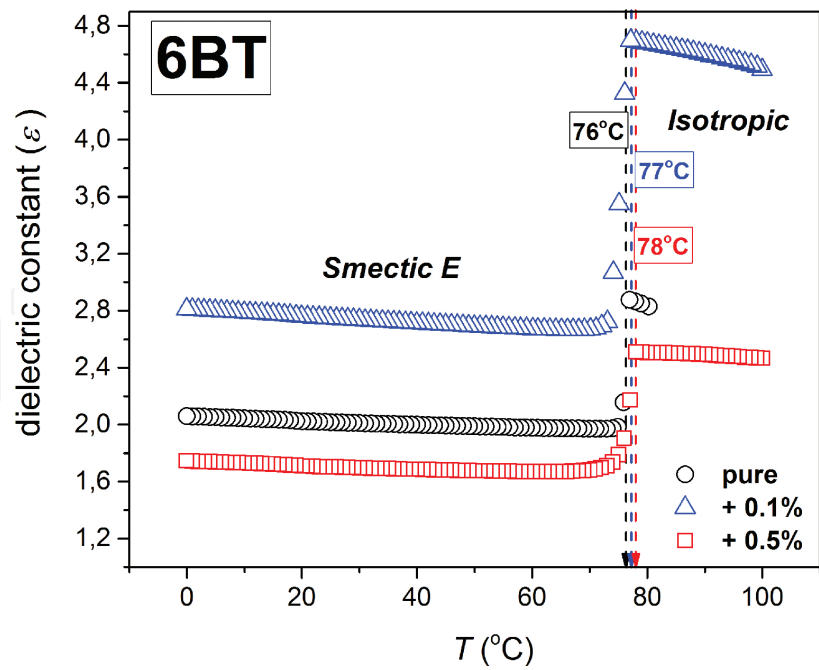


Figure 6. Changes of dielectric constant in 6BT + BaTiO3 nanocolloids, focused on the Smectic E phase.

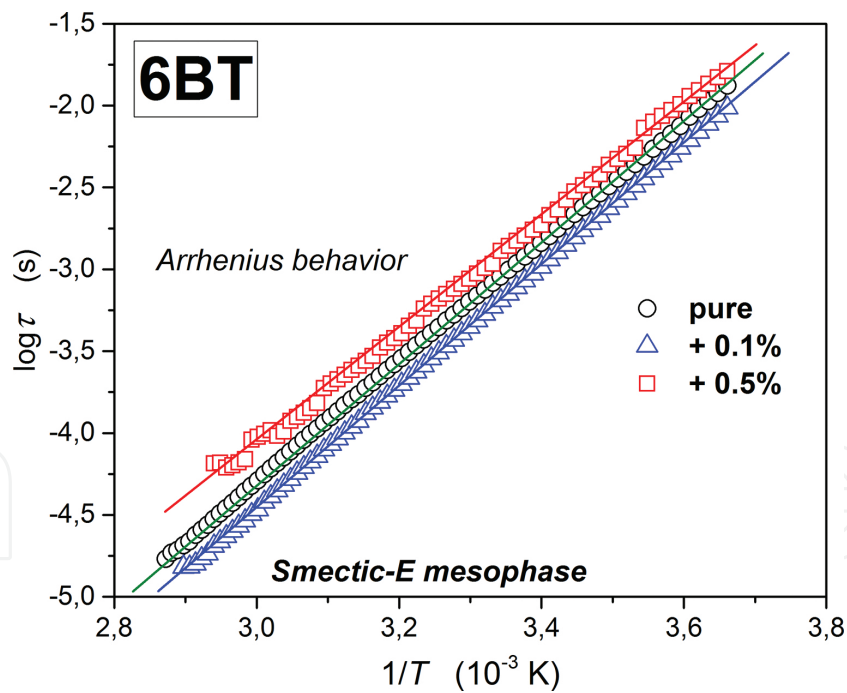


Figure 7. The “Arrhenius evolution” of the relaxation time for the main relaxation process in the SmE phase for 6BT + BaTiO3 nanocolloids.

Figure 5 presents dielectric spectra in 6BT, both for the imaginary (ϵ'') and real components (ϵ') of dielectric permittivity. For the latter, the “flat part” for $f > 3 \text{ kHz}$, indicates the static domain $\epsilon = \epsilon' \approx \text{const.}$

For the imaginary part of dielectric permittivity, the peak of the primary relaxation loss curve makes it possible to estimate the key relaxation time in the given system $\tau = 1/(2\pi f_{peak})$.

Figure 6 shows the evolution of dielectric constant in the SmE mesophase, for the pure 6BT and its nanocolloids with BaTiO₃, and the similar behavior for the relaxation time is given in **Figure 7**. Contrary to the case of 12CB based nanocolloids (**Figure 1**), the small concentration strongly increases dielectric constant, whereas it decreases when increasing the concentration.

Figure 7 shows the impact of BaTiO₃ nanoparticles on the key relaxation time in the 6BT matrix. In the broad range of temperatures, exceeding 80 K, is purely Arrhenius, i.e., described by the Arrhenius relation $\tau(T) = \tau_0 \exp(\Delta E_a/RT)$. This issue is worth stressing since in complex viscoelastic systems most often the super-Arrhenius evolution occurs, with the temperature dependent on the apparent activation energy $\Delta E_a(T)$. It is notable from **Figure 7** that the small addition of BaTiO₃ speeds up the key relaxation process where the increase of the dopant slows the relaxation.

Concluding, although the studies of LCs + NPs nanocolloids have already a notable history, the impact of nanoparticles on basic properties of phase transitions, relevant for modeling within the physics of liquid crystals is almost unknown. The only report focusing on this topic has appeared only very recently. This contribution presents the resume of these results and presents preliminary insights into nanocolloids based on 5CB, with the isotropic–nematic transition and for 6BT with the long-range Smectic E phase, although the addition of nanoparticles seems to have no impact on the value of the leading “critical” exponent. It influences very strongly on the value of the isotropic–mesophase discontinuity. There is also a qualitative impact on the value of dielectric constant or dielectric relaxation time. However, for the given type of nanoparticles such an impact depends both on the type of liquid crystalline materials and the mesophase.

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