
ORIENTATIONAL BEHAVIOR OF A NEMATIC LIQUID CRYSTAL FILLED WITH INORGANIC OXIDE NANOPARTICLES

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We report the results of dielectric spectroscopy, Fourier transformed infrared spectroscopy (FTIR) and atomic force microscopy (AFM) studies performed on the nematic liquid crystal (LC) mixture Merck ZLI-1132 filled with TiO₂ (rutile and anatase) and SiO₂ nanoparticles. The observed static dielectric permittivities are interpreted in terms of orientation of the LC with respect to the measuring electric field. Adding of SiO₂ particles mainly induces a statistical orientation of LC molecules, whereas TiO₂ particles promote the perpendicular orientation. The dynamics of LC molecules in all systems is very similar. The reason for the slightly faster reorientation observed in the mixtures may be connected with a disturbed nematic order near the surface of solid particles.

Introduction

Nowadays, the investigations of heterogeneous systems with solid / liquid crystalline interfaces have been drawn increasing interest among scientists [1]. Droplets of LC dispersed in a polymer matrix (PDLC), LC filled with small inorganic particles (filled LC), LC stabilized by polymer networks, porous glasses and membranes filled with LC, LC filled in aerogels, etc. are a few examples of such systems [2–7]. Possible technical applications of LC filled with nanoparticles of different origins and shapes require a detailed basic research of electric, magnetic, optical and thermodynamic properties of these systems, as well as studies of superstructures which may be formed in such systems under certain conditions [8–11].

SiO₂ is now widely used for different nanocompositions of organic-inorganic materials. Though TiO₂

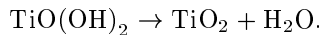
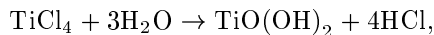
is also a promising material for filled LC [12], the basic physical properties of the related systems were not studied in detail. It is expected that LC filled with TiO₂ nanoparticles will improve the electrooptical switching characteristics as the contrast ratio and response time. Additionally, such materials may exhibit interesting optical properties. In the present work, we have undertaken the first dielectric studies of these systems with the purpose of detecting the effect of TiO₂ nanoparticles on the static permittivity and the low-frequency relaxation process. Additional spectroscopic and topological measurements were performed to confirm the results. A special attention was paid to a change in dielectric properties of a filled LC depending on the concentration and crystal structure of nanoparticles.

1. Experimental

1.1. Materials

Opty-pure TiO₂ particles were synthesized according to a procedure described in [13] using thermal hydrolysis of titanium tetrachloride solved in hydrochloric acid. The synthesis was carried out under normal pressure at 100 °C in the presence of specially prepared titanium nuclei which were added to the solution in order to control the formation of the crystalline modifications, rutile (R) or anatase (A). In the result, a polycrystalline sediment consisting of hydrated titanium

dioxide and hydrochloric acid was obtained according to the following scheme:



This procedure allows one also to change physico-chemical properties of the obtained TiO_2 material such as its phase composition, size and morphology of particles, their surface activity, porosity, and other characteristics by adjusting the synthesis conditions [14]. The so obtained material was subjected to an additional heat treatment at ambient conditions at 300 °C (A300 and R300). Additionally, rutile was heated to 900 °C (R900). The specific area of the samples was determined by means of nitrogen adsorption and was found to be about 95 m²/g for A300 and R300 and 3 m²/g for R900. The structure of the particles has been confirmed by X-ray analysis with a DRON-2 instrument by taking the $\text{CuK}\alpha$ radiation. Morphological investigations by electron microscopy did show that TiO_2 crystallites are 5–15 nm in size and they are aggregated to spherical particles of 10–30 μm in diameter [15]. It is worth mentioning that, before the dielectric measurements, all powder samples were mechanically milled (dry milling), and therefore the actual size of particles was smaller, and their specific surface area was larger than that initially determined. This was confirmed by the AFM analysis of A300 samples, whereby the particle size was found to be about 100–200 nm (see Section 2.3). Furthermore, a aerosil (particles of 7–10 nm in size) and polydisperse SiO_2 (particles of less than 1 μm in size) were used as a filler, too.

ZLI-1132 (Merck, Germany), a thermotropic nematic mixture of three trans-4'-alkyl-(4-cyanophenyl)cyclohexanes with propyl, pentyl, and heptyl as alkyl groups and trans-4'-n-pentyl-(4-cyanobiphenyl)cyclohexane in the weight ratio 24/36/25/15, with a mesophase range from –10 to 71 °C has been used as an LC matrix. All the components of the mixture show a relatively high positive dielectric anisotropy in the nematic mesophase that makes them suitable for the technical use and investigation by dielectric spectroscopy.

The LC nanocomposites were obtained by loading TiO_2 powders of a chosen crystalline modification and a thermal history and SiO_2 into the LC held in the nematic phase.

1.2. Experimental Methods

The measurements of complex dielectric permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ with $i^2 = -1$ were performed from 10 Hz to 10 MHz in the temperature range of (–10 ÷ 70) °C on non-oriented samples using a Solartron Schlumberger Analyzer in combination with a Chelsea Interface. The applied measuring voltage was 1 V. A double plate capacitor with an area of 2 cm² and a distance between the gold coated brass electrodes of 0.150 mm was used. The temperature was stabilized with the Eurotherm equipment. The capacitor was calibrated with cyclohexane. The experimental points for ε' and ε'' were fitted to the real and imaginary part of Eq. (1) consisting of two Cole–Cole mechanisms:

$$\varepsilon^* = \varepsilon_2 + \frac{\varepsilon_0 - \varepsilon_1}{1 + (i\omega\tau_1)^{1-\alpha_1}} + \frac{\varepsilon_1 - \varepsilon_2}{1 + (i\omega\tau_2)^{1-\alpha_2}} + \frac{iA}{f} + \frac{B}{f^N}. \quad (1)$$

Here, the 4th term stands for the conductivity contribution, and the last term refers to the description of the capacitance of double layers at low frequencies, ε_i are the low- and high-frequency limits of the dielectric constant, $\omega = 2\pi f$ (f – frequency), τ_i – relaxation times, α_i – Cole–Cole distribution parameters, A – conductivity factor, B and N – additional fitting parameters responsible for the slope of conductivity and capacity of the double layer.

Fourier transformed infrared spectroscopy FTIR (IFS-88 Bruker spectrometer) at room temperature in the transmission mode has been applied to the initial ZLI-1132 and the TiO_2/LC nanocomposites. The spectral slit width was 2 cm^{–1}, and the number of scans was 32.

AFM measurements were performed using a Discoverer TMX 2010 (TopoMetrix) at room temperature. The images were obtained by the non-contact method with Si tips (the cantilever frequency was about 162 kHz). The samples were prepared by the application of TiO_2 powder on the mica substrate coated with a nail lacquer (for the particle size evaluation) or a glass-forming nematic LC heated to the clearing temperature.

2. Results and Discussion

2.1. Dielectric Spectroscopy

Fig. 1 presents the dielectric dispersion ε' and absorption ε'' data obtained for the initial LC ZLI-1132 and its different colloidal nanocomposites with TiO_2 and SiO_2 . The spectra were analyzed using the two-frequency

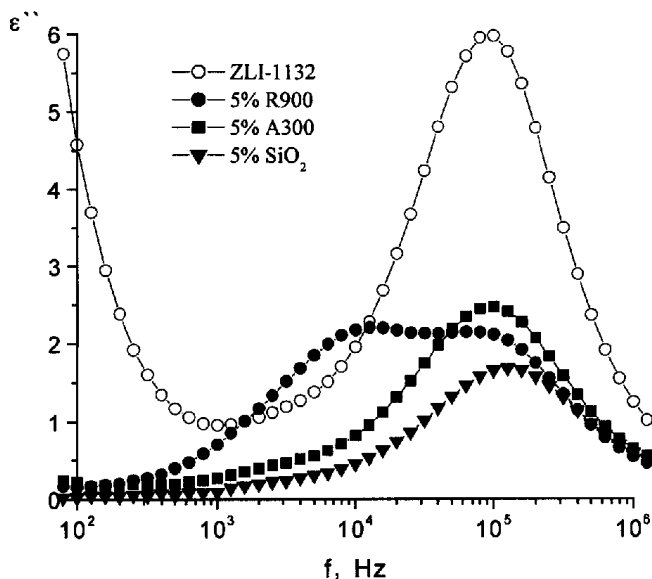
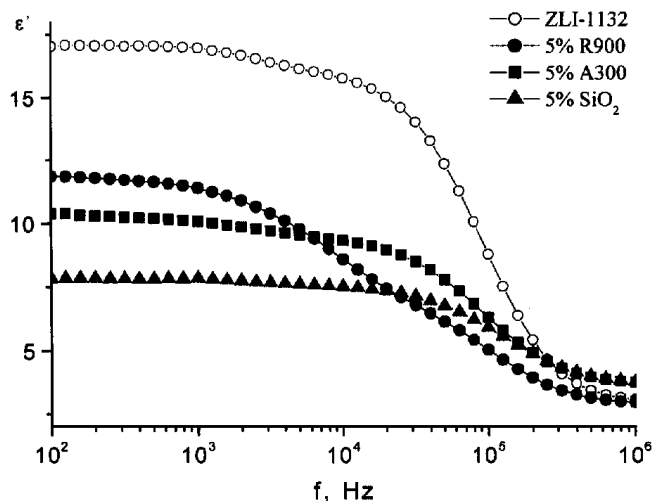


Fig. 1. Dielectric constants ϵ' and losses ϵ'' of LC ZLI-1132 filled with different TiO_2 and SiO_2 particles at $T=0$ °C

relaxation process given in Eq. (1). The existence of two relaxation processes is clearly seen for the ZLI-1132+5%R900 mixture at $T=0$ °C. These two relaxation processes originate from the reorientation of molecules about their short molecular axis. The faster relaxation process with τ_2 corresponds to the reorientation of trans-4'-n-alkyl-(4-cyanophenyl)cyclohexanes whereas the slower one with τ_1 originates from the trans-4'-n-pentyl-(4-cyanobiphenyl)cyclohexane.

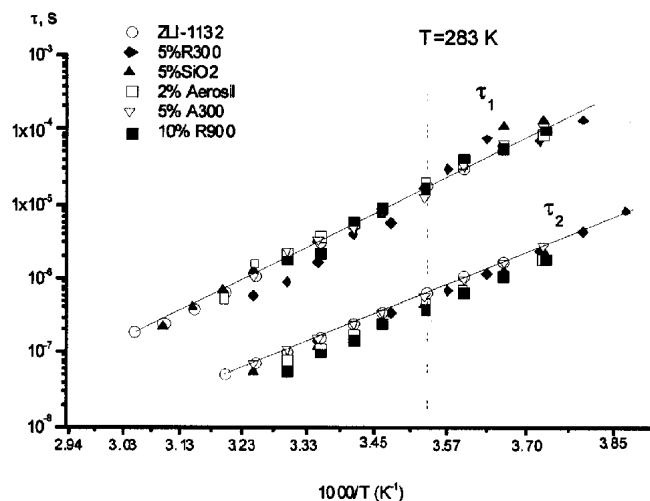


Fig. 2. Relaxation times of ZLI-1132 filled with different TiO_2 and SiO_2 nanoparticles. Both relaxation times refer to a reorientation of components of the ZLI mixture about the molecular short axes

The relaxation times calculated for all the systems are presented in Fig. 2 as Arrhenius plots. Thereby, the error of the data for the low-frequency mechanism is higher due to the separation procedure. The lines are related to the data of the pure LC ZLI-1132. As one can see in Fig. 2, the dynamics of the LC is very similar in all studied cases. A slightly faster reorientation, in comparison with the pure ZLI-1132, is observed for all filled LC. The values of activation enthalpies calculated from the slopes for LC ZLI-1132 are 79.6 ± 1.3 and 63.8 ± 0.3 $\text{kJ} \cdot \text{mol}^{-1}$ for the motions characterized by τ_1 and τ_2 , respectively. These values practically do not change when the LC is filled with small solid particles. This suggests that the interaction with the solid surface is not sufficient enough to change the LC dynamics significantly. This fact is additionally supported by FTIR spectroscopy.

2.2. FTIR Spectroscopy

In the IR spectra of the LC filled with different solid particles (Fig. 3), no marked changes in position, intensity, and shape of the fundamental bands were observed in relation to that of the initial ZLI-1132. This is in contrast with our previous spectroscopic and dielectric data [12, 16, 17] for the more polar 5CB filled with TiO_2 and SiO_2 particles, where a fairly strong molecular interaction between LC molecules and active centers on the surface of oxide particles has been found. The obtained FTIR results suggest that the interaction of the cyclohexane derivatives in ZLI-1132 with TiO_2

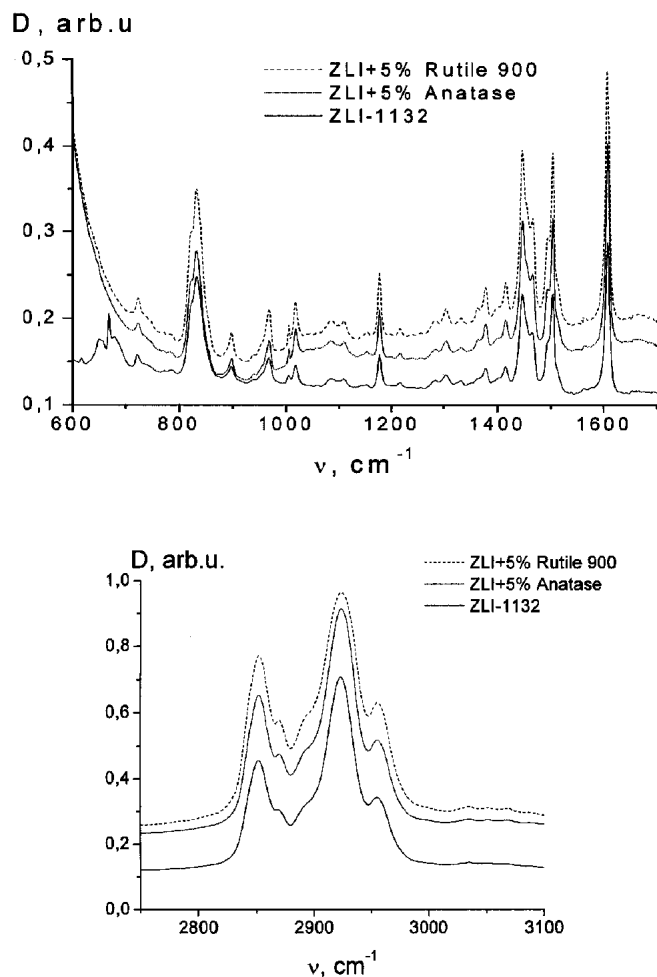


Fig. 3. FTIR absorption spectra of pure LC ZLI-1132 and its mixtures with different nanoparticles at room temperature

particles is smaller than that of 5CB as the phenyl derivative of cyanophenyl. This may result from the differences of both chemical classes, especially in the formation of mesomeric structures and the resulting lower dipole moments of the cyclohexane derivatives. Therefore, the spectral changes induced by surface interactions are concealed under the background of a bulk absorption of the LC mixture.

2.3. AFM Results

AFM measurements were performed only on A300 samples. At first, the samples of A300 particles were prepared on the mica substrate coated with a nail lacquer to evaluate the size and morphology of TiO₂ particles (Fig. 4). These particles show a tendency to form aggregates consisting of small nanosized crystallites. The data related to the distance and height

differences between points on the line are indicated by the differently numbered pairs of inverted triangles. The averaged size of the agglomerates of TiO₂ particles was determined by AFM to be 200 nm. AFM images (Fig. 4) also show the tendency of TiO₂ particles to form aligned structures on the solid surface, which may be expected to be even more pronounced in an electric field. After that the TiO₂ particles were immersed in a nematic LC in order to characterize the morphological behavior under anisotropic conditions. For this purpose, the samples were prepared by loading the TiO₂ powder into a drop of the glass forming nematic LC deposited directly on the mica substrate heated to the clearing temperature and then cooled to room temperature. The AFM image and line profile measurements of TiO₂ particles immersed in a nematic LC (Fig. 5) show a disturbed surface ordering near solid particles.

2.4. Discussion

Fig. 6 presents the temperature dependence of the static permittivity, ϵ_0 , in the nematic phase for the initial LC ZLI-1132 and for the LC filled with different oxide particles. In the ZLI-1132 mixture, the dipole moments are determined by strong polar terminal CN group ($\mu \approx 4.7 D$). As clearly seen from the Fig. 6, even small concentrations of the solid dopants result in a strong decrease of ϵ_0 . According to [18], the static dielectric constant ϵ_0 of a colloidal mixture of LC with spheroid particles, fulfilling the condition

$$V_{LC} < \frac{\epsilon_D + 2\epsilon_{LC}}{|\epsilon_D - \epsilon_{LC}|}, \quad (2)$$

can be calculated from the equation

$$\epsilon_0 = \epsilon_{LC} + 3\epsilon_{LC}V_{LC} \frac{\epsilon_D - \epsilon_{LC}}{\epsilon_D + 2\epsilon_{LC}}. \quad (3)$$

Here, V_{LC} is the volume fraction of spherical particles, ϵ_D and ϵ_{LC} are the dielectric constants of solid particles and LC, respectively [18, 19].

For a simple approximation of the static dielectric constant in the parallel direction, let us consider a sample containing 2 wt. % of SiO₂. With $\epsilon_D = 3.0$ and $\epsilon_{LC} = \epsilon_{||0} = 17.7$ [20], the right-hand side of inequality (2) is equal to 2.6. This is much more than mass content (0.02) of spherical particles in LC. Taking into account the smaller density of LC as compared with SiO₂, inequality (2) is satisfied more strongly. Therefore, one can use Eq. (3) to calculate the dielectric constant of the colloidal LC. Using the available data for the LC filled with 2 wt. % SiO₂, one can obtain $\epsilon_{||0} = 17.3$.

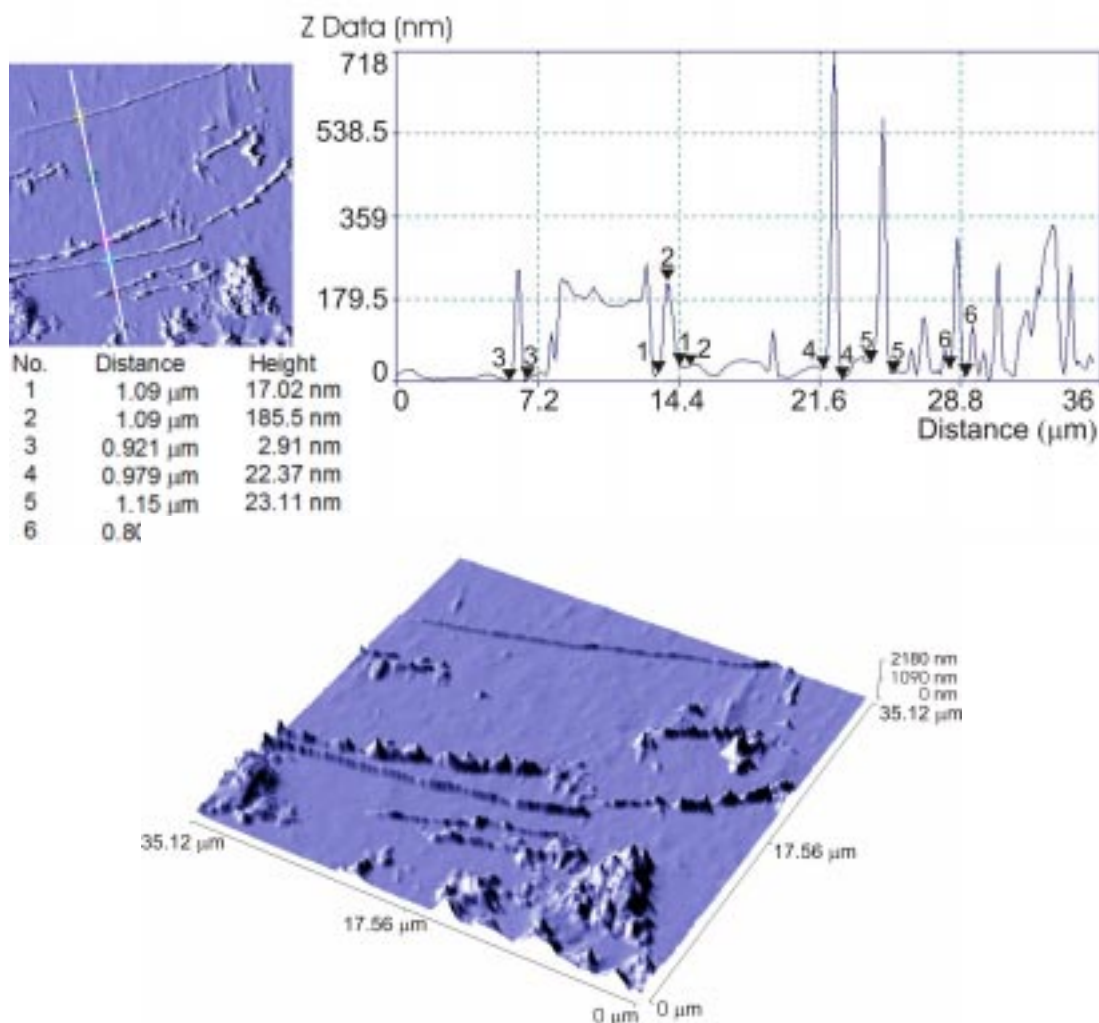


Fig. 4. AFM image and line profile measurements of A300 particles immersed in a nail lacquer showing the agglomeration and the alignment tendency. The data relate to the distance and height differences between points on the line indicated by the differently numbered pairs of inverted triangles

The comparison of this value with the data presented in Fig. 6 indicates that the experimental data cannot be explained only by taking into account the dielectric constant of the added particles. This suggests that changes in the orientation of LC molecules might have a stronger effect on dielectric properties of the colloidal mixture. The initial ZLI-1132 shows a tendency to be oriented in parallel to the measuring field, and therefore the dielectric constant is high ($\epsilon = 17$) and increases with decrease in temperature. With the mean dielectric constant of $\langle \epsilon \rangle = 9$ measured in the isotropic phase at $t > 70^\circ \text{C}$, it follows from Fig. 6 that the addition of SiO_2 particles results in a statistical orientation of LC.

This may result from the stronger interaction between the solid particles and the LC, which is extended to the volume phase by elastic forces.

In the case of TiO_2 particles, we have a more parallel orientation of LC molecules, if their concentration does not exceed 5% by weight. If the concentration increases, the solid component may be deposited on the electrodes forming a certain surface geometry, which may provoke a planar orientation of LC, as the experimentally found data are near to $\epsilon_{\perp} = 4.6$. One can expect that, in the case of the chaotic orientation of LC molecules by the addition of SiO_2 particles, a certain part of solid particles may be accumulated on the metal electrode surface and

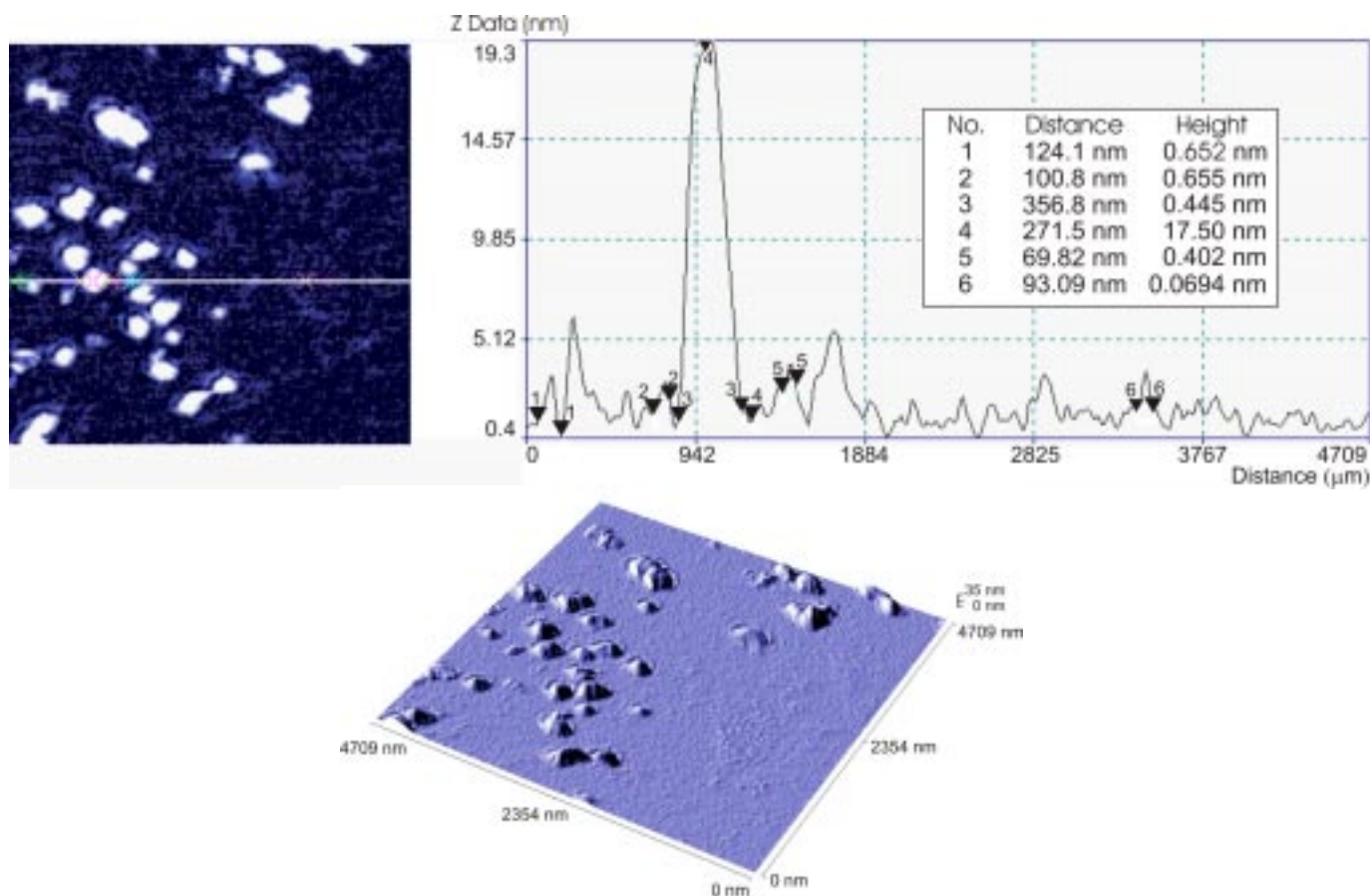


Fig. 5. AFM image and line profile measurements of A300 particles immersed in nematic LC showing the disturbed surface ordering by defects

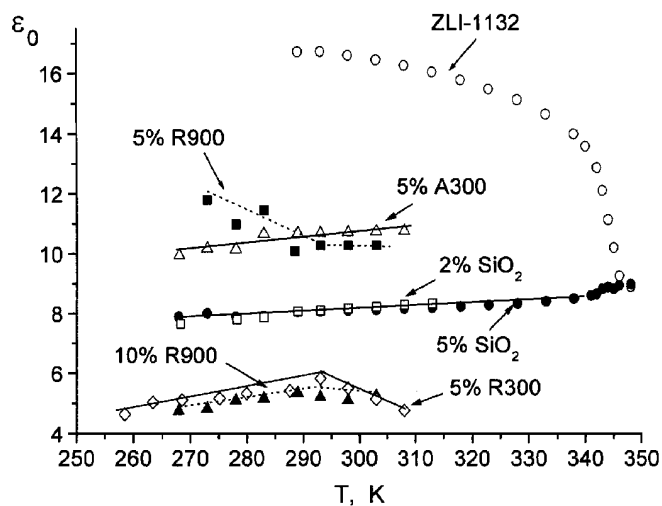


Fig. 6. Static dielectric permittivity as a function of temperature in the nematic phase of ZLI-1132 filled with different TiO₂ and SiO₂ nanoparticles

form “islands”, which enforces the planar orientation of LC in the near-surface areas. Adjacent areas of the clean metal surface would induce the homeotropic orientation of LC molecules, and these two effects would result, on the average, in a disordered orientation of LC. Such orientation effects are known from the example of the solid particles of rubbed polyimide and can be studied by AFM.

Conclusions

We interpret the differences in static dielectric permittivity, which are observed for the studied systems, as a result of the spontaneous orientation of the nematic LC in an external electric field. The addition of SiO₂ particles promotes the statistical orientation of LC molecules, while the adding of TiO₂ particles in smaller concentrations results in their more parallel orientation with respect to the electric field. At a higher content

of TiO₂ particles, the perpendicular orientation was detected. These effects are caused by the interplay of the solid particles within the LC and at the surface of the electrodes.

The dynamics of LC molecules in all systems is very similar. The reason for the slightly faster reorientation observed in the mixtures may be connected with a disturbed nematic ordering near the surface of solid particles as revealed by AFM measurements.

According to IR spectroscopy data, the molecular interactions of LC ZLI-1132 with the surface of TiO₂ particles in the nanocomposites are not strong enough to cause significant changes in the IR absorption spectra.

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ОРІЄНТАЦІЙНІ ВЛАСТИВОСТІ НЕМАТИЧНОГО РІДКОГО КРИСТАЛА, НАПОВНЕНОГО ЧАСТИНКАМИ НЕОРГАНІЧНИХ ОКСИДІВ

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Резюме

Наведено результати досліджень нематогенного рідкого кристала (РК) ZLI-1132, наповненого нанорозмірними частинками оксиду титану TiO₂ (рутил та анатаз) та діоксиду кремнію SiO₂, проведених методами широкосмугової діелектричної спектроскопії, ІЧ-спектроскопії та атомної силової мікроскопії. Показано, що одержані значення статичної діелектричної проникності досліджуваних систем можна пояснити впливом орієнтації РК у вимірювальному електричному полі. Додавання частинок SiO₂ веде до переважно статистичної орієнтації молекул РК, натомість додавання частинок TiO₂ сприяє їх перпендикулярній орієнтації відносно електричного поля. Динамічні властивості всіх досліджуваних систем виявилися досить близько. Більш високі значення часу реорієнтації молекул у наповнених РК можуть бути пов'язані з порушенням нематичного упорядкування поблизу поверхні неорганічних частинок.