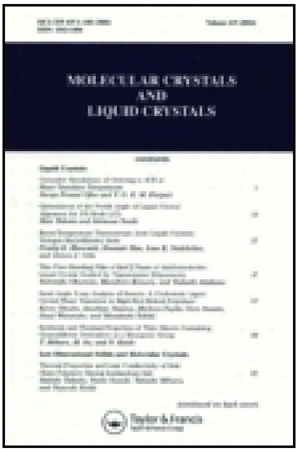

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Dielectric and electro-optical properties of nematic liquid crystals (LCs) doped with diamond nanoparticles (DNPs) have been investigated. It is established that the effect of DNPs on the electric conductivity depends on the purity of LC; the nanoparticles adsorb ions from LCs with a substantial content of ionic impurities, but release their own ions in highly pure LCs. The DNPs also influence LC permittivity due to orientational disordering of LC and contribution to overall permittivity of the samples. In contrast to LC-Carbon Nanotubes counterparts, the LC-DNPs composites do not show memory type electro-optic switching that may be assigned to isotropic shape of DNPs and their relatively weak interaction with LC hosts.

Keywords Diamond nanoparticles; filled liquid crystals; liquid crystal composites; liquid crystals

1. Introduction

Last decade was marked by great interest to liquid crystal (LC) dispersions of nanoparticles (NPs). Filling with NPs is usually used to extend range of LC properties and to reduce some parasitic effects typical for the LC electro-optic cells. LC suspensions of magnetic [1], ferroelectric [2], dielectric [3], semi-conducting [4] and metal [5] nanoparticles have been recently investigated. It was demonstrated that small amounts of these NPs substantially modify viscoellastic, dielectric, optical, electro- and magnetooptical properties of LC hosts [6].

The carbon particles have also been investigated as fillers for LCs. Among them special attention is currently paid to carbon nanotubes (CNTs) [7–9]. Having shape similar to LC molecules and effectively interacting with these molecules they disperse

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well in LC matrices copying their orientational order. Addition of CNTs improves operational parameters and weakens various troublesome effects in the LC electro-optic cells. Besides influencing intrinsic properties of LCs, CNTs result in new effects. One of them is the effect of electro-optic memory caused by stabilization of the field induced alignment of LC by a continuous network of CNTs formed in this state [9,10]. The stabilizing effect comes from the partial alignment of CNT network according to the alignment of LC host and effective LC-CNT interaction. The CNT network reveals itself in a sharp increase of conductivity of LC-CNTs dispersions with concentration of CNTs.

In the present work, we investigate LCs filled with nanoparticles of diamond (DNPs). Due to the small size and inert surface, DNPs are currently of especial interest for biomedical applications as potential enterosorbents, drug delivery and labeling agents [11]. Our basic goal was to compare the effect of DNPs on dielectric and electro-optic properties of LCs with the effect of CNTs. These two sorts of carbon particles have some important distinctions. First of all, they are composed of two different allotropic forms of carbon. In contrast to multiwalled CNTs with a quasi-metallic conductivity (along the tube axis), DNPs are non-conductive. Finally, in contrast to the tubes, DNPs have spherical form. We demonstrate that DNPs greatly influence conductivity of LCs as well as modify their electro-optic response by keeping this response reversible.

2. Experimental Section

2.1. *Samples*

As LC hosts we used nematic mixtures E7 ($T_{NI} = 58°C$, $\varepsilon_{\|} = 19$, $\varepsilon_{\perp} = 5.2$) and MLC6609 ($T_{NI} = 91.5°C$, $\varepsilon_{\|} = 3.4$, $\varepsilon_{\perp} = 7.1$) from Merck with positive and negative dielectric anisotropy, respectively. To reorient these LCs in an electric field, planar alignment was set for E7 and homeotropic alignment for MLC6609. This was attained by using aligning films of polyimides AL3046 (JSR, Japan) and SE5300 (Nissan, Japan), respectively. These films were spin coated on the glass slides with indium tin oxide (ITO) electrodes, properly backed and unidirectionally rubbed with a velvet cloth.

The DNPs were purchased from Aldrich and used as received. The particle diameter according to supplier specification was less than 10 nm. The particles and LC at the desirable proportion were manually mixed and then subjected to ultrasonic mixing for 10 min. The concentration of DNTs in the mixture, C_{DNP}, was 0.25–4% by weight. The dispersions prepared in such way were filled in the antiparallel electro-optical cells (antiparrallel orientation of rubbing directions) with a thickness of 16 μm.

The quality of LC alignment and the sample morphology were studied by using a polarizing optical microscope POLAM 213 M equipped with a digital camera conjugated with PC. The microscopic photos of some samples are presented in Figure 1. It is apparent that DNPs, like other types of nanoparticles [12,13], effectively aggregate in LCs forming continuous network at $C_{DNP} > 3$ wt.%.

2.2. *Experimental Techniques*

The dielectric measurements were conducted by using oscilloscopic method [14,15]. The frequency f dependencies of real ε' and imaginary ε'' components of complex

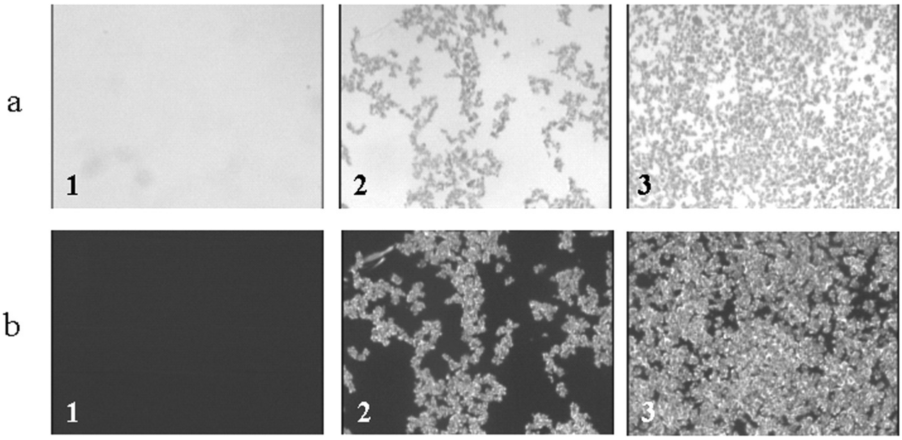

Figure 1. Polarizing microscope pictures of MLC6609-DNPs samples with concentration of DNPs equal to 0; 1 and 3 wt.% in case 1, 2 and 3, respectively. The pictures in row (a) correspond to one polarizer setting (the analyzer is removed). In case of row (b) the polarizer and analyzer are crossed. The room temperature observation.

dielectric constant $\varepsilon^* = \varepsilon' - \varepsilon''$ in the frequency region $5 \cdot 10^{-2} - 10^6$ Hz were obtained by measuring frequency dependences of resistance and capacitance of LC cell. In these measurements the voltage signal applied to the tested cells had a triangle form with amplitude of 0.25 V. As an example, Figure 2 presents the $\varepsilon'(f)$ and $\varepsilon''(f)$ spectra for pure LC E7 as well as for the E7 doped by 4 wt.% of DNPs.

Based on the ε'' data the sample conductivity σ was determined using the formula:

$$\sigma = 2\pi\varepsilon_0\varepsilon'' f, \tag{1}$$

where ε_0 is a dielectric constant of the free space. For this estimation the frequency $f = 100$ Hz was used. It corresponded to the linear part of double logarithmic plot of $\varepsilon''(f)$ curves (Fig. 2) to ensure frequency independence of conductivity. This allowed us to attribute the measured conductivity to the ionic conductivity of LC.

The electro-optical studies were carried out by using experimental set up minutely described in [16]. The cell was set between two crossed polarizers so that the angle between the polarizer axes and the rubbing direction was 45°. It was powered by sinusoidal voltage $U = 60$ V ($f = 2$ kHz), which was stepwise increased from 0 to 60 V and then decreased back to 0. The transmittance T of the beam of He-Ne laser ($\lambda = 0.63\,\mu$m) was measured as a function of voltage using the formula $T = (I_{out}/I_{in}) \cdot 100\%$, where I_{in} and I_{out} are intensities of the incident and transmitted light, respectively.

All measurements were carried out at room temperature, except the dielectric spectra of LC MLC6609 and the MLC6609-CNT colloids, which were measured at room temperature, as well as at 70°C. In the latter case, the temperature was raised to increase conductivity of the probes, which at room temperature approached sensitivity limit of our setup.

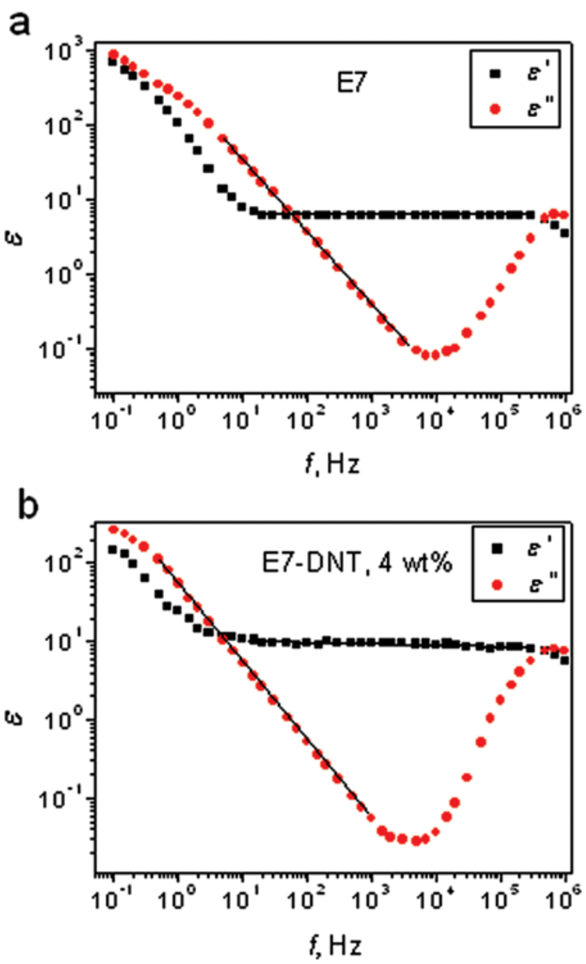

Figure 2. Frequency dependences of real ε' and imaginary ε'' parts of complex dielectric constant for (a) E7 and (b) E7-DNPs (4 wt.%) samples at room temperature. (Figure appears in color online.)

3. Results and Discussion

3.1. *Dielectric Characteristics*

According to Figure 2, three parts of the $\varepsilon'(f)$ and $\varepsilon''(f)$ spectra can be distinguished. The low frequency range ($f < 10$ Hz) corresponds to first relaxation process primarily caused by double electric layers and space-charge polarization essentially changing the near-electrode concentration of ions [17]. The intermediate frequency range ($f = 10 - 5 \cdot 10^{3}$ Hz) reflects polarization and charge transfer in the LC bulk. Finally, the high frequency range ($f > 10^{4}$ Hz) corresponds to second relaxation process, which is commonly assigned to dipole relaxation associated with the rotations around short molecular axis [18]. Collective character of such rotations in LCs leads to essential fall of frequency of this relaxation.

Comparing the dielectric spectra for pure and DNP doped LC E7, the following distinctions can be noticed. The spectra for the doped sample are shifted to the lower frequencies that might reflect a change of LC ionic conductivity and ion concentration. This is supported by the fact that dielectric loss ε'' decreases by adding the nanoparticles. This implies reduction of ionic conductivity, which is, according to (1), directly proportional to ε''.

Figure 3 demonstrates values of permittivity ε' and conductivity σ for the series of LC-DNP samples with different DNP loading. The data for E7-DNT series correspond to room temperature. At the same time, the results for MLC6609-DNT series are presented for 70°C, since the room temperature data were not sufficiently reliable (close to sensitivity level of our measuring device). For both LCs, permittivity ε' quasi-linearly grows with concentration of DNP C_{DNP} at the initial stage of C_{DNP} increase ($C_{DNP} < 3$ wt.%). The growth of $\varepsilon'(C_{DNP})$ curves results in rather high permittivity values of doped LCs. At $C_{DNP} = 4$ wt.% the growing factor is about 1.7–1.9. Two reasons of this effect have been considered. Firstly, one can suggest

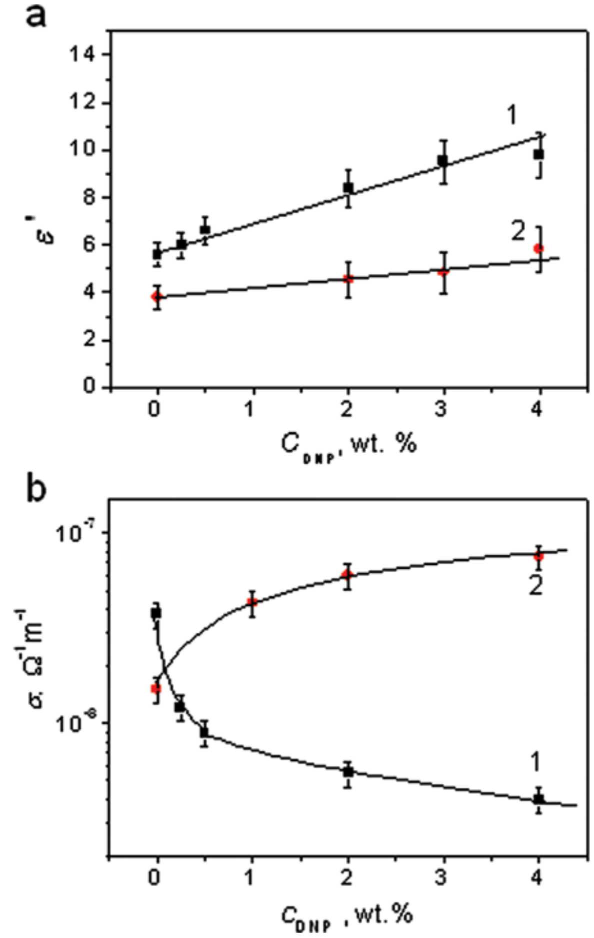

Figure 3. Permittivity and conductivity of LC-DNPs samples as functions of DNP concentration. Curves (1) and (2) correspond to LC E7 and LC MLC6609 series, respectively. The data for the E7 series correspond to 18°C, and the data for the MLC6609 series are acquired at 70°C. (Figure appears in color online.)

that grows of ε' is a result of high permittivity of diamond particles. The permittivity of macroscopic samples of diamond ε_D is about 5.7, i.e., close to permittivity of LCs. However, as demonstrated in paper [19], the permittivity of diamond particles sharply grows if the particle size reduces to hundreds of nanometers. At 100 nm the estimated permittivity value is 31, while at 4 nm it approaches $7 \cdot 10^4$. This increase is consistent with the Moss equation connecting permittivity with the band gap of nanocrystal E_g:

$$\varepsilon^2 \cdot E_g = const \tag{2}$$

The permittivity increases, because E_g of diamond decreases upon decreasing particle size [20]. The value $\varepsilon_D = 10^3 - 10^4$ was set in the Maxwell-Garnett equation for the effective dielectric constant ε_e of the composite media [21]

$$\varepsilon_e = \varepsilon_{LC} \frac{2\varepsilon_{LC}(1-\varphi) + \varepsilon_D(1+2\varphi)}{\varepsilon_{LC}(2+\varphi) + \varepsilon_D(1-\varphi)} \tag{3}$$

where φ is the volume fraction of the embedded DNPs. The estimation of ε_e was made for $C_{DNP} \leq 0.5$ wt.%, i.e., for rather small concentrations of DNPs. Thereby we intended to avoid percolation of DNPs, since Eq. (3) is invalid in the percolation regime. Whereas density of diamond is roughly 3.5 times higher than the density of LC, this loading corresponded to volume concentration $\varphi = 1.4 \cdot 10^{-3}$. By setting values of ε_D, ε_{LC} and φ in Eq. (3) we realized that calculated parameter $\varepsilon_e/\varepsilon_{LC}$ is several orders of magnitude lower than that one obtained in experiment. So, it was concluded that permittivity of DNPs plays minor role in overall permittivity of LC-DNPs composites.

The other factor which might result in growing of the composite dielectric constant is disturbing of LC alignment by DNP aggregates. Really, orientational disordering of both planar aligned LC E7 ($\Delta\varepsilon > 0$) and vertically aligned LC MLC6609 ($\Delta\varepsilon < 0$) shall result in growing of LC dielectric constant. Figure 1 demonstrates that LC alignment is essentially destroyed in the vicinity of DNPs aggregates. The alignment randomization is especially strong at high concentrations of DNPs. The values of ε' obtained at high C_{DNP} are close to $<\varepsilon'>= \frac{1}{3}(\varepsilon'_{LCII} + 2\varepsilon'_{LC\perp})$, i.e., to orientationally averaged value of LC dielectric constant. This evidences for major contribution of LC randomization to growing of dielectric constant.

While permittivity always grows with concentration of DNPs, the behavior of conductivity curve $\sigma(C_{DNP})$ depended on the LC used. For MLC6609 the curve slightly increased, while for E7 it considerably decreased (for more then one order of magnitude). It is worthwhile mentioning that conductivity of LC MLC6609 at room temperature was extremely low ($\sigma < 10^{-9}\ \Omega^{-1}\,\mathrm{m}^{-1}$) and almost at the sensitivity level of our measuring device. In contrast, the conductivity of E7 was rather high even at room temperature. This agrees with a general opinion about high ionic contamination of this material appearing due to its strong polarity. The behavior of $\sigma(C_{DNP})$ curves can not be explained by randomization of LC alignment with nanoparticles due to anisotropy of LC conductivity. In turn, it can be easily explained by the balance of ionic impurities in the system. The results suggest that DNPs effectively rectify LC with strong ionic contamination, that was previously observed for other types of nanoparticles [22,23]. At the same time, they introduce some ions to pure LC. One can explain this by the ionic adsorption/desorption processes at nanoparticle surface. It is reasonable to assume that surface of DNPs contains some adsorbed ions, whose number depends on preparation and storage conditions of these particles. In case that these particles are mixed with pure LC, the ions partially desorb and migrate to the less contaminated LC surroundings causing some contamination of LC. On the other hand, if the particles are mixed with the LC enriched with ions, the LC ions preferably adsorb on the relatively pure particles.

3.2. *Electro-optic Curves*

The transmittance *T vs.* applied voltage *U* curves for the pure MLC6609 and the MLC6609-DNPs ($c = 1$ wt.%) sample are presented in Figures 4a and 4b, respectively. The oscillations of *T*(U) curve are caused by the phase shift change between the *e* and *o* light waves in a course of homeotropic-to-planar reorientation, $\Delta\varphi$, higher than $\pi/2$. The phase shift *vs.* voltage curves derived from the experimental

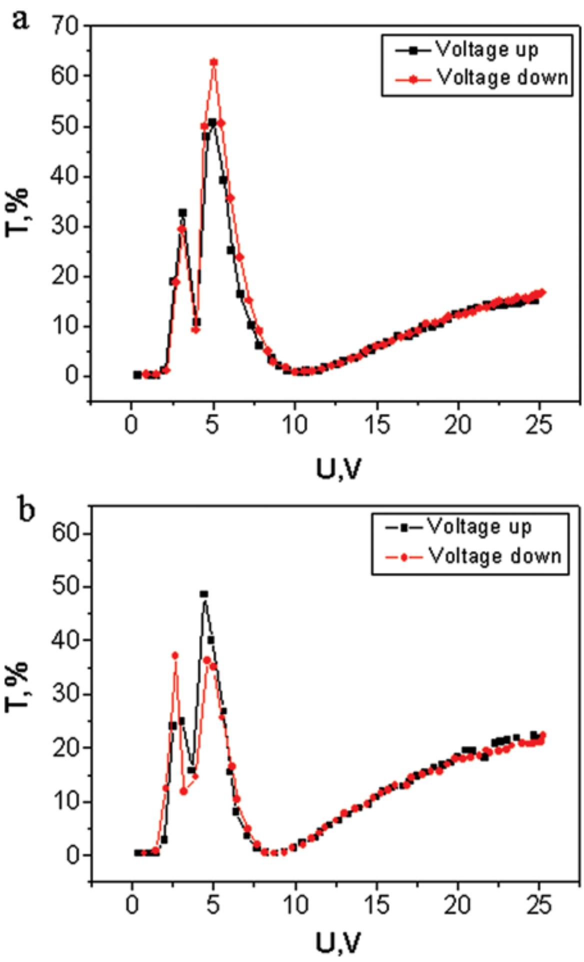

Figure 4. Transmittance *vs.* applied voltage curves for (a) MLC6609 and (b) MLC6609-DNPs (1 wt.%) samples. (Figure appears in color online.)

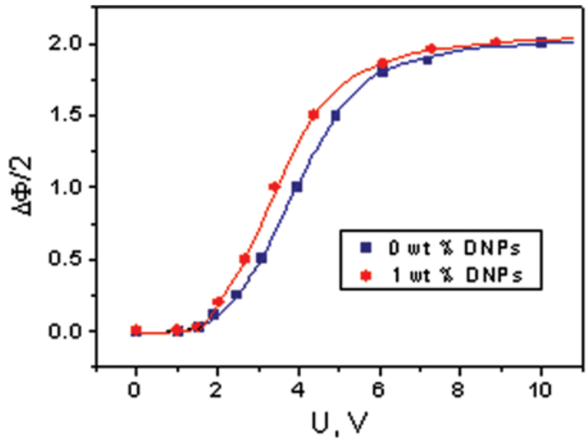

Figure 5. The phase incursion in the (a) MLC6609 and (b) MLC6609-DNPs (1 wt.%) samples as a function of applied voltage. (Figure appears in color online.)

curves $T(U)$ on a base of equation $T = \sin^2(\Delta\varphi/2)$ are presented in Figure 5. They demonstrate some reduction of the threshold and controlling voltages for the DNPs doped sample. This is seemingly caused by randomization of LC alignment giving fraction of LC molecules with the dipole moment oriented out of the plane perpendicular to the electric field. The reorientation of these molecules has no threshold character. At $C_{DNP} \geq 3$ wt.%, however, the opposite tendency was observed. This might be caused by increasing fraction of LC adjacent to DNPs, for which the driving voltage is higher than for the bulk part.

There is also apparent from Figure 4 that the MLC6609-DNPs sample, same as the pure MLC6609, demonstrates reversible electro-optic response. This contrasts with the irreversible response of MLC6609-CNTs samples. The observed difference is seemingly caused by the difference in properties of DNPs and CNTs. Comparing with the ball-shaped DNPs, the highly anisotropic nanotubes perfectly build into aligned LC layers and effectively form networks in these materials. Furthermore, because of specific graphene structure, CNTs strongly interact with LC molecules via $\pi\pi$ stacking [24]. As result of this, nanotube skeleton effectively stabilizes LC alignment realized in the electric field [9,10,25]. This seems to be not the case for DNTs having isotropic shape and inert surface. However, indisputable advantages of DNPs are high electrical resistance, chemical inertness and mechanical stability. These particles can be successfully used for doping conventional LC cells without danger of electrical shorting, chemical degradation and essential mechanical damage of the particles in a process of preparation and exploitation of LC-DNPs composites.

4. Conclusions

In the present study, dielectric properties and electro-optic response of liquid crystals doped by nanoparticles of diamond are investigated. It is found out that insertion of DNPs may result in significant ionic rectification of LCs because of trapping of the ionic impurities by the nanoparticles. In parallel, at sufficiently high loading, such a doping essentially increases permittivity of LC layers due to randomization of LC alignment as well as contribution of DNP to overall permittivity of the composites.

Small quantities of DNPs (<2 wt.%) cause slight reduction of threshold and controlling voltages of LC cells. Unlike carbon nanotubes, particles of another allotropic form of carbon, they do not provoke electro-optic memory and electric shorting. Besides, they are chemically and mechanically stable. This makes these objects rather suitable for filling LCs with a purpose of improving their operating characteristics.

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