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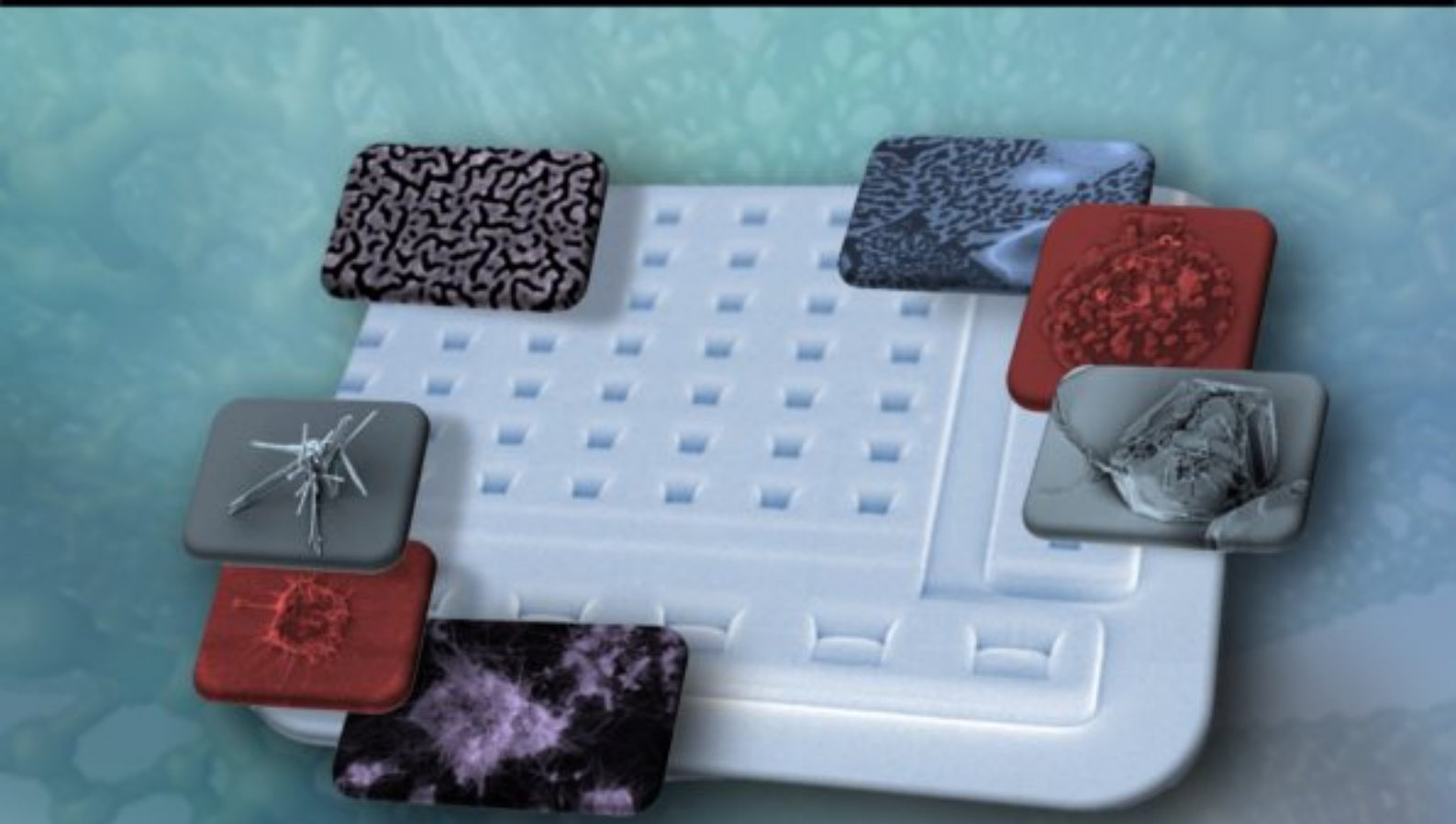

Nanomaterials and their Composites: from Fabrication to Applications

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Effect of $Mo_6S_xI_{10-x}$ Nanotubes Addition on Electrooptical Properties of Polymer-dispersed Liquid Crystals

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Abstract: We investigated the effect of incorporation of about 0.1 wt% $Mo_6S_4I_6$ nanotubes in the (H)PDLC mixture composed of commercially available compounds. The effect of nanotube addition on optical contrast and switching voltage was analysed. The results show, that the switching voltage of the composites with nanotubes is considerably lower than the switching voltage of the analogous structures without the nanotubes. The structures with nanotubes also show less hysteresis upon increasing and decreasing the external voltage. The electron microscopy investigations reveal that the nanotube material accumulates inside the LC domains. We show that a presence of the nanotubes in the LC material causes a decrease of the threshold voltage and also improves the switching speed upon modification of an external voltage, which explains the phenomena observed in the (H)PDLC structures. *Copyright © 2011 IFSA.*

Keywords: Polymer-dispersed liquid crystals, Nanotubes, Electrooptic switching.

1. Introduction

Polymer-dispersed liquid crystals (PDLCs) and holographic polymer-dispersed liquid crystals (HPDLCs) are composite materials widely used to fabricate electrically switchable diffractive optical

structures. During the fabrication process a homogeneous mixture of photosensitive monomers and liquid crystal (LC) molecules is exposed to optical radiation, which induces photopolymerization reaction. At some specific level of polymerization the miscibility of the constituent compounds breaks down and phase separation occurs, which results in the formation of optical diffraction structures with high refractive index contrast ($\Delta n \leq 0.2$). The main advantage of these structures is that the refractive index of phase separated LC regions can be tuned by an external electric field thus modifying the mismatch between the polymer matrix and the LC domains [1]. Due to this property, (H)PDLCs are suitable for various optical devices such as switchable windows, display devices, optical limiters and interconnects, and different kinds of optical sensor elements [2, 3].
In an ideal configuration, the starting mixture has to be selected so, that refractive index mismatch between the LC domains and the polymer matrix completely vanishes at some specific external voltage. This requirement is, however, difficult to be realized in general, as the degree of photopolymerization-induced phase separation strongly depends on the illumination details and consequently the mixture, which is suitable for creation of a specific optical structure can be quite inappropriate for fabrication of a different structure. This problem can be solved by addition of the third component, which can be utilized for "fine tuning" of the optical and/or switching properties. Nanoparticles are very suitable for this purpose, as their addition in low fraction can on one hand bring desirable modifications of the physical properties, but on the other hand does not affect the phase-separation capability of the mixture.

One of the most frequently investigated type of nanodopands in (H)PDLCs are inorganic colloidal nanoparticles, which are primarily used to tune the light scattering features of the material through modification of the refractive index of the coexisting phases [4-9]. It was shown that functionalized nanoparticles can also enhance the phase separation process and consequently improve the electrooptic properties of the (H)PDLC structures [10, 11]. Nanopraticles like carbon nanotubes (CNTs), clay nanoplatelets, etc. were also studied as additives to (H)PDLCs [12-14].

We investigated the effect of incorporation of $Mo_6S_4I_6$ and $Mo_6S_2I_8$ (MoSI) nanotubes [15] into the (H)PDLC structures composed of commercially available photosensitive acrylate-based pre-polymer mixture and biphenyl-type liquid crystal molecules [16]. Due to the conductive nature of the MoSI nanotubes [17], the basic idea was that nanotube addition could presumably increase the conductivity of the polymer matrix. This should result in an increase of the effective electric field across the LC domains and consequently in lover driving voltages needed for electrooptic switching [18]. The effect of reduced driving voltage was indeed observed, however, its explanation was found to be very different from initial expectations.

2. Experiments and Results

The fraction of the nanotubes in the starting mixture was about 0.1 wt%. The SEM image of the nanotube powder is shown in Fig. 1. The nanotubes were introduced into the LC compound of the starting mixture from an ultrasonicated dispersion in isopropanole. After mixing the isopropanole was evaporated and polymer compounds were added. The resulting mixture was introduced by capillary flow into standard cells made of two ITO-coated glass plates separated by plastic spacers to set the thickness. The cells were than exposed to the UV radiation from an Argon ion laser operating at the wavelength of 351 nm. Exposure with one, two and four coherent laser beams was used to fabricate usual PDLC samples and 1D or 2D HPDLC lattices, respectively [16, 19].

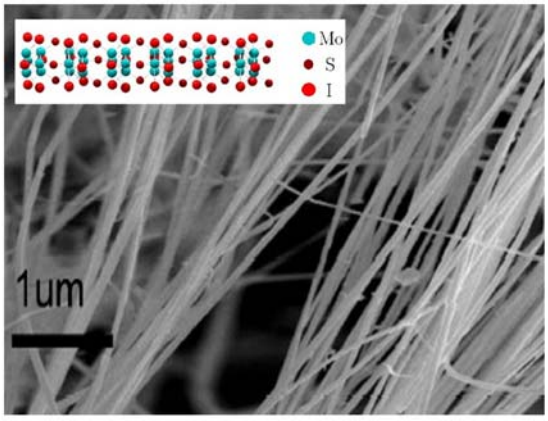
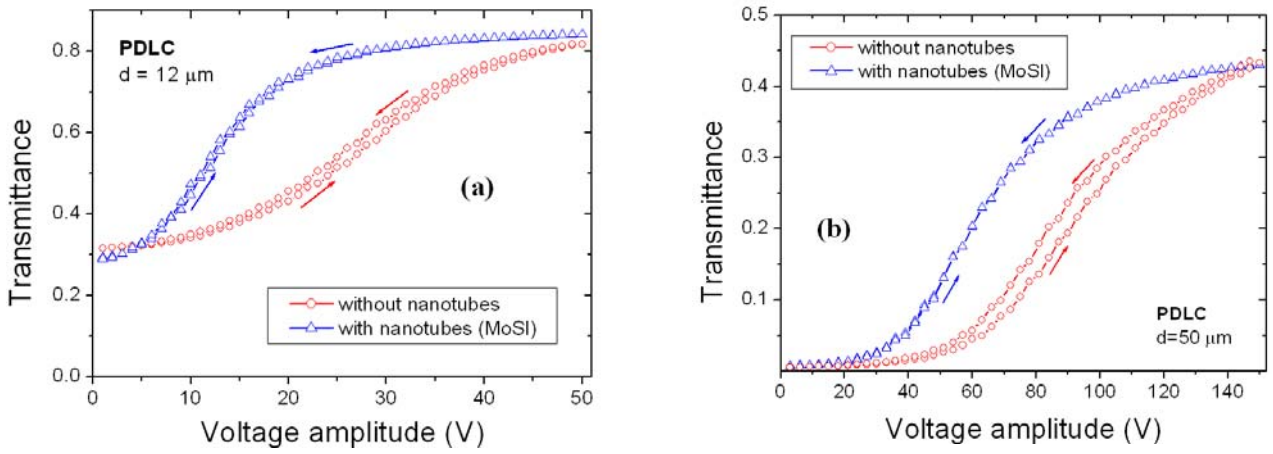


Fig. 1. SEM image of the starting nanotube material. The bar corresponds to 1 μm.

Diffraction properties of the samples were probed by a He-Ne laser beam at the wavelength of 633 nm and the one or more photodiodes. Square waveform voltage at the frequency of 1 kHz and variable amplitude was attached to the ITO electrodes to induce variations of the LC orientation. The effect of nanotube addition on optical contrast between the off- and the on- states and on transmitted/diffracted intensity as a function of voltage was analyzed. Fig. 2 shows the dependence of transmittance of the PDLC films with the thickness of 12 μm and 50 μm, respectively, on applied voltage. One can see that the switching voltage of the samples containing nanotubes is considerably lower. Besides this, the hysteresis observed during increasing and decreasing the voltage amplitude is practically absent in the doped samples. The contrast between the off and the on states is, however, not very different, which suggests that the morphology of the structures is very similar.



(a) (b)

Fig. 2. Transmittance of the PDLC films of two different thicknesses versus applied voltage. Red circles denote undoped and blue triangles doped samples, respectively.

To check in what amount the nanotubes are incorporated into the polymer matrix, LC material was removed from the structure and SEM imaging of the remaining material was performed. The result is shown in Fig. 3. Because the LC fraction in the starting mixture is relatively high (55 %), the polymer network does not show the conventional droplet morphology, but a morphology of interconnected pores with irregular shapes. We performed also elemental analysis of the sample surface (EDS), but did not

find any traces of Mo, S or I in the polymer. This suggests that MoSI nanotubes are phase separated from the polymer network together with the LC material. This was confirmed by observing the sedimentation of the washed-out LC material, which after some days showed a tiny black layer of aggregated nanotubes on the bottom of the container.

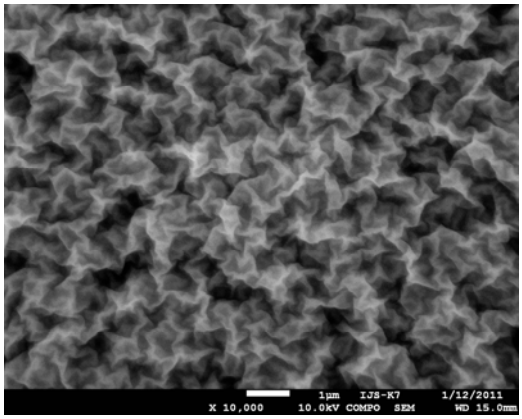


Fig. 3. SEM image of the polymer network of a PDLC film. The bar corresponds to 1 μm.

A similar analyis was performed also for 1D and 2D HPDLC grating structures. The effect of nanotubes was profound especially in the 1 D gratings. Fig. 4 shows the intensity of different diffraction orders as a function of applied voltage for the grating with the pitch of 4.6 μm and the thickness of 12 μm. To enable easier comparison, the intensities are rescaled to the same modification interval. One can notice that the switching voltage of the doped material is again considerably lower than for undoped material.

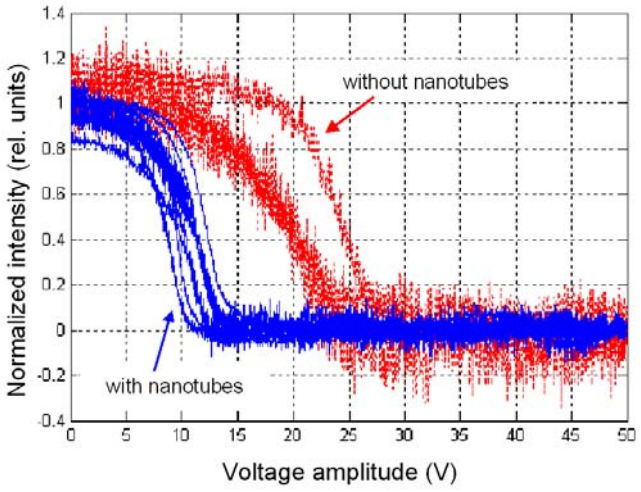
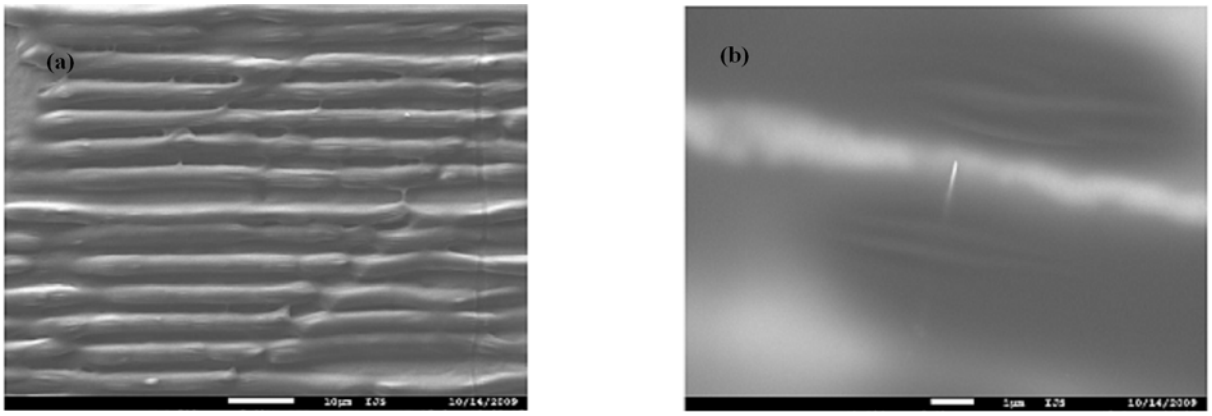


Fig. 4. Normalized diffracted intensity of the HPDLC grating versus applied voltage. The intensities of different diffraction orders were rescaled to the same modification interval. Red curves denote undoped and blue curves doped grating, respectively.

Also for this structure we performed a SEM analysis of the morphology of the polymer matrix. The result is shown in Fig. 5. The channel morphology with the periodicity of the granting structure can be resolved. The presence of MoSI material in the polymer matrix is again very low. A lot of efforts were needed to find a single isolated bundle shown in Fig. 5.(b). Therefore we can conclude that, similar to PDLC samples, also in the HPDLC structures the MoSI nanotubes accumulate in the LC regions.



(a) (b)

Fig. 5. SEM image of the HPDLC grating structure on two different scales: the bar in (a) corresponds to 10 μm and the bar in (b) to 1 μm, respectively. The white stripe in (b) is a single MoSI nanotube, as resolved with the EDS analysis.

Stimulated with the above-described findings, we decided to analyze the effect of nanotubes on the properties of the pure LC material used in (H)PDLC samples (nematic LC mixture TL203, Merck Ltd.). The nanotubes were introduced into the LC material in the same way as in the case of (H)PDLC samples. Then the LC material was introduced into the planarly aligned LC cells with rubbed polyimide surface layer. The thickness of the cells was 50 μm. The cell was placed between the two crossed polarizers and the field-induced reorientation of the nematic director field in the standard Freedericksz transition configuration was analyzed [20]. Fig. 6 shows the intensity of transmitted probe beam as a function of applied voltage for doped and undoped cells. Due to variations of sample thickness, optical phase retardation and the associated transmitted intensity at $U = 0$ have different values in different regions of the sample. The results for two limiting cases are presented. The threshold voltage U_c, at which the reorientation of the LC starts to take place, is around 1.6 V for undoped sample, while for doped sample it is around 1.2 V. This is in agreement with the lower switching voltages observed in PDLC and HPDLC structures.

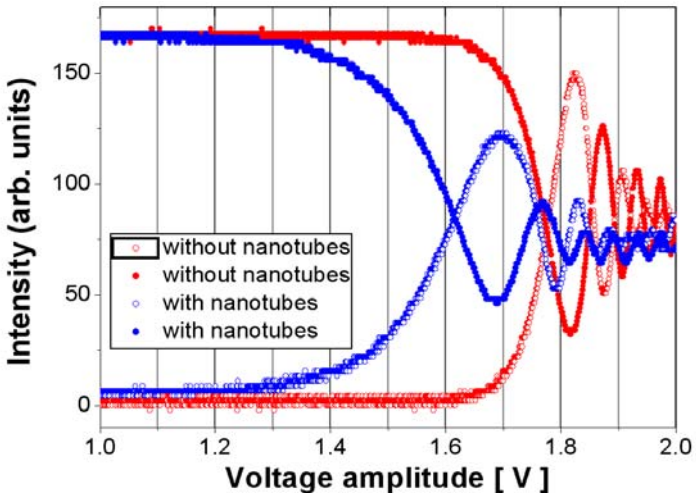


Fig. 6. Transmitted intensity of a planarly aligned LC cell placed in-between two crossed polarizers as a function of applied voltage amplitude: undoped sample (red curves), doped samples (blue curves).

The threshold voltage U_c of an aligned LC cell is determined by two parameters: the elastic constant of the nematic director field and the dielectric anisotropy of the LC material. For the configuration used in our study the corresponding relation is given as [20]:

$$U_c = \pi \sqrt{\frac{K_{11}}{\varepsilon_0 \varepsilon_a}}, \tag{1}$$

where K_{11} is the splay elastic constant and ε_a is the dielectric anisotropy. The addition of nanotubes can in principle affect both, the elastic properties and the anisotropy of the LC medium. To probe the effect on elastic properties, we performed measurements of the viscoelastic constant K_{11}/η_{splay}, where η_{splay} is the effective viscosity for splay distortion, by performing dynamic light scattering (DLS) analysis of the thermally induced fluctuations of the nematic director field [21]. The results showed practically no difference between the values of the K_{11}/η_{splay} for doped and for the undoped LC material, therefore we concluded that addition of nanotubes does not modify the elastic properties of the LC medium.

To probe the effect of nanotubes on dielectric anisotropy ε_a of the LC phase, we investigated switching dynamics of the LC cell as a function of the applied voltage amplitude. For voltages above the threshold voltage U_c, the response time upon application of the voltage τ_{on} is given as [22]:

$$\frac{1}{\tau_{on}} = \left(\frac{\varepsilon_0 \varepsilon_a}{\eta_{splay} d^2} \right) \left(U^2 - U_c^2 \right), \tag{2}$$

where d is the thickness of the cell. The results of the measurement of $1/\tau_{on}$ as a function of U^2 are shown in Fig. 7. Solid lines are fits to linear dependence in accordance with the Eq. 2. One can see, that the addition of nanotubes causes two effects: an increase of the slope of the linear dependence and an increase of the inverse response time upon switching on the external voltage. The material doped with nanotubes hence exhibits larger dielectric anisotropy and reacts on application of an external voltage considerably faster than the material without the nanotubes. We analyzed also the response time upon switching off the external voltage and found out that it was practically independent of the voltage amplitude and had very similar values ($\tau_{off} \sim 25$ s) in doped and undoped cells.

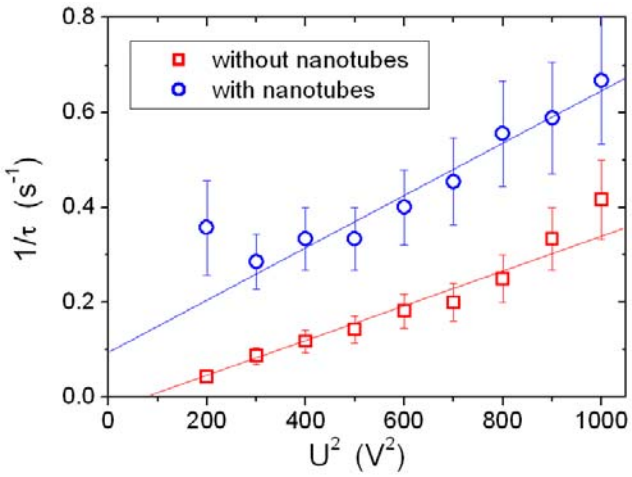


Fig. 7. Inverse response time of a planarly aligned LC cell upon application of an external voltage as a function of the square of the applied voltage amplitude: undoped sample (red squares), doped samples (blue circles). Solid lines are fit to linear dependence accordingly to the Eq. 2.

3. Discussion

Our results show that an addition of about 0.1 wt% of the MoSI nanotubes can significantly improve electrooptic properties of the nematic liquid crystals in their pure state as well as in their composites with polymer materials. The real part of the dielectric constant of MoSI thin films at 1 kHz is $\varepsilon' = 35$ [23]. Taking into account this value and the volume fraction of the nanotubes ($\sim 10^{-4}$), we calculated the effective dielectric function of the mixture using Maxwell-Garnett effective medium theory, which showed that the modifications of the dielectric function within this theory are negligible. The effect is therefore more complex than simple mixing and some additional phenomena seem to contribute to the increase of the effective dielectric anisotropy ε_a, which is relevant for electrooptic switching. Accordingly to the slopes of the linear fits shown in Fig. 7, the effective dielectric anisotropy ε_a of the nematic phase of TL203 doped with the nanotubes increases for a factor of 1.5. The increase of ε_a affects the threshold voltage U_c for the Freedericksz transition, which is consequently expected to decrease for a factor of $1.5^{-0.5} = 0.81$, while our measurements (Fig. 6) revealed a decrease for a factor of 0.75. The difference can be attributed to modification of the surface boundary conditions, like modification of pretilt angle, by the presence of the nanotubes. The modification of alignment layer was for instance observed in the LC mixtures doped with carbon nanotubes (CNTs) [24].

The reduced response time of the LC material upon switching on the external voltage is evidently not only the consequence of the increased effective dielectric anisotropy. One can notice in Fig. 7 that the linear fit of $1/\tau_{on}$ versus U^2 for doped sample crosses the y-axis at the value $1/\tau_{on}$ (U=0) > 0, which cannot be explained by the Eq. 2. This signifies the presence of an additional phenomenon that helps to speed up the reorientation process for $U > U_c$. One possible explanation is a weakening of the surface anchoring due to the presence of the nanotubes. Another possible scenario is that the applied electric field reorients nanotubes along the field and due to the coupling between the LC director and nanotube long axis an additional torque is imposed onto the LC director. Further investigations are needed to resolve the associated phenomena in more details. Nevertheless, the observed faster response of the LC material to variations of an external voltage explains the reduced hysteresis behaviour of the PDLC samples (Fig. 2). Because doped samples react faster on voltage modifications, they come closer to equilibrium during conventional slow ramping of the voltage amplitude used to probe the dependence of transmitivity on external voltage.

4. Conclusions

We showed that the addition of MoSI nanowires to the nematic LC mixture TL203 causes a significant improvement of the electrooptic properties of the LC material. It causes a decrease of the electrooptic switching voltage and also a decrease of the switching time upon application of the voltage. When such a nanowire/LC mixture is used for fabrication of the PDLC and HPDLC structures, the nanowires phase separate from the polymer network together with the LC material and hence remain dissolved in the LC phase. Consequently the improved effects on switching voltage and switching time, similar as observed in the pure LC compound, are observed also in the (H)PDLC structures.

Acknowledgements

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- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
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