

Photoresponsive azo-doped aerosil/7CB nematic nanocomposites: the effect from concentration of the azobenzene photoactive agent

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Abstract. We studied nanomaterials composed from 3 wt.% aerosil nanospheres and the room-temperature nematic liquid crystal 4-n-heptyl cyanobiphenyl (7CB), as doped with the photoactive liquid crystal 4-(4'-ethoxyphenylazo)phenyl hexanoate (EPH). The molecules of the azobenzene photoactive agent EPH were included at concentration ranging from 1 wt.% to 10 wt.%. The object of our interest is the effect of the EPH amount on the photosensitized electro-optical properties of thin films of aerosil/7CB/EPH nematic nanocomposites.

1. Introduction

Among the plenty of nanostructured materials with interesting properties and applications, the liquid crystals (LCs)-based nanocomposites, in particular those created by doping of LCs with nanoparticles (NPs) [1,2], have been attracted considerable research attention from the physics and engineering communities. At present, such nanomaterials are widely and intensely investigated because they have large potential to improve the performance of the LCs devices [3]. In this context, of special interest are the systems consisting of silica NPs doped into LCs [4]. Such nanostructured LCs have demonstrated advanced applications based on their valuable electric and electro-optic (EO) properties [1,4-6]. That is why, silica-nanostructured materials composed from aerosil NPs (ANPs) and nematic LCs have been extensively investigated [3,8,9].

Very recently, we have studied the EO properties of thin (25 μm) films of gel nanocomposites produced from nematic LC heptylcyanobiphenyl (7CB) and 3 wt.% hydrophilic ANPs [10,11]. Further, the photo-driven stimulation of the electro-optics of such nanomaterials doped with azobenzene LC 4-(4'-ethoxyphenylazo)phenyl hexanoate (EPH) is of research interest. Reasonably, the photo-stimulation of the electro-optics of EPH-doped ANPs/7CB films should be enhanced by use of higher intensity of light in reasonable limits. But also, the concentration of EPH photo-agent can affect their EO response. In the present work this was experimentally studied by varying the concentration of azobenzene EPH photoactive agent in the range 1 wt.% - 10 wt.%, by keeping fixed the UV light intensity.

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2. Experimental

ANPs (hydrophilic Aerosil 300 nanospheres having a mean diameter of about 7 nm and capped with silanol groups) at a concentration of 3 wt.% were added to the well known room-temperature nematic LC 4'-heptyl-4-biphenylcarbonitrile (7CB). The formed nanocomposite was doped with the azo-containing LC compound 4-(4'-ethoxy phenylazo)phenyl hexanoate (EPH). Four different blends of EPH with aerosil/7CB were made, with the composition of EPH being $X = 1$ wt.%, 3 wt.%, 5 wt.% and 10 wt.%. The plan-parallel EPH-doped ANPs/7CB gel films with a thickness of 25 μm were formed in cells assembled from two ITO (indium tin oxide)-coated glass plates, to serve as electrodes.

The experimental set up and the optical layout for the experiments performed, have been described in details elsewhere [12]. Briefly, the EO response of EPH-doped ANPs/7CB films to an alternating-current (AC) electric field was investigated by use of a circularly polarized He-Ne laser beam (wavelength $\lambda = 632.8$ nm, 1 mW power on the samples) and computer-controlled lock-in amplifier (SR830 DSP, Stanford Research Systems) coupled with a photodiode. The UV continuous light source was a LED ($\lambda = 375$ nm). The UV light intensity on the sample was fixed at ~ 3 mW/cm² and kept the same by all the measurements in this work.

The voltage-dependent transmittance of EPH-doped ANPs/7CB nanocomposite films were measured at 1 kHz frequency of the electric field applied on the films and with laser beam chopped at 90 Hz. The EO modulation characteristics of the films (the frequency spectra of the amplitude of the EO modulation of the laser beam passed through the films) were obtained in the range 1 Hz – 3 kHz at a fixed voltage of the electric field. In all cases, no polarizers were used. During the experiments, the temperature of the studied nanocomposite films was about 27° C.

3. Results and Discussion

Figure 1 reports UV-visible absorption spectra recorded for the EPH-doped aerosil/7CB nanogel samples we have prepared. The spectra show the absorbance change by variation of EPH concentration from 1 wt.% to 10 wt.%. The broad spectral band between 330 nm and 400 nm specific for EPH compound [13] (in fact, $\pi - \pi^*$ absorption band of the *trans*-azobenzenes at around 370 nm) is clearly seen. This implies that an efficient photoisomerization of EPH azo-molecules can occur by illumination with UV light at the wavelength of 375 nm that falls at the absorption band of EPH compound.

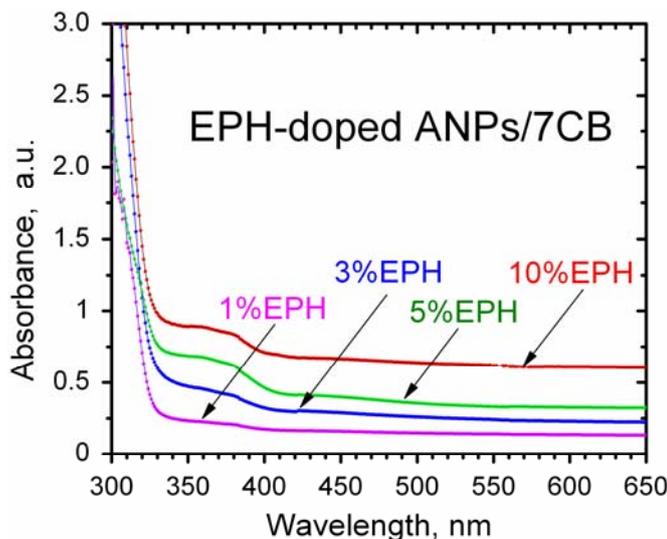


Figure 1. UV-Vis absorption spectra of ANPs/7CB nanocomposite films doped with azobenzene LC EPH molecules at various concentrations (denoted for each curve). All spectra were recorded under identical experimental conditions; the films were in cells assembled from quartz plates.

It should be noted that the shift of the baseline position of the spectra in figure 1 on the ordinate scale by increasing EPH concentration is mainly due to the increasing optical loss of EPH-doped aerosil/7CB films. This is resulting from strong light scattering (both specular and diffuse) by the films that takes place in the whole spectral range measured here. The light scattering problem has to be taken into consideration in the nematic state. Because of this, the optical transmission technique in our case provides qualitative results and actually the measured spectra may not represent the real absorption of the LC mixtures under study. Nevertheless, the effect from the azo-dopants is well distinguished.

It is well known that the strong light scattering by such a kind of nano-filled nematics is due to the formed gel structure [10,14,15]. Accordingly, the EO response of the examined three-component nanocomposites is determined from the gel network of nanoaerosil within the nematics, i.e. their EO response is directly related to the dispersed ANPs and their concentration. However, as seen from figure 1 the EPH dopants also strongly contribute to the light scattering even with no electric field applied on the films. Moreover, one can expect that the EPH doping does significantly change the structure of ANPs/7CB/EPH system where the azobenzene EPH molecules decorate the gel network of the nanostructured nematic.

By applying AC electric field, the nano(aerosil)-filled nematics scatter light due to electrically-controllable local inhomogeneities (ANPs-generated orientational defects in anisotropic LC matrix; the orientation of LC molecules in electric field leads to a disappearing the defects). By that, the electrically-induced changes do result from the electrically-driven reorientation of the LC molecules [11]. On the other hand, being exposed on UV light the ANPs/7CB/EPH nematic system should undergo changes due to *trans-to-cis* photoisomerization of azobenzene EPH LC molecules, i.e., from rod-shaped to bent-shaped conformation [12].

Figure 2 shows the light transmittance of ANPs/7CB/EPH films as a function of the applied AC electric field. The curves were obtained either without or with illumination of the films with UV light at 375 nm. For the sake of comparison, the voltage-dependent characteristics of the films doped with EPH at various concentrations were recorded keeping a constant intensity of the UV light. In general, the transparency of the ANPs/7CB films should be increased by the increase of the applied AC electric field [11].

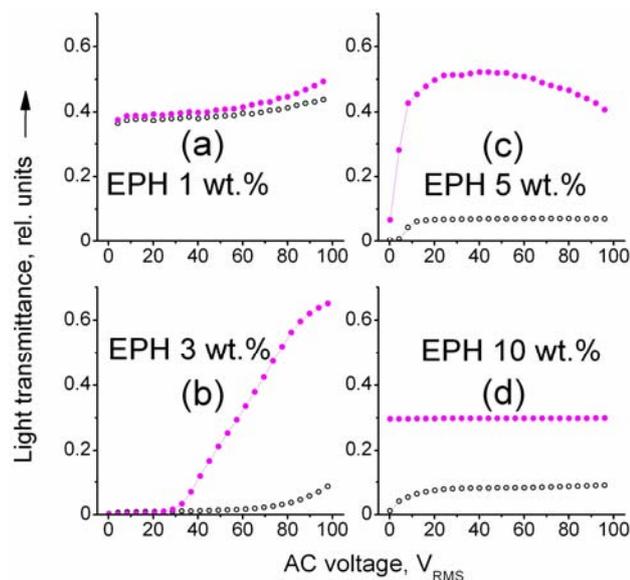


Figure 2. Voltage-dependent transmittance (at $\lambda = 633$ nm) of ANPs/7CB nanocomposite films doped with EPH at various concentration. All samples were in identical cells. Data obtained at a fixed UV-light intensity and under identical other experimental conditions. No UV light (open circles); with UV light (solid circles).

As seen from figure 2, the UV-light-induced changes of the EO response of the studied EPH-doped ANPs/7CB films are rather different as depending on the EPH concentration. So, instead of the smeared behavior of monotonic increase of light transmittance of the films at the lowest concentration (1 wt.%) of EPH we have used here (figure 2 a), a dependence with a well pronounced threshold of the electric field as well as an initiation of saturation of the film transparency, were present at the EPH concentration of 3 wt.% (figure 2 b). By increasing concentration of the EPH dopants (e.g., above 5 wt.%), a further UV-light-produced reduction of the voltage threshold takes place (figure 2 c). At higher concentration of EPH dopants, e.g., for the nanogel sample doped with 10 wt.% EPH, the voltage-dependent transmittance becomes threshold-less (figure 2 d), obviously because the sample is passed over its isotropic state at the given temperature (in our case 27° C). We have to point out that all the behaviors seen in figure 2 were consistent with our observations by optical microscopy of the samples.

Clearly, the observed UV-light-stimulated effect occurs due to *trans-to-cis* photoisomerization of azobenzene EPH LC molecules [13, 16-18] and is closely related to the UV-light-induced local Freedericksz transition of the examined nematic systems, as well as to their possible UV-light-induced transition to isotropic state at a given temperature. Furthermore, the observed UV-light-stimulated lowering of the threshold voltage of the local Freedericksz transition in the ANPs/7CB/EPH system can be attributed to an UV-light-induced increase of the characteristic size (δ_B) of the local bulk domains that undergo Freedericksz transition in this nano(aerosil)-filled nematic. Reasonably, the higher concentration of the EPH dopants that decorate the gel network, the larger δ_B .

In general, the enlargement of δ_B with the amount of EPH can be the reason for the changes observed in the amplitude-frequency EO modulation characteristics of the studied ANPs/7CB/EPH nanocomposite films by varying the EPH concentration. As an example, figure 3 compares the frequency spectra of second-harmonic (SH) modulation of light transmitted through such films doped with EPH at concentration 1 wt.%, 3 wt.% or 5 wt.%. The spectrum of SH amplitude-frequency EO modulation is relevant to the amplitude of the dielectric oscillations versus the field frequency, as measured for the LC films. These frequency characteristics were recorded without UV illumination, at a high intensity of the electric field applied (AC voltage of 100 V). As explained in [11], upon such electric-field strength the SH EO behaviors can be sensitive to the size of the bulk domains. It is seen from figure 3 that the larger the concentration of EPH dopants, the larger the slope of the SH EO modulation spectra. In accordance with [11], the results reported in figure 3 evidence the enlargement of the size δ_B of the active structural domains in the studied ANPs/7CB/EPH nanostructured nematic gel that scatter and modulate light. Note that these bulk domains are still smaller than those in pure (non-nanostructured and undoped) 7CB nematic LC. In the latter case, the slope of SH EO modulation spectra follows the reciprocal dependence on the field frequency [11].

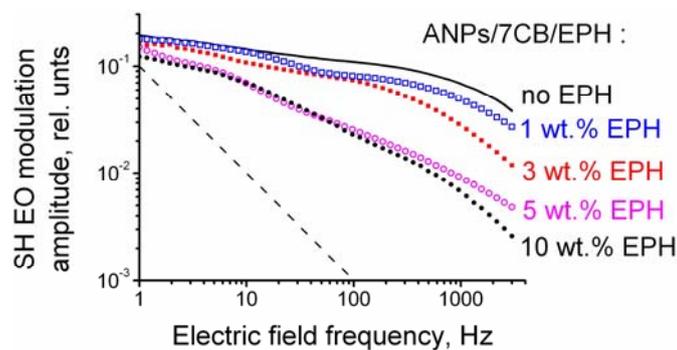


Figure 3. Frequency spectra of the amplitude of SH EO modulation of He-Ne laser beam transmitted through ANPs/7CB gel films doped with EPH at various concentrations. Data obtained by keeping the other experimental conditions the same; the driving AC voltage was 100 V_{RMS}. The dashed line represents the corresponding behavior relevant to pure 7CB nematic LC.

Figure 4 reports the UV light-induced change of SH EO modulation by ANPs/7CB films doped with EPH at various concentrations. For the sake of comparison, the spectra were scaled in identical manner. Again, the AC voltage applied on the films was fixed at 100 V_{RMS}, a voltage at which the UV-induced effect on the SH EO modulation behavior should be well pronounced. It is seen that even at the relatively low (1 wt.%) concentration of the azobenzene EPH dopants, the *trans*-to-*cis* photoisomerization of EPH is sufficient to photo-stimulate the electro-optics of EPH-doped ANPs/7CB films and to efficiently modify the SH EO modulation of intensity of the light transmitted through them. The illumination with UV light can considerably change both the amplitude of SH EO modulation and the slope of the SH EO modulation spectra of the films. Thus, the UV-light-modified SH EO modulation can become rather different than that achieved by the non-illuminated films. As seen, the UV-light-produced changes are enhanced at higher EPH-concentration (figure 4 c,d).

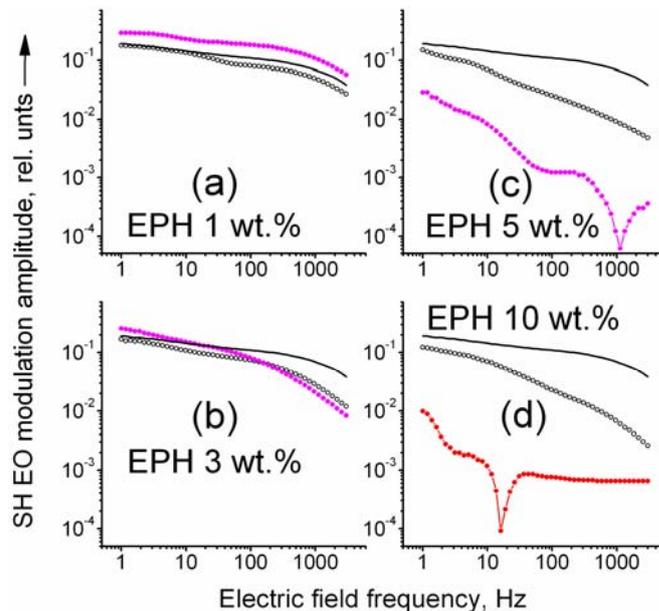


Figure 4. UV light-induced change of SH EO modulation response of ANPs/7CB/EPH films. The EPH concentration: 1 wt.% (a); 3 wt.% (b); 5 wt.% (c); 10 wt.% (d). The spectra were recorded either with (solid circles) or without (open circles) UV illumination (at the same level of the UV-light intensity as in the course of the experiments described above) by keeping the other experimental conditions identical; the driving AC voltage was 100 V_{RMS}. SH EO modulation spectrum achieved by undoped ANPs/7CB film is included as a reference (shown with lines).

Thus, at the presently used UV light intensity level, the UV illumination can increase the amplitude of SH EO modulation by the films doped with a small amount of azo-molecules (in our case, 1 wt.% of EPH, or at 3 wt.% of EPH - with a diminishing effect), or reduce the SH EO modulation amplitude (at 5 wt.% or 10 wt.% of EPH), as compared to the non-illuminated case. The UV-light-induced decrease of the SH EO modulation with increasing EPH concentration can be attributed to UV-light-produced enlargement of the bulk domains whose field-driven dielectric reorientation is heavily retarded. As a side effect, frequency dips can appear in the SH EO modulation spectra when the EPH concentration is high. Similar to the sharp single minima in the SH EO modulation spectra found for micro-confined nematic-based composites, such as micro-scaled polymer-dispersed LCs [19], the above mentioned dips upon UV illumination suggest that a strong scattering of light occurs at a given electric-field frequency, corresponding to a spatio-dielectro-optic coupling with the field-induced nematic director orientation deformations relevant to large-sized domains formed in the bulk of the UV-illuminated EPH-doped ANPs/7CB films.

It should be noted that at a low EPH-concentrations (like 1 wt.% and 3 wt.% in our experiments) an illumination with a blue light with intensity of about 30 mW/cm² restores the initial state of the films, i.e. SH EO modulation becomes close to that of the films non-exposed to UV light. This effect follows the back (*cis*-to-*trans*) transition of azobenzene molecules [20-22] after absorption of light in the blue spectral range ($n-\pi^*$ absorption band of the *cis*-azobenzenes at around 450 nm). In contrast, at higher EPH concentration the intensity of the continuous UV illumination at ~ 3 mW/cm² used here led to a change of the ANPs/7CB/EPH system that can not be restored by the same blue-light illumination. In our experiments this was clearly registered for EPH dopants at concentrations of 5 wt.% and 10 wt.%. Most probably, this is owing to UV-light-provoked formation of strongly-meshed agglomerate-like creatures-domains in the bulk of the azo-doped nano(aerosil)-filled nematic system under study.

4. Conclusion

We have studied the concentration effect of the of azobenzene photoactive molecules added to nano(aerosil)-filled nematic system, in particular EPH-photo-sensitized ANPs/7CB films, on the photo-driven stimulation of the electro-optics of such nanocomposite materials. It is demonstrated that at the relatively low-intensity (~ 3 mW/cm²) continuous UV light, the UV-produced effect on both the EO transmittance and the SH EO modulation by 25 μ m-thick EPH-doped ANPs/7CB films is well pronounced even at the relatively low (1 wt.%) concentration of the azobenzene EPH dopants. The UV-light-induced stimulation occurs due to *trans*-to-*cis* photoisomerization of EPH molecules that decorate the gel network of the nanostructured nematic and is enhanced at higher concentration of the EPH photoactive agent. Both factors (the optical density and the intensity of the activating UV light) should be considered and carefully balanced for proper photo-stimulated reversible function of the photoresponsive nematic nanocomposites such as the three-component system studied here. This balance is of importance for the practical application of the observed UV-stimulation effect in regular or specific scatter-based electro-optics of nematic LC systems doped with azo molecules.

Acknowledgments

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