

# Photoresponsive azo-doped aerosil/7CB nematic liquid-crystalline nanocomposite films: the role of polyimide alignment layers of the films

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**Abstract.** We studied thin films (25  $\mu\text{m}$ -thick) of nanomaterials composed from 3 wt.% aerosil nanospheres and the room-temperature nematic liquid crystal 4-*n*-heptyl cyanobiphenyl (7CB). The inclusion of 3 wt.% of the photoactive liquid crystal 4-(4'-ethoxyphenylazo)phenyl hexanoate (EPH) in the aerosil/7CB nanostructured nematics make them photoresponsive. The films had alignment layers from rubbed polyimide (PI). Our study is concentrated on the inspection of the PI-role for the photo-stimulated electro-optical properties of the considered EPH-doped aerosil/7CB nanocomposite films.

## 1. Introduction

Relatively recently, the research on the liquid-crystal (LC)-silica composites has demonstrated that such materials have a potential for a number of optical, electro-optical (EO) and electric applications [1]. The mechanism of light scattering of these nanostructured materials has been well established (see e.g., [2]). In particular, LC-aerosil systems have been extensively investigated [3-8]. The aerosil nanoparticles are silica nanoscale spheres whose surfaces are decorated to achieve hydrophilic or hydrophobic interactions.

Recently, we have studied the scatter-based electro-optics of nanocomposites formed from 3 wt.% hydrophilic aerosil nanospheres ( $\sim 7$  nm size) within the nematic LC 4-*n*-heptyl cyanobiphenyl (7CB) [9]. Further, the ultraviolet (UV) light-modified EO response of the aerosil/7CB nanofilled nematic doped with 4-(4'-ethoxyphenylazo)phenyl hexanoate (EPH) azo-molecules was reported [10]. In the work presented here, our aim is to be inspected the role of the rubbed polyimide (PI) alignment layers for the photo-stimulated EO response of EPH-doped aerosil/7CB films, in particular films with a thickness of 25  $\mu\text{m}$ . The LC alignment by thin layers of a PI is a most common way for inducing a homogeneous (planar) alignment of the LC molecules at the interfaces, and the alignment effect of PI layers on the optical films is widely exploited for a long time in organic electronics and LC devices for use in photonics products and displays [11-13]. The rubbed PI alignment layers serve to align LC molecules in a certain orientation and conformation with a specific pretilt angle (the angle between the

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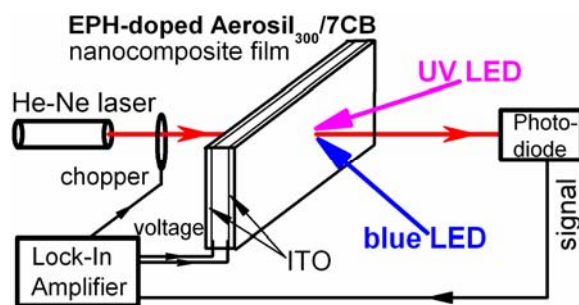
director of the LC molecules and the PI alignment layer). To a great extent, the pretilt angle determines the EO performance of the LC devices.

We have focused our study on the voltage-dependent optical transmittance (the static EO behavior) of visible light passed through the EPH-doped aerosil/7CB nanocomposite films, being under AC electric field and exposed to illumination with continuous light sources. The transmittance of such films with alignment PI layers was compared to the corresponding characteristics of the same nanocomposite films (either EPH-doped or undoped) but without PI layers, and the effect from the PI layers was elucidated by electrical and EO measurements.

## 2. Experimental

Nanospheres of hydrophilic Aerosil 300 having a diameter of  $\sim 7$  nm and capped with silanol groups) at a concentration of 3 wt.% were dispersed in the well known room-temperature nematic LC 4'-heptyl-4-biphenylcarbonitrile (7CB). The preparation of Aerosil<sub>300</sub>/7CB nanocomposite films has been described in details elsewhere [9]. The azo-containing LC compound 4-(4'-ethoxy phenylazo)phenyl hexanoate (EPH) [14] was added to the formed nanocomposite at a concentration of 3 wt.%. Thin films (with a thickness of 25  $\mu\text{m}$ ) of EPH-doped Aerosil<sub>300</sub>/7CB gel were sandwiched between a pair of indium tin oxide (ITO) conducting glass plates. The ultrathin transparent ITO layers on the glass plates were overcoated with a thin layer of polyimide (PI) (namely, PI-2555 from HD Microsystems, USA) having unidirectional mechanical rubbing. The orientation directions of the two PI-layered substrates of the cells were antiparallel. Identical planar cells with PI layers overcoating the ITO glasses, but filled with undoped Aerosil<sub>300</sub>/7CB, were also prepared in order to be used for reference measurements in our study. For the same purpose, the same two-component composite of undoped Aerosil<sub>300</sub>/7CB, as well as the above mentioned Aerosil<sub>300</sub>/7CB/EPH three-component nanocomposite were filled in cells with the same thickness of 25  $\mu\text{m}$  but without PI alignment layers (i.e., with ITO glasses only).

The experimental set up has been described in details elsewhere [15]. Briefly, the EO response of EPH-doped Aerosil<sub>300</sub>/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 (wavelength 375 nm). The UV light intensity on the samples was fixed at  $\sim 3$  mW/cm<sup>2</sup> and kept the same during all the measurements in this work. The same applies to the light in the blue spectral range (wavelength 450 nm, from another LED whose intensity on the samples was  $\sim 30$  mW/cm<sup>2</sup>, sufficient to restore the initial state of the samples).



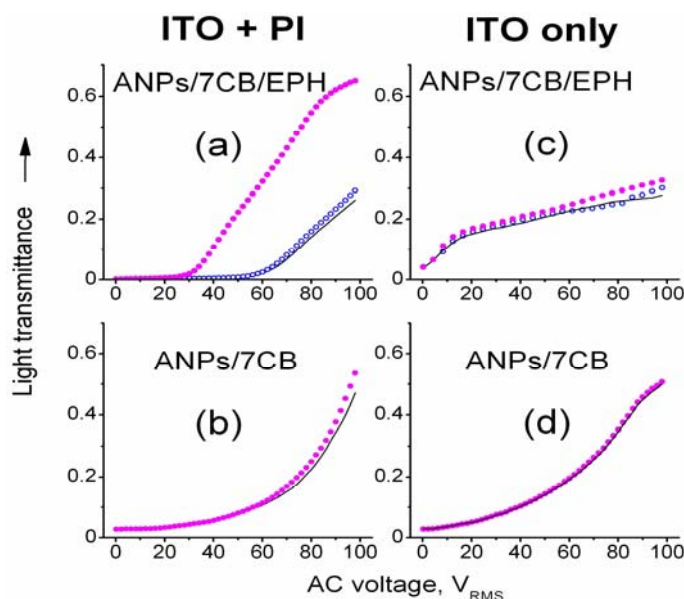
**Figure 1.** Schema of the optical setup used here.

The optical setup is schematically shown in figure 1. The voltage-dependent transmittance of EPH-doped Aerosil<sub>300</sub>/7CB nanocomposite films was measured at 1 kHz frequency of the electric field applied to the films and with He-Ne laser beam chopped at 90 Hz. No polarizers were used. By AC electric field transversally applied to the LC cells, the frequency dependent current through the nanocomposite films was measured by the lock-in instrument sweeping the frequency in the range

from 1 Hz to 3 kHz at a fixed voltage of the electric field. During all the experiments, the temperature of the studied nanocomposite films was about 26° C.

### 3. Results and Discussion

Like the dispersion of 3 wt.% Aerosil<sub>300</sub> in 7CB [9, 16], the prepared 3 wt.% Aerosil<sub>300</sub>/7CB doped with 3 wt.% EPH is also a soft gel nematic material. In the gel state of the filled nematics, an irregular network of hydrogen-bonded aerosil nanoparticles is formed that defines the geometrical confinement and the material properties, respectively. The inclusion of azo-bonded EPH mesogen makes possible to realize an efficient stimulation of the AC electric field-driven optical transmittance of EPH-doped Aerosil<sub>300</sub>/7CB nanocomposite films [10]. In particular, this effect can be achieved by continuous illumination with relatively low-intensity UV light at the wavelength of 375 nm that coincides with the wavelength peak position of *trans-cis* absorption band of EPH compound [14]. In this case, the UV light-induced effect on the electro-optics of EPH-doped Aerosil<sub>300</sub>/7CB occurs through *trans-to-cis* photoisomerization of EPH azo-bonded molecules (the transformation from rod-shaped *trans* isomers to bent-shaped *cis* isomers) [14,17-19]. The photoisomerization is reversible by employing continuous blue-light illumination. The latter leads to *cis-to-trans* photoisomerization of EPH that restores the initial state of the azo-molecules, and thereby the initial state of the EPH-doped Aerosil<sub>300</sub>/7CB nematic system. The common mechanism of *trans-cis-trans* conversion by azobenzene molecules is well known, e.g., [20-22].



**Figure 2.** Voltage-dependent transmittance of: (a) EPH-doped Aerosil<sub>300</sub>/7CB and (b) net Aerosil<sub>300</sub>/7CB, both in identical cells with PI and ITO layers. The second couple: (c) EPH-doped Aerosil<sub>300</sub>/7CB and (d) net Aerosil<sub>300</sub>/7CB, both in identical cells without PI alignment layers (ITO glasses only). Data obtained by use of He-Ne laser beam, under identical experimental conditions. No UV light (lines); by exposure on UV light (solid circles) and by subsequent illumination with blue light (open circles).

Figure 2 summarizes the voltage-dependent light transmittance curves measured for the four kinds of samples we have prepared. The light intensity changes were fully consistent with our observations by optical microscopy. The transmittance curves in figure 2 were obtained either without or with illumination of the films with UV light at the wavelength of 375 nm. For the sake of comparison, the voltage-dependent characteristics of all the examined films were recorded keeping a constant intensity

of the UV light. Also in order to be compared, the behaviors were measured in a way that equally scales the levels of transmittance of the four samples.

The voltage-induced increase of the transparency of Aerosil<sub>300</sub>/7CB films by increase of the applied AC electric field has been demonstrated and the electrically-controllable scatter-based mechanism of voltage-dependent light transmittance of this nematic gel material has been discussed in details in [9]. Basically, the same physical mechanism takes place for the Aerosil<sub>300</sub>/7CB/EPH gel films. This mechanism is governed by the aerosil network formed within these nanofilled nematic systems, but it is strongly influenced by EPH azo-molecules that decorate the network. In particular, the EPH LC molecules can be bond with the network nanostructures, and thereby create larger structures. This reflects in the very distinct threshold voltage of the local Freedericksz transition observed for Aerosil<sub>300</sub>/7CB/EPH (figure 2 a) in contrast to the smeared one for the net Aerosil<sub>300</sub>/7CB (figure 2 b). Clearly, the large reduction of the threshold voltage of the local Freedericksz transition in Aerosil<sub>300</sub>/7CB/EPH nematic films upon UV illumination ultimately occurs through the *cis*-isomers of the EPH molecules. The bent-shaped EPH *cis*-isomers formed by UV irradiation can additionally enhance the disorder in the photosensitive Aerosil<sub>300</sub>/7CB/EPH nanocomposites studied here. The disorder is intrinsic to the non-photosensitive Aerosil<sub>300</sub>/7CB dispersion [9,16], like similar aerosil-disordered LCs [1-5,23-25].

As seen from figure 2, a well pronounced UV light-produced stimulation (an increase of the film transparency at a given voltage, in fact a large shift of the voltage-transmittance behavior to the lower values) occurs only for EPH-doped Aerosil<sub>300</sub>/7CB films in cells having PI alignment layers (figure 2 a). The contrast to the same azo-doped nanocomposites formed in counterparts of cells with no PI (figure 2 c) indicates the paramount importance of the PI alignment layers for the UV light-induced effect.

There are two impacts of the PI layers. The first is the LC alignment through the rubbing of the PI layers. In thin films of pure 7CB nematic, the orienting relief formed by the groove pattern on the surface of the parallel-rubbed PI layers of the LC cells should totally align the nematic 7CB. In spite of the parallel-rubbed PI layers, in Aerosil<sub>300</sub>/7CB nanocomposite films the aerosil network prevents the alignment in volume, where, actually, a lot of pretilt variations are possible. By that, some alignment of this nanostructured nematic occurs only in a small region close to the PI surface. It should be noted that in EPH-doped Aerosil<sub>300</sub>/7CB nematic films with parallel-rubbed PI layers the azo-bonded EPH LC molecules can support the alignment of the 7CB LC molecules. In this case, the role of the azo-molecules is to transpose the LC alignment in the bulk of the system structure. Upon UV light, most probably the bent-shaped *cis*-isomers of the azo-molecules modify the anchoring in the nanoscale vicinity of the network nanostructure.

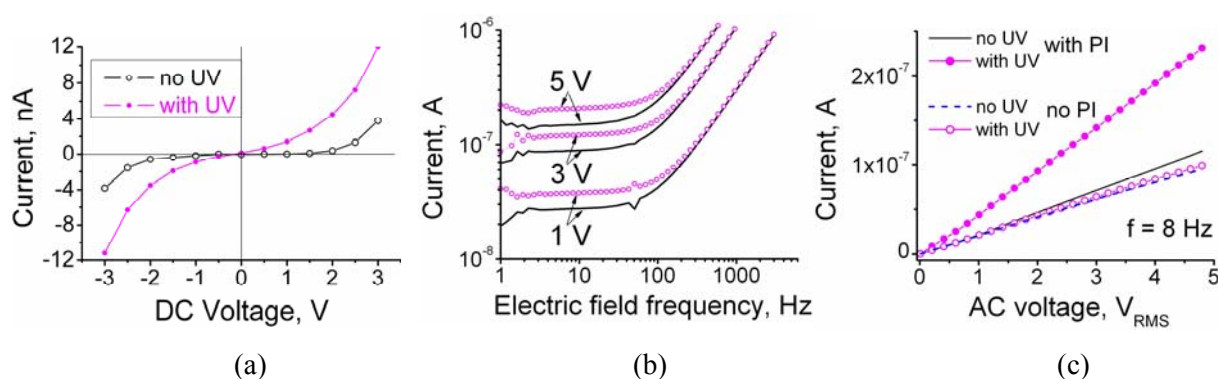
The second impact of the PI layers is the generation of free charge carriers by the PI polymer subjected to UV light. The creation of net negative charges in the PI alignment layers of LCs (at the PI surface and inside in the bulk of LCs) by UV exposure, as well as the surface modification of the PI alignment layers by UV illumination (changes in the surface composition and in the pretilt angle of the PI surface), are known for a long time, e.g., [26,27]. For instance, a broadband UV irradiation an average power density of 4.5 mW/cm<sup>2</sup> (comparable to the intensity level of ~ 3 mW/cm<sup>2</sup> of the UV light we have presently employed here) has been used in [26] to be altered the pretilt angle of PI alignment layers for nematic LC, and thereby to change the interaction between the nematic LC and PI alignment layers (in particular, PI-2555). Indeed, the exposure of the UV light on the PI layer was found to change drastically the surface morphology and anisotropy due to photochemical dissociation, bond breaking and subsequent oxidation reactions [26,28].

In our experiment, the relative low UV-light intensity did not lead to irreversible surface modifications and direct photoalignment effect, but most probably is enough to (slightly) change the anchoring conditions close to the PI surfaces, as well as in the bulk of the nanostructured nematic system. The space charge generated via the PI layers that overcoat the ITO layers of the LC cell plates can assist the modification of LC anchoring conditions. Besides the diffusion of the photo-produced charges in the sample [29] and their subsequent migration or trapping in various pathways, the charges

created from the PI layers can give rise of photo-induced surface polarization that can lead to some changes of the nematic LC anchoring, an effect reported in a number of studies on PI-LC interface subjected to UV light, where the alignment mechanism of LCs by PI-layers on various substrates and the nature of surface modification have been elucidated [12,27,30,31]. Actually, the light-induced charge will not only modify the PI-LC interaction, but may also increase the direct current (DC) offset voltage generated in a planar LC cell aligned with PI layers [32]. Upon AC electric field, the trapping sites generated during UV illumination could trap the carriers and generate an additional DC offset voltage shift. The static electricity by rubbing PI is well known (e.g., [33]).

To address the situation with possible electrical charging effects in the studied nanocomposite nematic gels, complementary electrical measurements were performed. By the examined Aerosil<sub>300</sub>/7CB/EPH films having rubbed PI layers, the measurements evidence a sizable UV light-induced generation of charge (the results are given below). This effect is most efficient at DC or low-frequency AC field (e.g., below 100 Hz). Thus, under such conditions, an UV-induced weak effect of anchoring change due to UV-induced photo-electric effect provoked by the PI layers surely takes place for the Aerosil<sub>300</sub>/7CB nanocomposites studied here (either EPH-doped or undoped). However, this UV-induced effect is much weaker (both at the surface and in the bulk) than the UV-light controlled LC alignment achieved by the change of LC anchoring conditions through the LC azobenzene molecules. The contribution of the latter effect is much more pronounced.

At this point comes the question about the UV light-induced effect on the AC field-driven light transmittance still observed (especially pronounced at higher AC voltage) in EPH-undoped Aerosil<sub>300</sub>/7CB in LC cells having orienting PI layers (figure 2 b). In fact, this effect on the EO response was very weak in comparison with EPH-doped Aerosil<sub>300</sub>/7CB (figure 2 a), but well reproducible, too. The optical microscopy displayed no sizable UV-produced morphology changes in this case, in contrast to photo-sensitized Aerosil<sub>300</sub>/7CB/EPH in identical LC cells (with PI) at equal values of the applied AC voltage. The same applies to the same (non-sensitive to UV light at 375 nm) undoped Aerosil<sub>300</sub>/7CB gel, but in LC cells with no PI layers. Note, that in the latter case no UV light-induced effect on the EO response of the films was detected (figure 2 d). In the context of the discussion above, the UV light-induced effect on the electro-optics of undoped Aerosil<sub>300</sub>/7CB in LC cells having orienting PI layers (figure 2 b) can be ascribed to an affect from alignment of this nanostructured nematic in a region close to the PI surface, or can originate in the local field change owing to free charge carriers generated by the PI-coating of the LC walls when exposed to UV light.



**Figure 3.** (a) DC current-voltage dependence measured for EPH-doped Aerosil<sub>300</sub>/7CB nanocomposite film; (b) The frequency dependence of amplitude of the alternating current in EPH-doped Aerosil<sub>300</sub>/7CB nanocomposite film. The spectra were obtained under identical experimental conditions. Pairs measured with no UV light (lines) and with UV light (circles), by applying AC voltages of 1 V, 3 V and 5 V (RMS); (c) AC current-voltage dependences measured for EPH-doped Aerosil<sub>300</sub>/7CB in cells: (i) with PI coatings; (ii) with no PI coatings (ITO glasses only), under identical other experimental conditions. The frequency of the AC electric field applied on the cells was 8 Hz. Pairs measured with no UV light (lines) and with UV light (circles).

The generation of an excess free carriers due to UV illumination of the examined Aerosil<sub>300</sub>/7CB/EPH nanocomposite films can be evidenced by electrical measurements upon static (DC) or dynamic (AC) field in the low-voltage regime. By that, a transversal electric-field configuration was used, through the ITO electrodes of the examined cells. The symmetric DC current-voltage ( $I$ - $V$ ) characteristics curve measured for the films (figure 3 a) displays a non-Ohmic behavior of increasing current by increasing voltage. Further, this behaviour gives an indication of very low leakage current and enhanced DC conductivity of the films being illuminated with UV light (under the experimental conditions of our measurements discussed above).

Figure 3(b) reports the frequency dependence of the alternating current by varying the strength of the AC electric field applied on the same EPH-doped Aerosil<sub>300</sub>/7CB film under the same other experimental conditions. As seen, a well pronounced UV light-induced effect occurs for the current at relatively low frequency ( $f < 100$  Hz) where the Ohmic component is predominant. At higher frequency, the capacitance component prevails. In this case, the increase of the current is due to reduction of the resistance of the nematic system (decrease of both real and imaginary part of the complex impedance, as we have further verified by means of impedance spectroscopy).

Figure 3(c) compares the  $I$ - $V$  behaviors obtained at a low-frequency (8 Hz) AC field (in order to exploit the pure Ohmic effect) for the same EPH-doped Aerosil<sub>300</sub>/7CB nanogel in two cells of identical thickness, but either with PI or without PI layers (ITO only), both measured either without and with UV light illumination, under identical other experimental conditions. As seen, the examined films exhibit linear  $I$ - $V$  dependence (Ohmic conductance). It should be noted that at 8 Hz the linear  $I$ - $V$  dependence holds up to 100 V<sub>RMS</sub>. Under the present level of the UV light intensity, there is a significant difference for the UV-induced increase factor of the AC conductivity ( $\Delta\sigma_{UV}$ ) measured from the  $I$ - $V$  behaviors of both samples. An important result is that  $\Delta\sigma_{UV}$  is larger ( $\sim 2$ ) for EPH-doped Aerosil<sub>300</sub>/7CB films with PI layers than that measured for the same nanocomposite films with ITO glasses only (figure 3 c, pairs (i) and (ii), respectively). Indeed, in the latter case  $\Delta\sigma_{UV}$  was negligible (1.04 – 1.05) - a detectable change but hardly discernible within the experiment uncertainty. This significant difference is strongly indicative of the generation of free carriers in our EPH-doped Aerosil<sub>300</sub>/7CB nanogel through the impinged PI layer after absorption of the UV light energy.

#### 4. Conclusion

For EPH-photo-sensitized Aerosil<sub>300</sub>/7CB nanocomposite films studied here, the surface orienting effect of unidirectional rubbed PI alignment layers is of paramount importance for the UV photo-driven stimulation of their electro-optics. The large UV light-induced change in the transparency of 3 wt.% nano(aerosil)-filled nematic doped with 3 wt.% azobenzene photoactive molecules (in our case EPH, a mesogen itself) is closely related to the alignment owing to the rubbed PI layers. In our Aerosil<sub>300</sub>/7CB nanocomposite films in planarly-orienting cells, the *cis*-isomers formed by UV irradiation modify the LC anchoring conditions. An UV light-induced change of anchoring conditions due to space charge generation by the PI layers (close to the PI surfaces) is also possible to contribute to the UV-light-modified electro-optics of such photoresponsive nematic systems, but the role of this mechanism is much less.

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