

Photo-controllable electro-optics of aerosil/7CB nanocomposite nematic doped with azo-bonded molecules

Y G Marinov^{1,*}, G B Hadjichristov¹, A G Petrov¹ and S Krishna Prasad²

¹ Georgi Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences,
72 Tzarigradsko chaussee, Sofia 1784, Bulgaria

² Centre for Nano and Soft Matter Sciences, Jalahalli, Bangalore 560 013, India

E-mail: ymarinov@issp.bas.bg

Abstract. We demonstrate that the electro-optics of nanostructured nematic liquid crystal (LC) doped with a small amount of photoactive LC molecules can be efficiently controlled by light. In particular, the inclusion of 3 wt.% azobenzene LC 4-(4'-ethoxyphenylazo)phenyl hexanoate (EPH) into a gel nanocomposite material produced from nematic LC heptylcyanobiphenyl (7CB) and 3 wt.% hydrophilic silica nanoparticles of size ca. 7 nm (Aerosil 300) allows both the static (the transmittance versus the voltage) and the dynamic (amplitude-frequency electro-optic modulation) characteristics of thin films (25 μm) of such a complex LC system in an alternating-current electric field to be enhanced by UV light at a wavelength of 375 nm. This photo-effect that is reversed with white light is based on the photo-isomerization of the doped azobenzene molecules. The efficient photo control makes the considered EPH-doped Aerosil/7CB photo-responsive nematic nanocomposites attractive for specific electro-optic applications.

1. Introduction

Nanostructured materials with unique physical properties obtained by the doping of liquid crystals (LCs) with nanoparticles (NPs) have recently attracted much attention [1-4]. The significance of such promising nanocomposite materials comes from the fact that they can provide an improvement of LC device performance by the development of new switching modes and tuning the physical properties of the LC materials [5-7]. Since in most cases the NPs-induced effects are due to their special physical properties such as ferroelectric, magnetic or anisotropic shapes, it is of special interest to investigate dispersions of spherical NPs with no special properties, in particular, quartz nanospheres – aerosil NPs (ANPs) having a diameter of about 7 – 10 nm dispersed in LCs. The confined geometry leads to the introduction of disorder in such heterogeneous nanostructured LC systems [1,7-12]. By varying the concentration of such filled nematics, the random disorder can be created *in situ* [13,14]. Very recently, we have studied the electro-optics of thin (25 μm) films of gel nanocomposites produced from nematic LC heptylcyanobiphenyl (7CB) and 3 wt.% ANPs [15].

On the other hand, it is of a great practical interest to make the nanostructured materials photo-responsive. A simple way for this is to dope them with photoactive agents. Good candidates can be the azo-containing compounds that possess an efficient *trans-cis* photoisomerism. For instance, azobenzene-doped nematics exhibit a photo-induced response [16,17] useful for a variety of

* To whom any correspondence should be addressed.



applications [18-21]. Recently, we have investigated photo-induced effects in guest-host systems composed of a nematic LC (as a host) and a photoactive azobenzene-containing LC compound (as a guest) [22-24].

Here, we present an experimental study of the electro-optics of ANPs/7CB films (25 μm thick, 3 wt.% hydrophilic ANPs) doped with 3 wt.% azobenzene LC 4-(4'-ethoxyphenylazo)phenyl hexanoate (abbreviated hereafter as EPH). Our research is focused mainly on the photo-stimulation of the electro-optics of such photoactive nematic nanocomposite materials, relevant to their practical applicability.

2. Experimental

The preparation of EPH-doped ANPs/7CB nanocomposite films was similar to that described in [15]. Hydrophilic ANPs (Aerosil 300 nanospheres having a diameter of ~ 7 nm and capped with silanol groups) at a concentration of 3 wt.% were added to LC 7CB mixed with 3 wt.% LC EPH. EPH-doped ANPs/7CB films with a thickness of 25 μm were formed in cells assembled from two glass plates, to serve as electrodes, each coated inside by ultrathin transparent conductive layers of indium tin oxide (ITO) overcoated with a polyimide layer with a unidirectional rubbing. The cells were assembled with antiparallel orientation directions of the two substrates.

The experimental set up and the measurement configuration have been described in our previous paper [24]. The electro-optical response of EPH-doped ANPs/7CB films to an alternating-current (AC) electric field was investigated by use of an unpolarized laser diode (wavelength $\lambda = 635$ nm, 1 mW power) and computer-controlled lock-in amplifier (SR830, Stanford Research Systems). The intensity of the diode laser beam transmitted through the films (I_{out}) was measured with a photodiode. The transmittance of the films was calculated as $T = I_{out}/I_{in}$, where I_{in} was the intensity of the incoming laser beam. The interval between data acquisitions was equal to 8 s (the same applies to the recording of frequency spectra). The UV continuous light source was a LED ($\lambda = 375$ nm), and the UV light intensity on the sample was ~ 1.5 mW/cm². The measurements were performed at room temperature.

3. Results and Discussion

Figure 1 shows the texture of EPH-doped ANPs/7CB film as viewed by optical microscopy. Separate microscale regions of chaotically disordered texture of the LC containing ANPs agglomerates (cloudy texture) can be seen. The nematic phase of the ANPs/7CB nanocomposite is a weak gel [15] with an irregular and fragile gel network of hydrogen-bonded ANPs [25]. The changes induced by illumination with UV light ($\lambda = 375$ nm) appear as a brightening of the texture. This morphological modification occurs via UV-induced photoisomerization of the doped azobenzene EPH LC, i.e. light-driven molecular conformation change of the EPH molecules (the transition from rod-shaped *trans* isomers to bent-shaped *cis* isomers) [16,17,22-24]. No such textural change was observed in ANPs/7CB nanocomposite under the same experimental conditions and in identical cells but without EPH, i.e. the undoped ANPs/7CB nanocomposite itself was photo-insensitive, as further confirmed by other measurements.

At zero electric field, a strong light scattering by EPH-doped ANPs/7CB nematic films takes place due to their gelly structures. The mechanism of light scattering in filled nematics due to the gel network and aggregation structures is well known (see, e.g., [8]). Applying an AC electric field to the films, the low-density gel state can be electrically driven through the dielectric orientation of the nematic director, so that the light-scattering properties (and thereby, the light transmittance) of the films can be electrically controlled. Reasonably, the voltage-dependent light transmittance of the EPH-doped ANPs/7CB nematic films (figure 2) should follow the reorientation of the 7CB LC molecules. By increasing the electric field, the 7CB molecules are forced to orientate along the field direction due to the positive dielectric anisotropy of 7CB, and at higher fields they tend to the homeotropic alignment. This is why the optical scattering is reduced and the optical transmission of the EPH-doped

ANPs/7CB films is increased by the increasing AC field (like the undoped NPs/7CB nanocomposite gel films [15]).

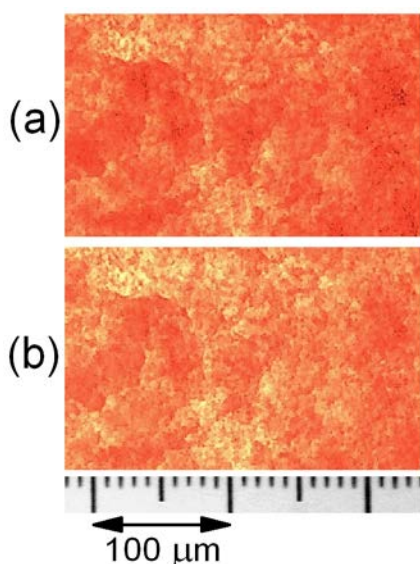


Figure 1. Micrographs of a film of the studied EPH-doped ANPs/7CB nanocomposite gel at an AC voltage of 30 V_{RMS} . No polarizers were used. The frequency of the electric field applied to the film was 300 Hz, and the temperature of the film was 29° C. Pictures taken without (a) or with (b) illumination by UV-LED ($\lambda = 375$ nm).

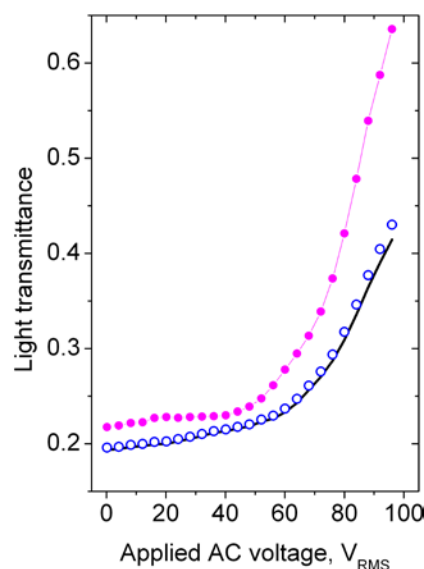


Figure 2. Laser beam ($\lambda = 635$ nm) transmission through EPH-doped ANPs/7CB film measured as a function of AC voltage applied to the film, either without (solid line) and with (solid circles) UV illumination at 375 nm, as well as by subsequent illumination by white light (open circles). The laser beam was chopped at 90 Hz, the frequency of the electric field applied to the film was 300 Hz, and the temperature of the film was 29°C. No polarizers were used.

By using UV light illumination, the transmittance of the considered EPH-doped ANPs/7CB films is enhanced (figure 2). The UV-produced change can be considered as a photo-stimulation of the film transmittance (up to ~ 60 % at 100 V, in the case shown in figure 2), and could have useful practical applications. After the UV illumination, by subsequent white light (from room lighting), the EPH-doped ANPs/7CB system tends to return back to its original state (figure 2, open circles) due to the *cis-to-trans* photoisomerization of the EPH azo-bonded molecules.

Our supplementary tests indicated that the polyimide layers that overcoat the ITO layers of the LC cell glass plates could play a role for the UV-induced change in the light transmittance of the studied EPH-doped ANPs/7CB gel films (the optical, electro-optical and electrical experimental proofs of the UV-induced photo-effect through the polyimide layers will be presented elsewhere). However, in the present case the contribution of the surface and bulk photoisomerization of EPH is considerably stronger, and thereby the UV-induced effect due to photoactive EPH dopants is much more pronounced than the UV-induced effect from the polyimide layers themselves.

The presence of the photoactive agent EPH in the ANPs/7CB nanocomposite films also strongly modifies their electro-optical modulation response which is rather an interesting feature. Thus, the electro-optic modulation characteristics of the azo-doped nanostructured nematic system studied here can be efficiently photo-controlled. As an example, figure 4 shows frequency spectra of the electro-optic modulation of transmitted laser light by EPH-doped ANPs/7CB films at a 100 V AC driving

voltage. The relatively flat and rather extended electro-optical frequency-modulation response of the examined nanocomposite towards the higher frequencies (except for the first harmonic – the modulation at the fundamental frequency) results from the enhanced role of the very small structural domains formed in this nanostructured nematic [15]. The UV-induced modulation changes were reversible (a white-light illumination restores the amplitude-frequency electro-optical response of EPH-doped ANPs/7CB system (figure 4) that is of great importance for the practical application of photo-responsive azo-doped ANPs/7CB nanocomposite films considered here.

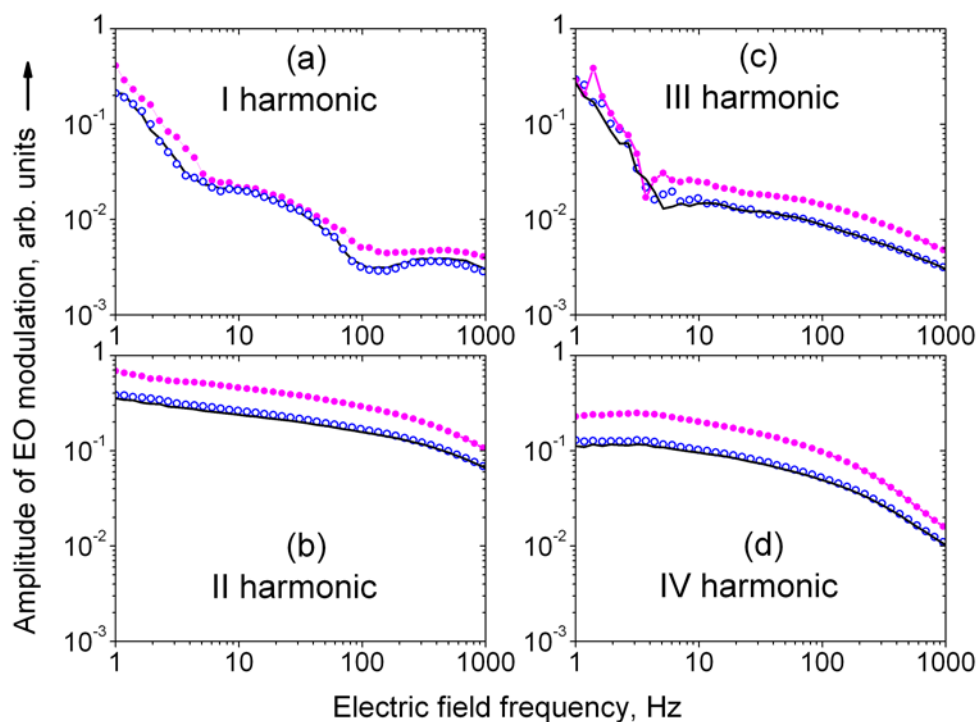


Figure 4. Frequency spectra of the amplitude of electro-optic modulation by EPH-doped ANPs/7CB film measured with a laser beam ($\lambda = 635$ nm) transmitted through the film at a 100 V_{RMS} driving voltage. Data obtained for the first (a); the second (b); the third (c) and the fourth (d) harmonic of the modulated signal versus the applied electric field frequency. No polarizers were used. The temperature of the film was 30° C.

4. Conclusion

We have shown that UV light illumination of aerosil/nematic nanocomposite films doped with photoactive azobenzene (in our case, the LC EPH at concentration of 3 wt.%) can enhance their electro-optical voltage-transmittance behavior and amplitude-frequency electro-optic modulation. Based on the light-driven molecular conformation change of the azo-bonded EPH molecules, the UV-induced stimulation of the electro-optics of EPH-doped aerosil/nematic nanocomposites is reversible (the initial state of the system is restored by white-light illumination). The observed photo-effect and the photo-responsive room-temperature filled nematic considered here could find various photo-controllable electro-optic applications for control and modulation.

Acknowledgments

The authors acknowledge the INERA EU project Research Potential "Research and Innovation Capacity Strengthening of ISSP-BAS in Multifunctional Nanostructures" (FP7 REGPOT-2012-2013-1) support for their participation at the LNN2015 conference. Work supported by the research project DFNI-TO2/18 "Nanostructured liquid crystals for tunable photonic devices" by the Ministry of Education and Science, National Science Fund of Bulgaria. This study was carried out as a part of Indo-Bulgarian joint research project DNTS/In-01/4/2013 "Investigation of photo-stimulation effects in nano-structured liquid crystalline systems" supported by the Department of Science and Technology, New Delhi and the Ministry of Education and Science, National Science Fund of Bulgaria.

References

- [1] Iannacchione G S 2004 *Fluid Phase Equilibria* **222-223** 177
- [2] Zakharov A V and Thoen J 2004 *Phys. Rev. E* **69** 011704
- [3] Cloutier S G, Eakin J N, Guico R S, Sousa M E, Crawford G P and Xu J M 2006 *Phys. Rev. E* **73** 051703
- [4] Prasad S K, Rao D S S and Nair G G 2009 *J. Indian Inst. Sci.* **89** 211
- [5] Ouskova E, Buchnev O, Reshetnyak V, Reznikov Y and Kresse H 2003 *Liq. Cryst.* **30** 1235
- [6] Li F, Buchnev O, Cheon C, Glushchenko A, Reshetnyak V, Reznikov Y, Sluckin T and West J 2006 *Phys. Rev. Lett.* **97** 147801
- [7] Li Q 2012 *Liquid Crystals Beyond Displays: Chemistry, Physics, and Applications* (Hoboken, NJ: Wiley & Sons)
- [8] Kreuzer M and Eidenschink R 1996 Filled Nematics *Liquid Crystals in Complex Geometries Formed by Polymer and Porous Networks* eds G P Crawford and S Zumer (London: Taylor & Francis) chapter 15 pp 307–324
- [9] Mercuri F, Ghosh A K and Marinelli M 1999 *Phys. Rev. E* **60** R6309
- [10] Bellini T, Buscaglia M, Chiccoli C, Mantegazza F, Pasini P and Zannoni C 2000 *Phys. Rev. Lett.* **85** 1008
- [11] Marinelli M, Ghosh A K and Mercuri F 2001 *Phys. Rev. E* **63** 061713
- [12] Jin T and Finotello D 2001 *Phys. Rev. Lett.* **86** 818
- [13] Lobo C V, Prasad S K, Yelamagad C V 2006 *J. Phys.: Condens. Matter* **18** 767
- [14] Bapat P N, Rao D S S, Prasad S K and Yelamagad C V 2010 *J. Phys. Chem. B* **114** 12825
- [15] Kumar M V, Prasad S K, Marinov Y, Todorova L and Petrov A G 2015 *Mol. Cryst. Liq. Cryst.* **610** 51
- [16] Prasad S K, Nair G G, Hegde G, Sandhya K L, Rao D S S, Lobo C V and Yelamagad C V 2005 *Phase Transitions* **78** 443
- [17] Yelamagad C V, Prasad S K and Li Q 2012 Photo-Stimulated Phase Transformations in Liquid Crystals and Their Non-Display Applications *Liquid Crystals Beyond Displays: Chemistry, Physics, and Applications* ed Q Li (Hoboken, NJ: Wiley & Sons) chapter 5 p 157
- [18] Tsutsumi O and Ikeda T 2002 *Mater. Sci.* **6** 563
- [19] Urbas A, Klosterman J, Tondiglia V, Natarajan L, Sutherland R, Tsutsumi O, Ikeda T and Bunning T 2004 *Adv. Mater.* **16** 1453
- [20] Barrett C J, Yager K G, Mamiya J and Ikeda T 2007 *Soft Matter* **3** 1249
- [21] Yager K G and Barrett C J 2009 Azobenzene Chromophores in Photo-Reversible Materials *Smart Light-Responsive Materials: Azobenzene-Containing Polymers and Liquid Crystals* eds Y Zhao and T Ikeda (Boca Raton, Florida: John Wiley and Sons) chapter 1 p 1
- [22] Petrov A G, Marinov Y G, Hadjichristov G B, Sridevi S, Hiremath U S, Yelamagad C V and Prasad S K 2011 *Mol. Cryst. Liq. Cryst.* **544** 3/[991]
- [23] Sridevi S, Hiremath U S, Yelamagad C V, Prasad S K, Marinov Y G, Hadjichristov G B and Petrov A G 2011 *Mater. Chem. Phys.* **130** 1329
- [24] Hadjichristov G B, Marinov Y G and Yelamagad C V 2014 *J. Phys.: Conf. Ser.* **558** 012026
- [25] Jayalakshmi V, Nair G G and Prasad S K 2007 *J. Phys.: Condens. Matter* **19** 226213