Light Transmittance of Aerosil/7CB Nematic Nanocomposite Electro-Optical Material Doped with Photoactive Azobenzene Nematogenic Liquid Crystal

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Abstract. Being of practical importance for photo-controllable electro-optical applications and devices based on nematic liquid crystals (LCs), the photo-induced modification of the light transmittance of photoactive nematic nanocomposites was studied as depending on both temperature and applied alternating-current electrical field. The studied nanocomposite material was produced from nematic LC 4-*n*-heptyl cyanobiphenyl (7CB) filled with 3 wt.% aerosil nanoparticles of size ~ 7 nm, and further doped with 3 wt.% azobenzene-containing nematogenic LC molecules. By doping with photoactive azobenzene-containing LC, the aerosil/7CB nematic nanocomposite becomes photoresponsive. Thin nematic films (25 μm thickness) of the produced azo-doped composite nanomaterial were examined. When illuminated with UV light at the wavelength of 375 nm, they exhibit a significant enhancement of their electro-optical response. In a certain temperature range, the electric-field driven optical transmittance of azo-doped aerosil/7CB films can be efficiently controlled by light through *trans-cis* photoisomerization of azobenzene nanodopants.

Keywords: Silica-nanostructured liquid crystal, nematic liquid crystalline nanocomposites, photoactive nanomaterials, azobenzene.

1. INTRODUCTION

The photoresponsive nematic liquid crystals (LCs) are a specific class of materials that have a wide spectrum of applications utilizing the unique electrical, dielectric, optical and electro-optical (EO) properties of the nematic LCs. In particular, photoactive nano-filled nematic systems efficiently controllable by both electrical field and by light, are attractive for scatter-based EO applications at room temperature, such as photo-controllable EO switches and attenuators, as well as for photonics and sensorics based on photo-sensitive electro-optics (Jayalakshmi et al, 2007; Hadjichristov et al, 2014; Marinov et al, 2016a; Hadjichristov et al, 2018). By doping with a small amount of photoactive agent, the dispersions of silica nanoparticles (NPs) in LC hosts (Hauser et al, 1999; Iannacchione, 2004), in particular nematic LCs (Kreuzer & Eidenschink, 1996; Garbovskiy & Glushchenko, 2011), become photoresponsive nematic nanocomposite materials (Prasad et al, 2005; Jayalakshmi et al, 2007; Yelamaggad et al, 2012).

Recently, in (Hadjichristov et al, 2018) we have proposed photoactive nematic optical nanomaterial based on nanogel composites produced from nematic LC heptylcyanobiphenyl (abbreviated name 7CB) and 3 wt.% hydrophilic aerosil NPs (ANPs) (Aerosil 300) of size ~ 7 nm (Kumar et al, 2015; Marinov et al, 2016b). The nanogel composite was additionally doped with 3 wt.% azobenzene nematogenic LC 4-(4'-ethoxyphenylazo) phenyl hexanoate (EPH, for short) (Sridevi et al, 2011). Thin (25 μm) optical films of EPH-dopedANPs/7CB photoactive nanocomposite nematic have shown strongly modified electro-optics based on *trans-cis* photoisomerization of azo-bonded molecules of the photoactive agent (in our case, EPH), a feature very useful for practice, e.g., for photo-controllable scatter-based electro-optics.

Reasonably, the relevant photo-stimulation of EO response of EPH/ANPs/7CB photoactive nematic nanocomposites depends on the light intensity and the concentration of the EPH photoactive component in the ANPs/7CB dispersion, as well as on the temperature. In the present report we consider the temperature-dependent behavior of EPH-doped ANPs/7CB. The photo-induced modification of the voltage-dependent optical transmittance of this photoactive nematic nanocomposite was studied by thermo-optical and electro-optical measurements.

2. EXPERIMENTAL

The preparation of EPH-doped ANPs/7CB nanocomposite material and the thin films thereof, as well as the apparatus and the experimental setup used in the present study have been described in details elsewhere (Hadjichristov et al, 2018). For EO and thermo-optical measurements, a probe He-Ne laser beam was employed. The light was directed normally to the studied ANPs/7CB/EPH films. The frequency of the external alternating-current (AC) electric field (if applied to the sample) was 1 kHz. In all experiments described here, the samples were illuminated with continuous UV light from light-emitting diode (LED) whose emission was at the wavelength λ = 375 nm. The UV-light intensity on the sample was ~ 3 mW/cm^2).

3. RESULTS AND DISCUSSION

As reported in (Hadjichristov et al, 2014; Marinov et al, 2016a; Hadjichristov et al, 2018), a significant stimulation of the transparency by UV light and a large UV-light-induced lowering of the threshold of the voltage-dependent light transmittance take place for the considered azo-doped aerosil/7CB nematic nanocomposites. The effect is illustrated in Fig. 1 and is determined by *trans-cis* photoisomerization of azo-bonded molecules of EPH NLC (Prasad et al, 2005; Petrov et al, 2011; Sridevi et al, 2011; Yelamaggad et al, 2012; Hadjichristov et al, 2018).

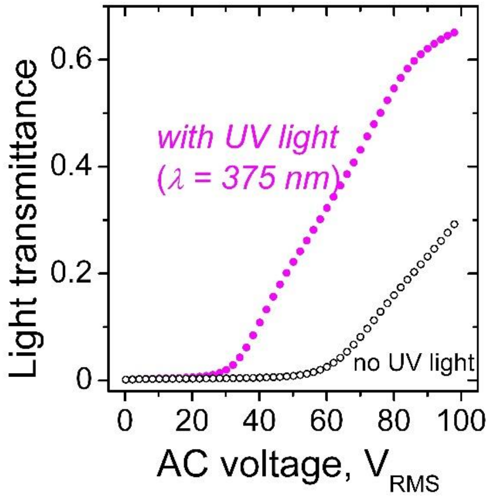

Fig. 1 Voltage-dependent transmittance of EPH-doped ANPs/7CB nanocomposite film. Data obtained without illumination with UV light (open circles), as well as with UV light (solid circles). The temperature of the film was 26 °C.

The UV-light-stimulated enhancement of the transparency of the EPH/ANPs/7CB nanocomposite films strongly depends on the temperature of the films. For instance, Fig. 2(a) reports the light transmittance of such a film as a function of temperature in the range from 25 °C to 42 °C, when the AC voltage applied to the film was 60 V (RMS). At this value of the AC voltage, the UV-light-induced effect by the studied EPH/ANPs/7CB nanocomposite films was maximum at the given dose of their exposure to UV light (Hadjichristov et al, 2018). For comparison, corresponding temperature scans, but at zero voltage, are given in Fig. 2(b). The latter behavior reflects the phase transition from isotropic to nematic state (I-N) of the EPH/ANPs/7CB nematic nanocomposite. The UV-light-induced change in the I-N temperature (T_{I-N}) is clearly seen. In Fig. 2, both transition temperatures, without UV light (T_{I-N}) and with UV light (T_{I-N}^{UV}) are indicated with asterisks. Their values are the same for the EPH/ANPs/7CB film at both zero voltage and voltage of 60 V.

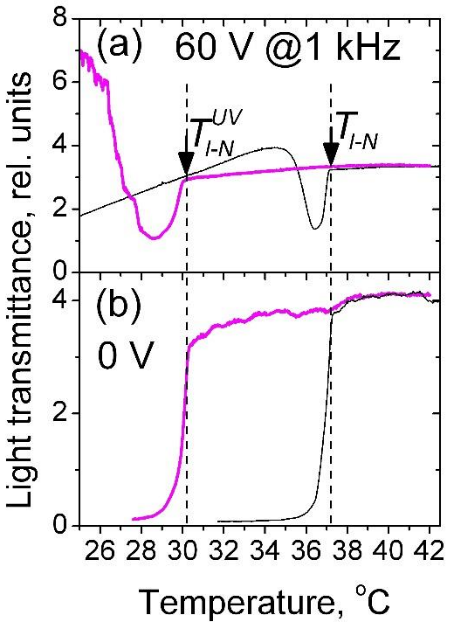

Fig. 2 Light transmittance versus the temperature of EPH-doped ANPs/7CB nematic nanocomposite film at AC voltage: (a) 60 V_{RMS}; (b) 0 V. The change of the curves of temperature-dependent optical transmittance due to UV illumination is also given (bold lines colored in magenta). The thermo-optical behaviours were measured at cooling under the same conditions. The intensity of the UV light was kept fixed and the other experimental conditions were also identical in both cases (a, b).

The UV-light-induced lowering of T_{I-N} is due to the presence of EPH nanodopants. Their bent-shaped *cis*-conformers produced by UV light (Sridevi et al, 2011) modify the local nematic order and the material parameters of the ANPs/7CB nematic nanocomposite (Hadjichristov et al, 2018). The *cis*-isomers of the EPH molecules introduce disorder, more than the disorder introduced from the *trans*-isomers of EPH in the ANPs/7CB nanocomposite. Accordingly, the UV-light-induced change in the light transmittance can strongly vary, in some temperature range the UV-light-induced effect can be even negative (Fig. 2a). Upon AC field applied to the EPH/ANPs/7CB film, a maximum UV-light-induced effect can be achieved in the range of the nematic state of the EPH/ANPs/7CB nanocomposite, but well below T_{I-N}^{UV} ($T_{I-N}^{UV} \approx 30$ °C in our case). In particular, at 26 °C.

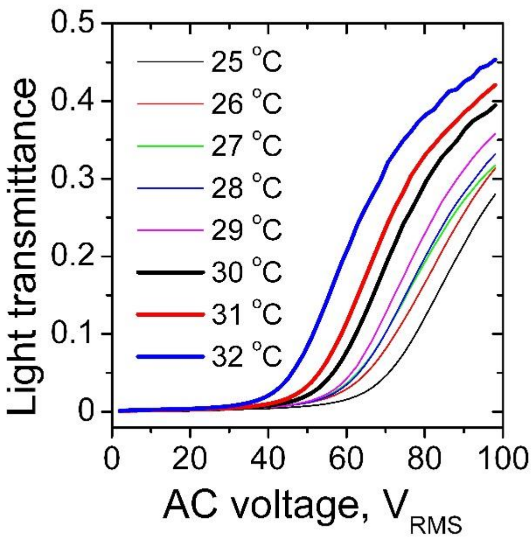

Fig. 3 Voltage-dependent transmittance of EPH-doped ANPs/7CB nanocomposite film recorded at various temperatures.

Fig. 3 presents the temperature-induced change of the curves of voltage-dependent transmittance of EPH/ANPs/7CB nematic nanocomposite film measured within the temperature range of nematic state. The elevated temperature results in a shift of the curves towards the lower voltage values, i.e. at a fixed voltage the higher transmittance occurs at the higher temperature. This experimental fact is consistent with the reduction of the order parameter (S) of the considered nematic system, because of anisometry reduction of the EPH LC molecules due to their conformation into *cis*-forms upon UV light.

Correspondingly, Fig. 4 shows the temperature-dependent light transmittance curves of the same EPH/ANPs/7CB film at various values of the applied voltage. In the nematic state, a strong enhancement of transmittance of the film is evident by increasing voltages starting from 0 V, as well as some lowering of T_{I-N} value and corresponding shift of the I-N phase transition curve in vicinity of T_{I-N} (by that, the slope of the I-N phase transition curve in vicinity of T_{I-N} remains the same). These features should be also taken into account when one consider the efficient control of the electro-optics of the EPH/ANPs/7CB nematic nano-composites (with or without illumination with UV light).

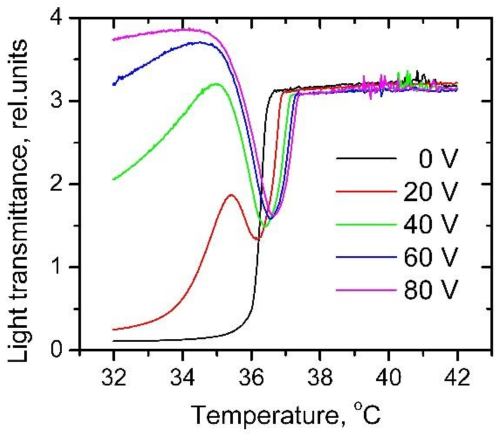

Fig. 4 Temperature-dependent light transmittance of EPH/ANPs/7CB film recorded (by cooling) at various applied voltages (RMS values).

4. CONCLUSIONS

We have demonstrated that there is a distinct part of the temperature dependence of the voltage-dependent light transmittance of thin optical films of aerosil/7CB/EPH nematic nanocomposites where their electrically-driven light transmittance displays a significant increase when the films are illuminated with UV light (at appropriate wavelength and intensity). This is a result from a disordering effect due to the UV-light-produced *cis*-isomers of the azobenzene LC EPH molecules, having more distorted configuration and being less delocalized than their *trans*-isomers. Thus, the efficient light-induced photoisomerization within the illuminated area of the considered photoactive nematic nanocomposite films does strongly influence their electro-optics. In this temperature range one can successfully use such light-controllable photoresponsive smart nanomaterials. Accordingly, an efficient control by light can be achieved, useful for photo-controllable EO applications and corresponding devices.

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