

Photosensitive Soft Matter: Mixtures of Nematic Liquid Crystal with Azo Molecules*

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Abstract. Photosensitive soft matter based upon guest-host liquid crystal systems was prepared by mixing azobenzene-containing mesogens with the nematic liquid crystal 4-butyl-cyclohexane carboxylic acid 4-pentyloxy-phenyl ester (CM80). Binary mixtures of the host CM80 with three azo-bonded compounds as UV-active dopants (guests) at a relatively small concentration of 1 wt.% were characterized by thermo-optical, dielectric, spectral and flexoelectric measurements. The study aimed to determine the mechanisms that result in variations of material parameters caused by light-driven molecular conformation change of the azo-dye guest molecules (the transition from rod-shaped *trans* isomers to bent-shaped *cis* isomers).

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1 Introduction

In the last years, the photo-controllable optical, dielectric and electro-optical response of liquid crystal (LC) materials using photo-isomeric molecules, in particular azobenzene-containing LCs and azobenzene-doped LCs, have attracted a great interest owing to their potential for photo-responsive applications [1,2]. For such systems, in particular azobenzene-doped nematics, upon UV irradiation the photoinduced change of molecular shape due to *trans*–*cis* isomerization of the azo-bond can also induce a change of the material properties [3–5]. The photoflexoelectric effect in photosensitive LCs and in other soft materials is also well established [6,7]. UV light-induced change of flexoelectric deformations has been reported for bulk thermotropic LC materials [7] and for guest-host dye-nematic mixtures [3,8].

The azobenzene and its derivatives are good examples of photo-isomerizable molecular systems, which are also called photochromic/photoactive/ photore-

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sponsive compounds. Here, we study azobenzene-doped nematic LC which exhibits both photosensitivity and photoflexoelectricity [9,10] based on UV light-induced isomerism. Three guest-host mixtures were examined. They were prepared from azobenzene-containing compounds as UV-active dopants (guests) at 1 wt.% in the host matrix of the nematic 4-butyl-cyclohexane carboxylic acid 4-pentyloxy-phenyl ester (hereafter denoted as CM80). The photosensitivity of these systems leads to a modification of their spectral, thermo-optical and dielectric properties upon UV light illumination, an effect that is certainly of practical interest.

2 Experimental

The samples were mixtures of the nematic LC CM80 (serving as a host matrix) and one of the three azobenzene compounds at a concentration of 1 wt.%, also liquid crystalline mesogenes, that acts as a guest, shown in Figure 1. The substances were synthesized in the Centre of Liquid Crystal Research in Bangalore, India, and were specially chosen in order to obtain mixtures having a high degree of both photosensitivity and photoflexoelectricity based on UV light-induced isomerism of the azobenzene dopants. These compounds exhibit maximum absorption at the wavelength of 365 nm. The host nematic CM80 was optically transparent in the wavelength range from 340 nm to 750 nm.

LC cells (with ITO-coated glass plates and a cell gap of 10 μm) with the guest-host mixtures were prepared as described in [11]. A good homeotropic orientation was achieved for the layers of the LC mixtures in the cells. Using a white light, the thermo-optical and dielectric measurements were carried out by cooling of the mixtures from their isotropic phase. The experimental setup and apparatus employed were described in details elsewhere [11].

3 Results and Discussion

As found by conoscopy and phase retardation measurements, both UI-147/CM80 and EPH/CM80 mixtures have shown a significant photoflexoelectricity [9,10]. From thermo-optical transmission changes we determined the isotropic-to-nematic (N-I) phase transition temperature (the clearing temperature, T_C) of our soft photosensitive nematic materials of azobenzene-doped CM80. The UV light-induced shift in T_C of the mixtures was evidenced. T_C of the guest-host systems was reduced (Figure 2, left). Since the host CM80 does not absorb the light at the wavelength of 365 nm, the effect obviously results from the azobenzene dopants.

The UV light-induced photoisomerization of the azo-containing dopant molecules leads to a diminution of the material anisotropy (and thereby, the optical anisotropy in our case) that does result in the decrease of T_C of the guest-

HOST

CM80

4-butyl-cyclohexanecarboxylic acid 4-pentyloxy-phenyl ester

N 65.5°C Iso

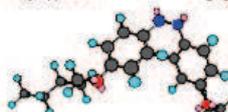
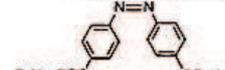
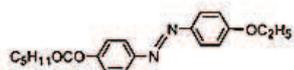


GUESTS

EPH

4-(4'-ethoxyphenylazo)phenyl hexanoate

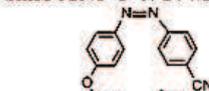
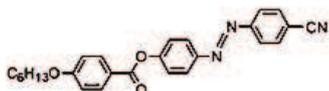
Cr 74.4°C N 215°C Iso



UI-147

4-hexyloxybenzoyloxy-4'-cyano azobenzene

Cr 92°C SmA 125.3°C N 274.2°C Iso



UII-34

α, ω -bis (4'-*n*-butylazobenzene-4-oxy) butane

Cr 128°C SmA 207°C N 215°C Iso

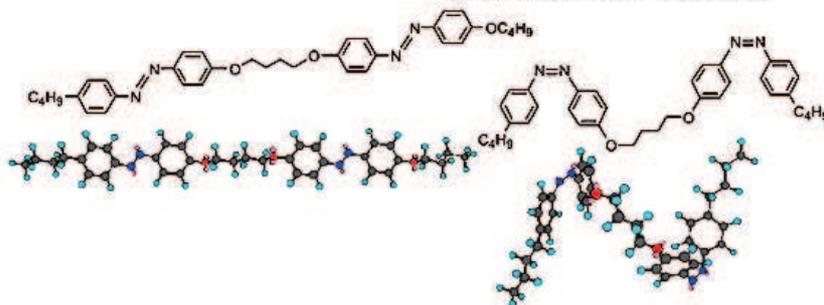


Figure 1. Molecular structure of the LC CM80 and azobenzene compounds used as dopants: *trans* (shown in the left) and *cis* (in the right) conformers.

host mixtures. Owing to the small concentration of azobenzenes, the material still remains a room-temperature nematic. The reduction of T_C of the guest-host mixtures upon UV light can be associated with the change of both intermolecular interactions and ordering parameter of the resultant binary mixture

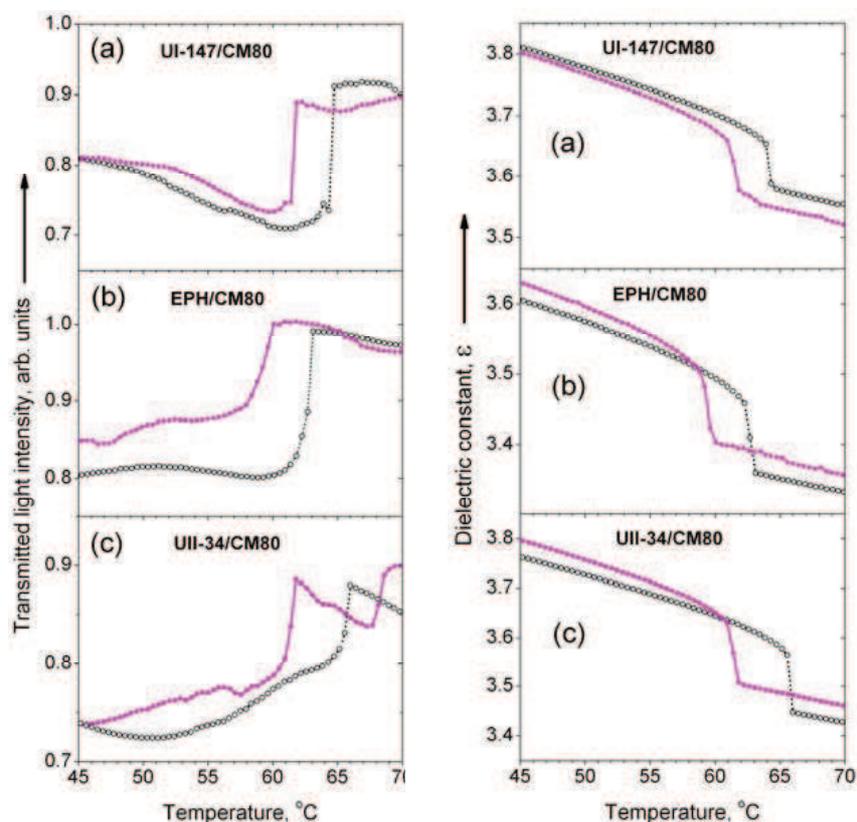


Figure 2. Variation of optical transmittance (left) and dielectric constants (right) of the three guest-host mixtures measured as a function of temperature. Data obtained without (open circles, dotted lines) and with (solid circles, solid lines) UV light illumination ($\lambda = 365$ nm, 2 min illumination, 4 mW/cm^2 intensity).

[5,12]. The corresponding change in the thermal behavior of the dielectric and flexoelectric properties of the mixtures due to molecular conformation (*cis*- and *trans*-isomers) of the azo-dopants upon UV light illumination at a wavelength in the absorption region, was also registered.

Our measurements indicated that among the three guest-host mixtures exposed to UV light, the UII-34/CM80 mixture exhibits the strongest UV light-induced shift of T_C . This effect is probably due to the presence of two azo bonds in each molecule of the UII-34 dopant. By measuring the thermal behaviour of the dielectric constants for the three mixtures upon identical conditions with and without UV light illumination, we have found the same effect, i.e. the highest UV light-induced 'shift' was for UII-34/CM80 mixture, then for EPH/CM80, and the lowest for UI-147/CM80 (Figure 2, right).

The UV light-induced shift of T_C and the corresponding temperature change of the dielectric constant of the three guest-host systems under study can be correlated. The host material used in the present investigations has a negative dielectric anisotropy, i.e., $\varepsilon_{\parallel} - \varepsilon_{\perp} < 0$, where ε_{\parallel} and ε_{\perp} are the dielectric constants parallel and perpendicular to the director, respectively. Since the azobenzene concentration is low, the magnitude and thermal behaviour of the dielectric constant of the mixture may be expected to be determined by that of the host material. Hence, as for any material with a negative dielectric anisotropy, the onset of the N-I transition is marked by an abrupt increase in ε_{\perp} . The transition from rod-shaped *trans*-isomers to bent-shaped *cis*-isomers weakened the intermolecular ordering interactions and the decreasing order parameter caused variations of material parameters [5,12]. However, the shift of dielectric response cannot be solely explained by the weakened intermolecular interactions and decreased molecular ordering. Most probably, it is also significantly influenced by the shape of the guest *cis*-isomer itself.

As for the UV light-induced change in the absorption spectra of the examined guest-host systems, the same sequence of the mixtures takes place when the degree of the UV light-induced spectral change is considered, i.e., the highest UV light-induced change for UII-34/CM80 mixture, then for EPH/CM80, and the lowest for UI-147/CM80. Accordingly, the same applies for the corresponding alteration of the percentage of the *cis*-conformers in the mixtures upon UV light illumination [11]. Thus, the data obtained from spectral measurements are consistent with the above results from thermo-optical and dielectric measurements. As explained in [11], the difference between the data obtained for each of the mixtures upon the same UV light impact comes from specificity of the molecular structure of the azobenzene dopants.

On the other hand, the measurement of flexoelectro-optic effect by the studied guest-host systems under identical conditions clearly indicated a UV light-induced enhancement in the flexoelectric response of about 30% and 40% for UI-147/CM80 and EPH/CM80, respectively, but a negligible effect of the UV light for UII-34/CM80 mixture [10]. The difference can be attributed to the structure and photo-induced conformation of the dopant azo-molecules. Under UV illumination the guest molecules isomerize from *trans*- to *cis*-form, the latter having a pronounced banana shape. This shape alteration could change the bend flexo-coefficient of the mixture, and also the longitudinal dipole moment of the surface-adsorbed guest molecules, and in turn the value of surface polarization. The algebraic sum of the bend flexo-coefficient and the surface polarization governs the amount of the flexoelectric bending [8]. That is why, a marked increase of the flexoelectro-optic effect upon UV light illumination was found for the guest molecules having a longitudinal dipole moment. In contrast, the molecule of the UII-34 compound is a double azo-bond, fully symmetric with no longitudinal component of the dipole moment, and no surface polarization contribution is possible.

In total, the thermo-optical, dielectric, spectral and flexoelectric measurements provide information how the azo-dopants do influence the properties of the mixtures being exposed to UV light. This is of importance when the aim is to achieve an UV photosensitivity and UV light-induced flexoelectricity of the guest-host mixtures, while still keeping the nematic nature of the mixed material. In particular, if the values of the material constants of the mixture depend straightforward (within a some limited region) on the percentage of the components in the binary system [13], then one can expect also a straightforward change of the photosensitivity of the guest-host soft-matter systems when the concentration of photosensitive agent is changed.

4 Conclusions

In view of the possibility for practical application, three photo-sensitive nematic LC materials have been studied being two-component guest-host mixtures of a photo-insensitive nematic host and a photochromic azobenzene-containing mesogen (at a relatively small concentration) that acts as a guest. The UV light sensitivity of these azobenzene-doped nematics is based on the photo-induced *trans-cis*-isomerization of the azobenzene guest component. The molecular conformation (*cis*- and *trans*-forms) upon UV light illumination at the wavelength of 365 nm in the region of the maximum absorption results in a modification of the spectral, thermo-optical and dielectric properties of the guest-host systems. Three different mechanisms are involved in the variations of the material properties: (i) weakened intermolecular ordering interactions, (ii) direct contribution of *cis* isomers, and (iii) molecular morphological interactions of the *cis* isomer with the host LC. It was also demonstrated that the optical transparency and dielectric properties of the mesogen guest-host mixtures can be controlled by both UV illumination and temperature. The information reported here may be useful in the design of functional photosensitive and flexoelectric molecular systems and soft materials for molecular electronics and optoelectronics.

Acknowledgments

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