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Photoinduced Nematic – Cholesteric Structural Transitions in Liquid Crystal Cells with Homeotropic Anchoring

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By doping a nematic liquid crystal with two chiral agents of opposite handedness and distinctly different spectral ranges of molecular absorption a photoinduced structural transition from the nematic (non-helical) to cholesteric (helical) state was realized, as well as a transition between two cholesteric states with the opposite handedness. This finding extends our knowledge about formation of cholesteric structures and opens new horizons for application of cholesteric liquid crystals.

Keywords Chiral dopant; cholesteric; compensated nematic; fingerprint; structural transition

1. Introduction

It is known that dissolution of chiral molecules in a nematic liquid crystal (LC) results in induction of the helically twisted cholesteric phase characterized by director \mathbf{n} (the preferred orientation of the long axes of anisometric molecules) rotating along the helical axis. Depending on the nature of chiral dopants (ChD) and molecular interaction between ChD and solvent molecules, the cholesteric helix can be right- or left-handed. The cholesteric LC (CLC) phase induced by a chiral compound with concentration C is characterized by helical pitch $p = 2\pi/q_0$, with the wave number $q_0 = 4\pi \cdot \beta \cdot C$, where β is the ChD helical twisting power [1].

Depending upon alignment boundary conditions at the surfaces, CLCs can form different textures [1,2]. In the *planar texture*, the director \mathbf{n} is parallel to the substrates, and the helical axis is perpendicular to the cell plane. One of the best-known properties of CLCs is selective light reflection from the planar texture with maximum wavelength $\lambda_{\max} = np$, where n is the average refractivity index. The helical pitch,

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and, correspondingly, λ_{\max} , can be very sensitive to temperature changes and external fields, which is the basis for various practical applications of CLCs (thermal sensors, adjustable color filters and reflective polarizers, voltage-controlled light attenuating films, mirrorless lasers, etc.) [3–5].

In the *homeotropic texture*, the director is normal to the substrates, and the cholesteric axis is parallel to the cell plane. This texture in CLCs is also called “fingerprint texture” due to its specific appearance. It can be controlled by varying the cell gap, pitch, intensity of an applied field, etc. If the cholesteric pitch is changed by external electric or magnetic field, cholesteric texture transitions from the fingerprint to homeotropic or planar nematic alignment can be observed [6]. The fingerprint textures with well oriented “fingers” are used to realize switchable diffraction gratings and beam steering devices [7,8].

It has long been known that the cholesteric helix could be frustrated (distorted or even completely unwound) in a cell with sufficiently strong homeotropic anchoring [9]. Suppression of the helix was experimentally observed in [10,11]. The conditions for the fingerprint texture formation are determined by the ratio of the helical pitch p and LC thickness d . If p is smaller than the threshold pitch $p_{th} = 2 \cdot d \cdot K_{22}/K_{33}$ [12], the chiral torque is strong enough with respect to the anchoring energy of the aligning surfaces and twisted cholesteric structure can be observed. When $p_{th} < p$, the chiral torque is too small, and the system would not be able to twist. In this case, the structure is similar to that of homeotropically aligned nematics.

Besides external thermal, electrical and magnetic fields, the cholesteric helix can also be effectively controlled by light. The use of light offers certain advantages due to relatively easy spatial, temporal and remote control of irradiation. The main attention was previously paid to the planar texture, in which a phototunable selective reflection could be realized ([13] and the references therein). In these systems, photoirradiation leads to changes in conformation of ChD molecules and, correspondingly, to changes in their helical twisting power. In one of the few works related to photoinduced effects in the homeotropic texture [10], transition from the fingerprint cholesteric texture to the nematic texture was realized. In this work, the authors used 4-*n*-pentyl-4'-cyanobiphenyl (5CB) as a nematic matrix, and helical twisting was induced by ChD 2-(4'-phenylbenzylidene)-*p*-menthane-3-one (PBM). UV irradiation caused *trans-cis* isomerization of PBM molecules [14], which resulted in a substantial decrease in their twisting ability. When the increasing helical pitch exceeds the threshold value p_{th} , the chiral torque becomes too small to overcome the anchoring force, and helical twisting is suppressed.

In this article we further develop the idea of structural transitions between different mesophases in cells with homeotropic anchoring. We demonstrate the transition from a nematic (non-helical) to cholesteric (helical) state, i.e., the transition inverse to the case described in [10]. Furthermore, we realize the transition between two cholesteric states with opposite chirality.

2. Our Concept

The simplest way to realize these transitions is to use a chiral dopant that would change the sign of its chirality due to photoisomerization. Let us assume that the initial *trans* isomer demonstrates left-handed chirality, while the *cis* photoisomer is right-handed. Then, the CLC helical twisting in the initial state is left-handed.

During irradiation, the concentration of left-handed *trans* isomers would decrease, and the concentration of right-handed *cis* isomers would increase. At strong anchoring and sufficient exposure dose the left-handed helix would disappear, with a left-handed cholesteric transformed to the non-twisted nematic state. Under further irradiation, the right-handed torque induced by *cis* isomers can overcome the anchoring, resulting in right-handed cholesteric helix. Thus, one could obtain an induced CLC with the opposite chirality.

Since it is not easy to find an efficient chiral dopant with such properties, we realized this scheme in a different way. Our idea was to use two photoisomerizing chiral dopants of opposite chiralities. The exposure conditions should ensure much higher photoreaction yield for one of these dopants. Photoisomerization of this dopant would change the resultant torque and eventually lead to structural transitions in the LC system. Note that a similar “two-dopant” approach was previously applied in [15] to expand or compress the cholesteric helix without change in a sign of helical twisting.

3. Materials and Methods

To realize the experimental situation described in section 2, we used two different ChDs. The right-handed dopant was ZLI-3786 (R-811) obtained from Merck. The left-handed ChD was PBM synthesized at Institute for Single Crystals, NAS of Ukraine [14]. The chiral dopants were dissolved in nematic LC MLC6882 (Merck, Germany) of negative dielectric anisotropy. Two different mixtures were prepared, with weight concentrations of ChDs $C_{\text{PBM}} = 1.1\%$ and $C_{\text{R811}} = 1.65\%$ (mixture M1), and $C_{\text{PBM}} = 1.4\%$ and $C_{\text{R811}} = 1.1\text{ wt}\%$ (mixture M2), respectively.

To obtain homeotropic alignment of CLC, we used polyimide SE1211 (Nissan, Japan) ensuring strong anchoring energy. The polyimide films were deposited on glass substrates by spin-coating method (4000 rpm, 30 sec), and then annealed (180°C, 30 min) and unidirectional rubbed.

For studies of structural transformations in the mixtures under UV radiation, we used plane-parallel LC cells with thickness $d = 12 - 15\text{ }\mu\text{m}$. The cell thickness was determined by the interference method.

Illumination of LC cells was carried out by a high-pressure UV lamp UV-P 280 (Panacol, Germany). The integral UV radiation intensity was 40 mW/cm^2 . The LC textures were observed using a polarizing microscope Polam 213 M (LOMO, Russia) equipped with a PC-connected digital camera. The UV absorption spectra of the samples prior to UV irradiation and after fixed exposure doses were recorded in 230–450 nm range using a Hitachi 330 spectrophotometer.

4. Results and Discussion

At first, we checked whether the selected dopants satisfied the conditions mentioned in section 2. For this purpose, we recorded UV spectra of ChDs in hexane solution ($C = 10^{-4}\text{ mol/l}$) before and after UV irradiation. The solutions were placed in quartz cuvettes with a thickness $d = 1\text{ cm}$. The filled cuvettes were irradiated directly or through the glass plate used for preparation of LC cells. This plate acted as a filter cutting off the light with wavelengths shorter than 300 nm, thus preventing light absorption and photo-excitation of R-811 molecules (Fig. 1).

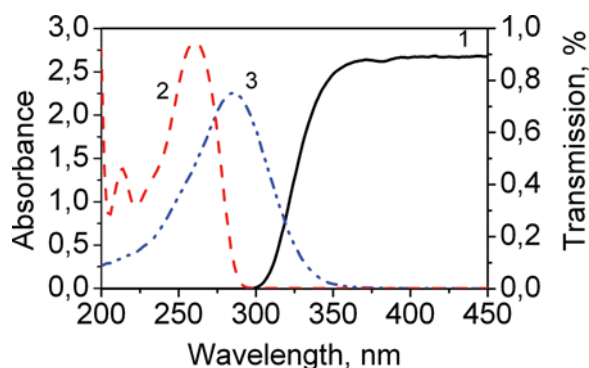


Figure 1. Transmission spectrum of glass plate (1) and absorption spectra of chiral dopants R-811 (2) and PBM (3). (Figure appears in color online.)

This is confirmed by spectra of PBM and R-811 before and after irradiation (Fig. 2). One can see a clear difference between the two cases of irradiation. Under full-spectrum UV irradiation, both dopants are involved in photoreactions, while when the short wavelength range is cut off, only PBM dopant demonstrates its

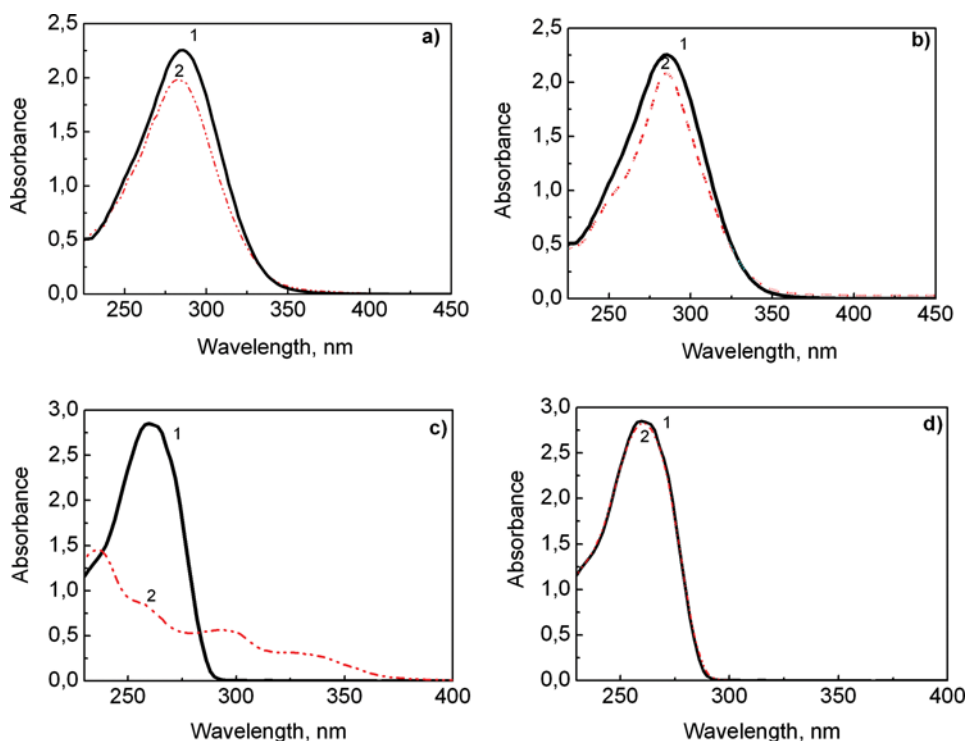


Figure 2. Spectral kinetics of PBM (a, b) and R-811 (c, d) in hexane upon UV irradiation. (a, c) Irradiation through quartz plate, and (b, d) irradiation through glass plate. Numbers 1 and 2 stand for the spectra before and after 45 min irradiation, respectively. (Figure appears in color online.)

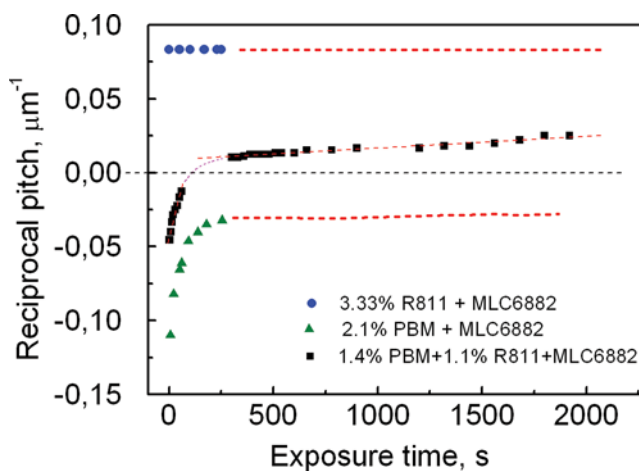


Figure 3. Inverse pitch vs. exposure time for induced cholesteric systems: 3.33% R811 + MLC6882 (circles); 2.1% PBM + MLC6882 (triangles); 1.4% PBM + 1.1% R811 + MLC6882 (squares). The filled symbols correspond to actually measured values, while the dashed lines represent calculated values that would ensure additivity of p^{-1} in the mixed system. The saturation value of the triangles' line represents the expected p^{-1} value for *cis*-isomers of PBM. (Figure appears in color online.)

phototransformation. According to [14], this process is *trans-cis* isomerization. Thus, though both ChDs are photoreactive, transformation of R-811 can be avoided by using a filter (glass plate) cutting off UV radiation with $\lambda < 300$ nm.

Using the above-described glass plates for our LC cells, we studied changes in helical pitch under UV irradiation. The helical pitch values were determined from the fingerprint texture periods under a polarizing microscope. The measured values of the inverse pitch p^{-1} as function of irradiation time for cholesteric phases induced by PBM and R-811 are shown in Figure 3.

One can observe UV-induced unwinding of the initial left-handed helix for the nematic matrix doped with PBM. At the same time no observable changes could be noted for the R-811 right-handed helix under similar conditions. When both ChDs were introduced into the nematic matrix, the resulting p^{-1} value, as it should be expected, was very close to its additive value. Upon irradiation, unwinding of the initial left-handed helix was observed, and then helix inversion occurred, i.e., the cholesteric helix became right-handed. In other words, with increasing exposure dose the left-handed cholesteric was first converted to a nematic, and then the nematic turns into a right-handed cholesteric. Typical textures corresponding to these phases are shown in Figure 4. The initial and final fingerprint textures correspond to left-handed and right-handed cholesterics, respectively. The observed photo-switching between these phases occurs through nematic state, which is reasonable from topological point of view.

One can note the absence of experimental points in the range 65–270 s for the sample with two chiral dopants (Fig. 3). This gap is caused by suppression of cholesteric helix in this range of exposures. This fact clearly illustrates that the nematic (unwound) state is not a momentary state corresponding to a certain exposure dose at which the torques induced by different dopants are mutually compensated. In fact,

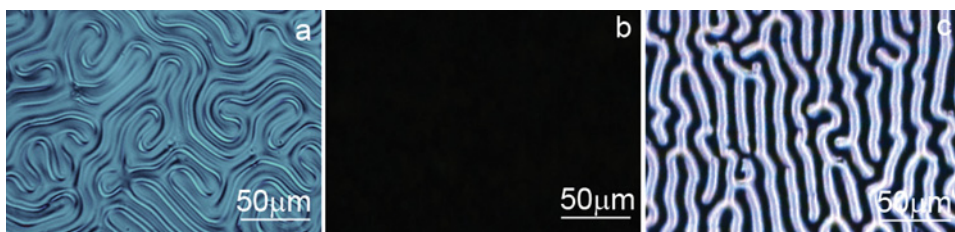


Figure 4. Microphotographs demonstration the photoinduced structural transitions in the homeotropically aligned layer of the induced cholesteric containing two chiral dopants with opposite chiralities (mixture M2): (a) left-handed helical texture before irradiation; (b) compensated nematic texture (after 2 min irradiation); (c) right-handed helical texture (after 10 min irradiation). The cell is placed between two crossed polarizers. The magnification is $\times 100$.a. (Figure appears in color online.)

the nematic state exists in quite a broad range of exposure times, because of threshold character of helix formation. This time range corresponds to the pitch range $-p_{th} < p < p_{th}$.

The data presented in Figure 3 were obtained for mixture M2, which had higher content of left-handed dopant PBM. The sequence of structural transitions for the other mixture (M1) is not so rich. Before irradiation, this mixture shows homeotropic nematic structure, implying that torques induced by two different dopants are roughly balanced. Irradiation of this mixture results in transition to right-handed cholesteric with fingerprint texture, as shown in Figure 4 (photo 3).

5. Conclusions

Thus, light-induced nematic-cholesteric structural transition in the LC cells with homeotropic anchoring has been realized, and the conditions required for this effect have been determined. As a variant of this effect, a sequence of photoinduced structural transitions was observed, starting from left-handed helix (manifested by fingerprint texture) via homeotropic nematic to right-handed helix. The observed effect is based on the interplay of the opposite handedness and different light sensitivities of two chiral dopants introduced into a transparent nematic matrix, as well as competition between helical twisting and surface anchoring. These results extend our knowledge about structural transitions in cholesteric LC materials and open new horizons for their application. They suggest new principles for information processing and storage devices, optically re-writable LC displays, polarization switches, etc.

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