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Collective Character of Previtamin D *cis-trans* Isomerization in Liquid-Crystalline Matrices

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Significant increase of the previtamin D cis-trans *isomerization efficiency with increased concentration of initial provitamin D was observed in both nematic and cholesteric LCs at room temperature, but the effect revealed reduced progressively with heating, and in isotropic phase it disappeared. The results obtained indicate on the collective character of* cis-trans *isomerization in liquid crystals due to the ordering of LCs. Here we present our results on the dynamics of the cholesteric phase induction and its propagation in response to the UV-induced geometry change of the provitamin D dopant molecule.*

Keywords *cis-trans* isomerization; collective processes; induced cholesteric; photosensitive chiral dopant; provitamin D; quasi-nematic phase

1. Introduction

It is known that the properties of liquid crystalline (LC) matrices can be modified by photochemical reactions of photoactive dopant molecules, and photochemically driven *trans-cis* isomerization of azobenzene derivatives is the reaction most often used for this purpose. Although the light-driven phase transitions in doped liquid crystals are surveyed in the literature, little is known about relations between the photochemical processes and the phase transition. We pioneered in studying provitamin D_3 (7-dehydrocholesterol, 7-DHC) photoisomerization in a liquid crystalline matrix [1,2] using UV absorption spectroscopy.

It has been found that dissolution of chiral molecules of provitamin D_3 in a nematic LC induces the cholesteric phase with right-handed helix ($\beta = +3{,}4\,\mathrm{mkm}^{-1}$ wt.-%$^{-1}$ [3]). Upon UV irradiation the conformationally flexible molecules of previtamin D are formed by hexadiene ring-opening, and further previtamin D undergoes *cis-trans* photoisomerization into tachysterol which is left-handed chiral molecule ($\beta = -8{,}5\,\mathrm{mkm}^{-1}$ wt.-%$^{-1}$ [3]) (Fig. 1). Evidently, these phototransformations change the sign and the pitch of the induced cholesteric phase.

At room temperature significant growth of the efficiency of *cis-trans* isomerization was observed with the dopant concentration rising from 0.04 wt.-% up to 3 wt.-% in both nematic and cholesteric LCs [4,5]. However, its remarkable reduction was

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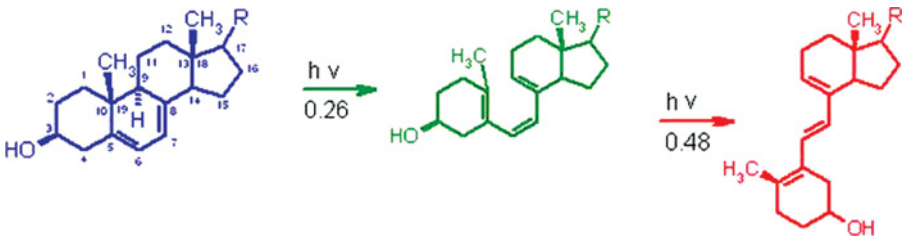

Figure 1. The key photoconversions of provitamin D in a LC matrix. The numbers at arrows denote the quantum yields. R = C_8H_{17} – Vitamin D_3 series, R = C_9H_{17} – Vitamin D_2 series. (Figure appears in color online.)

established with the temperature increase from 22°C up to 70°C. Finally, in isotropic phase no dependence on the dopant concentration was observed [5]. Such anomalous behavior depending on the matrix viscosity testifies that in contrast to volume-demanding 'classic' mechanism of *cis-trans* isomerization in isotropic solvents defined as torsion relaxation around double-bond, in a LC matrix non-classical volume-conserving 'hula-twist' (HT) *cis-trans* photoisomerization takes place. Such mechanism is common in confined media [6] where only one C-H unit undergoes out-of-plane translocation, while the remaining portion of the molecule slides in the plane.

A comparison between the numerical calculation and experimental data showed that the increase in individual quantum yield of *cis-trans* isomerization alone failed to explain its enhancement with the initial provitamin D concentration [4]. We suggest that the previtamin D *cis-trans* isomerization acquires collective character in the ordered LC medium with reduction in the distance between neighboring previtamin D molecules. Inasmuch as the concentration dependence is lacking in isotropic media and is observed solely in the mesophase, obviously, the LCs short-range order governs the *cis-trans* isomerization enhancement. This raises the question of whether the cooperative movements inherent in liquid crystals and elastic properties of a LC matrix ensure so-called 'domino' mechanism of *cis-trans* isomerization?

2. Experimental Methods

Studies of the photoinduced nematic – cholesteric phase transitions were performed using nematic MLC-6815 (Merck) doped with 7-dehydrocholesterol (Sigma) in sufficiently low concentration to preserve quasi-nematic phase within planar oriented LC cells of $15 \div 60\,\mu m$ thickness.

The dynamics of cholesteric – nematic phase transition was investigated using special regime of UV irradiation of the LC cells with planar-oriented nematic LC doped with provitamin D_3. In the initial stage of the experiments one half of the LC cell surface was irradiated whereas another half of surface was covered with black paper. Later on the LC cell surface was partitioned into three domains, and only the left and right extreme domains were irradiated while the central one was light protected.

UV irradiation of the samples was done with a low-pressure mercury lamp ($\lambda_{irr} = 254\,nm$, total nominal power 30 mW). The power of the incident radiation was measured with the calibrated spectrometer EPP2000C-UV+VIS (StellarNet Inc.), and in the sample plane it amounted to $0.3\,mW/cm^2$. Measurements of UV–VIS absorption spectra were performed with Perkin Elmer Lambda 25

spectrophotometer. The photoisomerization kinetics was measured by monitoring the UV absorption spectra transformations because accumulation of *trans*-isomer tachysterol is accompanied by significant absorbance increase thereby allowing estimation of the *cis-trans* isomerization efficiency [3].

To investigate optical properties of the system, a polarizing microscope POLAM L213 was used equipped with a camera Sony H5. All measurements were performed in ambient atmosphere.

3. Results and Discussion

3.1. *UV Irradiation of the Two-Domain LC Cell*

The LC cell (d = 16,9 μm) doped with provitamin D_3 (C = 0,53 wt.-%) was prepared, and before UV exposure the UV absorption spectra of both domains were recorded (Fig. 2, solid curve). After short UV exposure (t = 60 sec) of the left domain no changes in the LC structure were observed with a microscope when the LC cell was inserted between crossed polarizers, although remarkable changes were found in the absorption spectrum (Fig. 2, dotted line 1).

Nevertheless, after additional UV exposure of 20 sec significant changes in the UV spectrum (Fig. 2, dotted line 2) and in the LC structure of the left domain were observed (Fig. 3a). As was shown previously [6], just 80 sec exposure is needed to form tachysterol in amount sufficient for induction of the cholesteric helix.

Immediately after the exposure the small 'islands' of induced planar-oriented left-handed cholesteric phase were observed (Fig. 3a) which further enlarged and merged with each other (Fig. 3b), and finally, homogenous left-handed cholesteric phase filled in the UV irradiated left domain (Fig. 3c). Such a picture was not changed after prolong storage.

What is more important, no propagation of the left-handed cholesteric phase induced by the UV created *trans*-isomer to the non-irradiated quasi-nematic part of the LC cell was observed, and the phase boundary remained sharp, as well as the UV absorption spectra of the two domains fixed immediately after UV irradiation remained unchanged after prolonged keeping.

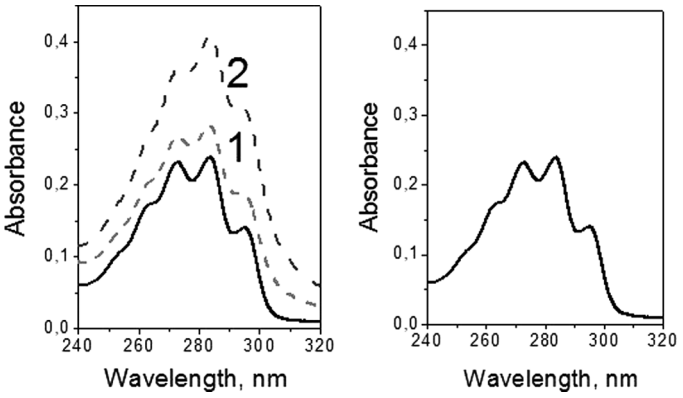

Figure 2. The UV absorption spectra of the irradiated (left) and non-irradiated (right) domains of the two-domain LC cell: solid line – before UV exposure, dotted lines – after 60 (1) and 80 sec (2) UV exposures.

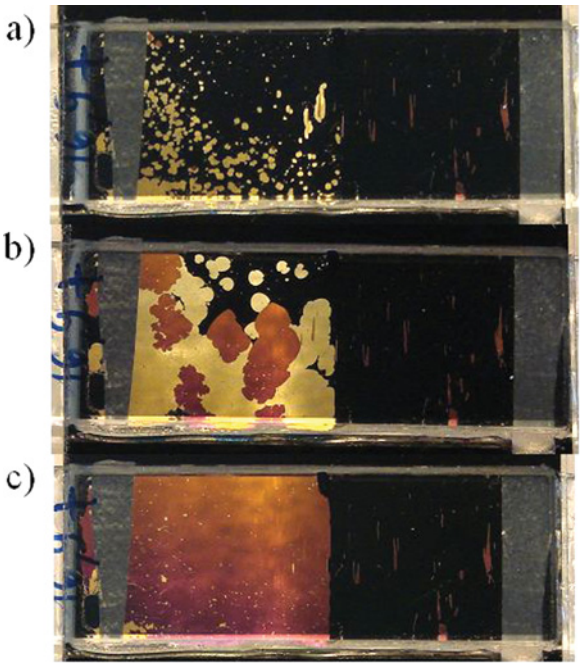

Figure 3. Photographs of the two-domain LC cell mounted between crossed polarizers immediately after UV exposure (a), and after 5 (b) and 60 min (c) storage. (Figure appears in color online.)

3.2. *UV Irradiation of the Three-Domain LC Cell*

To gain greater insight into the behavior of cholesteric phase with variously twisted helices, the three three-domain planar-oriented nematic LC cells of different thickness and different 7-DHC concentrations were prepared, and two side parts were UV irradiated with different exposures to accumulate different tachysterol concentrations (Fig. 4).

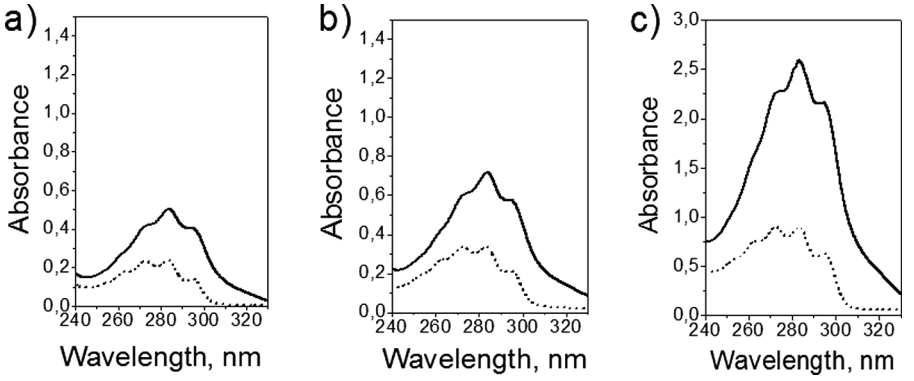

Figure 4. Initial absorption spectra (dotted line) of the three LC cells: a) $d = 15{,}5\,\mu m$, $C_{7\text{-DHC}} = 0{,}5$ wt.-%, b) $d = 15{,}8\,\mu m$, $C_{7\text{-DHC}} = 0{,}65$ wt.-%, c) $d = 55\,\mu m$, $C_{7\text{-DHC}} = 0{,}5$ wt.-% and after UV exposure (solid line) of 6 min (a), 6,5 min (b) and 13 min (c).

Photographs of the three LC cells mounted between crossed polarizers after UV exposures are shown in Figure 5. From different colors of the irradiated side parts it may be deduced that cholesteric helices were formed with different half-turn numbers N. Interestingly, due to diffraction at the shield edges additional color stripes are clearly seen at the phase boundaries (Fig. 5b, c, d) that offers a clearer view of how many half-turns of the cholesteric helix were formed in every LC cell.

As in the previous case of two-domain LC cell, the phase boundaries as well as the UV absorption spectra fixed immediately after UV irradiation remained unchanged after prolonged keeping of all the three LC cells. And as before, it was necessary to irradiate central domain during 80 sec to initiate cholesteric phase propagation (Fig. 6) and additionally to keep the cell about 1 hour to get homogenous cholesteric phase within the whole LC volume. More importantly, the UV absorption spectra of the central domain (as well as the side ones) fixed immediately after short UV exposure remained unchanged during the cholesteric phase propagation.

More complicated phase behavior was observed in the 2nd LC cell with $N = 2$ (Fig. 7). After 80 sec UV exposure of the central domain and 1 hour dark storage homogenous cholesteric phase with $N = 1$ filled in the central domain (Fig. 7a), and additional storage time was needed to get homogenous cholesteric phase within the whole LC volume (Fig. 7b). In this case, too, the absorption spectrum of the central domain remained unchanged during the cholesteric phase propagation.

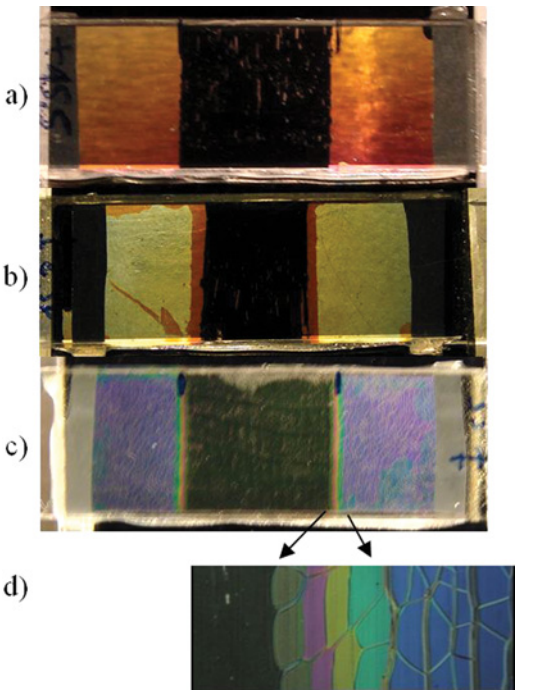

Figure 5. Photographs of the three-domain LC cells after UV exposures of the side parts: a) $d = 15{,}5\,\mu m$, $C_{7\text{-DHC}} = 0{,}5$ wt.-%, $N = 1$; b) $d = 15{,}8\,\mu m$, $C_{7\text{-DHC}} = 0{,}65$ wt.-%, $N = 2$; c) $d = 55\,\mu m$, $C_{7\text{-DHC}} = 0{,}5$ wt.-% and d) the right boundary (magnification $* 20$), $N = 5$. (Figure appears in color online.)

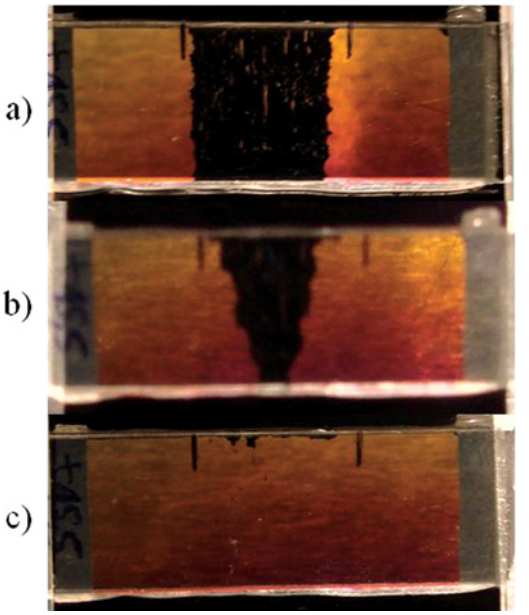

Figure 6. Creation and dynamics of the cholesteric phase propagation into the central part of the 1st (Fig. 5a) LC cell: immediately after 80 sec UV exposure (a) and after 30 (b) and 60 min (c) storage. (Figure appears in color online.)

It is evident that much more time would be needed to get homogenous cholesteric phase in the 3rd LC cell (Fig. 5c) in which more half-turns of the cholesteric helix (N = 5) were formed. Really, as one can see from Figure 8 even after many days storage the formation of homogenous cholesteric phase over the whole LC cell was not observed. But again no noticeable changes in the absorption spectrum of the central domain were observed during the cholesteric phase propagation.

Just the UV spectrum stability observed in all the above cases over the course of the cholesteric phase propagation might be taken as evidence of absence of 'domino effect' on *cis-trans* isomerization of dopant molecules.

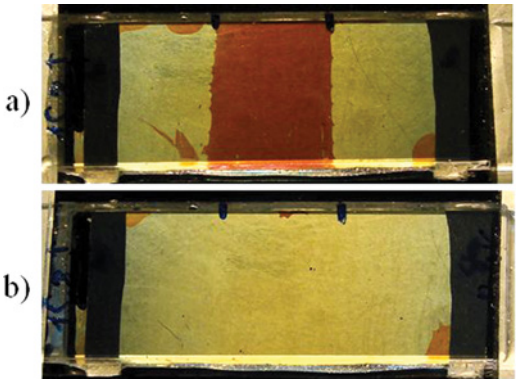

Figure 7. Photographs of the 2nd (Fig. 5b) LC cell after 1,5 h (a) and 2 days (b) storage. (Figure appears in color online.)

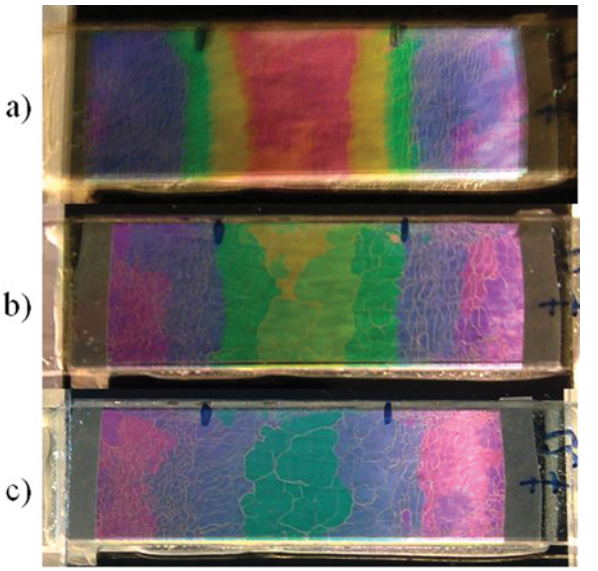

Figure 8. Photographs of the 3rd LC cell after 1 (a), 4 (b) and 15 days (c) storage. (Figure appears in color online.)

4. Conclusions and Perspectives

Previously observed significant increase of *trans*-isomer accumulation upon UV irradiation as compared with less viscous isotropic media was evidence of a volume-conserving hula-twist (HT) mechanism of previtamin D *cis-trans* isomerization. In addition, its collective character in the mesophase was established [1,2].

To clarify a possible role of 'domino effect', the dynamics of the cholesteric phase induction was studied by partial UV irradiation of a planar oriented LC cell, and the chirality transfer to the whole system was investigated using polarizing microscopy and UV absorption spectroscopy.

It was found that provitamin D dissolved in nematic LC mesophase in small concentration (less than 0.5 wt.%) did not transmit its chirality to the whole system, and the host matrix maintained its initial quasi-nematic order.

Upon UV irradiation the photoconversions of provitamin D induced a left-handed cholesteric helix, and well-defined edge between irradiated and non-irradiated parts of the LC cell was observed for a long time independent on the helix twist after UV exposure. Probably, provitamin D molecules with rigid steroid skeleton prohibited from the chirality transfer.

Nevertheless, critical UV exposure was found to observe the cholesteric phase propagation over the whole volume. Evidently, the well-determined ratio between the initial right-handed provitamin D, the conformationally flexible previtamin D and, what is most important, the left-handed tachysterol is needed for chiral perturbation in quasi-nematic LC, opening the locks to cholesteric phase expansion. However, stability of the UV absorption spectrum during this period disproved the suggestion on the 'domino effect'.

We think the enhancement of *cis-trans* isomerization with dopant concentration occurs due to excited energy transfer as a result of dipole–dipole resonance

interaction which critically depends on the distance between dopant molecules and the relative orientation of the dopant dipoles.

As the energy of the UV quantum is much more above 0–0 transition, the provitamin D excited molecule can transfer excess of energy (during a nonradiative relaxation into initial state or into a photoproduct) to the neighboring molecules, exciting their rotation and vibration degrees of freedom and thus promoting *cis-trans* isomerization. This could lead to the increase of photoconversion probability of the next dopant molecules, so that for every molecule with absorbed quantum of light there might be on the average more than one photoproduct.

We think the time–resolved spectroscopy could elucidate the microscopic mechanism of cooperative *cis-trans* isomerization of previtamin D in ordered LC media.

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