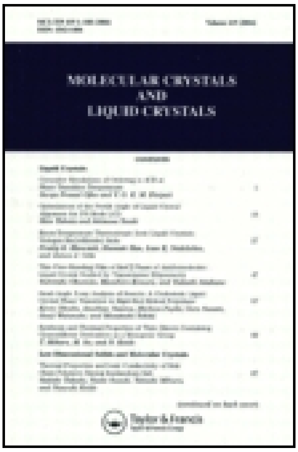

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Polarization Properties and Structure Changes of Plane-Oriented Nematic LCs with Provitamin D_3 Chiral Dopant

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At the first time a combined method of UV-absorption spectroscopy and Stokes-polarimetry were used for investigations of cholesteric liquid crystals induced by UV-photosensitive steroid provitamin D_3 molecules. It is determined that trans-*isomer tachysterol is the left-handed chiral dopant in contrary to initial provitamin D_3. The measurements of detailed distributions of light polarization ellipticity after passing through planar liquid crystal cells have shown that ellipticity changes are in close agreement with the variations of calculated equilibrium cholesteric pitch. It has been shown that UV-induced changes of cholesteric structure and alignment depend both on the liquid crystal thickness and initial concentration of provitamin D_3 dopant.*

Keywords Induced cholesteric LC; LC optical properties; LC structure dynamics; polarization light ellipticity; provitamin D_3 chiral molecule; UV-photosensitive dopant

1. Introduction

It is known that photoinduced order–disorder phase transitions of liquid crystals (LCs) or their order–order alignment changes induced by photochemical reactions of photochromic molecules give rise to the optical properties changes of the LC cells that constitutes basic principle for LC devices [1].

One of the popular methods to induce phase transition as well as modulation of alignment in cholesteric LCs is based on photochemical reaction of dopant molecules. Usually azobenzenes and stilbenes molecules are incorporated in LC matrices as photochromic guest molecules and then irradiated to cause specific photochemical reaction – E/Z isomerization. Such host/guest LC systems is very useful for different photonic applications, especially LC displays, polarizing optical elements, etc.

On the other hand, the UV-induced photoreaction of steroid provitamin D_3 (7-dehydrocholesrerol, 7-DHC) molecule is one of the well-studied photochemical reaction nowdays because it's the first stage of natural vitamin D_3 synthesis. It is known that the most efficient transformation in this complex photoreaction is

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Z/E isomerization of intermediate photoproduct previtamin D_3 into *trans*-isomer tachysterol. Obviously, the photoinduced changes in molecular geometric structure of initial right-handed chiral 7-DHC molecules [2] should affect its helical twisting power (HTP) and, as a result, the properties of induced cholesteric LCs.

In this paper we focused on the photochemical modulation of polarization properties and LC structure in planar LC cells caused by cholesteric pitch changes under UV-induced photoreaction of provitamin D_3 dopant.

2. Experimental Methods

2.1. *Features of 7-DHC Photoreaction in Nematic LCs*

The kinetics of 7-DHC photoreaction is described in details in literature [3–5]. In ethanol solution, under UV irradiation ($\lambda = 254\,\text{nm}$) 7-DHC is mainly transforms to *trans*-isomer tachysterol (~60%) (Fig. 1). The phototransformation is accompanied by increasing of maximum absorbance at 282 nm that can be measured by UV-absorption spectroscopy and thus can be used as indirect assessment of tachysterol concentration. As was shown in our previous papers [6–9], in nematic LCs the efficiency of tachysterol accumulation depends on initial 7-DHC concentration and varies in wide range up to 100%.

Mathematical model of 7-DHC photoreaction kinetics [10] allows calculation of photoisomer concentrations C_i after various UV exposures, and then equilibrium cholesteric pitch P is calculated from: $P_0^{-1} = \sum_i w_i \beta_i^{-1} C_i^{-1}$, w_i – weight fraction of each chiral photoisomers [11], using known HTPs (β_i) of chiral dopants and ignoring specific intermolecular interactions.

2.2. *Stokes-Polarimetry*

It is known that at normal incidence of linearly polarized light on planar-oriented cholesteric liquid crystal (CLC), one of the circularly polarized components is passed through CLC without significant reflection but another one is mainly reflected [12]. Thus the light polarization is transformed from linear to elliptical.

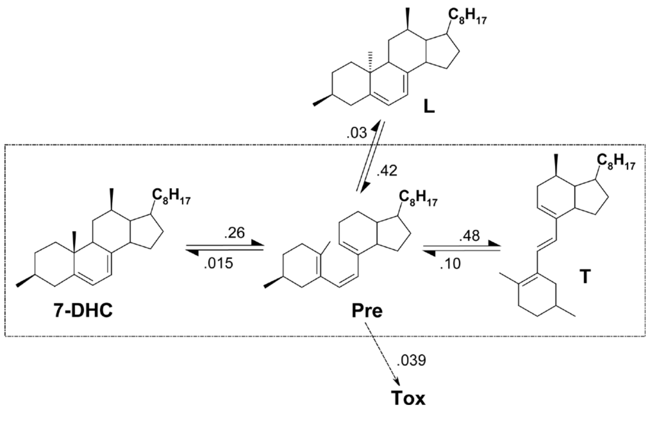

Figure 1. Scheme of 7-DHC photoreaction, Pre-previtamin D_3, T – tachysterol, L-lumisterol, Tox – toxysterols. Numbers at arrows represent the photoconversion quantum yields.

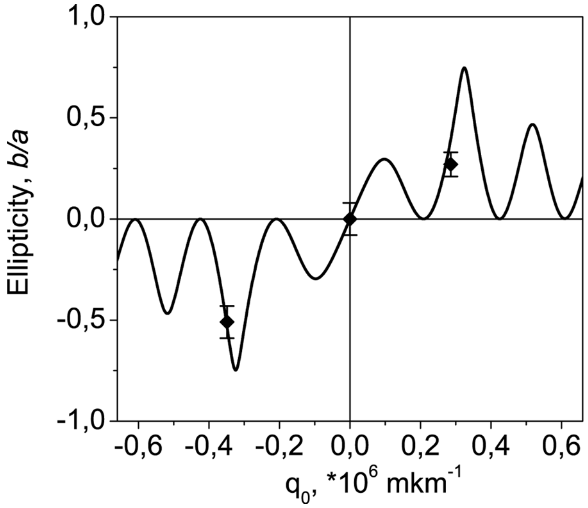

Figure 2. Comparison of calculated (line) and measured (symbols) light polarization ellipticity ($\lambda = 633$ nm) passed through planar cholesteric LC structure.

The calculated light polarization ellipticity ($\lambda = 633$ nm) passed through planar-oriented cholesteric LC [13] with normal incidence depending on the cholesteric helix twist wave number q_0 is presented at Figure 2 (line). The incident wave polarization was linear and parallel to the polishing direction on substrates.

We used Stokes-polarimetry technique to obtained detailed data on light polarization ellipticity after passing through a LC cell (Fig. 3) and to measure three orthogonal pairs of polarization component intensities (two linear and one circular) needed for construction of Stokes vector and ellipticity calculation [14,15]. For each sample, measurements were provided in several places (1.5 × 1.5) mm^2 of the LC cell (3 × 1) cm^2.

2.3. *LC Cell Preparation*

Induced cholesteric LCs were placed in planar cells of different thickness *d*, (15 ÷ 20) mkm and (58 ÷ 62) mkm. Both quartz substrates were coated with orientation layer of polydimethylsiloxane and rubbed for strong planar anchoring to fix the angle between incident light polarization and LC director at the first substrate.

For experimental testing of calculated dependence presented in Figure 2, we used nematic MLC-6815 (Merck) doped with right-handed chiral dopant R-811

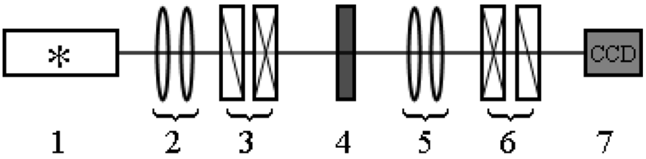

Figure 3. Stokes-polarimetry setup, 1 – He-Ne laser ($\lambda = 633$ nm), 2, 5 – collimating systems, 3, 6 – $\lambda/4$ plates and polarizers, 4 – LC cell, 7 – CCD camera connected to PC.

(Merck) and left-handed S-811 (Merck) with known HTPs. Hence dopant concentrations were chosen to provide integer half-turns of cholesteric pitch in the LC cells.

Then we measured ellipticity of light passing through LC cells filled by mixture of MLC-6815 with 7-DHC (Sigma) before UV irradiation and after several UV exposures. Additionally, wedge-shaped LC cells with thickness $(55 \div 65)$ μm were used for estimation of the photoisomer HTPs.

3. Results and Discussion

3.1. *Estimation of Provitamin D_3 and Tachysterol HTPs*

First, Stokes-polarimetry was tested by series of experimental measurements of light polarization ellipticity passing through planar LC cells filled by referent CLCs (with known dopant HTPs and well-defined thickness). The obtained results (Fig. 3, symbols) were in close agreement with calculated ellipticity data.

Further we studied UV spectral kinetics and light polarization ellipticity changes under UV irradiation of LC cells filled by induced cholesteric LC (MLC-6815 + 7-DHC) at $C_{7\text{-}DHC} = 0.6 \pm 0.05$ wt.%. The initial positive ellipticity value (Fig. 4a) corresponds to right-handed cholesteric helix induced provitamin D_3 in consistency

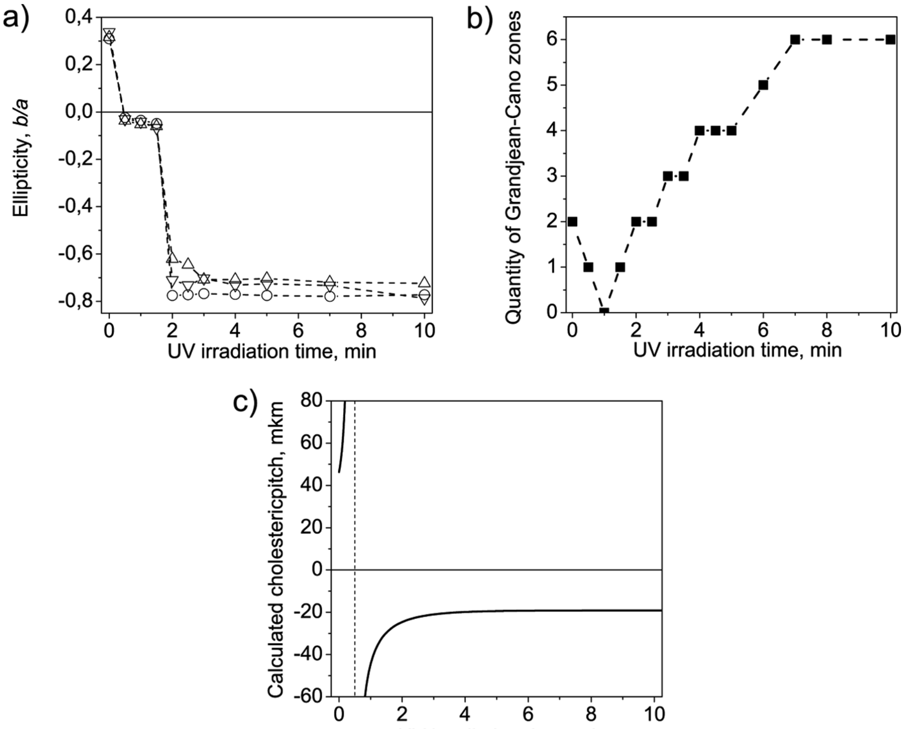

Figure 4. Experimentally measured changes of light polarization ellipticity ($\lambda = 633$ nm) in 3 places of planar-oriented LC cell with thickness 18 mkm (a) and of Grandjean-Cano zones quantity in wedge-like LC cell with thickness 56 mkm and wegde angle 6,4′ (b), and also calculated dynamics of equilibrium cholesteric pitch (c).

with previous results [2]. Next under UV irradiation ellipticity reduces to zero due to dopant photoconversions and establishing of nematic phase that is confirmed by polarized microscope observations. At last, sign of ellipticity became reverse to initial that indicated the left-handed cholesteric phase formation under UV irradiation. As was shown earlier [8,9], at specified initial 7-DHC concentration the efficiency of tachysterol accumulation is reached almost 100%, and thus we assumed that tachysterol is the left-handed chiral dopant.

This suggestion was confirmed by observation in changes of Grandjean-Cano zones quantity in the wedge-shape cells (Fig. 4b). In this Figure, the decrease of zones quantity indicates the increasing of cholesteric pitch up to quasi-nematic phase when right-handed and left-handed helixes are compensated each other. Further increase in zones quantity demonstrates the reversion to the cholesteric phase with tachysterol accumulation. Using known formula, we obtained HTPs of provitamin

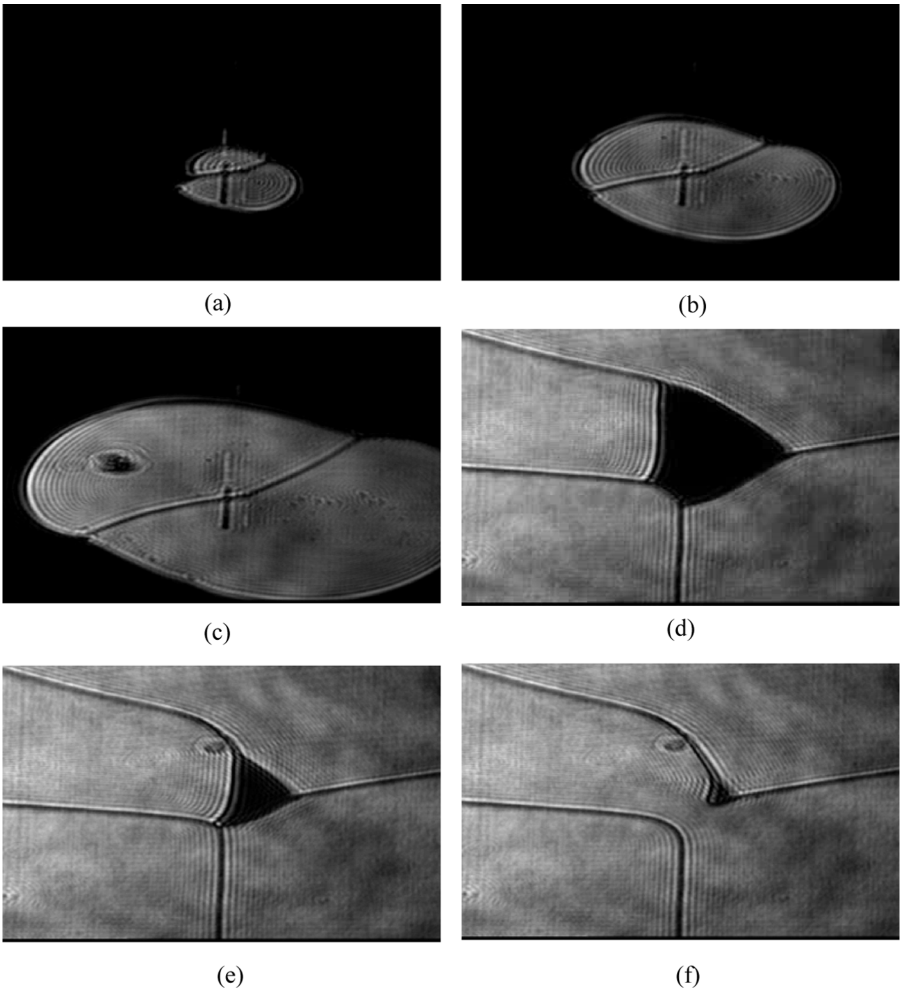
(a) (b) (c) (d) (e) (f)

Figure 5. Initial spreading (a–c) of left-handed cholesteric phase in quasi-nematic after 80 sec. of UV exposure, and the last stage of LC re-orientation (d–f). View in crossed polarizers, LC cell place (1.4×2.1) mm^2.

D_3 $\beta_{7\text{-}DHC} = +3.4\,\mathrm{mkm}^{-1}\,\mathrm{wt.\%}^{-1}$ and tachysterol $\beta_T = -8.5\,\mathrm{mkm}^{-1}\,\mathrm{wt.\%}^{-1}$ in assumption of 100% efficiency of 7-DHC = >T transformation.

At last, we calculated changes of cholesteric pitch value depending on UV exposure using photoreaction mathematical model with determined photoisomer HTPs (Fig. 4c). Simulated dynamics of cholesteric pitch is extremely close to experimental measurements of light polarization ellipticity changes, and asymptote (dotted line) represents the time of quasi-nematic phase appearance. However, the comparison of pitch dynamics with changes in quantity of Grandjean-Cano zones shows good agreement only at the initial stage of UV irradiation. Subsequent increase in zones quantity can be explained by differences in thickness of wedge-shape and planar LC cells.

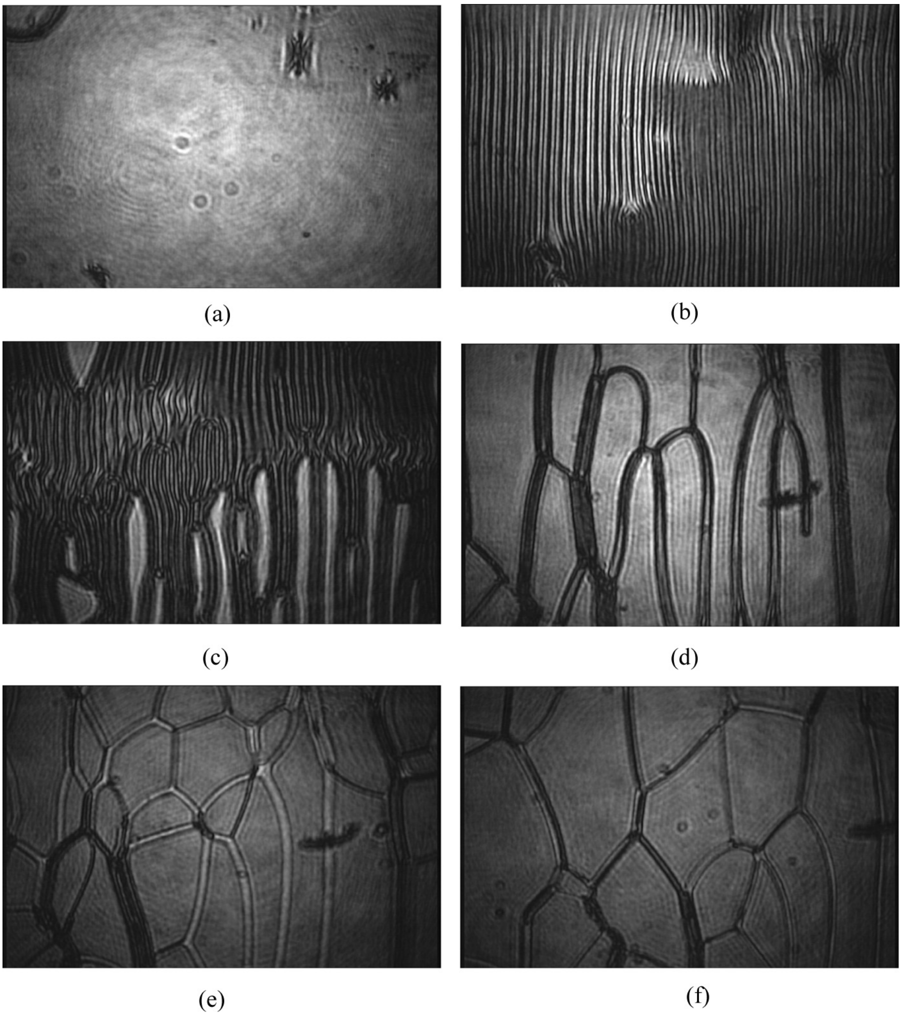
(a) (b) (c) (d) (e) (f)

Figure 6. Transformation of right-handed cholesteric phase into left-handed one under UV irradiation via re-orientation of cholesteric axis into the fingerprint structure, (a) – 1 min 05′ of UV exposure, (b) – 1 min 10′, (c) – 1 min 15′, (d) – 2 min, (e) – 4 min, (f) – 15 min, LC cell place $(1.3 \times 1.6)\,\mathrm{mm}^2$.

3.2. *The LC Structure and Alignment Dynamics*

Depending on initial 7-DHC concentration and LC cell thickness, two types of left-handed cholesteric LC phase establishing under UV irradiation were observed.

In the thin LC samples with $d = (15 \div 20)$ mkm and $C_{7\text{-}DHC} = (0.5 \div 0.6)$ wt.%, initial quasi-nematic phase is observed in LC cell because half-pitch of cholesteric LC induced by 7-DHC is larger than the cell thickness ($P_{7\text{-}DHC}/2 > d$). After 80 seconds of UV irradiation, the small islands of left-handed cholesteric phase were formed, increased in size (Fig. 5a–c) and merged with each other without any additional UV exposure (Fig. 5d–f). At that time, the boundaries between nematic and cholesteric phases spread with velocity $(1.5 \div 3)$ mkm/sec in the LC cell plane depending on room temperature and boundaries shape.

Analogous process was observed in thick LC cells with $d = (58 \div 62)$ mkm at $C_{7\text{-}DHC} \approx 0.2$ wt.% which provided the same initial ratio ($d/P_{7\text{-}DHC}$) as in thin LC cells.

In case of thick LC cells at higher 7-DHC concentration ($C_{7\text{-}DHC} \approx 0.5$ wt.%), initial right-handed cholesteric phase was observed before UV irradiation (Fig. 6a).

After UV exposure, the cholesteric phase reoriented into homeotropic state (Fig. 6b) which saved up to 30 minutes without UV irradiation. An important point is that experimentally measured cholesteric pitch from fingerprint texture ($P = 107$ mkm) is close to the calculated equilibrium pitch ($P_0 = 105$ mkm). Further UV irradiation destroyed the fingerprint texture (Fig. 6c) and led to formation of planar-oriented left-handed cholesteric poly-domain structure (Fig. 6d–f).

4. Conclusions and Perspectives

The polarization properties and structure changes of cholesteric LC induced by UV-sensitive steroid provitamin D_3 molecules have been studied in detailed. It is found that initial provitamin D_3 is right-handed chiral dopant with positive HTP while its main photoproduct – *trans*-isomer tachysterol – is the left-handed molecule with negative HTP. The Stokes-polarimetry technique was used to obtained detailed data on light polarization ellipticity after passing through a LC cell, and excellent correlation between measured ellipticity and simulated cholesteric pitch were established. Additionally, alignment changes were studied using polarizing microscope, and two types of LC phase re-orientation were revealed depending on the ratio between LC cell thickness and 7-DHC concentration (or initial cholesteric pitch value). The obtained data open the perspective of practical use of cholesteric LC induced by provitamin D_3 in different LC polarizing devices.

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