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UV Biodosimeter with Visual Detection of Vitamin D Synthesis Using θ-cell

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It has been shown that the LC cell, with parallel to the x-axis rubbing of a front face and circular rubbing of a rear face (θ-cell), filled with a nematic LC-805 doped by 7-Dehydrocholesterol (Provitamin D_3) allows visual monitoring of the UV photoinduced conversions of Provitamin D by deviation of the disclinaton line. After an UV exposure, relaxation processes in the LC matrix result in further dark change in the deviation angle that complicates the use of θ-cell as a UV biodosimeter. Temperature dependence of dynamic behavior of the disclinaton line was investigated additionally since it is important for a UV biosensor.

Keywords Induced cholesteric LC; Provitamin D phototransformation; UV monitoring; disclination line; θ-cell

Introduction

The cholesteric mesophase, sensitive to the smallest changes in molecular structure, is an excellent medium for optical sensors with visual detection, suitable for various applications. Wide usage of the ultraviolet (UV) electromagnetic radiation necessitates particular care in its applications where human beings are involved. High energy UV photons are absorbed by UV sensitive molecules in human skin and initiate a variety of photochemical reactions with subsequent alterations in their structures.

Since UV induced cancer is probably initiated by photochemical changes of DNA, simple biological dosimeters such as uracil molecule [1], DNA [2], bacteriophages [3] and bacteria [4, 5] are suitable for estimating the potential carcinogenic hazards of solar UV radiation.

On the other hand, initiation of endogenous synthesis of Vitamin D_3 in human skin is an important positive biological function of solar UV-B (280-315 nm) radiation. In view of its dramatic seasonal and latitudinal changes, an *in situ* control of the vitamin D synthetic capacity of sunlight demands particular care. Since UV-B portion of sunlight converts 7-Dehydrocholesterol (7-DHC, Provitamin D_3) into Previtamin D, which, in turn, undergoes thermo-conversion into Vitamin D_3 at a body temperature [6], Previtamin D quantity accumulated during UV exposure is closely related to the accepted specific 'antirachitic' UV biodose.

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The 'Vitamin D' biodosimeter [7, 8] is based on the Previtamin D photosynthesis *in vitro*, and therefore satisfies the most important criterion for assessing its applicability, that is the measured photoreaction is UV-specific and indicative of a critical photobiological process of Vitamin D synthesis [9].

Dissolution of optically active molecules of 7-Dehydrocholesterol in nematic liquid crystalline (LC) matrix was shown to induce cholesteric phase with right-handed helix [10]. Upon UV irradiation alteration of molecular geometry of 7-DHC by the photoinduced conversion into Previtamin D (with its further *cis-trans* isomerization into Tachysterol) significantly affects its helical twisting power resulting in helical pitch changes and allowing visual detection of Previtamin D synthesis [10–12]. In particular, *trans*-isomer Tachysterol was shown to have much higher helical twisting power and its accumulation appeared to be accompanied by a decrease in the cholesteric pitch. Significant effect of UV irradiation on the number of Cano-Grandjean zones in the wedge-shaped LC cell, extremely useful for personal UV dosimetry *in situ,* has been observed for the first time [10]. Later, the shift of selective reflection peak and, as a result, the LC cell color change, was observed under UV irradiation in a sandwich-like LC cell. This enables the easiest detection of Previtamin D synthesis and evaluation of the accumulated UV dose *in situ* by comparison of the LC cell color with the calibration scale [11, 12]. Such LC-based D-biodosimeter meets the most important requirements of applications as personal UV dosimeter [9].

Here we discuss a new method for visual detection of Provitamin D photoconversions, as well as the monitoring of biologically active UV dose, based on measuring the angular deviation of the disclination line in the so-called θ-cell designed by Stalder and Schadt [13, 14].

In a LC θ-cell, the rubbing of a front face is parallel to the x-axis and is circular on a rear face. As a result, the boundary conditions on the substrates align director to be parallel to the x-axis at one side and oriented circularly at another. Started from the orientation parallel to the x-axis, director then rotates gradually to finally satisfy the alignment angle determined by the circular rubbing of the rear substrate. The molecules located along the y-axis do not experience any twist, while along the x-axis ($y = 0$) the twist angle becomes undetermined and a topological defect occurs in the form of a disclination line [13, 14]. In a θ-cell filled with an achiral nematic liquid crystal the disclination line is oriented parallel to the unidirectional rubbing [15].

A simple method for detecting and measuring of LC compound chirality by determination of the azimuth orientation of a disclination line in θ-cell is discussed in [16].

For a UV dosimeter, the LC matrix must be transparent in the UV range, stable to UV and visible radiation action; besides it should be a good solvent for 7-Dehydrocholesterol. An important point is that helical pitch of the UV biosensor should be thermally stable to temperature changes in the range of $(10 \div 50)^{\circ}$C.

Materials and Methods

H-bonded LC-805 (50:50 mixture of trans-4-butylcyclohexane-carboxylic ($C_{11}H_{20}O_2$) and trans-4-hexylcyclohexane-carboxylic ($C_{13}H_{24}O_2$) acids) has been chosen as a nematic LC matrix. Experiments were performed with a composition of LC-805 (KANTO Chemical Japan) and 7-DHC (Sigma) ($C_{7\text{-DHC}} = (0.2 \div 0.8)$ wt.%).

The LC cells were made from two 2.5-mm-thick quartz substrates covered (spin-coated) with a polyimide film (Kapton). The rubbing was produced mechanically unidirectional for

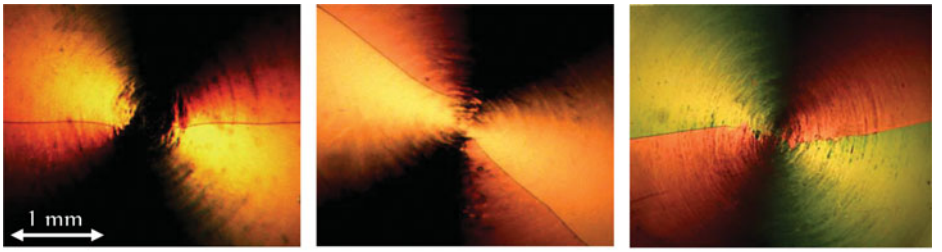

Figure 1. Microscope view of a θ-cell between crossed-polarizers: (a) filled with pure nematic LC-805, (b) filled with composition LC-805 and 7-DHC (C = 0.2 wt.%), (c) filled with composition LC-805 and 7-DHC (C = 0.8 wt.%). The LC cell thickness ~55 μm.

one substrate and using a rotating disk for another one. The cells thickness was ~50 μm with transversal dimensions 1 × 3 cm^2.

Monitoring the behavior of disclination line was performed using a polarizing microscope POLAM L-213M (LOMO), and temperature studies – by using polarizing microscope Olympus BX 51 with Instec HS-1 heater.

UV irradiation of the samples was carried out at room temperature with a fluorescent lamp EL-30 (270-380 nm). Spectral irradiance of the UV lamp at the sample distance of 7 cm was measured with the calibrated spectrometer EPP2000C-UV+VIS (StellarNet Inc.), and in the sample plane it amounted to 0.11 mW/cm^2 in the UV-B spectral range. The kinetics study of 7-DHC photoisomerization in the θ-cells was followed by recording the UV absorption spectra before and after several UV exposures using Lambda 25 spectrophotometer (Perkin Elmer).

Results and Discussion

The first LC sample used in the experiment was θ-cell filled by a pure nematic LC-805 at ~60°C. The prepared cell was inspected in a microscope and it appeared that equilibrium position of a disclination line was reached within two hours. Figure 1(a) shows the observed picture, with the θ-cell placed between the crossed polarizers. The disclination line between two twist domains with opposite orientations is seen as black horizontal line on the bright background [16, 17]. The orientation of the disclination is mainly parallel to the unidirectional rubbing as expected.

Then, the θ-cell was filled with a LC composition containing 0.2 wt.% of 7-DHC which is right-handed chiral dopant with the helical twisting power $\beta = +3.4$ mkm^{-1}wt.$^{-1}$ [18]. Despite the fact that at such a low concentration quasi-nematic phase was observed (due to the fact that half-pitch of cholesteric LC induced by 7-DHC was larger than the cell thickness), the effect of the disclination reorientation caused by LC chirality is clearly seen in Figure 1(b). With the increase of 7-DHC concentration, the pitch variations will be reflected in the amount of the angular deviation of the disclination line from the unidirectional rubbing direction in accordance with the relationship $\theta = 2p/d$, where p is the helix pitch and d is the cell thickness [17]. At C = 0.8 wt.% the disclination line makes more than 360 degrees rotation (Figure 1c).

Initially temperature dependence of the disclinaton line was investigated since it is an important point for a UV biosensor. The phase transition temperatures to isotropic state were

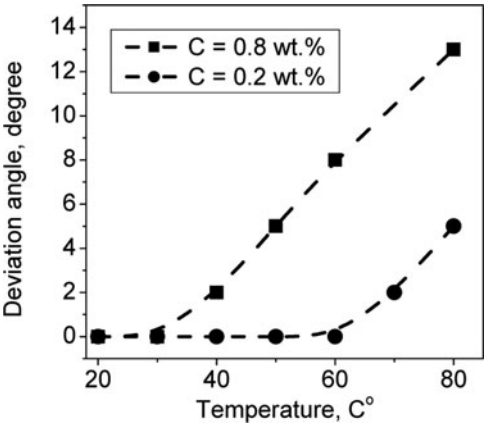

Figure 2. Deviation angle of the disclination line from the unidirectional rubbing axis as a function of temperature for LC-805 doped with 7-DHC.

measured for the LC-805 and for the two LC samples doped with 7-DHC. The following values were obtained: T = 94°C for pure LC-805, T = 93°C for $C_{7\text{-DHC}} = 0.2$ wt.% and T = 91.5°C for $C_{7\text{-DHC}} = 0.8$ wt.%.

The temperature behavior of the disclination line in two θ-cells with the same concentrations of 7-DHC was studied with the temperature increase from room temperature in increment of 10°C. At the each temperature, the sample was kept for a 1 hour before reaching the equilibrium position of the disclination line. It appeared that in quasi-nematic phase (C = 0.2 wt.%) the disclination line was stable when heated up to 60°C, whereas at high concentration of 7-DHC the line began to turn slowly with increased temperature starting from 40°C (Figure 2). The clockwise direction of deviation corresponded to decreasing of cholesteric pitch as it expected for the highly anisometric chiral dopant molecules [19]. Interestingly, for both concentrations the angle increased nearly equal with increasing temperature $\Delta\varphi/\Delta T \approx 0.25$ degrees/°C. Physical origin of this behavior remains to be explored and published as an independent research.

The experiments on UV irradiation of the θ-cells showed deviation of the disclination line during UV exposure. After the termination of UV irradiation, however, the line did not stop turning, and the deviation angle continued to grow slowly until it reached a certain equilibrium value wherein molecules on either side of the disclination line have the same free energy [17].

Therefore, UV irradiation of the LC samples with two concentrations of 7-DHC (C = 0.2 wt.% and C = 0.8 wt.%) was performed as follows. Before UV exposure the initial position of the disclination line was fixed and the initial absorption spectrum of the sample was recorded. Then, immediately after each UV exposure, both the deviation angle of the disclination line and absorption spectrum of the irradiated θ-cell were recorded. Further observation of the disclination line behavior was carried out without UV exposure as long as the slow variation of the angle stopped. It should be noted that almost no changes occur in the absorption spectrum of the θ-cell during this period.

The photos of the θ-cell with two concentrations of 7-DHC made prior to UV irradiation and after several UV exposures are shown in Figure 3.

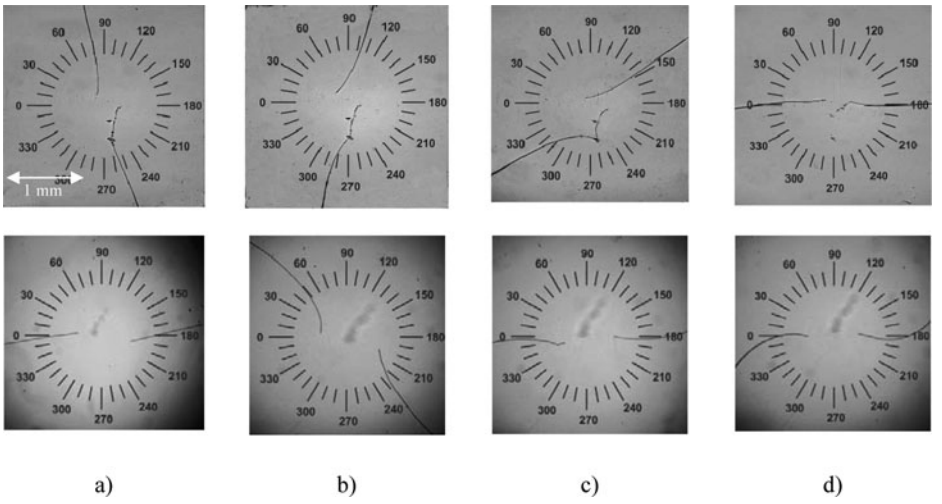

Figure 3. Microscope view of the two θ-cells in polarized light before UV irradiation (a) and after several UV exposures: 2 min (b), 5 min (c), and 10 min (d). Top row: $C_{7\text{-DHC}} = 0.2$ wt.%, bottom row: $C_{7\text{-DHC}} = 0.8$ wt.%.

The process of the angular deviation is depicted in Figure 4 for the two samples with different concentrations of 7-DHC. Open symbols show the angle values measured immediately after UV exposures, and solid symbols show equilibrium values of the deviation angle. Solid lines show the angle changes measured immediately after UV exposures, and vertical dashed lines represent further 'dark' changes in the deviation angle.

It is obvious that the angle changes correspond to two different mechanisms of changing the cholesteric pitch. The first mechanism is directly related to the UV photoinduced conversion Provitamin D → Previtamin D and its further *cis-trans* isomerization into Tachysterol that affects the pitch of the cholesteric helix. Accumulation of the *trans*-isomer T with much greater helical twisting power determines final reduction of cholesteric pitch [18].

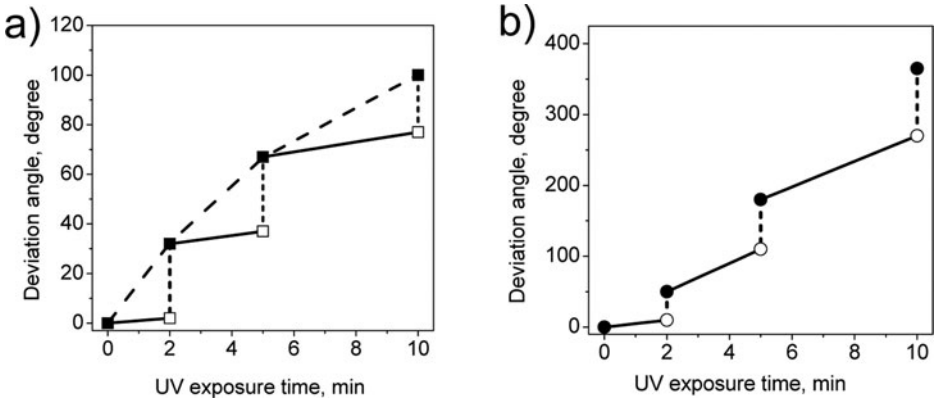

Figure 4. Effect of UV irradiation on the increase of deviation angle of disclination line in two samples with $C_{7\text{-DHC}} = 0.2$ wt.% (a) and $C_{7\text{-DHC}} = 0.8$ wt.% (b).

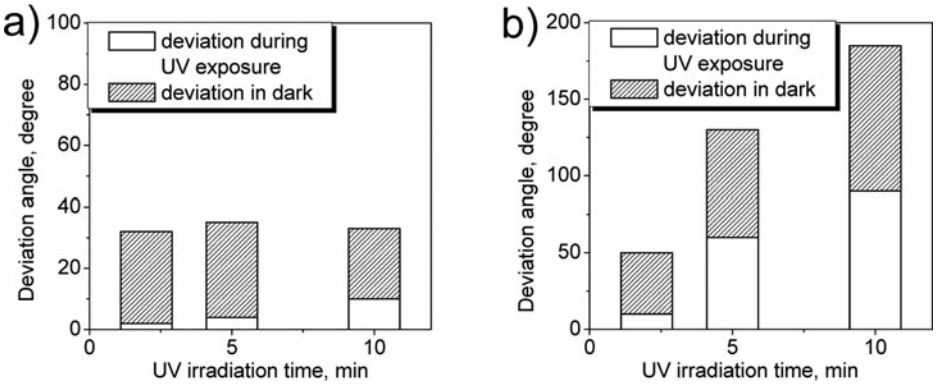

Figure 5. Deviation angle changes on the irradiation time for the two θ-cells with $C_{7\text{-DHC}} = 0.2$ wt.% (a) and $C_{7\text{-DHC}} = 0.8$ wt.% (b).

The second mechanism of the 'dark' changes in the deviation angle is a slow process that is associated with the reorientation of the LC molecules. Indeed, if the energy of the molecules on both sides of the disclination line is unbalanced, the LC structure is appropriately adjusted via reorientation of the LC molecules by molecule-molecule interaction. As a result, the disclination line moves to reach a stable equilibrium configuration. According to our understanding the rate of such dark reorientation is mainly dependent on the LC viscosity and defined by the elastic constant K_{22} for the director *twist*-deformation.

Comparing the angle increment in Figures 4a) and b), it becomes evident that the cell with high concentration of 7-DHC is more UV sensitive, especially due to collective character of *cis-trans* isomerization [20], but it is less suitable for personal UV dosimetry because during total UV exposure the disclination line deviates in excess of 360 degrees. Indeed, since the angles φ and $(\varphi + n\pi)$ corresponding to two different values of helical pitches have the same apparent deviation of the disclination line from the unidirectional rubbing axis, for measuring UV dose it is important to determine exactly how many turns the disclination line has experienced.

The envelope (dotted curve) connecting the equilibrium values of the deviation angle at low concentration (Fig. 4a) has a shape of function $y = A_{total}\ (1 - exp(-B_{total} * t_{UV}))$ where A_{total} reflects the total value of the deviation angle change, and B_{total} – the change rate. The values of function parameters obtained from interpolation of the experimental data are equal to $A_{total} = 133.4$ degrees and $B_{total} = 0.14\ \text{min}^{-1}$ (or, going from the time dependence of deviation angle to the UV-B dose dependence, $B_{total} = 0.0021\ (\text{J/m}^2)^{-1}$). This curve can further be used for comparison with the accumulation of Previtamin D in ethanol and the calibration curve construction.

The relationship between the 'light' and 'dark' changes of the deviation angle for the two cells is clearly seen in Figure 5, and the dynamic behavior of the disclinaton line during keeping in dark after several UV exposures is given in Figure 6.

Graphs showing the dark relaxation of deviation angle in Figure 6 can also be approximated by the function $y = A0_{dark} + A_{dark}\ (1 - exp(-B_{dark} * t_{dark}))$ where $A0_{dark}$ reflects the initial absolute value of the deviation angle immediately after each UV exposure, A_{dark} - the absolute value of 'dark' growth of the deviation angle, and B_{dark} - its change rate. Similar to previously described, the values of function parameters were obtained from the interpolation of the experimental data. It is worth noting that in case of low 7-DHC

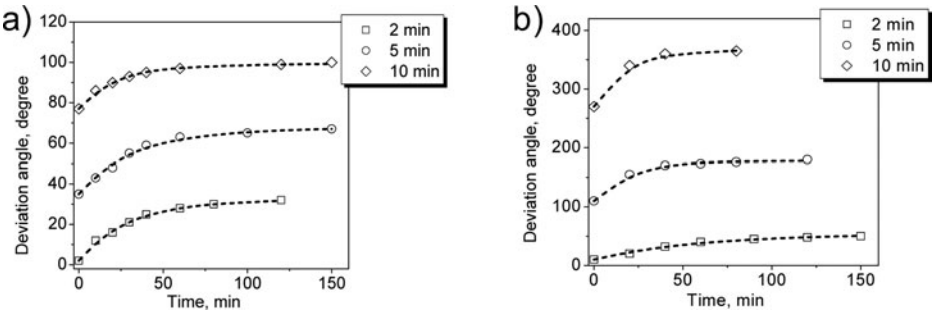

Figure 6. Dark relaxation of the deviation angle after each UV exposure for the two θ-cells with $C_{7\text{-DHC}} = 0.2$ wt.% (a) and $C_{7\text{-DHC}} = 0.8$ wt.% (b).

concentration, the coefficients A_{dark} and B_{dark} vary slightly with exposures ($A_{dark} \sim (22 \div 32)$ degrees, $B_{dark} \sim (0.03 \div 0.04)$ min^{-1}), but their variations become more significant for high concentration of 7-DHC (A_{dark} changes from 44 to 96 degrees, and B_{dark} changes from 0.02 to 0.07 min^{-1}).

Interestingly, the contribution of the dark growth is reduced with the accumulation of Tachysterol, i.e. the energy balance is achieved faster as the cholesteric helix becomes more twisted.

Since the rate of Tachysterol accumulation depends on the UV-B irradiance, it can be expected that at a lower intensity the angle adjustment will occur during longer UV exposure, and, as a result, the 'dark' contribution of the angle change will decrease. Furthermore, for UV dosimetry it is important to check whether the final deviation angle corresponding to UV dose is independent of the intensity, i.e. whether the reciprocity law is valid.

With this aim two θ-cells were prepared with the same concentration of 7-DHC (C = 0.25 wt.%) that showed the same initial deviation angle $\varphi_0 = 100^0$. One LC cell was irradiated during 10 min at a distance of 7 cm, and the other one – at a distance twice as large (14 cm). The exposure time for the second LC cell was four times greater (40 min), so that the obtained UV doses for both θ-cells were almost the same.

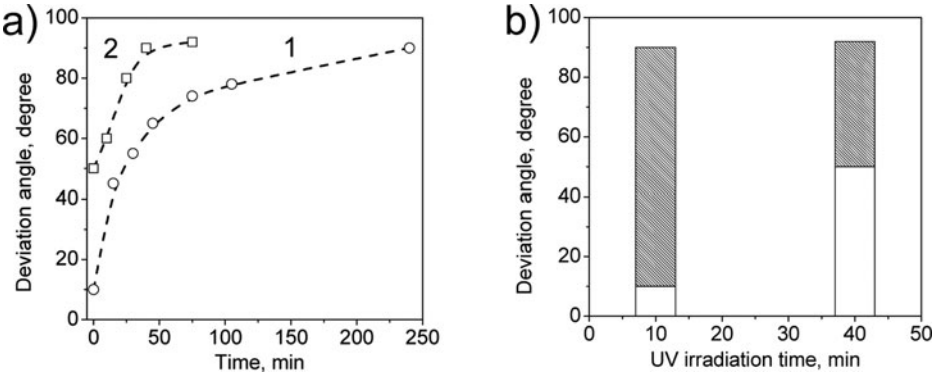

Figure 7. Dark increase of the deviation angle (a) in the θ-cells irradiated at a distance of 7 cm (1) and 14 cm (2) and contribution of 'light' and 'dark' changes into the total increase of the deviation angle (b).

The deviation angle was measured immediately after UV exposure and then recorded every 10 min. The dark changes of the deviation angle for both LC cells are shown in Fig. 7a) and the total increase of the angle – in Figure 7b). As expected, the contribution of dark change into the total value of deviation angle was smaller at longer exposure with lower intensity of UV radiation, and the equality of the total values of deviation angles proves the validity of the reciprocity law.

Conclusions

The experiments with θ-cells filled with a composition LC-805 and 7-DHC showed close relationship between the deviation of disclination line and phototransformations of Provitamin D. The long-term dark relaxation observed in the doped LC-805, however, complicates application of the θ-cell as a personal UV dosimeter, and a less viscous LC matrix would be more appropriate. Our further studies will clarify the usability of the θ-cell as a UV biodosimeter by testing additivity and reproducibility of initial and final values of deviation angle in the range of 7-DHC concentrations and UV exposures.

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