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Development of Personal UV Biodosimeter Based on Vitamin D Photosynthesis

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A new approach to monitoring of vitamin D synthetic capacity of UV solar/artificial radiation is described. Nematic liquid crystal (LC) was converted into cholesteric phase by chiral dopant of 7-dehydrocholesterol (provitamin D₃), and the effects of UV irradiation were studied using spectral and polarized observations. Significant changes in optical characteristics of the LC films depending on UV exposure were observed as a result of UV initiated photoisomerization that changed helical twisting power of dopant molecules.

Keywords: liquid crystal; provitamin D₃; cholesteric; UV dosimeter.

INTRODUCTION

Concerns of the environmental and health effects of solar UV radiation penetrating into the biosphere through the depleted ozone layer have greatly emphasized the urgency of reliable measurements of biologically effective UV radiation. Excessive solar UV exposures cause sunburn, premature skin aging and skin cancer, but in appropriate doses UV sunlight plays an important positive biologic function initiating vitamin D₃ synthesis in skin. This suggests the use of an *in situ* monitoring of vitamin D synthetic capacity of solar UV radiation.

The UV-B portion of sunlight (280-315 nm) converts provitamin D₃ into previtamin D₃, which, in turn, undergoes thermoconversion into vitamin D₃ at body temperature [1]. Consequently, accumulation of previtamin D₃ during UV exposure can serve as a measure of biological UV dose. However, side photoconversions of previtamin D₃ give rise to a multicomponent mixture that complicates the issue.

The method of UV dosimetry (D-dosimeter) based on an *in vitro* model of vitamin D^{*} synthesis (solution of provitamin D in ethanol) had been recently introduced as a result of comprehensive studies of the photoreaction kinetics with tunable dye-laser [2,3,4]. Original spectrophotometric analysis has been specially designed to ensure *in situ* measurements of accumulated UV doses [5]. However, necessity of UV spectrophotometer and computer processing of the absorption spectra hinders the use of D-dosimeter for personal UV dosimetry.

Here we report on the first experiments directed to elaboration of personal UV dosimeter based on nematic liquid crystal doped with chiral biomolecules of 7-dehydrocholesterol (provitamin D₃).

EXPERIMENTAL

Material and sample preparation.

To comply with the requirements, the LC matrix should be transparent in UV range, thermally stable over the interval at least 10-40 °C, be a good solvent for 7-DHC and be stable with respect to the visible light. Nematic LC-805 (1:1 mixture of 4-n-butyl- and 4-n-hexyl-trans-cyclohexanecarboxylic acids) (CHCA, NIOPIK, Russia) has been selected as a host matrix [6], and 7-DHC (Sigma, Germany) was dissolved in the LC material in concentration 5 ÷ 10 wt.%.

Three types of cells (15x20mm²) were prepared. The first one was a sandwich-like cell whose substrates were usual quartz plates. It

* Further the term vitamin D is employed in the general sense although two principal chemical species of vitamin D are available. Vitamin D₂ (C₂₈H₄₄O), is photochemically produced in plants from ergosterol (provitamin D₂), similar to vitamin D₃ (C₂₇H₄₄O) which is produced in animals and humans from 7-dehydrocholesterol (7-DHC, provitamin D₃). It is significant that basic monomolecular isomerizations of the two steroid species occur in perfect analogy.

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was used for comparison of the photoreaction kinetics in LC matrix with known kinetics in ethanol solvent by absorption spectroscopy.

The second type was the wedge-like cell consisted of two indium-tin-oxide (ITO) glass substrates with rubbed polyimide films (Merck, Korea) which are widely used as aligning layers. The wedge-like cells were made using Mylar spacer, and their thickness ($L = 63\ \mu\text{m}$) was measured by interferometer. This cell was used for polarized-light observations.

The other wedge-like cell was prepared using two quartz plates as substrates. To provide planar boundary conditions the quartz substrates were spin coated with poly(dimethylsiloxane), annealed on the hot plate at $200\text{--}250\ ^\circ\text{C}$ over 4 hours and further mechanically rubbed that ensured planar alignment of the LCs. With this cell it was possible to record the absorption spectra and carry out visual observations with polarizing microscope.

Methods

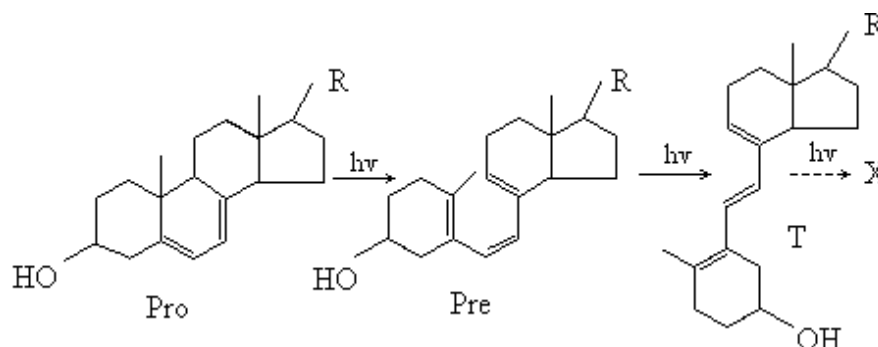
The samples were irradiated with fluorescent lamp (EL-30) that delivered integral intensity of $0.3 - 0.63\ \text{mW}/\text{cm}^2$ within the spectral range of $250\text{--}350\ \text{nm}$ depending on the distance $8\text{--}12\ \text{cm}$.

UV absorption spectra of the samples were recorded by KSVU-23 spectrometer (LOMO, St.-Petersburg) before UV irradiation and after certain exposures within the spectral range of $230 - 350\ \text{nm}$. In parallel, UV effects on the induced cholesteric phase were studied using polarizing microscope.

RESULTS AND DISCUSSION

Effect of the LC microenvironment on the photoreaction kinetics

Significant difference of the spectral kinetics of 7-DHC photoisomerization has been revealed in the LC matrix as compared with ethanol solution [7]. Significant increase in the absorbance in case of the LC matrix gave strong evidence for the enhancement in the efficiency of previtamin D *cis-trans* isomerization. This efficient photoconversion into rod-like molecule of tachysterol can be attributed to specific interaction with microenvironment in the nematic LC matrix (see Scheme 1).



SCHEME 1. Photoisomerizations of provitamin D in the nematic matrix: Pro – provitamin D, Pre – previtamin D, T – tachysterol; R = C₉H₁₇ (vitamin D₂ series); R = C₈H₁₇ (vitamin D₃ series).

Studies of the induced cholesteric phase

Transformation of the nematic LC-805 into cholesteric phase due to chiral dopant was evidenced by observation of Cano-Grandjean stripes in the wedge-shaped cell using polarizing microscope. Well known dependence of the number of Cano disclinations (N_C) on the dopant concentration (C) had been observed. $N_C = 10$ was found at $C = 10$ wt.% that corresponded to maximum solubility of 7-DHC. The cholesteric pitch length (P) was obtained from the number of disclination lines N_C : $P = 2L/N_C$ [9]. The length of the pitch depends on the dopant concentration as $PC = \text{const}$ (see Figure 1), and a selective reflection band for the calculated P lies outside the visible spectrum.

In an unsealed cell, on keeping in dark, the Cano stripes progressively declined in number with slow broadening starting from the cell borders [10]. We associate this instability with the loss of twisting power of 7-DHC in the course of oxidation [11]. To avoid this process, in subsequent experiments the cells were carefully stuck along the perimeter, and the number of Cano stripes was found to be unchanged in storage.

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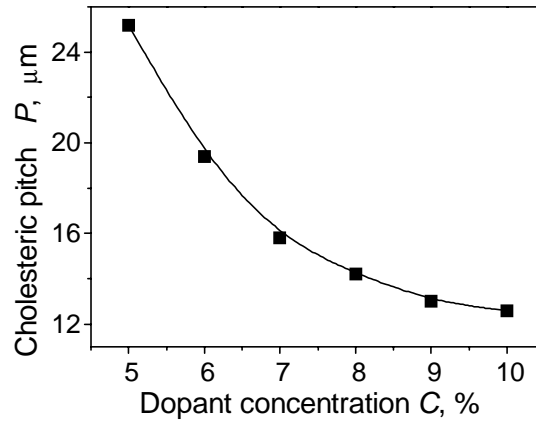


FIGURE 1. Dependence of an induced pitch length on 7-DHC concentration.

UV irradiation

Significant effect of UV irradiation on the number of Cano stripes has been revealed with polarizing microscope (see Figure2), and

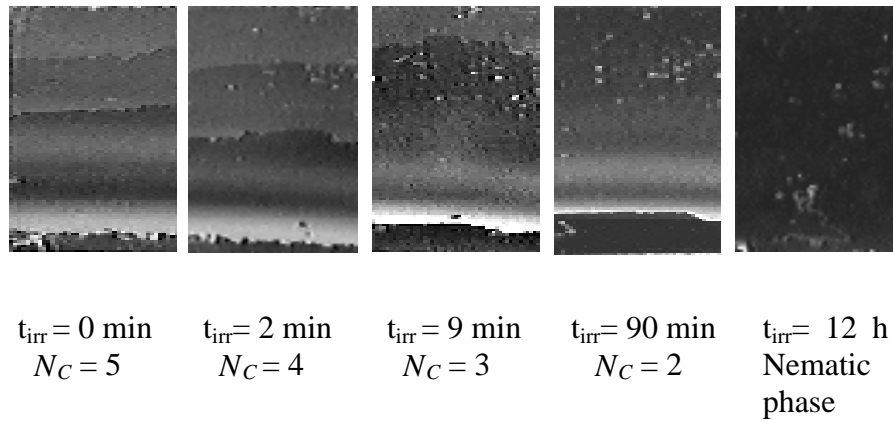


FIGURE 2. Cano stripes decrease during UV irradiation.

corresponding dependence of the cholesteric pitch length, P , on the UV exposure has been calculated (Figure 3). The decrease of the N_C with increasing irradiation time indicates that the chiral dopant undergoes phototransformations into isomers possessing considerably lesser helical twisting power (HTP).

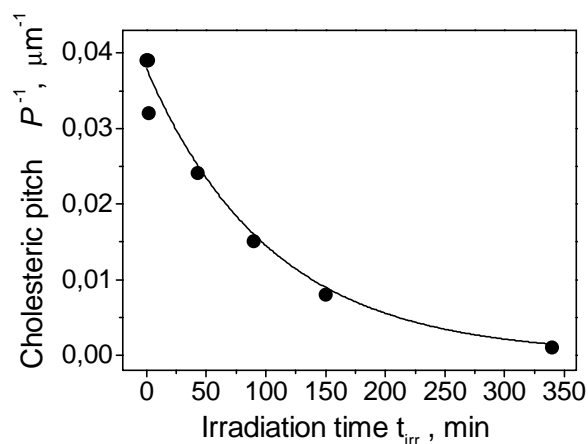


FIGURE 3. Dependence of an induced pitch reverse length on the UV exposure.

Observation on the spectral kinetics (Figure 4) suggests that efficient accumulation of *trans*-isomer tachysterol occurred at the beginning of UV irradiation as evidenced by significant increase in the absorbance (Figure 4a). Obviously, HTP of 7-DHC molecule with its rigid steroid skeleton should be significantly decreased by hexadiene ring-opening and further *cis-trans* isomerization into rod-like molecule of tachysterol. Thus, accumulation of tachysterol gives rise to the increase in the cholesteric pitch length and, as a result, is accompanied by the N_C decrease. Irreversible photodegradation of tachysterol (Figure 4b) under prolonged UV irradiation is accompanied by further decrease in N_C to the point of disappearance of cholesteric phase (see Figure 2).

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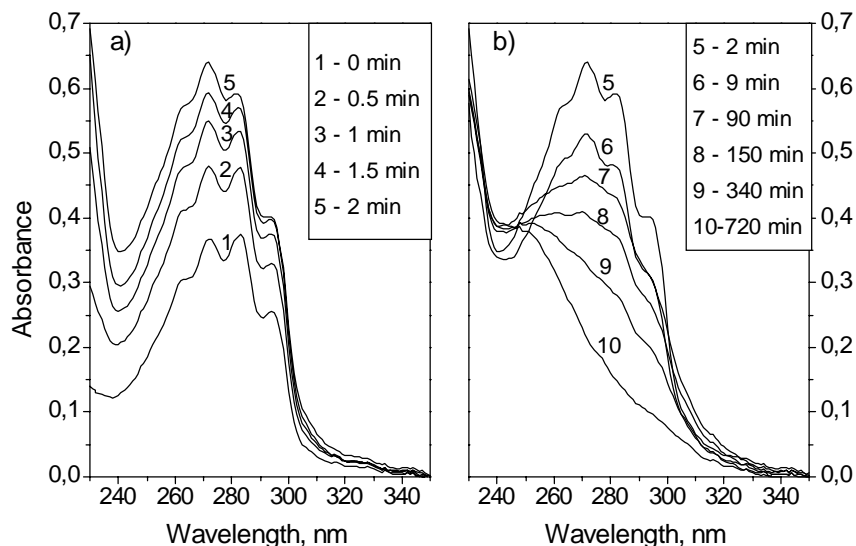


FIGURE 4. Transformations of the absorption spectrum of the LC sample during UV exposures.

CONCLUSIONS

For the first time, it has been experimentally found that chiral molecule of 7-DHC induces stable cholesteric phase when doped into nematic LC. Substantial changes in the spectral kinetics of provitamin D photoisomerization in the nematic matrix as compared with ethanol solution argues in favour of the increase in the efficiency of *cis-trans* isomerization of previtamin D. Clearly defined dependence of the cholesteric pitch on the UV exposure has been observed, which may be applied for personal UV dosimetry. It is expected that intercalibration of doped LC film with D-dosimeter can ensure monitoring of vitamin D synthetic capacity of solar UV radiation by visual observation using crossed polarizers. Further investigations will be directed to simplification of the procedure by shifting the selective reflectance band to visible spectral region.

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