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■論 文■

Cholesteric Liquid Crystals as Multi-Purpose Sensor Materials

L.N.Lisetski
Institute for Scintillation Materials of STC "Institute for Single Crystals"
of the National Academy of Sciences of Ukraine, Kharkov, Ukraine

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Abstract - New possibilities are discussed for cholesteric liquid crystals (CLC) as sensor materials for detection of ionizing radiation, biologically active UV radiation, and the presence of hazardous vapors in atmosphere. A distinguishing property of CLC-based detectors is their "bioequivalence", i.e., mechanisms of their response to external factors essentially imitate the corresponding mechanisms of biological tissues. Such detectors can ensure sufficiently high sensitivity to make feasible their use as alarm indicators or in biophysical studies. Specific examples are given of sensor compositions and their response characteristics.
Key words : cholesteric liquid crystals, ionizing radiation, UV radiation, vapor detection, bioequivalent detectors

Introduction

Cholesteric liquid crystals (CLC) have been known since 1960-ies as promising material for various sensor applications. The helical pitch of CLC can be, in appropriate conditions, extremely sensitive to different external factors ; at the same time, its variation can be easily recorded using the routinely measured selective reflection/transmission spectra or, if large enough, even visually observed as changes in color. This property had been evoking much interest reflected in numerous developments of design and operation principles of CLC-based sensors or meters of temperature, electric or magnetic fields, pressure, IR radiation, acoustic waves, etc. [1,2].

In this paper, we will consider several sensor applications of CLC that are related to technogenic factors affecting the environment and life conditions of human organisms. Since these factors grew more and more important with the development of technological world, these applications were re-visited several times after their initial discovery. In particular, they include detection and monitoring of ionizing radiation, biologically active UV radiation, and the presence of toxic vapors in the atmosphere.

In early works, CLC were used for detection of large doses of ionizing radiation. The action principle of such devices was based on radiation-induced chemical destruction of a substance present in the cholesteric mixture (e.g., cholesteryl iodide). The sensitivity obtained was rather low, with the smallest doses that could be detected being of the order of~1 krad. Efforts in this direction resumed after the Chernobyl catastrophe, a new principle was proposed [3]-to use processes of *trans-cis* isomerization of certain substances introduced to the cholesteric solvent. In such a way, sensitivities of the order of mrad were obtained ; in addition, these detectors were claimed to be bioequivalent, i.e., the mechanism of their response was similar to that occurring in biological tissues. Such detectors are expected to be especially efficient at low (<10 keV) gamma-radiation energies.

The main ideas for the development of liquid crystalline bioequivalent detectors of ionizingradiation can be summarized as follows.

Let us compare the radiation response mechanisms of two substances. One of them is lecithin (phosphatydilcholine), which is (alongside with other phospholipids of similar structure) one of the main components of cell membranes. The other is a typical mesomorphic (liquid crystalline) substance-4-methoxybenzylidene-4′-butylaniline (MBBA). The chemical structure of these substances is shown in Fig.1.

In both cases, the relevant reactions are not strictly radiochemical, but rather radiation-stimulated. The radiation does substantially accelerate the processes that naturally go at a slow rate under air oxygen and water vapor-

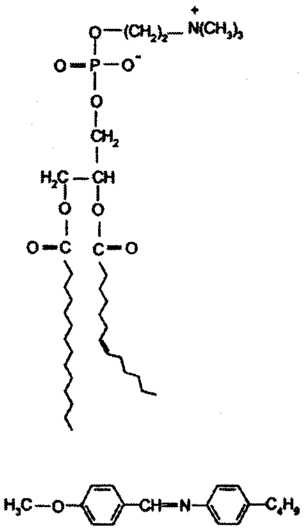

Fig. 1. Chemical structure of lecithin and 4-methoxybenzylidene-4′-butylaniline (MBBA).

Table 1. Response mechanisms of lecithin and MBBA affected by ionizing radiation.

Substance	Low doses (stage 1)	Higher doses (stage 2)
Lecithin	Formation of lyso-forms (reversible)	Oxidative destruction at the double bond (irreversible)
MBBA	*trans-cis* isomerization (reversible)	Decomposition into butylaniline and Methoxybenzaldehyde (irreversible)

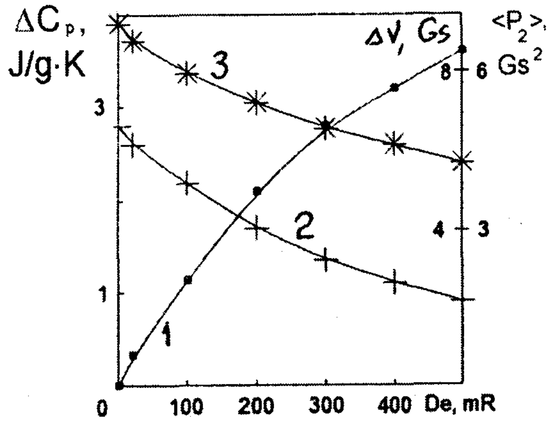

Fig. 2. Measured characteristics of the radiation response of water dispersions of egg yolk lecithin as function of exposure dose ($^{241}Am\gamma$ -source) [4] : 1 - heat capacity (50% of lecithin, lamellar structure, Mettler TA 3000) ; 2 and 3 - second moment (2) and halfwidth (3) of NMR absorption line (10% of lecithin, vesicular structure, Bruker AM-250, D_2O).

both MBBA and lecithin acquire brownish color after prolonged storage in ampoules, which is well known to chemists.

The radiation response of a model membrane structure (i.e., water dispersion of egg yolk lecithin) is shown in Fig. 2.

The observed changes in the measured characteristics reflect the effects of radiation at relatively low doses (Stage 1 processes), which show a tendency to saturation at ~0.5 R, with the Stage 2 effects remaining negligibly small (this, by the way, can be taken as a criterion of the "low"dose). Similar effects in a bioequivalent material (e.g., MBBA) can be made much more pronounced by an appropriate choice of measured characteristics. In our case, we observe radiation-induced changes in the selective reflection spectra of MBBA that is doped with a chiral (optically active) additive to obtain the cholesteric mesophase. In a specific example shown in Fig. 3, we use the eutectic mixture of MBBA and its ethoxy homologue EBBA.

One can see that effects of small radiation doses (at the level of 0.1 R) can be clearly detected (e.g., by using a photoreceiver fixed at ~1.2μm and recording the changes in the intensity of the transmitted light). This illustrates

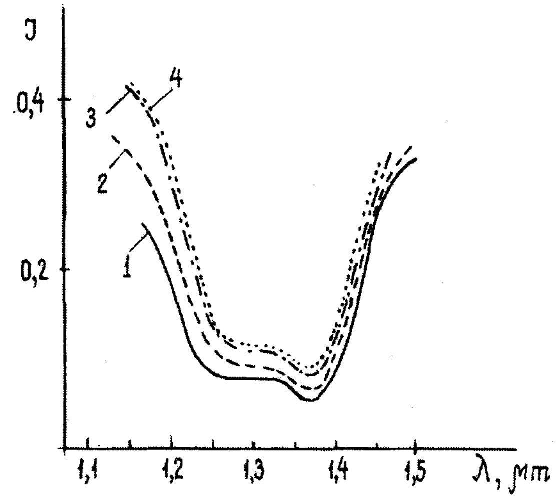

Fig. 3. Radiation response of a bioequivalent liquid crystalline system (MBBA/EBBA+3.6% of chiral dopant) : initial sample (1) and the same sample after irradiation for 3 min (2), 5 min (3) and 10 min (4). Radiation source : ^{241}Am, 0.7 R/h [3].

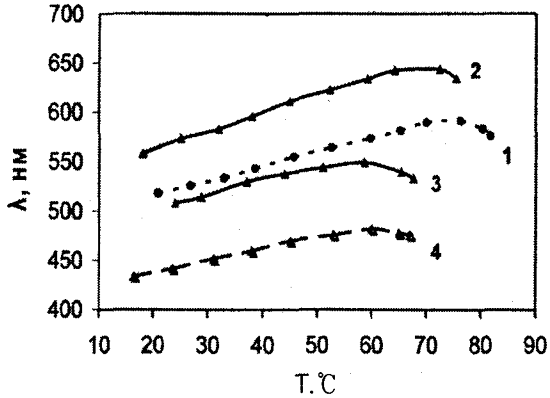

Fig. 4. Selective reflection maximum of cholesteric sensor compositions for UV detection : 1 - Matrix 8 ; 2 -Matrix 8+5% ProD$_2$; 3 - Matrix 8+5% ProD$_2$, after 60 min. UV irradiation ; 4 - Matrix 8+5% vitamin D$_2$.

a principle of a bioequivalent detector of weak ionizing radiation.

The ideas developed for CLC ionizing radiation detectors were successfully used for detection of biologically active UV-radiation.

This problem became popular worldwide because of the situation of ozone layer depletion and allegedly increased dangers of harmful UV-C radiation (and, accordingly, an increasing demand for simple UV radiation indicators to be used in mountain resorts, sunlit beaches, deserts, Antarctic, etc.). It has been proposed to monitor UV radiation using CLC mixtures doped with provitamin D (the photochemical reaction provitamin D-vitamin D resulted in observable changes in helical pitch) [5,6].

In Fig. 4, the operation principle of a liquid crystal bioequivalent UV-detector is shown. Provitamin D$_2$ (ergosterol) and vitamin D$_2$ (ergocalciferol) shift the selective reflection maximum into opposite directions. Formation of vitamin D$_2$ under UV-irradiation is accompanied by a shift of the selective reflection peak to shorter vavelengths (towards values characteristic for the vitamin D$_2$-containing mixture). This can be visually observed as change of color of the cholesteric mixture from orange to green (decrease of λ_{max} by >60 nm).

In Fig. 5, data are shown on the effects of UV irradiation of the cholesteric sensor mixtures obtained using three different optical filters (UFC-2, K-8 and K-108). The transmission band of UFC-2 was essentially similar in its wavelength range to the absorption spectrum of ProD$_3$. The K-8 filter cut out the wavelength range below ~280 nm, i.e., the shorter wavelength half of the ProD$_3$ absorption spectrum. The K-108 filter transmitted only at wavelengths above the ProD$_3$ absorption spectrum. The experimental conditions were essentially the same as described in [5,6], with the UV lamp pre-calibrated to obtain the illuminance values from the exposure time and the distance to the irradiated sample.

These results imply that the only factor that caused λ_{max} shifts for cholesteric mixtures doped with provitamin D in our experiments was UV light absorbed by provitamin D (i.e., the fraction of UV light that could be considered as "biologically active" in a certain sense).

Finally, another promising use of CLC sensors is detection of hazardous vapors in atmosphere. Such works were actively carried

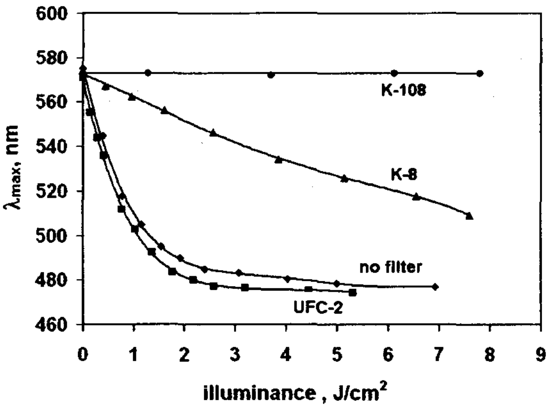

Fig. 5. Shifts of the maximum selective reflection wavelength λ_{max} under UV-irradiation of the cholesteric sensor composition (Matrix 8 + 10% $ProD_3$) as function of illuminance.

out in the late 1970-ies (expecting their possible use for detection of poisonous gases in chemical warfare), and a revival of interest in this field was recently noted (see, e.g., [7,8]). This was largely related to the increasing importance of anti-terrorist activities (e.g., poisonous substances getting into ventilation systems ofsubways, large supermarkets, etc.). The ideas originating from CLC radiation sensors were found to be useful in development of simple, cheap and sufficiently reliable CLC indicators of toxic vapors.

Further progress in all the above-described fields is to be made by passing from the stage of laboratory experiments and model devices for demonstration purposes to the development of operable instruments ensuring qualitative dosimetry or, at least, a reliable alarm indication. This requires cooperation and investments (which can be relatively small in comparison with competing devices, such as, e.g., biosensors based on carbon nanotubes or semiconductor-based UV and ionizing radiation detectors requiring sophisticated microelectronics and processing schemes).

Conclusions

1. Cholesteric liquid crystals are a class of materials that allow bridging the gap between biophysics and optoelectronics (traditionally based on solid state materials).
2. Basing on cholesteric liquid crystals, sensor materials can be developed for detection of biologically active UV radiation, bioequivalent detection of ionizing radiation, and detection of harmful vapors and gases in the atmosphere.
3. Two main directions in practical application of these sensor materials are :
   - development of simple and inexpensive detectors of the above-mentioned harmful factors (e.g., alarm indicators) ;
   - development of "bioequivalent" detectors/ dosimeters designed for biophysical and medical studies.
4. The problems of this field of studies are open for discussion with Korean colleagues with the aim of arranging further cooperation and eventual joint R&D projects.

References

1. P.L.Carroll, Cholesteric liquid crystals : their technology and application. Ovum Ltd. : London, 280(1973)
2. G.M.Zharkova, A.S.Sonin. Liquid crystal composites. VO Nauka : Novosibirsk, Part 2, pp.37-112(1994)
3. B.S.Prister, V.N.Borzenko, L.N.Lisetski e.a., Mol.Materials, 5, 175(1995)
4. V.N.Borzenko, L.N.Lisetski, B.S.Prister, Yu.E.Shapiro, Functional Materials, 3, 365 (1996)
5. L.N.Lisetski, O.V.Vashchenko, V.D.Panikarskaya e.a., Proc.SPIE, 5257, 97(2003)
6. M.Aronishidze, G.Chilaya, L.N.Lisetski e.a., Mol.Cryst.Liq.Cryst., 420, 47(2004)
7. F.L.Dickert, A.Haunschild,P.Hofmann, Fresenius J.Analyt.Chem., 350, 577(1994)
8. D.A.Winterbottom, R.Narayanaswamy, I.M.Raimundo, Sensors and Actuators, B90, 52(2003)