

## The Study of Phase Transition in Some Irradiated Cholesteric Liquid Crystalline Mixtures<sup>1</sup>

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**Abstract**—We present the study of binary and multicomponent cholesteric mixtures undertaken with the aim of forming a system with the temperature of the phase transition close to the room temperature, which could be suitable for the detection of ionizing radiation. The phase diagrams were established on the basis of data from the optical microscopy and differential scanning calorimetry (DSC). The mixtures were exposed to the continual spectrum of X-Ray radiation in the period of 30/60 min. The mixtures react by changing the color of the mesophase, and a shift of the mesophase transition towards lower temperatures. The duration of the effects exceeds six months.

**Keywords:** cholesteric crystals, optical properties, X-ray radiation, molecular parameters, reflectance spectra.

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### INTRODUCTION

Various factors can have an influence on the pitch of the cholesteric helix: temperature, composition of mixtures, some chiral additives which do not have any liquid crystalline phases and radiation [1–5]. The spectroscopic properties should also change when guest molecules are intercalated between host molecules [6–8]. Studying factors affecting liquid crystalline self-assembly may also have a biophysical significance, having in mind that most components of living systems, from DNA through cell membranes to muscles, exist in liquid crystalline state. Losing or changing of their liquid crystalline integrity may have serious effects on living systems [9, 10].

In this paper we examine the influence of ionizing radiation (X-ray irradiation) on different mixtures of cholesteric substances, inspired by the fact that literature data available on this field are extremely scarce. When cholesteric mixtures have been exposed to the continual spectrum of X-ray radiation for the period of 30/60 minutes, they have reacted by changing the color of the mesophase and have shifted the mesophase towards lower temperatures. The properties of the studied mixtures (before and after the irradiation) have been characterized by various experimental techniques, including polarizing optical microscopy, optical reflectance spectroscopy, differential scanning calorimetry (DSC) and X-ray diffraction. We note that the color changes induced by the

irradiation have persisted for at least six months. This property enables the use of such samples as indicators of absorbed radiation dose.

### EXPERIMENTAL

Optical microscopic studies were performed in transparent light using a polarizing microscope Carl Zeiss, Jena, equipped with a hot-stage Mettler FP-5 for the controlled heating and cooling of the sample. For DSC analysis Du Pont Instrumental Thermal Analyzer 1090 910 was used. Combination of microscopy with DSC studies enabled us to identify mesophases and to construct the phase diagrams.

Optical reflectance spectra were measured in the wave number range of 10000–30000 cm<sup>-1</sup>, within the mesophase temperature region of the investigated compounds, using a monochromator SPM-2 (Veb Zeiss, Jena) with an R-45/0 type reflection cell. MgO was used as “white” standard. From the reflectance spectra the pitch of the cholesteric helix could be calculated using the formula  $P = \lambda/\bar{n}$ . Here  $\lambda$  is the wavelength belonging to the maximal reflectance, while  $\bar{n}$  is the average refractive index which was measured by an Abbe refractometer (Zeiss-Jena).

By X-ray diffraction unoriented samples were investigated in transmission geometry using a conventional powder diffractometer, Seifert V-14, equipped with an automatic high temperature kit Paar HTK-10, at CuK<sub>α</sub> radiation of 0.154 nm. Some molecular parameters: the thickness of smectic layers and the

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longitudinal spacing distance in the cholesteric phase ( $d$ ) as well as the average distance between the long axes of neighboring molecules ( $D$ ) were calculated from the positions of the small angle and the wide angle diffraction peaks, respectively.

## RESULTS AND DISCUSSION

The optical microscopic and DSC studies have been started with checking the pure substances: cholesteryl oleyl carbonate (ChOC), cholesteryl nonanoate (ChN) and cholesteryl benzoate (ChB) and shown good agreement with existing literature data [11–14]. We have examined the phase transitions of the binary (50–50 wt %) mixtures: Mix1 (ChOC–ChN), Mix2 (ChOC–ChB), Mix3 (ChN–ChB), as well as of the three component mixture, Mix4 [ChN (55%)–ChOC (35%)–ChB (10%)]. It was found that they form mesophases at room temperature which are stable for several days, while Mix4 produces a cholesteric phase in a broad temperature range (19–60°C) stable for several months. All mixtures have cholesteric phase in a wide temperature region, with a change of color from red to blue. Smectic A ( $S_A$ ) phase—which is present in the pure compounds ChOC and ChN—did not occur in any of the mixtures. The results of optical and DSC investigations are presented in Table 1.

The binary mixtures were also studied by the Kofler contact method. A representative snapshot taken at crossed polarizers (for Mix1) is presented in Fig. 1. The black patch on the left side of Fig. 1 is the isotropic (Iso) phase of ChOC, the fan-shaped patterns on the right side represent the crystalline (Cr) phase of ChN, while the central contact region corresponds to the cholesteric (Ch) phase of Mix1.

The ternary mixture, Mix4, was selected for the irradiation tests. It was exposed to the continual

**Table 1.** Phase transition temperatures ( $T$ , °C) and transition enthalpies ( $\Delta H$ , J/g) evaluated on heating by DSC; helical pitch ( $P$ , nm) and wavelength of maximal reflectance ( $\lambda$ , nm) at  $T = 24^\circ\text{C}$

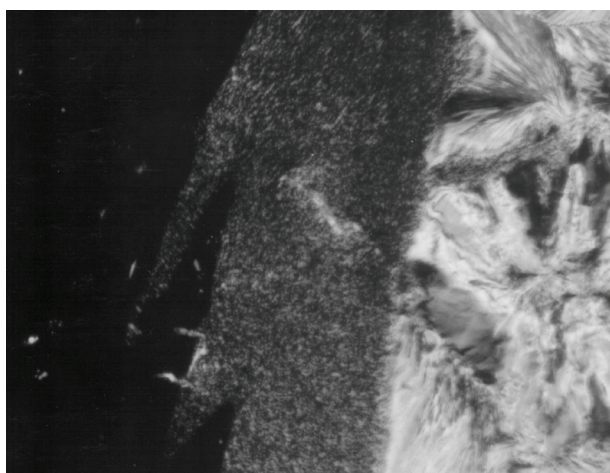
Code	$T$	$\Delta H$	$T$	$\Delta H$	$P$	$\lambda$
	Cr–Ch		Ch–Iso			
Mix1	n.i.		37.8	3.1	413	617
Mix2	n.i.		85.3	0.5	423	633
Mix3	94.8	1.03	125.0	0.6	418	626
Mix4	n.i.		71.2	9.3	452	685
Mix4A	n.i.		70.3	1.4	420	633
Mix4B	n.i.		71.7	3.0	369	556

Note: n.i.—the crystal (Cr)—cholesteric (Ch) phase transition could not be identified, because the mixtures did not crystallize within a few months.

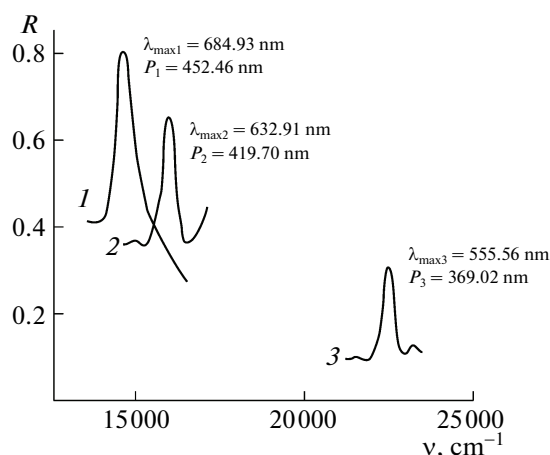
X-radiation spectrum with the energy of 0.03 MeV for 30 and 60 min. After irradiation the mixtures absorbed a dose of 1.25 Gy (Mix4A) and of 2.5 Gy (Mix4B), respectively, have been investigated by the same techniques.

Based on the measured reflection spectra (Fig. 2) it is obvious that the irradiation induces a shift of the maximum of the reflection peak towards lower wavelengths compared to that of the not irradiated mixtures; hence the helical pitch,  $P$ , decreases (Table 1). It is also seen in Fig. 2 that if the irradiation time increases, the shift of the maximum reflection peak towards shorter  $\lambda$  becomes more pronounced.

X-ray powder diffraction spectra have been recorded in all mesophases of the pure compounds as well as of the mixtures. As an example, in Fig. 3 we exhibit the spectra obtained for Mix4 at various temperatures, cooling from the isotropic phase down to



**Fig. 1.** Photo of the contact preparation of ChOC (left) with ChN (right) taken at 35°C. The central contact region corresponds to Mix1.



**Fig. 2.** Reflectance spectra at  $T = 24^\circ\text{C}$  of (1) Mix4, (2) Mix4A, and (3) Mix4B.

**Table 2.** Molecular parameters ( $d$  and  $D$ , Å) of pure compounds, binary and three component mixtures for all observed phases at a selected temperature ( $T$ , °C). The errors of the measurements were  $d \sim 0.05$  Å and  $D \sim 0.002$  Å, respectively

Compound	Phase	$T$	$2\theta$ , deg	$d$	$D$
ChOC	S <sub>A</sub>	25	6.4	13.79	—
			17.0	—	5.209
	Ch	38	2.8	31.52	—
			17.0	—	5.209
	Iso	40	17.2	—	5.149
ChN	S <sub>A</sub>	65	3.0	29.42	—
			16.0	—	5.533
	Ch	76	2.4	36.77	—
			15.8	—	5.602
	Iso	100	16.0	—	5.533
ChB	Ch	150	3.7	23.85	—
			15.85	—	5.585
	Iso	190	16.0	—	5.533
Mix1	Ch	35	2.75	32.09	—
			17.0	—	5.209
	Iso	55	16.8	—	5.271
Mix2	Ch	89	3.5	25.21	—
			16.5	—	5.366
	Iso	129	16.3	—	5.432
Mix3	Ch	117	3.62	24.41	—
			16.45	—	5.389
	Iso	130	16.1	—	5.506
Mix4	Ch	18	2.6	33.94	5.209
			3.0	29.42	—
		23	2.4	36.77	—
			3.0	29.42	—
		26	16.9	—	5.240
			2.6	33.94	—
		31	3.15	28.02	—
			16.8	—	5.271
	Iso	61	16.6	—	5.334
Mix4A	Ch	18	2.9	30.43	—
			17.2	—	5.149
		23	16.8	—	5.271
		26	3.0	29.42	—
			16.6	—	5.334
		30	3.1	28.47	—
			16.4	—	5.398
Mix4B	Iso	60	16.2	—	5.464
	Ch	19	2.6	33.91	—
			3.1	28.47	—
		23	16.8	—	5.240
			3.1	28.47	5.271
		30	16.8	—	5.334
	Iso	60	16.5	—	5.366

room temperature. In the diagram one can clearly identify two angle ranges. There is a wide, diffuse peak at large scattering angles (at  $2\theta \sim 16.8^\circ$ ) at all temperatures, while in the mesophase there is a sharp peak at small angles ( $2\theta \sim 2.6^\circ$ ). Diffraction spectra of the other compounds exhibit similar features. A peak at an angle  $\theta$  in the diffraction spectrum can be associated with a characteristic distance  $x$  according to Bragg's law:  $\lambda = 2x\sin(\theta)$ . The characteristic distance calculated from the large angle diffraction peaks corresponds to the average intermolecular distance  $D$  (i.e. the mean distance between the long axes of neighboring molecules). The appearance of peaks at small angles in the mesophases indicates anisotropy due to orientational order.

In the cholesteric phase they provide the average spacing  $d$  along the director, while in the smectic phase of the pure compounds the smectic layer thickness can be obtained from the small angle diffraction peak. The second peak seen at small angles in Fig. 3 for low temperatures may indicate a nucleation of a below ambient S<sub>A</sub> phase in Mix4 which has not yet been confirmed by optical measurements. The characteristic distances calculated from the diffraction spectra are summarized in Table 2.

Looking at the temperature dependence of the calculated parameters one can find that the average spacing distance ( $d$ ) along the director in the cholesteric phase decreases, while the average distance between the long axes of neighboring molecules ( $D$ ) increases with temperature. That indicates increased molecular mobility and less molecular packing density. As far as the influence of the irradiation is concerned, the changes in the molecular parameters  $d$  and  $D$  are much less pronounced than the variation of the helical pitch. Nevertheless, all irradiation induced changes in the cholesteric mesophases of the investigated mixtures were found to be irreversible.

Comparison of the properties of the irradiated and the non-irradiated samples implies the presence of two concurrent principal phenomena: first, a shift of the temperature of the cholesteric mesophase formation, and second, a change in the molecular packing resulting in a tighter pitch (a larger helical twisting power) and a slight variation of the parameters  $d$  and  $D$ . Both phenomena might have a common origin: an alteration of the conformation of molecules either due to excitation or due to chemical degradation. One probable mechanism is that under the influence of X-ray irradiation the substituent connected to the C<sub>17</sub> carbon atom of the sterane skeleton rotates around the C<sub>17</sub>–C<sub>20</sub> single bond, bringing the molecule into a metastable state which is energetically close to the initial conformation of the non-irradiated sample [9] and has a long lifetime. Another possibility is that the  $\pi$ -electrons of the –C=C– or –C=O double bonds of ChOC or ChN, become excited, or even break. Unfortunately, the correlation between the molecular structure and the parameters  $d$  and  $D$ , or the pitch are, at

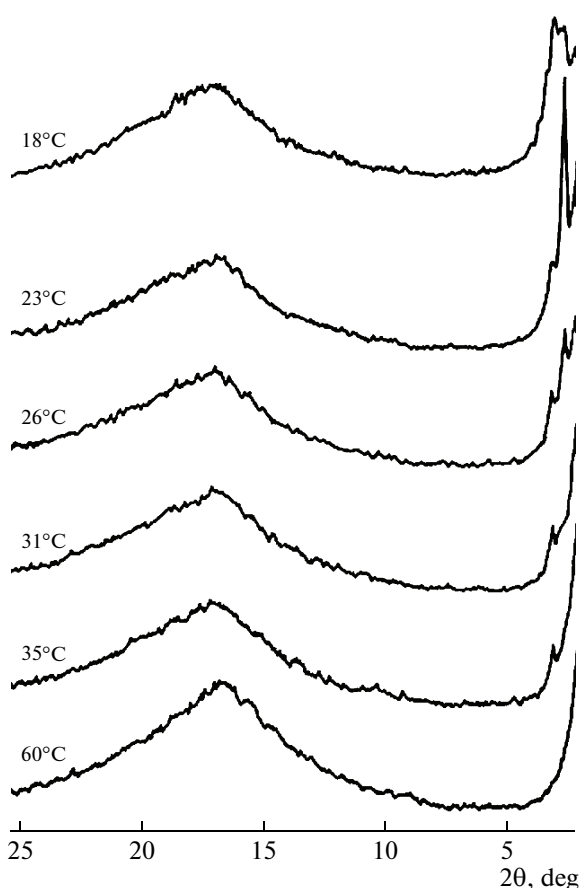


Fig. 3. X-ray diffraction spectra of Mix4 at various temperatures.

present, mostly unexplored. Therefore, the fact that irradiation increases the twisting power does not allow to single out the type of the radiation damage on the molecular structure.

### CONCLUSIONS

The above presented results imply that the X-radiation may directly influence the conformation/self-assembly of the molecules. The most probable mechanism is a degradation of the chemical structure. In order to decide whether the radiation damage occurs in the form of a metastable deformation of the sterane skeleton, or it is rather related to the break of the  $-C=C-$  or  $-C=O$  double bonds, further specific measurements should be carried out. Interestingly, the experiments have shown that the irradiation induced

molecular changes primarily affect the chiral packing of molecules in the cholesteric mesophase. Irradiation increases the twisting power and thus leads to a shortening of the cholesteric pitch which is detected as a permanent shift of the wavelength of the maximal light reflectance towards smaller wavelengths. This property enables the use of such samples as indicators of absorbed radiation dose.

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