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THE INFLUENCE OF X-RAY RADIATION ONTO THE PHASE TRANSITIONS OF SOME CHOLESTERIC LIQUID CRYSTAL MIXTURES

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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 mixture reacts by a change of the colour of the mesophase, and the shift of the mesophase transition towards lower temperature. The duration of the effects exceeds about six months.

Introduction

Various factors can have an influence on the pitch of the cholesteric helix [1-3]. In this paper we have examined the influence of X-ray irradiation. Optical and DSC studies have enabled the construction of the phase diagrams. X-ray diffraction data enabled the determination of some molecular parameters of the mixtures: the thickness of smectic layers and the longitudinal spacing distance in the cholesteric phase (d) and the average distance between the long axes of neighbouring molecules (D). The pitch of the cholesteric helix $P = \lambda/n$, was determined on the basis of reflection spectral analysis (λ is the wavelength belonging to maximal reflectance, n is the average refractive index).

Results and Discussion

The optical microscopic (polarizing microscope Carl Zeiss (Jena)) and DSC (Du Pont Instrumental Thermal Analyzer 1090 910) 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 [4]. We have examined the phase transitions of the binary (50-50%) 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%)]. The binary mixtures form mesophases at room temperature stable for several days, while **Mix4** produces a cholesteric phase stable in period of several months in a broad temperature range (19°C-60°C). This latter mixture was exposed to the continual X-radiation spectrum with the energy of 0.03 MeV for 30 min (**Mix4A**, dose 1.25 Gy) and for 60 min (**Mix4B**, dose 2.5 Gy) (Table 1).

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

Code	Cr	$T(^{\circ}\text{C})$ [$\Delta H(\text{J/g})$]	Ch	$T(^{\circ}\text{C})$ [$\Delta H(\text{J/g})$]	I	P (nm)/ λ (nm)
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

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

All mixtures have cholesteric phase in a wide temperature region, with a change of color from red to blue. Based on experimental reflection spectra data (SPM-2, Veb Zeiss, Jena), it is obvious that the irradiation induces a shift of the maxima of the reflection peak towards lower wavelengths, compared to the not irradiated mixtures (Figure 1, Table 1). On the base of X-ray diffraction data (Seifert V-14, $\text{CuK}\alpha$), it was concluded that the thickness of smectic layers (d) decrease, and an average distance between the long axes of neighboring molecules (D) increased with temperature (Figure 2).

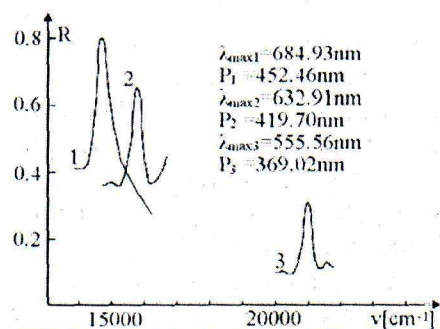


Fig.1. Reflectance spectra at $T = 24^{\circ}\text{C}$ of: Mix4(1), Mix4A(2), Mix4B(3).

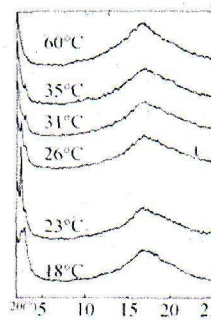


Fig.2. X-ray diffraction spectra of Mix4 at various temperatures.

Conclusion

The above presented results imply that the X-radiation may directly influence the conformation of the molecules. The most probable mechanism is a degradation of the chemical structure. One of possibilities is deformation of the sterane skeleton, which brings the molecule into a metastable state energetically close to the initial conformation of the non-irradiated sample. Another possible explanation is that π -electrons from the C=C or C=O double bonds in the cholesteryl oleyl carbonate or cholesteryl nonanoate become excited or even the bonds are broken, which can also influence the self-assembly of molecules in the cholesteric mesophase. These changes may increase the twist angle of the director from one layer to the other and thus may lead to a shortening of the cholesteric pitch and consequently, in a shift of the wavelength of the maximum of reflected light towards smaller wavelengths. This property enables the use of such samples as indicators of absorbed radiation dose.

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References

- [1] D. Ž. Obadović, A. Vajda, T. Toth-Katona, R. Marinković-Nedučin, *Mol. Cryst. Liq. Cryst.*, 1995, **265**, 135-142.
- [2] D.Ž. Obadović, M. Stojanović, S. Jovanović-Šanta, D. Lazar, A. Vajda and N. Éber, *International Journal of Modern Physics B*, 2006, **20**, 2999-3013.
- [3] A. Chanishvili, G. Chilaya, G. Petriashvili, D. Sikharulidze, *Mol. Cryst. Liq. Cryst.*, 2004, **409**, 209 – 218.
- [4] G.W. Gray and P. A. Winsor, *Liquid Crystals and Plastic Crystals*, J. Wiley and Sons, New York, 1974, **2**, 280.