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LIGHT INDUCED EFFECTS IN CHOLESTERIC MIXTURES WITH A PHOTOSENSITIVE NEMATIC HOST

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For the first time the photooptic effect in induced cholesteric mixtures using photosensitive nematic host has been observed. The changes of the pitch (color) and optical anisotropy (Δn) and also cholesteric-isotropic phase transition have been studied. Potential applications of these systems are color filters, UV image recording, UV sensors, and optical data processing systems.

INTRODUCTION

Light induced effects are extensively studied in liquid crystals (LC), particularly, in cholesteric LC [1–6]. There are at least three possible mechanisms for the change of the LC parameters under the light illumination: thermal, orientational (reorientation torque caused by dielectric coupling of the electric field of the light with the medium) and conformational.

Most of the studied absorbing liquid crystals, consist of conformationally active molecules, which are capable of *trans-cis* (E-Z) isomerization. In this case an elongated rod-like molecule (*trans* isomer) transforms under the influence of UV radiation into a bent form (*cis* isomer). Azobenzene liquid crystal films show a nematic phase with *trans* isomers and no LC phase when *cis* isomers are created by UV radiation. *Trans-cis* photoisomerzation of azobenzene LC with an applied laser pulse results in a nematic-to-isotropic phase transition with a rapid optical response of 200 microseconds [7–9].

The photostimulation of cholesteric LC, can cause a change of the pitch, and thus a shift of the wavelength of selective reflection. The effect can be attributed to a light-induced change of the helical twisting power (HTP). A colour shift has been observed when a conformationally active dye was

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doped to the cholesteric LC [10–11], or where a photoisomerizable chiral compound was used as a chiral dopant in an induced cholesteric mixture [12–13]. Photosensitive chiral dopants based on (-)-menthone have been successfully used in LC and LC polymers [14–16]. The binaphtol derivatives were used as a tunable chiral dopant in [17]. The liquid crystal compound cholesteryl p-phenylazophenyl carbonate has been added to cholesteric liquid crystal mixtures to produce the photoinduced effect [18]. Finally reversible and irreversible color changes, cholesteric-nematic, cholesteric-isotropic phase transitions due to photochemical decomposition, racemization or transformation of conformationally active components have been observed in LC mixtures [19–21].

Recently, use of a photo-isomerizable nematic component in induced cholesteric mixtures has been studied. [22]. Various nematic LC with different conformationally active moieties and thus with different wavelengths of absorption are investigated. Such systems possess wide possibilities. In this paper we present some photooptic effects observed in cholesteric mixtures when the azo- and azoxycompounds are used as a nematic host.

EXPERIMENTAL RESULTS

Induced chiral systems represent mixtures of nematic liquid crystals (NLC) with chiral dopants (CD) [23–27].

As an NLC azo and azoxy compounds were used:

NLC 1–ZhK 440 (NIOPIK): (2/3 p-n butyl-p-methoxyazoxybenzene + 1/3 p-n-butyl-p- heptanoylazoxybenzene), nematic phase temperature range between -5°C and $+75^{\circ}$C;
NLC 2 – ZhK 286 (NIOPIK): p-ethoxyphenyl-p′-azophenyl hexanoate, nematic phase range 56°C–116°C (for heating) and 116°C–45 (for cooling).

As a chiral dopants the following were used:

CD 1 – Cholesteryl Caprate (CC),
CD 2 – nonmesomorphic optically active dopant,
CD 3 – CB 15 (Merck).

The following cholesteric mixtures were investigated:

Sample 1 – 70% NLC 1 + 30% CD1 with clearing temperature $T_c = 75^{\circ}$C and positive temperature dependence of pitch P: $dP/dT > 0$;
Sample 2 – 85% NLC 1 + 15% CD2 with $T_c = 74^{\circ}$C and $dP/dT < 0$;
Sample 3 – 55% NLC 1 + 45% CD3 with $T_c = 50^{\circ}$C and $dP/dT = 0$;

Sample 4 – 60% NLC 2 + 40% CD3 with $T_c = 98°C$ and $dP/dT = 0$;
The thickness of the cells was 10 μm; measurements were made at room temperature for samples 1–3 and at 61°C for sample 4.
The spectrum transmission measurements were made by a spectrophotometer Specord M 40.

The irradiation was carried out by a 100 W Mercury lamp CBD-120 (USSR) and appropriate filters: F1 ($\lambda = 365$ nm); F2 ($\lambda = 400$ nm); F3 ($\lambda = 436$ nm).

Observed photooptic effects in the mixtures depend on the characteristics of the cholesteric LC and the dose of light irradiation. Figures 1–8 show the experimental results for all of the four samples. The results can be divided into two types: 1 – when the change of the pitch (color) is observed, and 2 – when the change of the refractive index n is observed.

It is known that the pitch in induced cholesteric systems depends on the structure of the both the nematic host and the chiral dopant [23–27]. Concerning the photooptic effect, it has been shown that the "giant" optical nonlinearity in nematic MBBA is due to the change of the polarizability and of the order parameter S of the LC molecules upon phototransformation [28–29]. The decrease of the order parameter S produces a change of the refractive indices and the lowering of the phase transition temperature T_c. Actually, the change of refractive indices is due both to the change

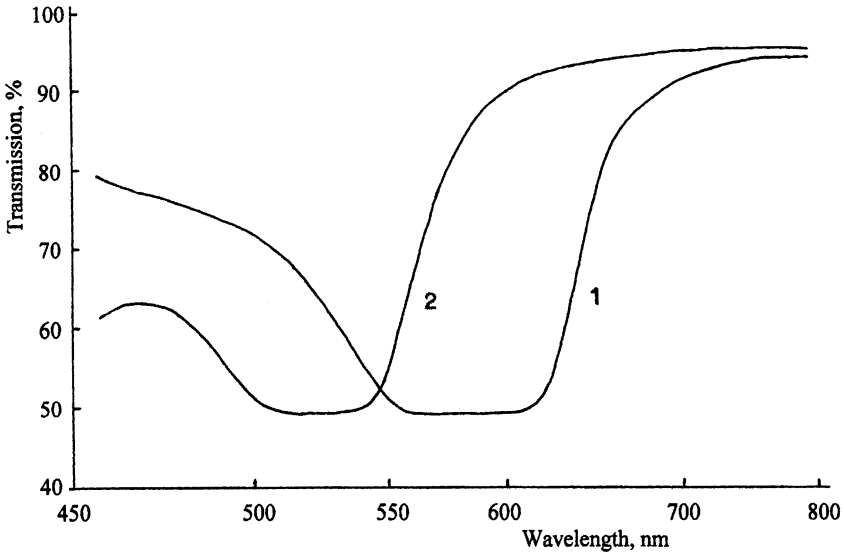

FIGURE 1 Transmission spectra for sample 1 – (70% NLC 1 + 30% CD 1) 1 – before irradiation; 2 – after 180 s irradiation with filter F1 ($\lambda = 365$ nm).

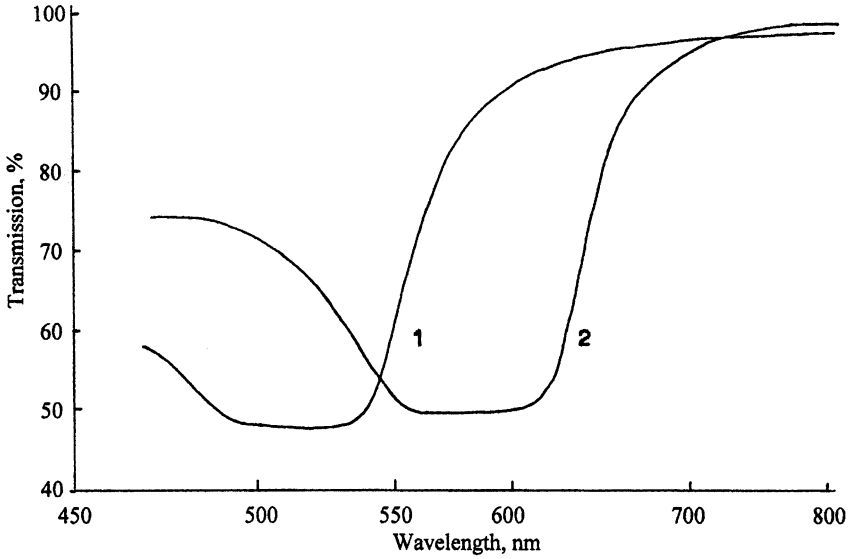

FIGURE 2 Transmission spectra for sample 1 – (70% NLC 1 + 30% CD 1) 1 – after 180 s irradiation with filter F1 ($\lambda = 365$ nm); 2 – next 180 s irradiation with filter F3 ($\lambda = 436$ nm).

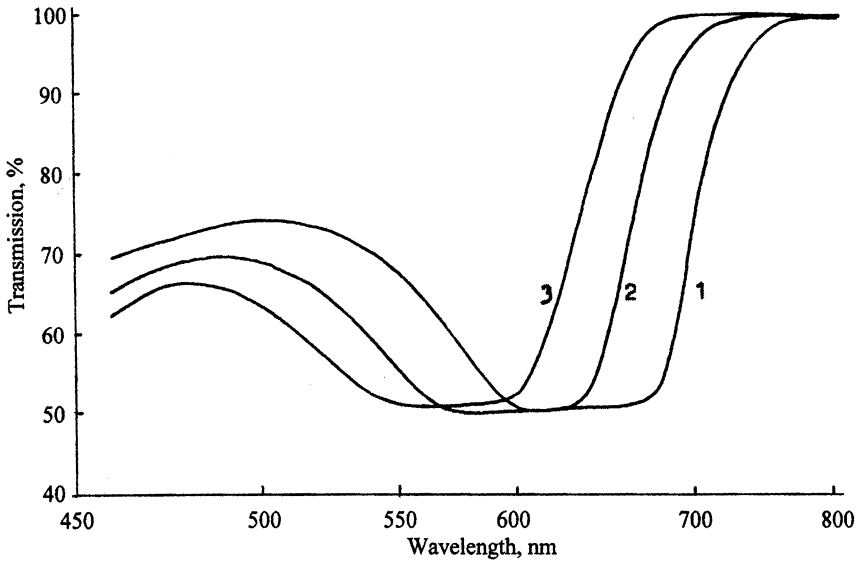

FIGURE 3 Transmission spectra for sample 2 – (85% NLC 1 + 15% CD 2) 1 – before irradiation; after irradiation with filter F1 ($\lambda = 365$ nm): 2–60 s; 3–120 s.

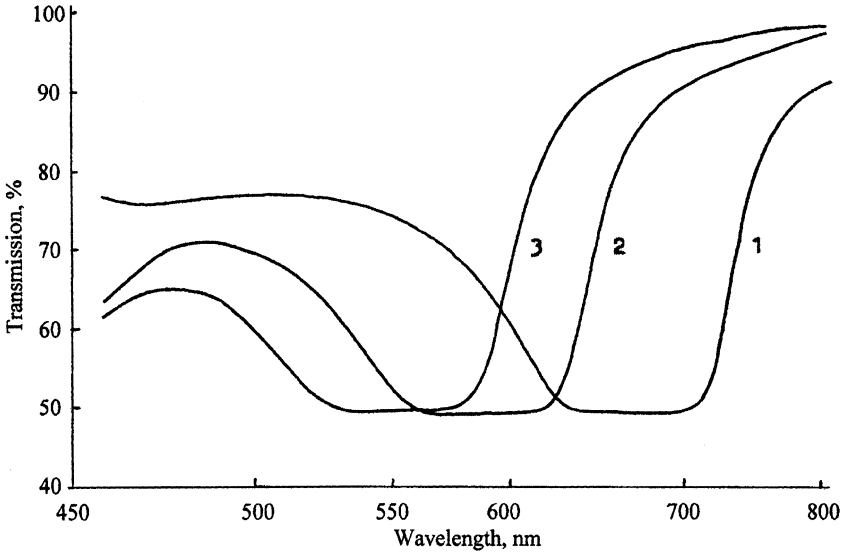

FIGURE 4 Transmission spectra for sample 2 – (85% NLC 1 + 15% CD 2) 1 – before irradiation; after irradiation with filter F2 ($\lambda = 400$ nm): 2–60 s; 3–150 s.

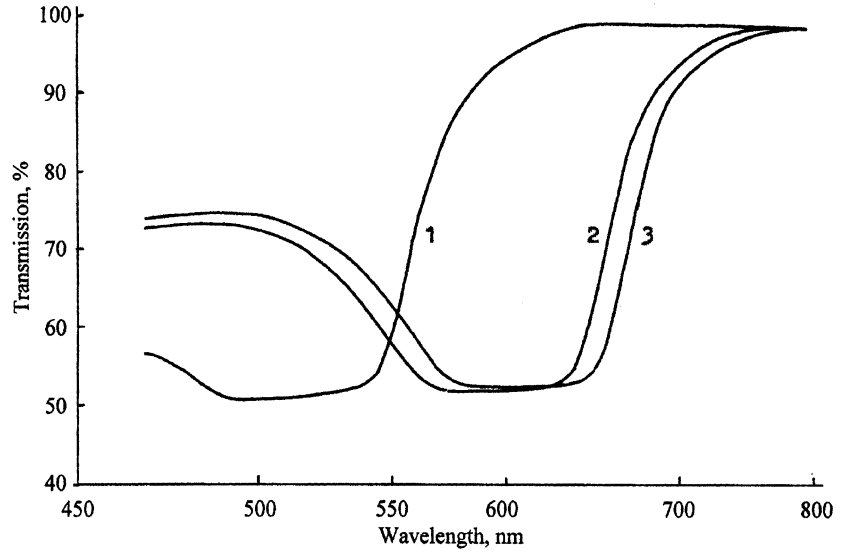

FIGURE 5 Transmission spectra for sample 2 – (85% NLC 1 + 15% CD 2) 1 – after 150 s irradiation with filter F1 ($\lambda = 365$ nm); the next irradiation with filter F3 ($\lambda = 436$ nm): 2–60 s; 3–150 s.

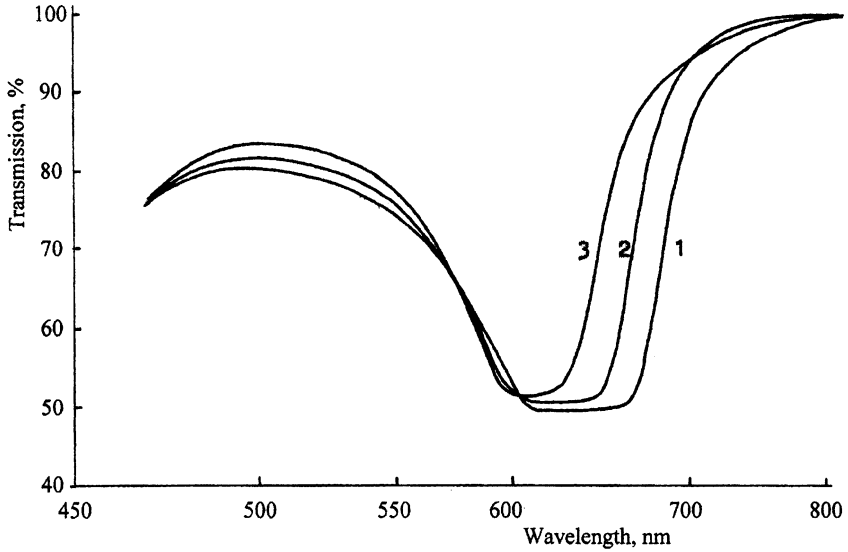

FIGURE 6 Transmission spectra for sample 3 – (55% NLC 1 + 45% CD 3) 1 – before irradiation; after irradiation with filter F1 ($\lambda = 365$ nm): 2–30 s; 3–60 s.

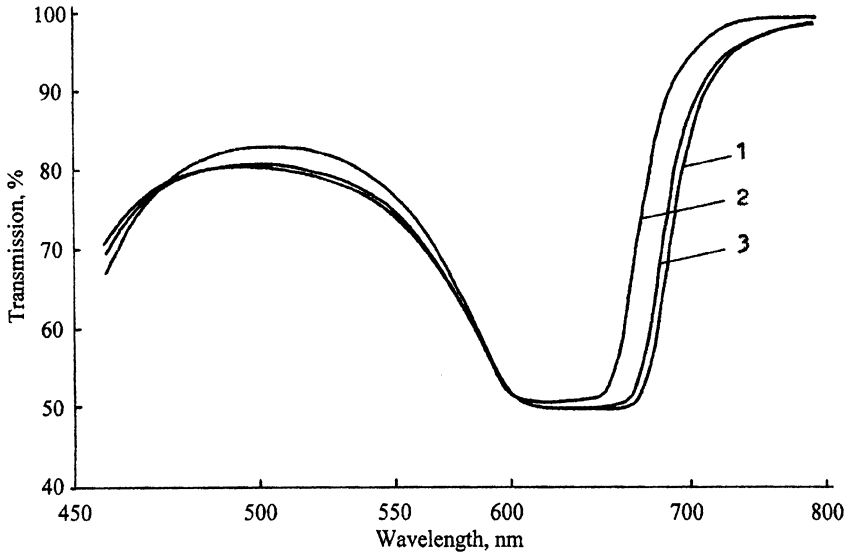

FIGURE 7 Transmission spectra for sample 3 – (55% NLC 1 + 45% CD 3) 1 – before irradiation; after irradiation with filter F1 ($\lambda = 365$ nm): 2–30 s; the next irradiation with filter F3 ($\lambda = 436$ nm): 3–30 s.

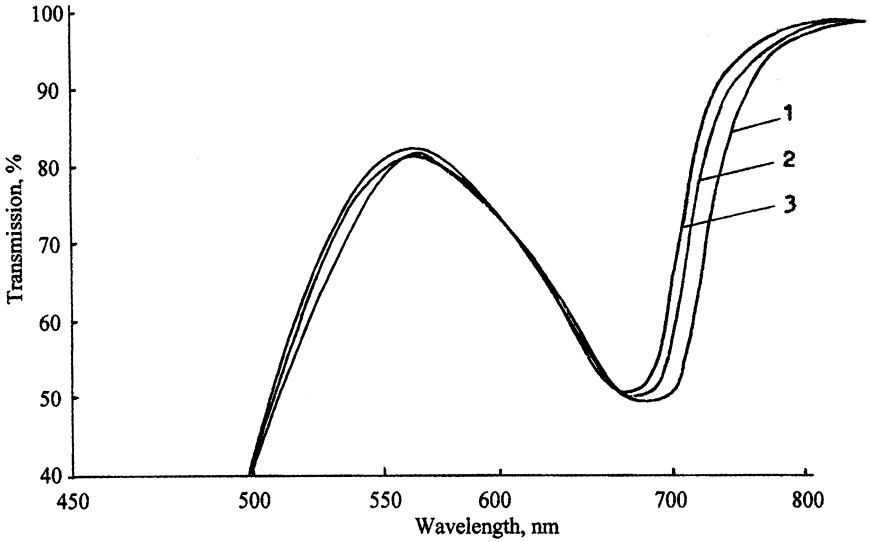

FIGURE 8 Transmission spectra for sample 4 – (60% NLC 2 + 40% CD 3) 1 – before irradiation; after irradiation with filter F1 ($\lambda = 365$ nm): 2–30 s; 3–40 s.

of the order parameter S and to the change of the anisotropy of the polarizability of these mesogenic molecules. For temperatures far below the phase transition, the contribution of both mechanisms to the nonlinearity are comparable, but as the phase transition is approached, the contribution due to the change in the order parameter increases. These observed changes in the refractive indices involve an increase in the ordinary index and a decrease in the extraordinary index.

Thus a change in the pitch under illumination (and therefore in the shift in the selective reflection band) in cholesterics is due to changes in both the polarizability and the order parameter. The increase of the wavelength of selective reflection (λ_0) with irradiation is explained by decrease in HTP, which in turn is a due of conformational changes of photoizomerisable dyes or chiral additives [10–18]. In [17] it was noted that increase of the pitch is connected with decrease of the concentration of the more chiral isomer. Azobenzenes and azoxybenzenes can form *cis*- and *trans*-isomers. Light induced periodic structures in induced cholesteric liquid crystals containing azoxybenzene compounds were observed in [30].

In our case, as follows from Figs. 1–5, we observe the decrease of P with short wavelength (365 nm and 400 nm) light irradiation. Long wavelength (436 nm) light irradiation sets pitch to the initial state. It is clear that the shape of selective reflection curve in Figs. 1–8 shows that we are far from T_c.

The experimentally observed pitch decreases under short wavelength irradiation (blue shift of the selective reflection peak) in Figures 1–5. For mixtures with $dP/dT > 0$ and $dP/dT < 0$, this can be explained only by lowering of the concentration of nematogenic isomers within the nematic host material. This idea suggests that the short wave irradiated state of the photoisomerizable azoxycompound do not possess nematic phase.

The change of extraordinary refractive index in Figures 6–8 can be explained by change of the polarizability.

With an increase in the short wavelength light intensity or with increased exposure times the broadening of the reflection band for all samples revealed a decrease in the order parameter S. In fact, the material goes from the cholesteric phase (colored) to isotropic phase (transparent) at higher short wavelength intensities. When the irradiated isotropic phase is cooled with the short wavelength radiation being maintained, blue phases are observed. This confirms the increase in chirality under short wavelength irradiation since the material does not possess blue phases when it has not been irradiated. These results need more detail investigations.

CONCLUSION

The photooptic effect in cholesteric mixtures with photoisomerizable nematic host has been experimentally investigated for the first time. Changes of the pitch (color) and optical anisotropy (Δn) and also cholesteric-isotropic phase transition are observed. These effects offer a wide range of possibilities for application: color filters, UV image recording, UV sensors, and optical data processing systems.

REFERENCES

[1] Tabirian, N. V., Sukhov, A. V., & Zel'dovich, B.Ya. (1986). Orientational optical nonlinearity of liquid crystals. *Mol. Cryst. Liq. Cryst.*, *136*, 1–139.

[2] Palffy-Muhoray, P. (1990). The Nonlinear Optical response of liquid crystals. In: *Liquid Crystals- Applications and Uses*, Bahadur, B. (Ed.), World Scientific, Singapore, Vol. 1, p.493.

[3] Khoo, I. C. & S. T. (1993). *Optics and Nonlinear optics in Liquid Crystals*, World Scientific: Singapore.

[4] Blinov, L. M. (1996). Photoinduced molecular reorientation in polymers, Langmuir-Blodgett films and liquid crystals. *J. of Nonlinear Optical Physics and Materials*, *5*, 165.

[5] Chilaya, G. (2000). Cholesteric Liquid Crystals: Optics, Electrooptics and Photooptics, chapter 6 in *"Chirality in Liquid Crystals"*, Bahr, Ch. & Kitzerow, H. (Eds.), series Partially Ordered Systems, Springer Verlag: New York.

[6] Chilaya, G. S. (2000). Effect of various external factors and pretransitional phenomena on strructural transformations in cholesteric liquid crystals. *Crystallography Reports*, *45*, 871–886, [Kristallografiya *45*, 944–960 (2000)].

[7] Ikeda, T., Miamito, T., Sasaki, T., Kurihara, S., & Tazuke, S. (1990). Photochemical phase transition behaviours of ternary mixtures of photochromic azobenzene derivative, low molecular weight liquid crystal and polymer liquid crystal. *Mol. Cryst.*, *188*, 235–250.
[8] Ikeda, T. & Tsutsumi, O. (1995). Optical switching and image storage by means of azobenzene liquid crystal films. *Science*, *268*, 1873–1875.
[9] Shishido, A., Kanazawa, A., Shionio, T., Ikeda, T., & Tamai, N. (1999). Enhancement of stability in optical switching of photosensitive liquid crystal by means of reflection mode analysis. *J. Mater. Chem.*, *9*, 2211–2213.
[10] Sackman, E. (1971). Photochemically induced reversible color changes in cholesteric liquid crystals. *J Am. Chem Soc.*, *93*, 7088–7090.
[11] Schnuriger, B. & Bourdon, J. (1976). Photoisomerisation dans les milieux mesomorphes cholsterique. Influence sur les proprietes optiques du mileu. *J Chim. Physique*, *73*, 795–798.
[12] Vinogradov, V., khizhniak, A., Kutulya, L., Reznikov, Yu., & Reshetnyak, V. (1990). Photo-induced change of cholesteric LC-pitch. *Mol. Cryst. Liq. Cryst.*, *192*, 273–278.
[13] Yarmolenko, S. N., Kutulya, L. A., Vaschenko, V. V., & Chepeleva, L. V. (1994). Photosensitive chiral dopants with high twisting power. *Liquid Crystals*, *16*, 877–882.
[14] Boiko, N. I., Kutulya, L. A., Reznikov, Yu. A., Sergan, T. A., & Shibaev, V. P. (1994). Induced cholesteric liquid crystal polymer as a new medium for optical data storage. *Mol. Cryst. Liq. Cryst.*, *251*, 311–316.
[15] Bobrowski, A. Yu., Boiko, N. I., & Shibaev, V. P. (1999). New chiral photochromic menthone-containing homopolymers and copolymers–synthesis, phase behavior and photo-optical properties. *Liquid Crystals*, *26*, 1749–1765.
[16] van de Witte, P., Brehmer, M., & Lub, J. (1999). LCD components obtained by patterning o chiral nematic polymer layers. *J. Mater. Chem.*, *9*, 2087–2094.
[17] Vicentini, F., Cho, J., & Chien, L.-C. (1998). Tunable chiral materials for multicolour reflective cholesteric displays. *Liquid Crystals*, *24*, 483–488.
[18] Goldberg, N. N. & Fergason, J. L. (March 1973). Cholesteryl p-phenylazophenyl carbonate. *U.S. Patent*, *3*, 720–658.
[19] Haas, W., Adams, J., & Wysocki, J. (1969). Interaction between UV radiation and cholesteric liquid crystals. *Mol. Cryst. Liq. Cryst.*, *7*, 371.
[20] Haas, W. E., Nelson, K. F., Adams, J. E., & Dir, G. A. (1974). U.V. imaging with nematic chlorostilbenes. *J. Electrochem. Soc.*, *121*, 1667–1669.
[21] Mioskowski, C., Bouruignon, J., & Candau, S. (1976). Photochemically induced cholesteric-nematic transition in liquid crystals. *Chem. Phys. Lett.*, *38*, 456–459.
[22] Chanishvili, A., Chilaya, G., Petriashvili, G., & Sikharulidze, D. Light induced effects in absorbing cholesterics, 6th European conference on Liquid Crystals, 2001, Halle (Germany), abstracts, # 2-P3.
[23] Chilaya, G. (1985). *Physical properties and applications of liquid crystals with induced helicoidal structure*, Metsniereba, Tbilisi (in Russian).
[24] Vinokur, K. D., Sikharulidze, D. G., Chilaya, G. S., & Elashvili, Z. M. (1988). *Liquid crystals with helical structure and their applications in displays*, Metsniereba, Tbilisi, (in Russian).
[25] Chilaya, G. (1981). Induction of chirality in nematic phases. *Rev. Phys. Appliq.*, *16*, 193–208.
[26] Chilaya, G. S. & Lisetski, L. N. (1981). Helical twist in cholesreric mesophases. *Sov. Phys. Usp.*, *24*, 496–510.
[27] Chilaya, G. S. & Lisetski, L. N. (1986). Cholesteric liquid crystals: physical properties and molecular-statistical theories. *Mol. Cryst. Liq. Cryst.*, *140*, 243–286.

[28] Odulov, S. G., Reznikov, Yu. A., Soskin, M. S., & Khizniak, A. I. (1982). Photostimulated transformation of molecules- a new type of "giant" optical nonlinearity in liquid crystals. *Sov. Phys. JETP*, *55*, 854–859.

[29] Odulov, S. G., Reznikov, Yu. A., Soskin, M. S. & Khizniak, A. I. (1983). Photostimulated change of the phase transition temperature and "giant" optical nonlinearity of liquid crystals. *Sov. Phys. JETP*, *85*, 1154–1158.

[30] Kitaeva, V. F. & Zolotko, A. S. (1992). Square periodic distortions of the director field in cholesteric liquid crystals. *Mol. Cryst. Liq. Cryst. Sci.Technol.* – Sec B: Nonlinear Optics, *2*, 261– 279.