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Natalia Boiko<sup>a</sup>, Alexey Bobrovsky<sup>a</sup> & Valery Shibaev<sup>a</sup>

<sup>a</sup> Chemistry Department, Moscow State University, 119899, Moscow, Russia

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## New Type of Chiral Photochromic Liquid Crystal Polymers for Colour Photo-Optical Recording

NATALIA BOIKO, ALEXEY BOBROVSKY and VALERY SHIBAEV

*Chemistry Department, Moscow State University, 119899 Moscow, Russia*

Photo-optical properties of a cholesteric copolymer based on nematogenic and photosensitive optical active lateral groups containing a benzeliden-p-mentan-3-on fragment have been investigated. The selective light reflection wavelength was found to be controlled by the UV irradiation that causes the photoisomerization of the chiral photochromic groups. As a result the selective reflection of light can be changed locally. That permits the recording of a color image on a color background. The copolymer's photo-optical properties are compared with properties of a blend of cholesterol-containing copolymer with a low-molar-mass chiral dopant based on menthone derivatives.

**Keywords:** Photochromic polymers; liquid crystal polymers; chiral polymers

### INTRODUCTION

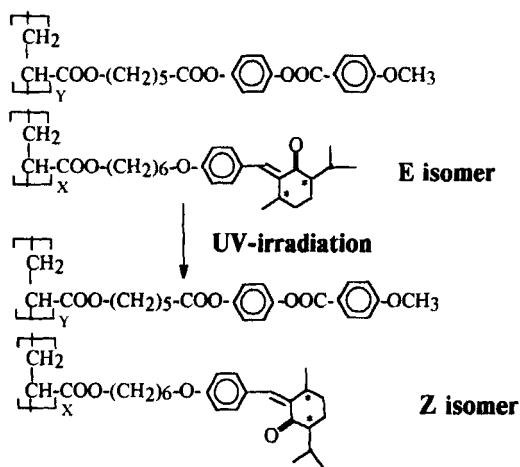
Liquid crystalline (LC) photochromic polymers have attracted particular attention due to their potential application for reversible optical data recording and as nonlinear optical media <sup>[1]</sup>. From this viewpoint, azo-dye containing LC and amorphous polymers have been extensively studied.

In contrast to above mentioned polymers there is a relatively limited number of publications devoted to synthesis and study of photochromic cholesteric polymers <sup>[1-4]</sup>. At the same time these systems may be considered as promising materials for color data recording due to the ability of chiral systems to change the parameters of helical structure (pitch of helix) and values of the selective light reflection ( $\lambda_{\text{max}}$ ) under the action of light. Note

that almost all publications on this matter reported the results for comb-shaped copolymers, in which photochromic properties are provided by low molar mass nematogens.

Meanwhile, it seems interesting to combine photochromic and chiral fragments in one monomeric unit. This combination would enable light-induced changes of both configuration of chiral photochromic fragment and its so-called helical twisting power  $A$ , so that the final values of  $A$  becomes less than initial  $A$  values<sup>[5-7]</sup>. As a result the selective reflection of light can be locally changed that permits to record the color image on the color background.

In previous works<sup>[6-7]</sup>, we developed a new approach to the synthesis of chiral photochromic copolymers, which involve chiral and photochromic fragments in the same monomer unit. The synthesized acrylate copolymers contained nematogenic phenyl benzoate and chiral non-mesogenic 2-benzylidene-p-menthan-3-one side groups:



The presence of the double ( $\text{C}=\text{C}$ ) bond in the chiral fragment predetermines light-induced E-Z isomerization.

The phase behaviour of copolymers has been considered<sup>[6-7]</sup>. All copolymers containing less than 30 mol.% of chiral units (X) form a cholesteric mesophase. Photochemical behaviour of solutions of such copolymers has shown the occurrence of only one photoprocess during the illumination, that was E-Z isomerization<sup>[6-7]</sup>. Note, that back 'dark' process has not taken place. In this paper we focused our attention on studying the

photooptical properties of one of such copolymers. In addition we have studied the mixture based on low-molecular-mass photochromic chiral dopant and cholesteric copolymer.

## EXPERIMENTAL

Phase transitions in copolymers were studied by differential scanning calorimetry (DSC) with a Perkin Elmer DSC-7 thermal analyzer at a scanning rate of 10 K/min. The polarizing microscopic investigations were performed using a Mettler TA-400 thermal analyzer and a LOMO P-112 polarizing microscope. Selective light reflection of samples was studied with a Hitachi U-3400 UV-Vis-IR spectrophotometer equipped with a Mettler FP-80 hot stage. The samples with a thickness of 20  $\mu\text{m}$  were sandwiched between two flat quartz plates and were annealed for 20-40 min.

Photo-optical studies were performed using a specially designed instrument equipped with a DRSh-250 mercury high-pressure lamp. Using the filter, we selected the 313-nm band of linear lamp radiation spectrum. To prevent heating induced by IR-radiation, a water filter was used. To obtain a flat parallel light beam, quartz lens was used. Under radiation, constant temperature of the samples was maintained using a Mettler FP-80 heating unit. After a certain time of irradiation, the samples were annealed at the temperature that was on 30°C higher than  $T_g$ . During annealing the selective light reflection spectra were recorded. The samples were annealed until no changes in the selective light reflection wavelength were observed (usually, for about 40 min). The intensity of UV radiation was  $2.03 \times 10^{-9} \text{ Es s}^{-1} \text{ cm}^{-2}$  or  $0.77 \text{ mW cm}^{-2}$ .

## RESULTS AND DISCUSSION

The copolymer containing 15 mol.% of chiral photochromic units was studied. This material displayed a wide interval of cholesteric mesophase between the glass transition temperature (28°C) and the clearing point (93°C). The cholesteric mesophase is capable of easy orientation under shear stress and produce the planar texture, which is characterized by the selective reflection of light. The copolymer films exhibit selective reflection of light with  $\lambda_{\text{max}} = 440 \text{ nm}$  (at room temperature).

Photooptical investigations have been performed using 20  $\mu\text{m}$ -thick films, which were illuminated at different temperatures (Figures 1 and 2). The colour of the films and the helix pitch are unchanged if the samples are irradiated at room temperature without subsequent annealing above  $T_g$ . However, the selective reflection of light of illuminated samples is shifted to a longer

wavelength region after annealing above  $T_g$ . This means that the helix can be untwisted after UV-irradiation and heating. As follows from Figures 1 and 2, an increase of the illumination time, shifts the selective light reflection wavelength to a longer-wavelength region. Let us emphasize that the higher the temperature during illumination, the higher the intensity of this process.

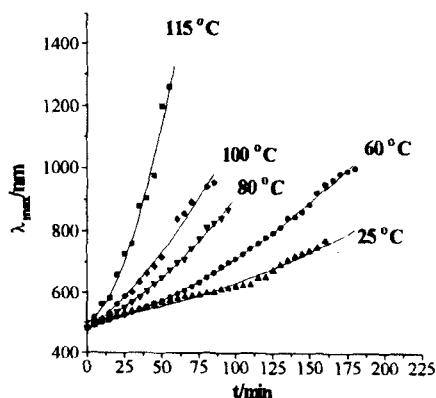


FIGURE 1  $\lambda_{\max}$  as a function of irradiation time for the copolymer. Irradiation temperature is shown in Figure.

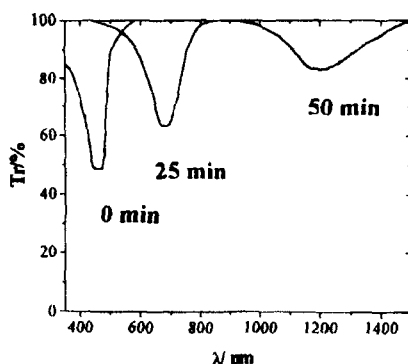


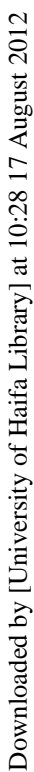
FIGURE 2 Change of the transmittance spectrum of the copolymer at the irradiation temperature  $T_{cl}+20^{\circ}\text{C}$  (irradiation time is shown in Figure).

The photochemical studies of copolymer solution<sup>[6]</sup> allows one to conclude that E-Z isomerization of chiral photochromic units is responsible for an increase in the pitch of the helix (Figure 1) and that the twisting power of Z-isomer is likely to be much lower ( $A_Z \ll A_E$ ). It is known that for the low-molecular-mass analogs, the twisting power of Z-isomers is lower by an order of magnitude<sup>[5]</sup>.

The shift in the maximum of selective reflection of light is accompanied by its pronounced broadening (Figure 2). The following speculations may be invoked to explain the broadening of the peak. In spite of the thickness of the test samples is 20  $\mu\text{m}$ , the photochemical reaction proceeds in a very thin (about 1  $\mu\text{m}$ ) surface layer<sup>[8]</sup> at extinction coefficient<sup>[6]</sup>  $\epsilon_E^{313} \approx 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ . During the illumination process, even in the isotropic melt, thermal "mixing" of E and Z-isomers in the test sample is extremely low. This leads to the accumulation of a marked fraction of the Z-isomer of chiral side groups in the thin reaction layer. In the bulk, most of chiral groups exist in the E-configuration. Annealing of the test sample is accompanied by the diffusion of macromolecules enriched by Z-isomer. Finally, noticeable fluctuations in the concentration of the Z-isomer in the sample are observed. This phenomenon is likely to be associated with a higher viscosity of polymers as compared with that of low-molecular-mass analogs and, consequently, with lower diffusion constants of photochromic fragments. As a result, peak of selective light reflection becomes more diffuse and then degenerates.

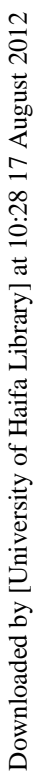
*A priori*, one may assume that mixing of low-molecular-mass additive with polymer, on the one hand, will accelerate the attainment of equilibrium and, on the other hand, will assist the "self-healing" of the radiation-induced defects in the planar texture. In the previous work<sup>[9]</sup> we have studied the photorecording in the system based on nematic homopolymer and photosensitive chiral additive (dopant) containing bezylidene-*p*-menthan-3-one fragment. However, a principal disadvantage of such mixtures is associated with their low stability: within one year. The above composition experiences separation induced by crystallization of chiral dopant. However, as shown in work<sup>[10]</sup>, when cholesteric copolymer with its own helical structure is used as a polymer matrix, introduction of 10 mol % of chiral dopant to this copolymer provides a complete miscibility between the components, and this system undergoes no phase separation.

In this work, we studied photo-optical properties of the mixture based on low-molecular-mass photochromic chiral dopant (Mtn) and cholesteric copolymer, which is characterized by left-hand helical structure:



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of the composition as compared with initial copolymer but leads to an additional twisting of the system.. However, the clearing temperature ( $T_{cl}$ ) decreases by  $30^{\circ}\text{C}$  ( $T_g=18^{\circ}\text{C}$ ), and this decrease is associated with the nonmesomorphic state of the dopant.

Thus, the above-mentioned mixture shows light reflection in the visible spectral region (Figure 4). Note that this mixture is stable over time.

For the investigation of the photo-optical behaviour of the above-mentioned mixture, the  $20\text{-}\mu\text{m}$ -thick films were illuminated at different temperatures. After certain exposure time, the mixtures were annealed at a temperature, which exceeds the glass transition temperature  $T_g$  by  $\sim 30^{\circ}\text{C}$ . Simultaneously, the corresponding selective light reflection spectra were recorded.

At the initial moment of time, the test sample shows selective light reflection in the blue spectral region. As a result of irradiation and subsequent annealing, the value of  $\lambda_{\text{max}}$  shifts to the red spectral region (Figure 5). It is seen that the shift of the selective light reflection peak is accompanied by no marked increase in its half-width. In this case, the half-width of the peak remains almost unchanged until the photostationary state is attained. No degeneration of the peak is observed.

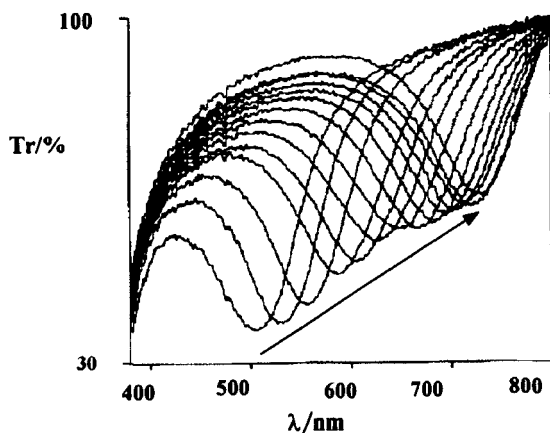


FIGURE 5. Change of the transmission spectra of the mixture during UV irradiation. Spectra were recorded at 5-min interval after UV irradiation. Temperature of the irradiated sample was  $60^{\circ}\text{C}$ .

Earlier we have assumed that the reason accounting for an increase in helix pitch is provided by E-Z isomerization of chiral groups and the corresponding twisting power of Z-isomer is much lower. According to the equation<sup>[11]</sup>:

$$A = \Delta\lambda_{\text{max}}^{-1}/X \quad (1)$$

for the unirradiated mixture, the helical twisting power ( $A$ ) of the chiral dopant (Mtn) is equal to  $9.4 \mu\text{m}^{-1}$ . In the case of the same mixture, the value  $A$  of the photostationary mixture of E and Z isomers of Mtn is calculated through Eq.(1) and it is equal to  $2.7 \mu\text{m}^{-1}$  (Figure 4, curve 2'). This marked change in helix twisting power is associated with a strong disturbance of an anisometry of chiral fragment.

In conclusion we may stress that the above chiral photochromic polymers and mixtures can be considered as universal coloured materials for coloured data recording and storage.

### Acknowledgments

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