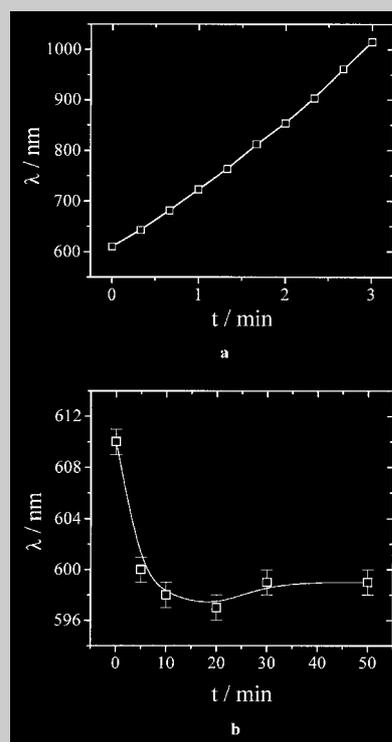


**Full Paper:** New photosensitive cholesteric mixtures (**I** and **II**) containing two different chiral-photochromic fragments were prepared. First mixture consists of phenyl benzoate nematogenic homopolymer and two low-molar-mass (LMM) chiral-photochromic dopants based on cinnamic acid and azobenzene. Mixture **II** consists of cholesteric copolymers with photosensitive azobenzene-containing side groups and LMM cinnamoyl-based dopant. Planar-oriented films of mixtures selectively reflect light in visible and near infrared regions of the spectrum. UV and visible light irradiation leads to the changing of selective light reflection wavelength which associated with *E-Z* photoisomerization and decreasing of the helical twisting power of chiral-photochromic fragments during light action. It was shown that direction of the pitch of the helix changing can be easily controlled by incident light wavelength: in the case of mixture **I** UV irradiation leads to the long-wavelength shift of selective light reflection but visible light action leads to the short wavelength spectral shift. In the case of mixture **II** reverse behavior was observed. The specific features of the kinetics of forward and back thermal processes were characterized. For such materials, their resistance with respect to the repeated “recording-erasing” cycles was tested, and the fatigue resistance was shown to be rather high. As was demonstrated, these mixtures containing chiral groups sensitive to the light of different wavelengths may be used for reversible as well as irreversible recording of optical information.



Change of selective light reflection wavelength during UV-irradiation, 365 nm (a), and visible light irradiation, >450 nm (b), for mixture **I**. Temperature of irradiated sample is 70 °C.

## New Variants of Photosensitive Polymeric Mixtures: Reversible and Irreversible Photoregulation of Helical Supramolecular Structure

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### Introduction

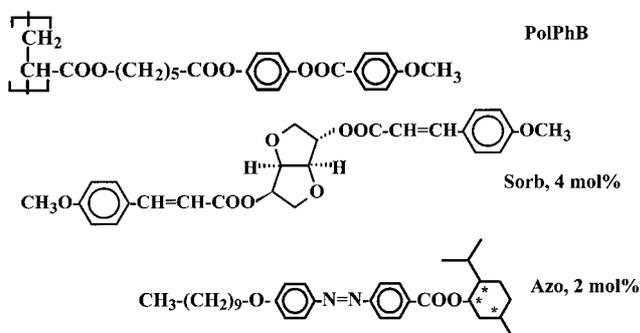
In recent years, a fast development of information technologies has triggered an intensive search for new materials for data recording and storage. In this connection, an evident interest is focused on photochromic polymer materials.<sup>[1–3]</sup> Quite recently, a new approach for the development of cholesteric polymer materials with controlled photo-induced changes in helix pitch has been advanced.<sup>[4–12]</sup> This approach involves the introduction of chiral photo-

chromic groups capable of *E-Z* photoisomerization to nematogenic or cholesteric matrix. In the course of this process, configuration of the above fragments is changed; this change is accompanied by a decrease in their anisotropy and, as a consequence, their twisting power. There were synthesized various polymers which are able to produce chiral nematic phase and capable of reversible or irreversible changes in the pitch of cholesteric helix and selective light reflection maximum. The derivatives of benzylidene

menthanone<sup>[4–9]</sup> and azobenzene<sup>[10–12]</sup> were used as functional chiral photochromic groups.

Quite recently, we have synthesized and studied a multifunctional copolymer containing both benzylidene menthanone and azobenzene chiral photochromic groups. Taking into account the fact the IR absorption bands of the groups are seen in somewhat different spectral regions, a quite unusual compound with a dual photochromism has been obtained. Upon UV irradiation, selective light reflection maximum is irreversibly shifted to a long-wavelength region whereas irradiation with visible light leads to reversible changes in optical properties. As in the case of UV irradiation, upon irradiation with visible light, one may observe an increase in both helix pitch and selective light reflection maximum. In this work, the class of photosensitive cholesteric systems has been widened and, using the synthesized chiral photochromic compounds,<sup>[11, 12, 14]</sup> two mixtures with dual photochromism have been prepared: upon irradiation with a certain wavelength, one may obtain either untwisting or twisting of cholesteric helix.

The first mixture is composed of phenyl benzoate homopolymer (**PolPhB**) responsible for the development of nematic phase and two chiral photochromic dopants containing both chiral fragments and double C=C (**Sorb**) and N=N bonds (**Azo**) which are capable of irreversible and reversible photoisomerization, respectively, cf. Scheme 1.



Scheme 1. Mixture I.

Figure 1 presents the schemes for irradiation-induced photoprocesses of dopants **Azo** (Figure 1a) and **Sorb** (Figure 1b). (In the case of dopant **Sorb** {2 + 2} photocycloaddition of dopants double bonds with formation of cyclobutane ring is also possible. However, the probability of this process in our case is very low, as it is controlled topochemically: a close contact of two C=C bonds is needed for this process.<sup>[15]</sup> In our previous work<sup>[14]</sup> the analysis by the gel permeation chromatography of the cholesteric mixtures irradiated during two hours by UV light showed that the concentration of the chiral dopant dimers after irradiation is negligible small.)

Mixture **I** displays chiral nematic phase (cholesteric mesophase) with a clearing temperature of 93–95 °C.

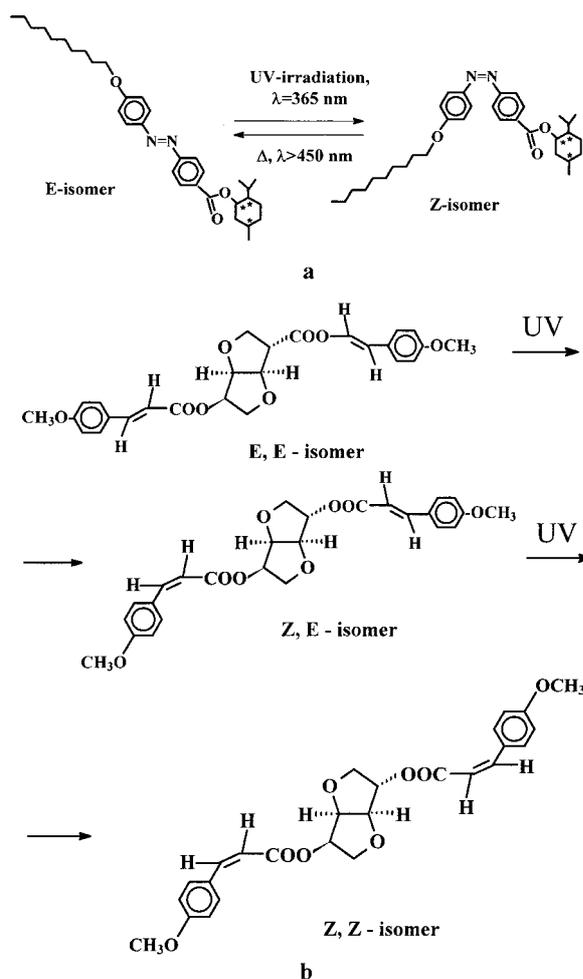


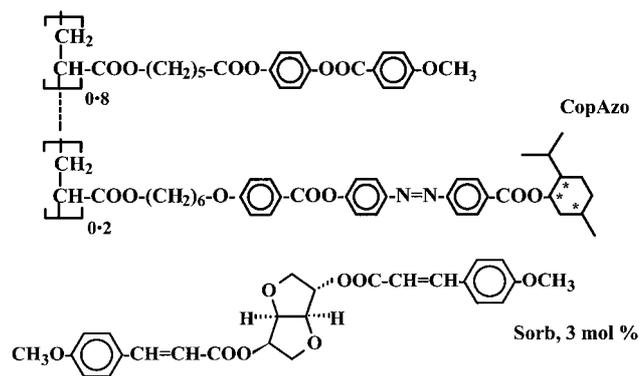
Figure 1. Schemes of *E-Z* photoisomerization processes taking place in dopants **Azo** (a) and **Sorb** (b) under light irradiation.

Note that dopant **Sorb** is a right-handed conformer; in other words, it is able to develop cholesteric helix with right twisting direction<sup>[14]</sup> whereas, in contrary, the second dopant **Azo** is a left-handed conformer.<sup>[11, 12]</sup> The composition of the mixture is selected so that the twisting direction of this ternary mixture is controlled by enantiomeric excess of **Sorb**, that is, the mixture is right-handed.

The second mixture is composed of left-handed cholesteric copolymer **CopAzo** containing nematogenic phenyl benzoate groups and chiral photochromic azobenzene groups as well a dopant **Sorb**, cf. Scheme 2.

Mixture **II** is also able to produce chiral nematic phase (cholesteric mesophase) with a clearing temperature of 102–103 °C. The composition of this mixture is selected so that twisting direction is left; in other words, in this case, azobenzene chiral photochromic groups are *dominate*. For both mixtures, glass transition temperature is equal to about 25 °C.

As is known, UV absorption bands of azobenzene chromophores of dopant **Azo** and azobenzene groups of copolymer **CopAzo** are located in a higher wavelength region



Scheme 2. Mixture II.

( $\lambda_{\max} = 367$  nm for **Azo** and  $\lambda_{\max} = 339$  nm for **CopAzo** in dichloroethane solution) as compared with that corresponding to dopant **Sorb** ( $\lambda_{\max} = 312$  nm in dichloroethane solution).<sup>[10–14]</sup> Furthermore, azobenzene chromophores are characterized by the existence of a high-wavelength  $n-\pi^*$  electron transition at about 450 nm; upon irradiation with a wavelength coinciding with this absorption band, *E-Z* photoisomerization also takes place.<sup>[11–13]</sup> Another important feature of cinnamoyl and azobenzene groups is that, when isomerization of azobenzene fragments is thermally and photochemically reversible, in the case of dopant **Sorb**, all light-induced changes are irreversible.<sup>[14]</sup>

Therefore, upon light irradiation with a wavelength coinciding with the UV absorption band of the dopant presenting in enantiomeric excess, one should observe a decrease in chirality of the system and, hence, helix untwisting; upon light irradiation with a wavelength overlapping with the UV absorption band of another dopant, integral chirality of the system, in contrary, should increase due to a decrease in helix twisting power. The above reasoning allows one to assume that, for mixture **I**, UV irradiation should lead to untwisting of cholesteric helix whereas irradiation with visible light results in helix twisting; in the case of mixture **II**, the whole behavior is quite the reverse.

Hence, the principal objective of the work involves the investigation of the specific features of photo-optical behavior of planar oriented films based on the above mixtures as a function of the wavelength of irradiation light and feasibility study on using the above systems for reversible and irreversible data recording.

## Experimental Part

### Synthesis

Phenyl benzoate homopolymer, azobenzene-containing copolymer and menthyl-, cinnamoyl-containing low-molar-mass photosensitive dopants were synthesized according to the procedures described in,<sup>[11, 12, 14, 16]</sup> respectively.

### Investigations of Phase Behavior and Optical Properties

Phase transitions of the mixtures were studied by differential scanning calorimetry (DSC) with a scanning rate of 10 °C/min. All experiments were performed using a Mettler TA-400 thermal analyzer and a LOMO P-112 polarization microscope. Selective light reflection of mixtures films was studied with a Hitachi U-3400 UV-Vis-IR spectrometer equipped with a Mettler FP-80 hot stage. The 20  $\mu\text{m}$ -thick samples were sandwiched between the two flat glass plates. The thickness of the test samples was preset by Teflon spacers. Planar texture was obtained by shear deformation of the samples, which were heated to temperatures above glass transition. Prior to tests, the test samples were annealed for 20–40 min.

### Photo-Optical Investigations

Photochemical properties investigations were studied using a special instrument<sup>[6]</sup> equipped with a DRSh-250 ultra-high pressure mercury lamp. Using filters, light with wavelengths 366, >450 and  $\approx 550$  nm was selected. To prevent heating of the samples due to IR irradiation of the lamp, water filter was used. To obtain plane-parallel light beam, quartz lens was used. During irradiation, the constant temperature of the test samples was maintained using a Mettler FP-80 heating unit. The intensity of light was equal to  $1.9 \times 10^{-8}$   $\text{Es} \times \text{s}^{-1} \times \text{cm}^{-2}$  (for light of 365 nm, as measured actinometrically<sup>[17]</sup>), the intensity of visible light ( $\lambda_{\text{ir}} > 450$  nm and  $\lambda_{\text{ir}} \approx 550$  nm) was equal  $\approx 8.0 \text{ mW} \times \text{cm}^{-2}$  (for  $\lambda_{\text{ir}} > 450$  nm) and  $\approx 0.7 \text{ mW} \times \text{cm}^{-2}$  (for  $\lambda_{\text{ir}} \approx 550$  nm), as measured by IMO-2N intensity meter.

Photochemical properties of copolymer were studied by illuminating the 20  $\mu\text{m}$ -thick films. Immediately after irradiation (in the case of visible incident light) transmittance spectra were recorded using Hitachi U-3400 UV-Vis-IR spectrometer. In the case of UV incident light the samples were annealed until no changes in the selective light reflection wavelength were observed (usually, for about 20 min).

## Results and Discussion

### Optical Properties of Mixtures

Selective light reflection of planar oriented films based on mixture **I** and **II** is observed in visible spectral region and near-IR region, respectively (Figure 2). Note that the profiles of temperature dependencies of selective light reflection maximum are different: in the case of mixture **I**, with increasing the temperature, helix untwisting takes place whereas, for mixture **II**, this trend is seen as the temperature is decreased. In the former case, this behavior is related to a decrease in orientational order parameter with increasing the temperature<sup>[18]</sup> whereas, in the latter case, this trend is provided by the development and intensification of smectic order fluctuations with decreasing the temperature.<sup>[12]</sup> In turn, one may expect an increase in twist elastic constant.<sup>[19]</sup> However, in both cases, at temperatures varying from 20 to 80 °C, the films based

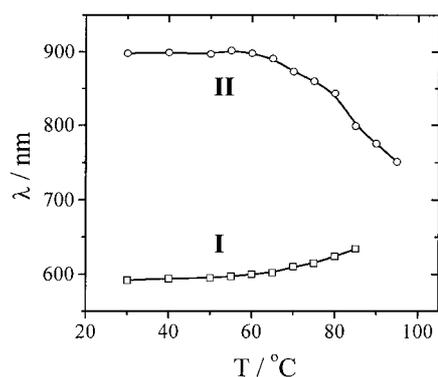


Figure 2. Temperature dependencies of selective light reflection wavelength for planar-oriented films of mixtures **I** and **II**. (Dependencies were plotted for non-irradiated samples.)

on the above mixtures are characterized by almost constant selective light reflection maximum.

The attempts were made to estimate the helix twisting power  $\beta$  for chiral photochromic dopants. The value of  $\beta$  characterizes the ability of chiral dopant or the ability of chiral groups to induce the cholesteric helix and may be expressed as

$$\beta = n(d\lambda^{-1}/dX)_{X=0} \quad (1)$$

where  $n$  is the mean refractive index;  $\lambda$  is the selective light reflection maximum, and  $X$  is the molar content of chiral dopant.

In the case of low content of chiral dopant in mixture, Equation (1) may be re-written as

$$\beta = n \Delta\lambda^{-1}/X \quad (2)$$

For dopant **Sorb** in nematogenic matrix **PolPhB**,  $\beta/n$  is equal to  $45 \mu\text{m}^{-1}$ . Taking into account the fact that the content of dopant **Azo** in mixture **I** is low (2%), one may expect that its introduction has no effect on helix twisting power of dopant **Sorb** in mixture. To calculate  $\beta/n$  for dopant **Azo** in mixture **I**, the assumption concerning an additive contribution of chiral components to selective light reflection maximum was made:

$$n\lambda^{-1} = \beta_1 X_1 + \beta_2 X_2 \quad (3)$$

$$\text{Hence, } \beta_2/n = (\lambda^{-1} - \beta_1 X_1/n)/X_2 \quad (4)$$

Reduced twisting power  $\beta/n$  of dopant **Azo** in mixture **I** (at  $T = 0.95 T_{ci}$ ) calculated through Equation (4) is equal to  $-8.7 \mu\text{m}^{-1}$  (here, sign (-) denotes the reverse direction of helix twisting for dopant **Azo** as compared with dopant **Sorb** (as was mentioned above, dopant **Azo** is characterized by left-handed of helix twisting). This value is close to  $\beta/n$  of dopant **Azo** in the matrix of menthyl-containing cholesteric copolymer which is equal to  $-9.6 \pm 2.0 \mu\text{m}^{-1}$ .<sup>[12]</sup>

For dopant **Sorb** in mixture **II**, calculation through Equation (4) provides a somewhat increased value of  $\beta/n$  which is equal to  $83 \mu\text{m}^{-1}$ . In this case, the assumption concerning an additive character and Equation (2) are not valid, and this fact is likely to be related to a high content of menthylazobenzene fragments in copolymer **CopAzo**.

Analysis of the calculated values of  $\beta/n$  allows one to conclude that twisting power of dopant **Sorb** is five times higher than that of dopant **Azo**.

### Photo-Optical Properties of Mixture **I**

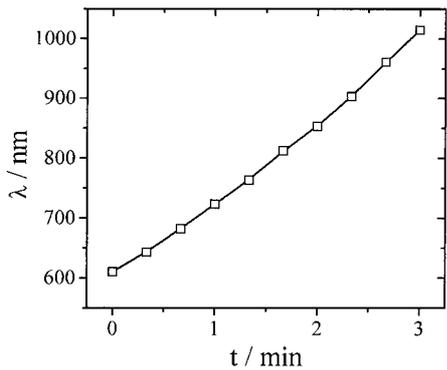
Let us consider the specific features of photo-optical properties of mixture **I**. As follows from Figure 3a and 3b, in this case, UV irradiation (365 nm) leads to untwisting of cholesteric helix and shift in selective light reflection maximum to high-wavelength spectral region whereas, upon irradiation with visible light (>450 nm), selective light reflection maximum is shifted to short-wavelength spectral region. Furthermore, upon irradiation with visible light, this shift in selective light reflection maximum is much lower and is observed once photostationary state is attained. Under irradiation with visible light, this shift in selective light reflection maximum is thermally reversible: upon annealing, this peak is shifted in reverse direction (Figure 4). However, it is interesting to note that even though, upon repeated recording-erasing cycles (Figure 4), the amplitude in changes of selective light reflection maximum remains almost unchanged, upon 12 recording-erasing cycles, a systematic shift in the position of selective light reflection maximum to long-wavelength region takes place (from 610 to 640 nm). This trend suggests that, upon light irradiation with a wavelength >450 nm, one may observe photoisomerization of not only dopant **Azo** but also irreversible *E-Z* photoisomerization of cinnamoyl dopant **Sorb**.<sup>a</sup>

Analysis of experimental data allows one to conclude that, upon UV irradiation, mixture primarily experiences photoisomerization of cinnamoyl dopant **Sorb** (Figure 1b) whereas irradiation with visible light leads to a preferential isomerization of azobenzene dopant **Azo** (Figure 1a).

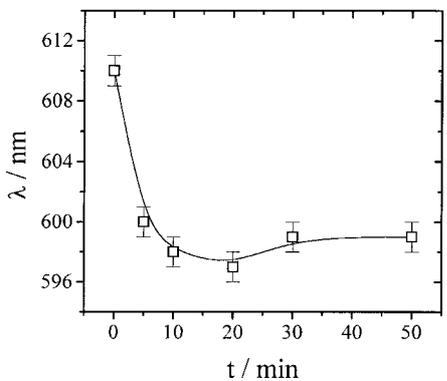
### Photo-optical Properties of Mixture **II**

In the case of mixture **II**, photo-optical behavior appears to be quite different: upon UV irradiation and annealing, selective light reflection maximum is shifted to short-wavelength region whereas, in the case of irradiation with visible light, this maximum is shifted to long-wavelength

<sup>a</sup> Note that, in the case of mixture **I**, irradiation with a wavelength  $\approx 550$  nm has no effect on cinnamoyl chromophores, however, shift in selective light reflection maximum to long-wavelength spectral region via isomerization of dopant **Azo** is very small ( $\approx 3$  nm).



a



b

Figure 3. Change of selective light reflection wavelength during UV-irradiation, 365 nm (a), and visible light irradiation, >450 nm (b), for mixture I. Temperature of irradiated sample is 70 °C.

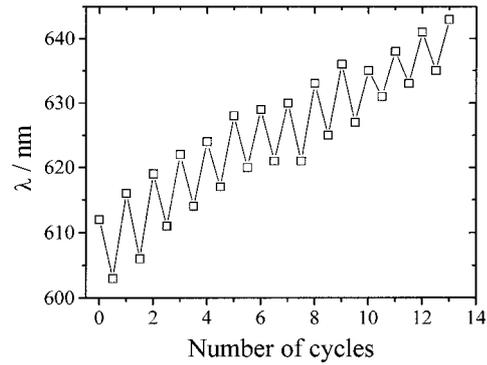


Figure 4. Fatigue resistance properties of the mixture I film under the “recording-erasing” processes. In each cycle the film was irradiated during 20 min by light (>450 nm) at 70 °C, then the film was annealed during 20 min at the same temperature.

region (Figure 5). As in the case of mixture I, irradiation with visible light leads to a preferential photoisomerization of azobenzene groups whereas, upon UV irradiation, photoisomerization of cinnamoyl groups of dopant **Sorb** and azobenzene groups of copolymer **CopAzo**. However, in the latter case, annealing leads to a reverse transformation of Z-isomers of azobenzene groups to E-form; hence, the resultant shift in selective light reflection maximum is controlled by the ratio between E and Z-isomers of dopant **Sorb**. Upon irradiation with visible light, the amplitude in changes in selective light reflection maximum is much higher than that in the case of mixture I; this trend is related to much higher content of azobenzene chiral photochromic groups in mixture II.

Quite impressive results were obtained when studying the feasibility of cyclic recording on planar oriented films

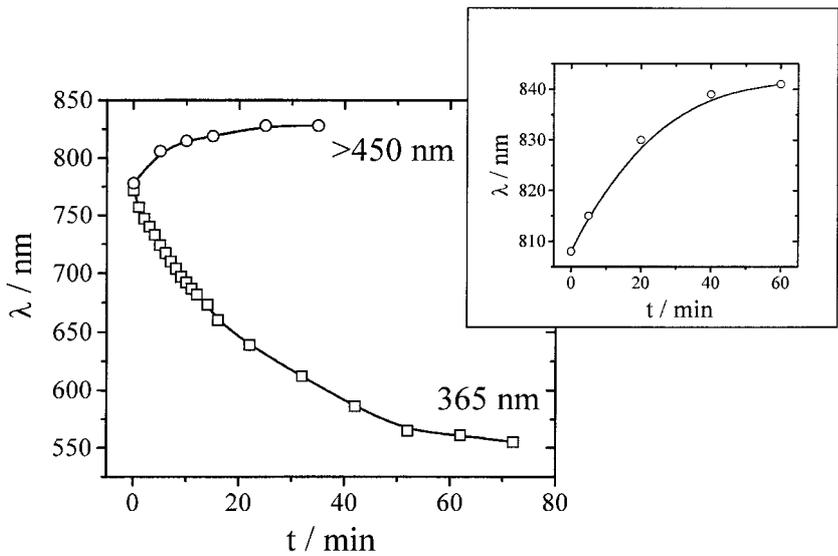
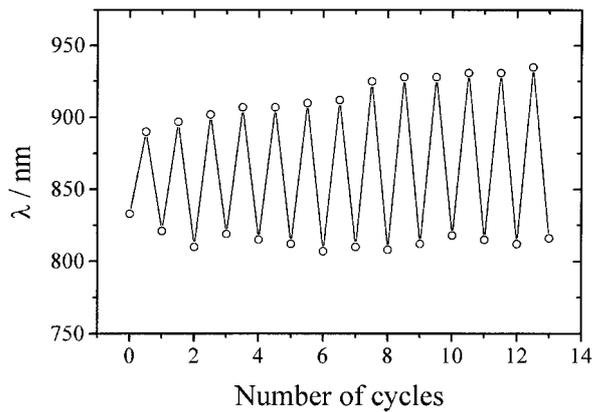
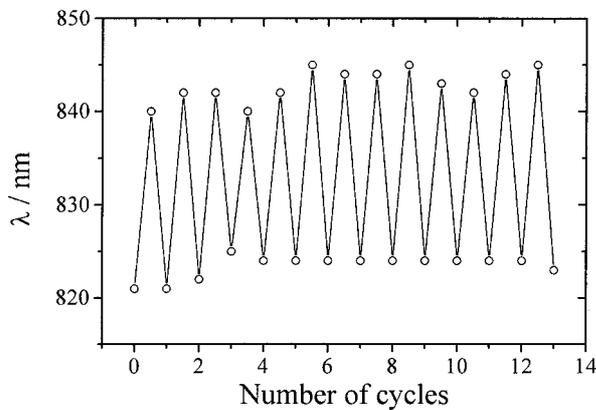


Figure 5. Changing of selective light reflection wavelength during irradiation with light of different wavelengths for mixture II (T = 90 °C). Inset: the change of selective light reflection wavelength during irradiation with light of 550 nm at 85 °C. In the case of irradiation with light of 365 nm the sample was annealed after each cycle of light action during 20 min at 90 °C.



a



b

Figure 6. Fatigue resistance properties of the mixture **II** film during the “recording-erasing” processes. In each cycle film was irradiated during 20 min by light  $>450$  nm (a) and  $\approx 550$  nm (b) at  $80^\circ\text{C}$ , then the film was annealed during 20 min at the same temperature.

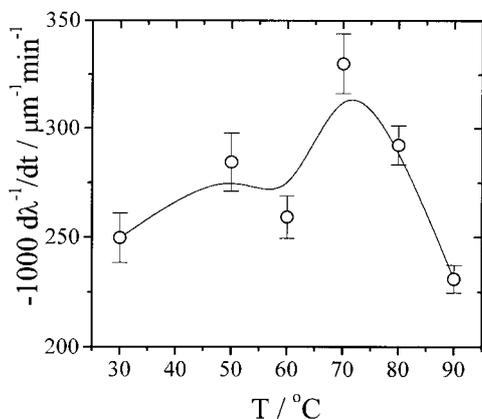
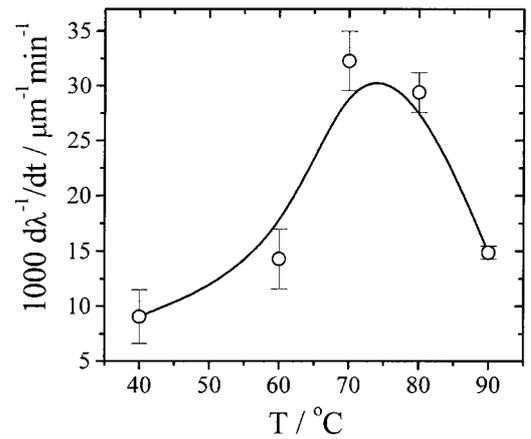
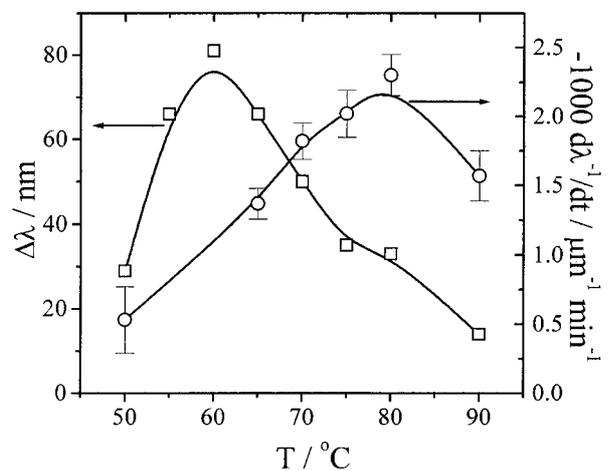


Figure 7. Temperature dependencies of the rate changing of reversal wavelength of selective light reflection during UV light action (365 nm) for mixture **I**.



a



b

Figure 8. Temperature dependencies of the rate changing of reversal wavelength of selective light reflection during irradiation by UV (365 nm) (a), and visible light ( $\approx 550$  nm) (b) and of the maximum selective light reflection shift (b) for mixture **II**.

of mixture **II** upon irradiation with visible light with  $\lambda > 450$  and  $\approx 550$  nm (Figure 6). Upon light irradiation with wavelength  $\lambda > 450$  nm, as the number of cycles is increased, the amplitude in the shift in selective light reflection maximum increases whereas, upon light irradiation with  $\lambda \approx 550$  nm, this amplitude remains almost unchanged. To understand the reasons of this behavior, further study is invited.

#### Effect of Temperature on Photo-optical Behavior of Mixtures

Let us consider the effect of temperature on the kinetics of changes in selective light reflection maximum for the above mixtures. Figure 7 and 8 show the temperature dependencies of initial rate of changes of reciprocal

selective light reflection maximum for mixtures **I** and **II** and for various wavelengths of incident light.<sup>b</sup>

Let us first mention that, in all cases, as temperature is increased, one may initially observe an increase in the rate of shift in selective light reflection maximum and, then, decrease. In this case, upon UV irradiation, maximum rate is observed at 70–75 °C for both mixtures (Figure 7 and 8a) whereas, upon irradiation with visible light ( $\approx 550$  nm), for mixture **II**, maximum rate is attained at about 80 °C (Figure 8b). This profile (the presence of maxima) is quite evident for mixture **II** irradiated with visible light: in this case, only azobenzene groups of copolymer **CopAzo** experience photoisomerization. This process is thermally reversible, and the rate of the back *Z-E* isomerization dramatically increases with increasing the temperature;<sup>[12]</sup> hence, the total rate of the transition of E-form to Z-isomer decreases with increasing the temperature. Below 80 °C, the rate of helix untwisting is limited by the viscosity of polymer medium. The above factors may be invoked to explain the temperature dependence of the rate of changes in selective light reflection maximum. Note that the temperature dependence of the amplitude of shift in selective light reflection wavelength also passes maximum (Figure 8b) but its position is shifted to lower temperatures. The lower the temperature, the higher the fractional content of Z-isomer of azobenzene side groups in photostationary mixture; at temperatures far below 55 °C, the viscosity is so high that one may hardly attain the equilibrium helix pitch value controlled by a certain ratio between E and Z-isomers of chiral photochromic groups.

In the case of UV irradiation, the appearance of maximum in the temperature dependencies of the rate of shift in selective light reflection maximum is not evident. This behavior may be explained as follows. Upon light irradiation with a wavelength of 365 nm, *E-Z* isomerization of both cinnamoyl fragments of dopant **Sorb** and azobenzene groups of dopant **Azo** and copolymer **CopAzo** is observed. Upon annealing, Z-form of azobenzene groups is transformed back to E-form and changes in selective light reflection maximum are provided only by irreversible *E-Z* isomerization of dopant **Sorb**. However, let us mention that the fraction of the light absorbed by dopant molecules strongly depends on the ratio between E and Z-isomers of azobenzene groups upon irradiation because the latter groups are able to absorb light with a given wavelength, and extinction coefficient of E-isomer is much higher than that of Z-form.<sup>[12,20]</sup> Therefore, the higher the temperature, the lower the fraction of Z-isomer of azobenzene groups, and the higher the ability of azobenzene fragments to absorb UV light and decrease the rate of photoisomerization of cinnamoyl dopant **Sorb**. At

<sup>b</sup> In the case of mixture **I**, shift in selective light reflection maximum is rather small; hence, a correct analysis of kinetic dependencies is hindered.

low temperatures, a decrease in the rate of shift in selective light reflection maximum is provided by the above increase in the viscosity of the system.

## Conclusion

Hence, let us emphasize a unique character of the above polymer cholesteric mixtures when the direction of the changes in helix pitch may be easily controlled by varying the wavelength of light irradiation. This approach allows one to widen substantially the possibilities of photo-optical control of optical properties of polymer materials. Such mixtures may be used for data recording and storage.

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