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Photo-optical behaviour of a photosensitive chiral nematic copolymer and mixtures containing non-chiral photoactive azobenzene groups

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For the first time, the phenomenon of the light-induced increase in helix pitch length is described for cholesteric polymer systems containing photosensitive *non-chiral* fragments. This phenomenon is observed for a copolymer and mixtures containing azobenzene fragments which are able to undergo *E-Z* photoisomerization. In all cases, upon UV irradiation, the selective light reflection maximum is shifted to the long wavelength spectral region. This shift appears to be quite appreciable and, in some cases for mixtures, it might be as high as 300 nm. This process is known to be thermally reversible: upon annealing, the selective light reflection maximum comes back to its initial position. The specific features of the kinetics of this photoprocess were studied, and the fatigue resistance of such systems investigated. The advantages of their application for reversible recording of optical information with a possible non-destructive data reading is outlined.

1. Introduction

Recently, a new approach for the development of chiral nematic (or cholesteric) low molar mass [1–6] and polymeric materials showing light-induced and controllable changes in the helical pitch lengths has been reported [7–15]. This approach is based on the introduction of chiral photosensitive fragments into the nematic matrix. These fragments are able to undergo light-induced *E-Z* photoisomerization. As a result of this process, *Z*-isomerization of the chiral photochromic groups takes place. This isomerization is accompanied by a decrease in the anisotropy of the photochromic groups and, as a consequence, also by a decrease in their helix-twisting power. Therefore, upon light irradiation, the macroscopic chirality of the system is reduced and, in the case of systems containing a single chiral component, the helical pitch length increases. Such systems appear to be quite attractive from the viewpoint of their practical application potential, because, upon light irradiation and the concurrent untwisting of the cholesteric helix, the selective light reflection maximum is shifted to the long wavelength region of the spectrum. Hence, the optical properties of films based on such systems may be easily controlled by light irradiation via local variations in the selective light reflection wavelength. In this case, the recorded ‘coloured’ image appears to be stable for rather

long periods of time. Furthermore, non-destructive data reading is possible; for traditional photochromic materials, this presents a challenging problem [16, 17].

However, for all these copolymers and their related mixtures, the photosensitive groups also show chiral properties; in other words, each side group of the copolymer or the low molecular mass dopant molecules combines both the function of providing photosensitive and the ability to induce the cholesteric helical supramolecular structure [7–15].

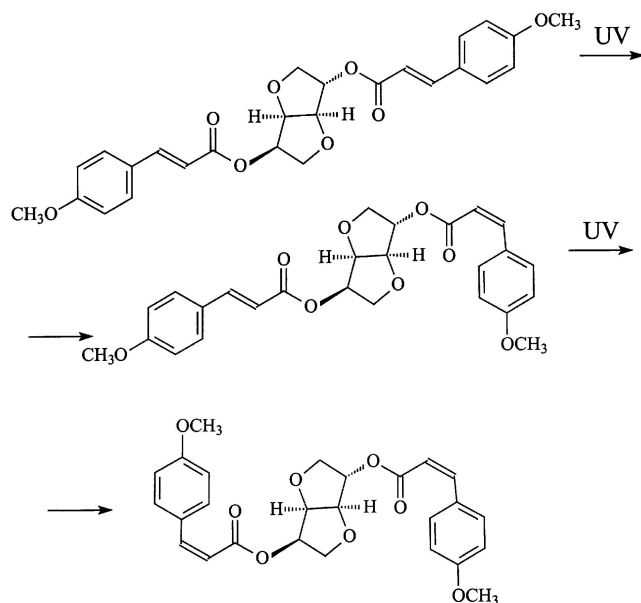
Shortly prior to the publications describing the cholesteric copolymers containing combined chiral and photochromic side groups, several publications [18–20] describing *co*-polycyclosiloxanes and polymethacrylates containing achiral mesogenic azobenzene [18, 19] or benzylidene cyclohexane fragments [20] as photosensitive groups appeared. In such cases, light irradiation leads to no smooth (continuous) changes in the helical pitch (in other words, macroscopic chirality). In the case of cyclosiloxanes containing azobenzene groups, the generation of higher selective light reflection orders is observed, and this process results from the distortion of helical supramolecular structure (at a fixed helix pitch length). For example, photoisomerization and {2 + 2} photocycloaddition of benzylidenecyclohexanone groups lead to a trivial breakdown of liquid crystalline order and a concomitant disappearance of the selective light reflection maximum [20].

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In this work, the possibility of smooth light-induced changes in the helix pitch and in the selective light reflection maximum has been demonstrated for the first time for polymeric systems, specifically by a copolymer and mixtures containing photosensitive achiral fragment (see the table). (For low molar mass cholesteric mixtures containing achiral photochromic azobenzene dopants [21, 22], the possibility of light-induced helix untwisting was already shown; however, the specific features of the kinetics of such photoprocesses were ignored.)

To this end, the copolymer containing azobenzene-based nematogenic groups and menthyl-containing chiral units was synthesized, and the three mixtures **I–III** containing chiral dopants based on an azobenzene-containing nematogenic homopolymer (mixtures **I** and **III**) and a copolymer (mixture **II**) were prepared. Note that, in the case of the copolymer and mixtures **I** and **II**, only the achiral groups are photosensitive; in the case of mixture **III**, the corresponding chiral group of the dopant Sorb is also photoactive as it contains two C=C bonds which are capable of *E–Z* photoisomerization [23] (see the scheme). The compositions of the copolymer and the mixtures were selected so that the selective light reflection wavelength is seen in the visible or near-IR spectral regions such that it does not overlap with the absorption bands associated with the azobenzene groups to any marked extent.

By varying the chemical structure of cholesteric systems, one may gain a deeper insight into the specific features of the photoinduced changes in the supramolecular structure under irradiation with various wavelengths; in the case of mixture **III**, one may also observe either



Scheme. Photoisomerization processes for the photosensitive dopant Sorb under UV light irradiation.

reversible (due to photoisomerization of azobenzene groups) or irreversible changes (due to photoisomerization of the molecules of chiral dopant) in the helix pitch as was shown earlier for systems containing chiral photochromic groups of both types [24, 25]. Therefore, the objective of the present work involves a study of the possible photochemically controlled changes in the optical properties of the copolymer and related mixtures shown in the table and the investigation of photoinduced transformations in cholesteric systems containing photosensitive non-chiral groups.

2. Experimental

2.1. Synthesis

The azobenzene-containing homopolymer and copolymers, and the cinnamoyl-containing low molar mass photosensitive dopant were synthesized according to the procedures described elsewhere [23, 26–28]. Relative molecular weights of the polymers were determined by gel permeation chromatography (GPC). GPC analyses were carried out with a GPC-2 Waters chromatograph equipped with an LC-100 column oven and a Data Modul-370 data station. Measurements were made using a UV detector, with THF as solvent (1 ml min^{-1} , 40°C), and a set of PL columns of 100, 500 and 10^3 \AA ; a calibration plot was constructed with polystyrene standards. The polymers obtained have the following molar mass characteristics: $M_n = 8000\text{--}12\,000$, $M_w/M_n = 1.3\text{--}2.1$.

2.2. Investigation of phase behaviour and optical properties

Phase transitions of the copolymer and mixtures were studied by differential scanning calorimetry (DSC) with a scanning rate of $10^\circ\text{C min}^{-1}$. The polarizing optical microscopy (POM) investigations were performed using a Mettler TA-400 thermal analyser and a LOMO P-112 polarizing microscope. X-ray diffraction (XRD) analysis was carried out using a URS-55 instrument (Ni-filtered CuK_α -radiation, $\lambda = 1.54 \text{ \AA}$).

Selective light reflection of the films was studied with a Hitachi U-3400 UV-Vis-IR spectrometer equipped with a Mettler FP-80 hot stage. The $\sim 20 \mu\text{m}$ thick samples were sandwiched between two flat glass plates. The thickness of the test samples was preset by Teflon spacers. A planar texture was obtained by shear deformation of the samples (by a slight shift of the cover glass plate), which were heated to temperatures $5\text{--}10^\circ$ below the clearing temperature. Prior to the tests, the samples were cooled to the required temperatures and annealed for 20–40 min.

2.3. Photo-optical investigations

Photochemical properties were studied using an instrument equipped with a DRSh-250 ultra-high pressure mercury lamp and N_2 UV laser ILGI-503 (337 nm). In

Table. Chemical structure and phase transitions ($^{\circ}\text{C}$) of the copolymer and mixtures.

Name	Chemical structure of components	Phase transitions
Copolymer		SmA 90–94 N* 104–105 I
Mixture I		SmA 94–95 N* 119 I
Mixture II		N* 97–98 I
Mixture III		SmA 94–98 N* 120 I

the case of the UV lamp, light with wavelengths 365, >450 and ~ 550 nm was selected using cut-off filters. To prevent heating of the samples due to IR irradiation by the lamp, a water filter was used. A quartz lens provided plane-parallel light beam. During irradiation, the constant temperature of the test samples was maintained using a Mettler FP-80 heating unit. The intensity of light was 1.9×10^{-8} Einstein $s^{-1} cm^{-2}$ (for light of 365 nm, as measured using actinometry [29]), the intensity of visible light ($\lambda_{ir} > 450$ nm and $\lambda_{ir} \sim 550$ nm) was ~ 8.0 mW cm^{-2} (for $\lambda_{ir} > 450$ nm) and ~ 0.7 mW cm^{-2} (for $\lambda_{ir} \sim 550$ nm); the intensity of the laser beam was ~ 66 mW cm^{-2} , as measured by an IMO-2N intensity meter.

The photochemical properties of the copolymer and mixtures were studied by illuminating the ~ 20 μm thick films. After irradiation, transmittance or absorbance spectra were recorded using the Hitachi U-3400 UV-Vis-IR spectrometer. In the case of UV incident light, the samples were annealed until no change in the selective light reflection wavelength was observed (usually, for about 20 min).

3. Results and discussion

3.1. Phase behaviour of photosensitive copolymer and mixtures

As revealed in data obtained by POM, DSC, and XRD, the development of a chiral nematic phase (N^*) is observed in all samples. For the copolymer and mixtures **I** and **III**, the glass transition temperature is about $35^\circ C$ whereas, for mixture **II**, it is $\sim 25^\circ C$. For the copolymer and mixtures **I** and **III**, a SmA mesophase is also observed (see the table). According to XRD this phase is characterized by a single-layer packing of the side groups: the X-ray patterns show a well pronounced small angle reflection with a period of 28 \AA , which almost coincides with the length of the azobenzene-containing side fragment (about 27 \AA).

3.2. Optical properties of the photosensitive copolymer and mixtures

Planarly oriented cholesteric films of the copolymer and mixtures show selective light reflection in the visible and near-IR spectra regions (figure 1). As follows from figure 1, the profiles of the temperature dependences of the selective light reflection wavelengths (λ_{max}) are different: for mixture **II**, the λ_{max} value is virtually independent of temperature, whereas for mixtures **I** and **III**, upon cooling, a slight untwisting cholesteric helix is observed; for the copolymer, λ_{max} is markedly shifted to the long wavelength spectral region. On cooling, an accompanying increase in the selective light reflection wavelength usually results from the development of smectic order when approaching the temperature of the

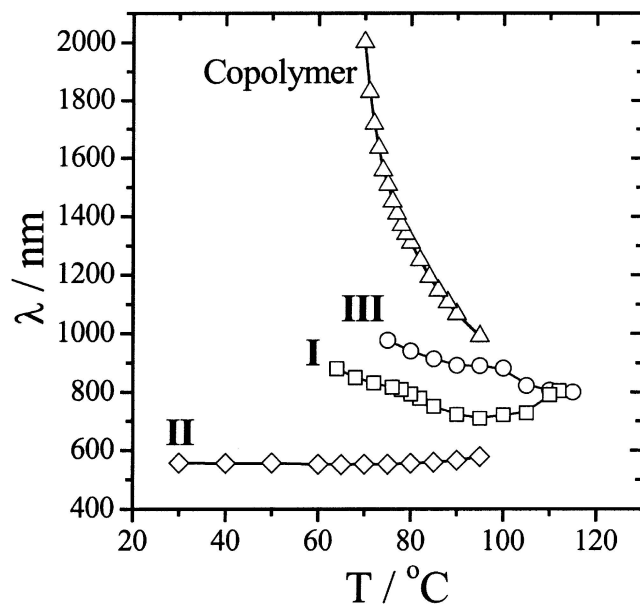


Figure 1. Temperature dependence of selective light reflection wavelength for the copolymer and mixtures **I–III**. Values of selective reflection wavelength were obtained during cooling. In the case of systems forming a SmA phase, supercooling of the chiral nematic phase and selective reflection at temperatures corresponding to the smectic phase was observed.

phase transition from N^* to the smectic phase [24]; this behaviour is observed for the copolymer and mixtures **I** and **III**. Note that for the copolymer this increase is more pronounced. This trend may be explained by the fact that, in this case, menthyl-containing chiral side groups assist in the development of the elements of layered order in the system. For mixture **II**, only a chiral nematic phase is formed, and the selective light reflection maximum remains unchanged over the whole temperature range of the mesophase (and below the glass transition temperature).

As a result of smectic order fluctuations, a decrease in the helical twisting power of the dopant in mixture **I** is more pronounced than it is in mixture **II**. In both cases, the structure of the dopant is the same, however in the case of mixture **I**, which is characterized by the formation of a low temperature SmA mesophase, the selective light reflection maximum is seen in a longer wavelength spectral region (figure 1). Therefore, the phase behaviour of the copolymer and mixtures exerts a strong effect on the optical properties of the planarly oriented films.

When films of the copolymer and mixtures showing the SmA mesophase are slowly cooled, the selective light reflection disappears and a non-typical texture capable of strong light scattering develops. However, due to the relatively high viscosity of the copolymer and mixtures, on rapid cooling of the samples from the cholesteric

mesophase to room temperature, both the helix pitch and selective light reflection maximum are fixed. Such film samples maintain their optical properties for a long period of time because the glass transition temperature is somewhat higher than room temperature (about 35°C).

3.3. Photo-optical properties of the photosensitive copolymer and mixtures in dilute solutions and thin films

We consider first the photochemical behaviour of dilute solutions of the photochromic homopolymer containing ethoxyazobenzene side groups which are the principal photosensitive fragments in the copolymer and mixtures:

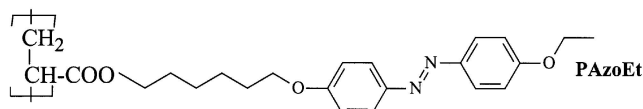


Figure 2(a) presents the absorption spectra of a dichloroethane solution of the polymer PAzoEt as recorded during UV irradiation. The nature of the spectral changes seen in figure 2(b) suggest unequivocally the occurrence of *E-Z* photoisomerization: in the region of the $\pi-\pi^*$ electron transition ($\lambda = 359$ nm), the optical density decreases and, in the region of the $n-\pi^*$ transition ($\lambda_{\max} \sim 450$ nm) of the azobenzene chromophore, the optical density slightly increases. This process is thermally, figure 2(b), and photochemically (upon irradiation with visible light) reversible. Even at room temperature, one may observe a gradual transformation of the *Z*-form back to the *E*-form, and this process is accompanied by the recovery of the initial spectrum of the solution, see figure 2(b).

The photochemical behaviour of the azobenzene groups in the films of the homopolymer and mixtures is somewhat different from their behaviour in solution (the films were prepared by slow evaporation from chloroform solution and a subsequent annealing at 80°C). First, the maximum of the $\pi-\pi^*$ electron transition is shifted somewhat to a shorter wavelength spectral region, (figure 2(c), $\lambda_{\max} = 325$ nm), and this shift may be explained by the

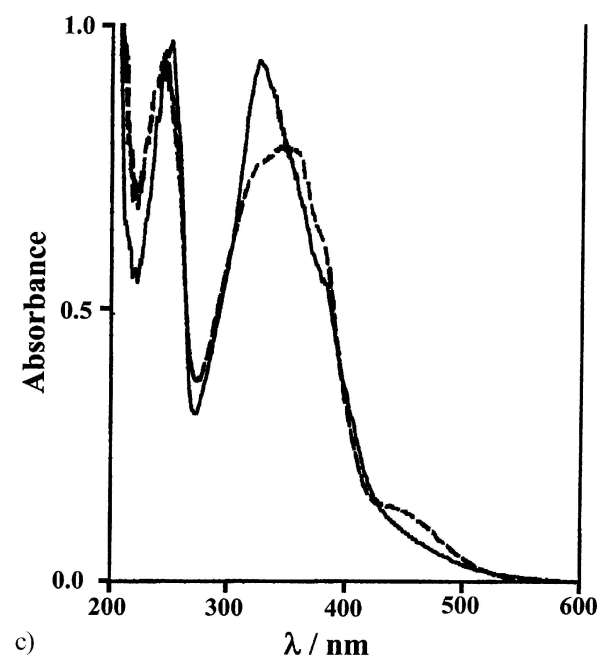
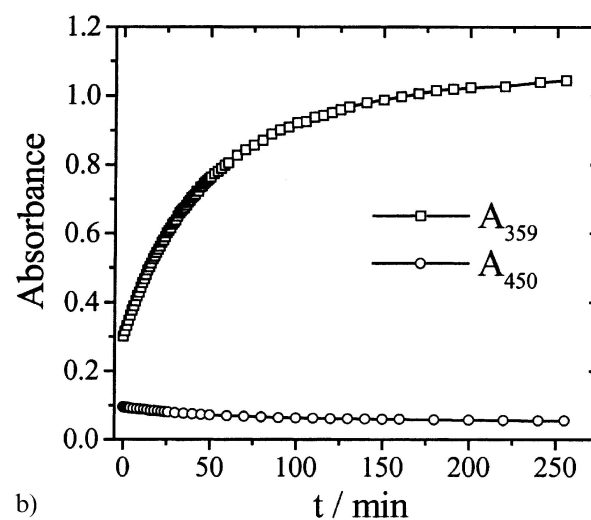
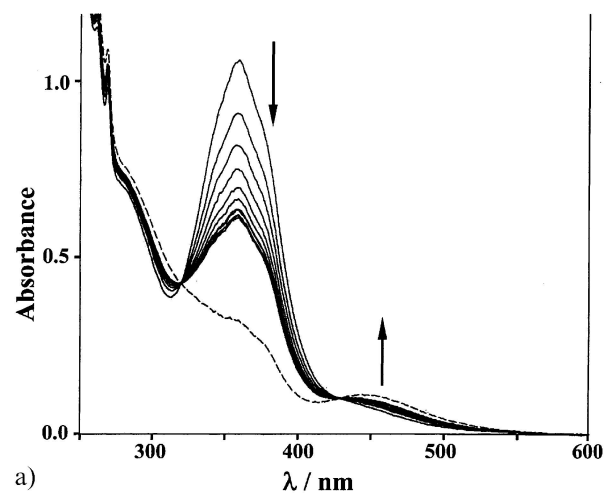


Figure 2. (a) Changes in the absorbance spectra of the homopolymer PAzoEt solution (dichloroethane, $0.85 \cdot 10^{-2} \text{ mg ml}^{-1}$) during UV irradiation. Spectra were recorded each 10 s of irradiation. Dashed line corresponds to the photostationary state (~ 10 min of irradiation). (b) Kinetics of absorbance changes of homopolymer PAzoEt solution during the thermal back *Z-E* isomerization process at wavelengths corresponding to $\pi-\pi^*$ and $n-\pi^*$ electronic transitions of the azobenzene chromophore. Before measurements the solution was irradiated by UV light for 10 min. (c) Changes in the absorbance spectra of a film of mixture II before (solid line) and after (20 min, dashed line) UV irradiation. Temperature of irradiated solutions and film was 25°C; wavelength of UV light was 365 nm.

formation of so-called H-aggregates [30–33]. Second, light irradiation leads only to minor spectral changes. This behaviour is likely to be related to the fact that the existing liquid crystalline order noticeably prevents photoisomerization [34, 35], and its conversion (i.e. concentration of *Z*-isomer produced during reaction) is reduced.

The photo-optical behaviour of the cyanoazobenzene-containing copolymer (in this work, this copolymer is used as a polymer matrix for mixture **II**) is similar to the photochemical properties of copolymers described elsewhere [36, 37]. Hence, the details of this phenomenon are beyond the scope of this publication but we would like to mention that, upon UV irradiation, the *E*–*Z* photoisomerization also occurs, and this process is either thermally reversible or reversible under the action of visible light.

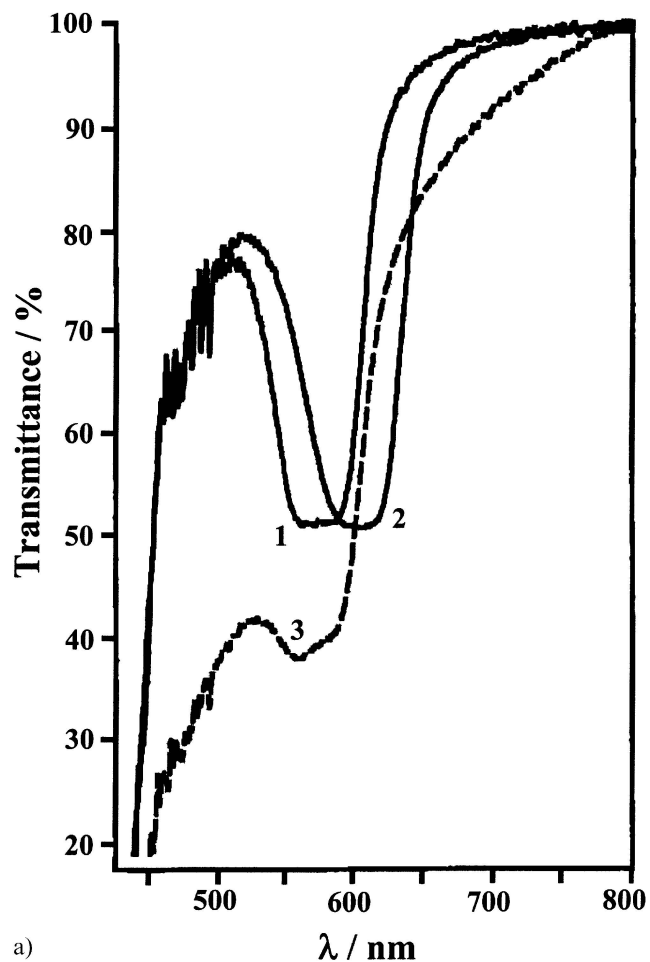
The photochemical properties of the cinnamoyl-containing chiral photochromic dopant (component of mixture **III**) have been described elsewhere [23]. As was shown, under the action of UV irradiation dilute solutions or films of cholesteric mixtures undergo *E*–*Z* photoisomerization about the double C=C bond in the dopant (see the scheme). Note that in this case this process appears to be thermally irreversible.

The experimental evidence described concerning the photochemical behaviour of solutions and films of the azobenzene-containing copolymer and mixtures allows one to conclude that, in all cases, light irradiation is accompanied by the transformation of the *E*-isomer of the mesogenic azobenzene fragments to the *Z*-form of low anisotropy.

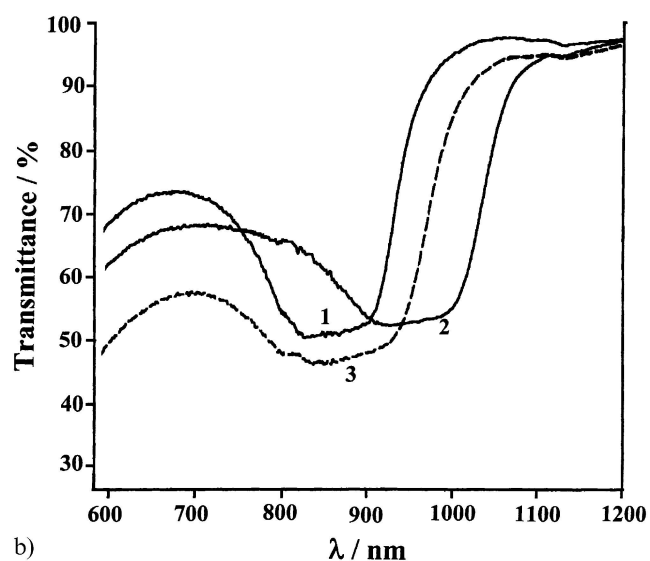
3.4. Photo-optical properties of planarly oriented films of photosensitive copolymer and mixtures

We now discuss the effect of light irradiation on the optical properties of planarly oriented films of the copolymer and mixtures. Upon UV and visible light irradiation the selective light reflection maximum is shifted to the long-wavelength spectral region (figures 3–6).

This phenomenon is more pronounced for the mixtures (shift in λ_{\max} is equal to ~ 300 nm!) and results from the *E*–*Z* photoisomerization of the azobenzene groups. This process leads to a decrease in the orientational order parameter due to the development of the bent-shaped *Z*-form of the azobenzene groups. In turn, as the orientational order parameter decreases, an untwisting of the cholesteric helix takes place [38, 39]. This explanation is supported indirectly by the well known phenomenon of the distortion of LC order accompanying the *E*–*Z* photoisomerization of azobenzene groups of comb-shaped polymers [40–44]. It is interesting to note that in this case the range of the shifts in the selective light reflection wavelength is much wider than that observed for the



a)



b)

Figure 3. Transmittance spectra of a planarly oriented film of mixture **II** at 90°C (a) and **III** at 100°C (b): (1) before irradiation; (2) after 10 min of UV irradiation (365 nm); (3) after annealing for 20 min at the same temperature.

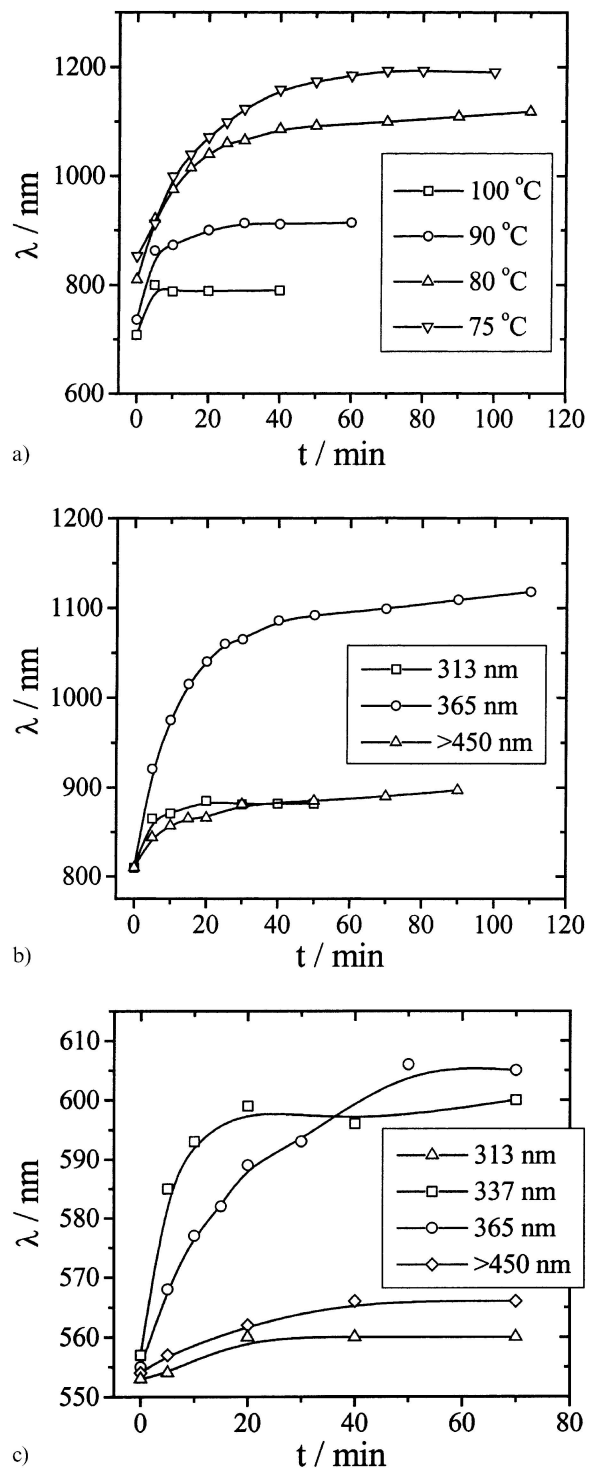


Figure 4. Changes of the selective light reflection wavelength for mixture I: (a) during UV irradiation (365 nm) at different temperatures (shown in figure); (b) during irradiation with light of different wavelengths (also shown in figure); $T = 100^\circ\text{C}$. (c) Changes of selective light reflection wavelength for mixture II during irradiation with light of different wavelengths at 70°C . After each irradiation cycle the transmittance spectra were recorded immediately.

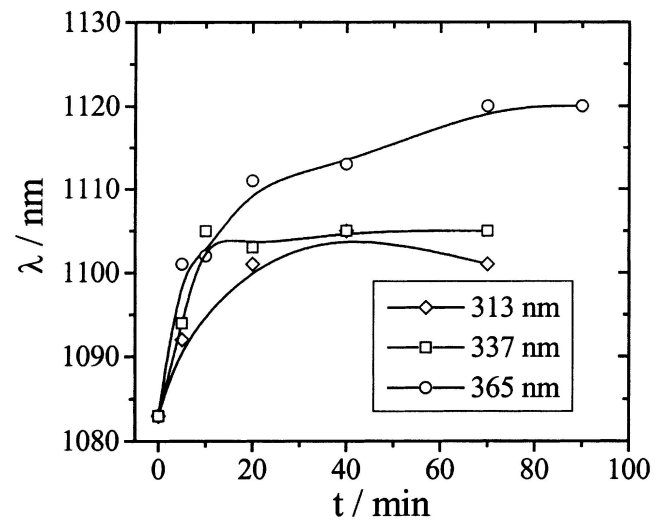


Figure 5. Changes of the selective light reflection wavelength for the copolymer during irradiation with light of different wavelengths ($T = 90^\circ\text{C}$). After each irradiation cycle the transmittance spectra were recorded immediately.

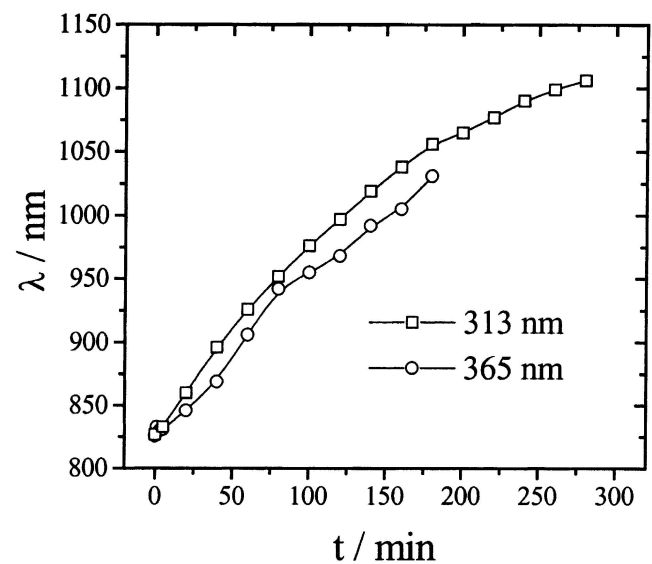


Figure 6. Changes of the selective light reflection wavelength during UV irradiation with light of different wavelengths for mixture III ($T = 100^\circ\text{C}$). After each irradiation cycle the sample was annealed for 30 min at the same temperature.

copolymers and mixtures containing chiral photochromic side groups or low-molecular-mass azobenzene dopants [14, 15] (in the latter case, the shift in λ_{max} is $\sim 30\text{--}90$ nm). The decrease in the order parameter can be associated with a decrease in the clearing temperature (T_{cl}); but according to our measurements the decrease in T_{cl} does not exceed 1° . Another possible explanation of the phenomena observed involves a change in the interactions between the chiral groups and azobenzene units during their photoisomerization.

For the copolymer and mixtures **I** and **II** in all cases, and for mixture **III** upon irradiation with visible light, the shift in the selective light reflection maximum is reversible: thus, upon annealing, the selective light reflection maximum recovers its initial position (figure 3). It is interesting to note that during the back reaction strong light scattering appears. This phenomenon has been observed earlier [14, 15] and is likely to be related to distortions in the planar texture upon twisting of the cholesteric helix. Nevertheless, as a result of prolonged annealing or shear deformation of the sample, a complete recovery of the initial profile of the selective light reflection peak takes place.

3.5. Kinetic features of the photo-optical behaviour of photosensitive copolymer and mixtures

We now consider in more detail the kinetics of the photo-induced twisting of the cholesteric helix and the effects of various factors on this process. The rate and range of changes in λ_{\max} are markedly controlled by temperature, figure 4(a), and by the light wavelength, figures 4(b), 4(c) and 5. In all cases, the higher the temperature, the smaller the shift in the selective light reflection maximum to the long wavelength spectral region, see figure 4(a). This behaviour is related to the fact that the rate of the back *Z*-*E* isomerization dramatically increases on increasing the temperature; hence, at higher temperatures, the content of the *Z*-isomer is lower.

On irradiation with visible or short wavelength UV light (313 nm), the shift in λ_{\max} is smaller than that observed upon irradiation at 365 nm, (see figures 4(b), 4(c), and 5). This behaviour may be explained by the fact that the degree of conversion of the *E*-*Z* photoisomerization is also controlled by the wavelength of light irradiation and appears to be a maximum when the light wavelength is close to the maximum of the π - π^* electron transition of azobenzene groups [45]; in the case of light irradiation at 365 nm, the degree of conversion of photoisomerization is greatest. Quite similar features of the kinetics of photo-optical processes were earlier observed for copolymers and mixtures with chiral photochromic azobenzene groups [14, 15, 24, 25].

The fact that the amplitude of the photoinduced shift in the selective light reflection maximum for the copolymer appears to be much smaller (less than 40 nm) than that of mixtures (figure 5), provided all other conditions are the same, seems to be rather unusual. Evidently, one may hardly compare systems with such difference in parameters such as chemical structure, and molecular-mass characteristics. At present, the only explanation of this phenomenon is the smectogenic character of the copolymer which manifests itself as a strong temperature dependence of λ_{\max} (figure 1). The presence of elements of layered order may reduce the rate and conversion of

photoisomerization due to a destabilization of the low anisometric *Z*-form of the azobenzene groups by the local environment.

A relatively low shift in λ_{\max} for mixture **II** (about 50 nm) induced upon UV irradiation, figures 3(a) and 4(c), may be rationalized by the fact that in this case the content of azobenzene groups is lower than in the copolymer and mixtures **I** and **III**.

3.6. Photo-optical properties of planarly oriented films of mixture **III** containing two different types of photosensitive fragments

The photo-optical behaviour of mixture **III** containing the two types of photosensitive fragment (azobenzene and cinnamoyl) appears to be far more complex. As was found, upon UV irradiation one may expect the *E*-*Z* photoisomerization of both the azobenzene groups and cinnamoyl fragments of the chiral photochromic dopant. At rather short exposure times, a reversible shift in the selective light reflection maximum is seen, figure 3(a), whereas upon prolonged irradiation and further annealing (during which the *Z*-form is transformed into *E*-form), the corresponding spectral changes are irreversible, see figure 6.

In the latter case, the shift in λ_{\max} is a result of the photoisomerization of the chiral photochromic dopant [23] according to the scheme. As was shown elsewhere [23] a {2+2} photocycloaddition process in the polymeric mixtures does not occur, due to the relatively low dopant concentration and the strong steric demand of this bimolecular reaction (close contact of two molecules is necessary for this reaction) [45]. Therefore, in the case of mixture **III**, irradiation leads either to helix untwisting and a reversible shift in λ_{\max} via a decrease in the orientational order parameter (resulting from a photoisomerization of azobenzene groups), or to an irreversible shift in λ_{\max} due to a decrease in the helical twisting power of the chiral photochromic dopant.

3.7. Fatigue resistance of planarly oriented films of the photosensitive copolymer and mixtures

To demonstrate the potential for repeated recording of optical information on the planarly oriented films of the copolymers and mixtures, the important property of fatigue resistance was studied (figure 7). To this end, the samples were repeatedly subjected to UV irradiation and annealing. As follows from figure 7, for the copolymer and mixtures **I** and **II**, the range of the shift in λ_{\max} and the selective light reflection maxima before and after irradiation remain unchanged. It seems interesting that for mixture **III** the amplitude of the shift in λ_{\max} remains virtually unchanged but one may observe a gradual shift in selective light reflection maximum to

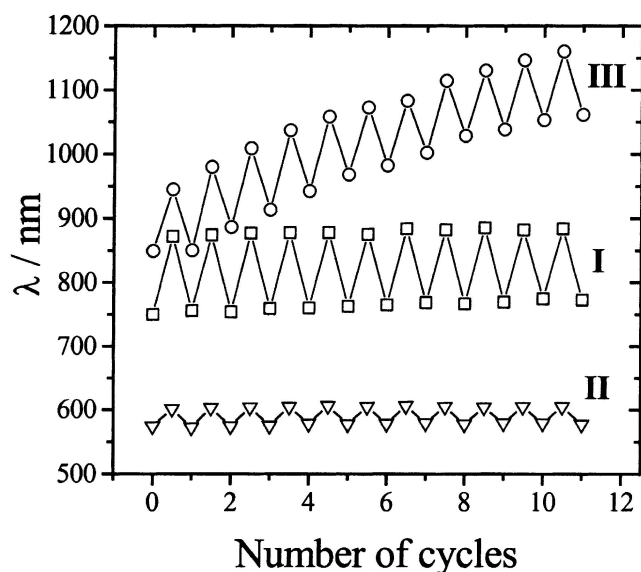


Figure 7. Fatigue resistance properties of films of mixtures I–III under recording–erasing conditions (recording was performed using 365 nm light). In each cycle the films were irradiated for 10 min by UV light at 100°C (mixtures I and III) or at 90°C (mixture II), then annealed for 20 min at the same temperatures.

the long wavelength spectral region. This behaviour is related to the accompanying reversible and irreversible photoisomerization of the azobenzene and cinnamoyl groups.

4. Conclusion

This work describes the first comprehensive investigation of photocontrolled changes in the helical pitch length for cholesteric polymer systems containing achiral azobenzene photosensitive groups. Photo-optical properties of copolymers and related mixtures are shown to be similar to the properties of polymer materials containing combined chiral photochromic groups: light irradiation also results in an untwisting of the cholesteric helix. However, for the systems with combined chiral photochromic groups, changes in the helical pitch length result from a decrease in helix twisting power, whereas for the copolymer and mixtures studied in this work, untwisting of the cholesteric pitch is likely to be related to a decrease in the orientational order parameter. Specific features of the kinetics of the photo-optical process were studied; as shown, such polymers and mixtures may be used for optical data recording and storage. Irradiation with UV and visible light at temperatures above the glass transition and corresponding to the chiral nematic state followed by cooling to room temperature, allows one to change locally the pitch of the helix and the selective light reflection wavelength. It should be pointed

out that the use of IR light, non-absorbing by the azobenzene groups but reflecting by the helical supramolecular structure, opens the possibility of non-destructive reading of optical information.

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