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ORIGINAL CONTRIBUTION

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Unexpected photoinduced phenomena in chiral–photochromic cholesteric copolymers with a triplet sensitizer

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Abstract For the first time the possibility of energy transfer from a triplet photosensitizer to chiral–photochromic fragments in photoactive cholesteric systems was demonstrated. For this purpose we prepared mixtures containing chiral–photochromic cholesteric copolymers with a triplet sensitizer—acrydine orange (AO). Chiral–photochromic groups in copolymers contain a C=C bond capable for undergoing E–Z isomerization during UV irradiation. All polymer mixtures form a chiral nematic phase displaying selective light reflection with λ_{max}~650–1,000 nm depending on the structure and concentration of the chiral groups. Irradiation of mixtures by visible light ($\lambda > 450$ nm) leads to a shift of the selective light reflection peak to a long-wavelength spectral region. This effect is associated with a decrease of anisometry of chiral–photochromic fragments in copolymers during their E–Z isomerization. It is important to emphasize, that chiral–photochromic side groups of copolymers do not absorb visible light themselves; therefore, the previously mentioned changes can be explained by the energy transfer from photoexcited AO molecules in the triplet state to isomerizable fragments. The study of the kinetics of this process revealed a rather unexpected phenomenon: after the first 60–80-min irradiation, the helix pitch of the supramolecular structure of the mixtures increases, but after successive irradiation the helix pitch decreases. The possible explanations of this phenomenon were suggested. It was demonstrated that these mixtures may be used for irreversible recording of optical information.

Keywords Chiral–photochromic copolymers · Cholesteric phase · Photocontrollable helix pitch

Introduction

Over the last 2 decades, the search for new materials for information processing, recording and optical storage has been an area of rapid development. In this connection increasing attention is being paid to the synthesis and study of photosensitive polymeric materials [1, 2, 3, 4]. Among different polymer systems cholesteric liquid-crystalline polymers present a unique class of materials owing to their very interesting and promising optical properties determined by helical supramolecular structures [5, 6, 7, 8, 9, 10, 11, 12, 13, 14].

In the works performed by the Philips research group and in our laboratory, pioneering approaches for the development of polymer cholesteric liquid crystals with photocontrolled helix pitch and a selective light reflection maximum have been advanced [5, 6, 7, 8, 9, 10, 11, 12]. Upon UV irradiation, such materials are able to experience the E–Z isomerization of chiral groups which is provided by the presence, for instance, of the C=C bonds in the side groups of the macromolecules. In turn, this process is accompanied by a decrease in the anisotropy and twisting power of the chiral groups. The helix twisting power is directly related to the concentration of the chiral component, x, and the helix pitch, P, in the helical supramolecular structure which is responsible for the selective light reflection maximum. $\lambda_{\max}$:

$$\beta = \frac{\mathrm{d}P^{-1}}{\mathrm{d}x} = \bar{n}\left(\frac{\mathrm{d}\lambda_{\max}^{-1}}{\mathrm{d}x}\right)_{x=0}, \quad (1)$$

where $\bar{n}$ is the average refractive index.

The value of the helical twisting power is strongly related to the anisometry of the chiral fragment; that is why the helix pitch and the selective light reflection maximum are changed during the action of light. Hence, irradiation by light provides an effective method for controlling the supramolecular structure and the optical properties of polymer films.

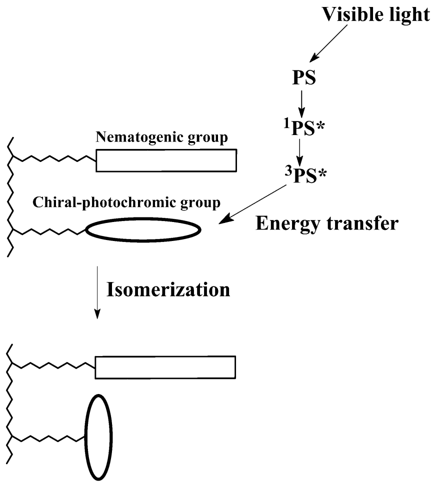
However, despite evident progress in this direction, synthesized materials of this type show a significant drawback: chiral–photochromic side groups are sensitive only to UV irradiation. This disadvantage can restrict the possible application of such systems and may be resolved by the introduction of chiral fragments containing photochromic groups which are responsive to visible light. Another possibility might be connected with the incorporation of an appropriate triplet photosensitizer into the polymer system. The first approach was successfully realized in our recent works [13, 14] in which we synthesized copolymers with a chirai–photochromic fragment composed of chiral (menthyl) and azobenzene-containing photochromic groups sensitive to UV and visible light.

The second approach is based on the preparation of cholesteric mixtures consisting of chiral–photochromic liquid-crystalline side-chain copolymers which do not absorb visible light and a triplet photosensitizer which can the transfer energy of the visible light to the photosensitive groups of the copolymer (Scheme 1).

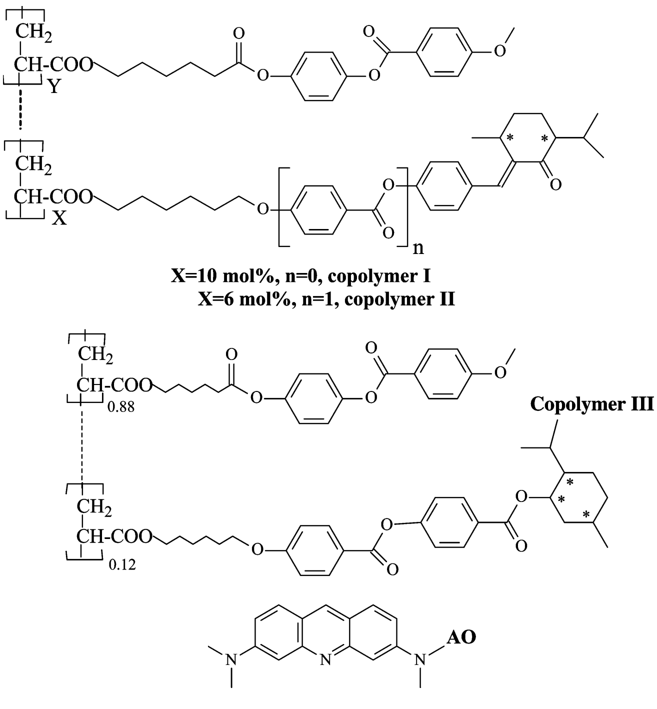
In present work we prepared cholesteric mixtures sensitive to visible light using the second approach, namely, by introduction of the triplet photosensitizer acrydine orange (AO) in well-studied [6, 7, 8, 9, 10, 11, 12] cholesteric photosensitive menthone-containing copolymers I and II (Structure 1).

As a "model" system we prepared a mixture containing nonphotosensitive menthyl-containing copolymer III without photoisomerizable groups. The contents of all the mixtures under investigation are shown in Table 1.

As mentioned in Refs. [15, 16] AO can be used as a triplet photosensitizer for benzilidenementhane-3-one, the structure of which is similar to chiral–photochromic side groups of copolymers I and II. But in previously



Scheme 1 Schematic representation of energy transfer from a photosensitizer (*PS*) absorbing visible light to the chiral–photochromic group of a liquid-crystalline copolymer forming a cholesteric (chiral nematic) phase. PS,^{1}*PS** and ^{3}*PS** correspond to the photosensitizer in ground, singlet and triplet excited states



Structure 1

Table 1 Clearing temperatures, T_{Cl}, for mixtures I–III

Sample	Content	T_{Cl} (°C)
Mixture I	Copolymer I + 3% acrydine orange	100–101
Mixture II	Copolymer II + 3% acrydine orange	114–115
Mixture III	Copolymer III + 3% acrydine orange	96–97

mentioned work only dilute isotropic solutions of low molar mass compounds were considered; a detailed study of the kinetics and other photochemical aspects of such systems was performed.

Hence, this paper is devoted to a study of the specific features of the photooptical behaviour of the previously mentioned systems under different conditions: temperature, incident light wavelength, etc. The main goal of this work deals with revealing the peculiarities of the triplet–triplet energy-transfer effect in new chiral–photochromic polymer systems with photovariable helix pitch and selective light reflection wavelength.

Experimental

Synthesis and mixtures preparation

The copolymers were synthesized according to the procedures described in Refs. [11, 17]. AO (Aldrich) was used as received. The mixtures were prepared by dissolving the copolymers in chloroform followed by solvent evaporation at 60 °C. The mixtures were then dried under vacuum at 120 °C for 2 h.

Investigations of phase behaviour and optical properties

Phase transitions of the copolymer mixtures were studied by differential scanning calorimetry (DSC) with a scanning rate of 10 °C min^{-1}.

The polarizing microscope investigations were performed using a Mettler TA-400 thermal analyzer and a LOMO P-112 polarizing microscope.

Selective light reflection of films of the mixtures was studied with a Hitachi U-3400 UV–vis–IR spectrometer equipped with a Mettler FP-80 hot stage. The samples of about 20-μm thickness were sandwiched between the 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 5–10 °C below the clearing temperature. Prior to the tests, the test samples were annealed for 20–40 min.

Photooptical investigations

Photochemical property investigations were performed using a special instrument equipped with a DRSh-250 ultra-high-pressure mercury lamp. Light with wavelengths 365 and above 450 nm was selected using cutoff filters. To prevent heating of the samples due to IR irradiation from the lamp, a water filter was used. To obtain a plane-parallel light beam, a 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 1.9×10^{-8} Es s^{-1} cm^{-2} (6.2 mW cm^{-2}, for light of 365 nm, as measured actinometrically [18]), the intensity of visible light ($\lambda_{\mathrm{ir}} > 450$ nm) was around 8.0 mW cm^{-2}, as measured with an IMO-2 N intensity meter.

Photochemical properties of the mixtures were studied by illuminating the films of around 20-μm thickness. After irradiation, transmittance or absorbance spectra were recorded using a Hitachi U-3400 UV–vis–IR spectrometer. The samples were annealed after the irradiation cycle until no changes in the selective light reflection wavelength were observed (usually, for about 20–30 min).

Results and discussion

Phase behaviour and optical properties of the copolymers and mixtures

According to the polarizing optical microscopy and DSC results all the mixtures studied form only a chiral nematic phase. The clearing temperatures for the mixtures are presented in Table 1; the glass-transition temperatures, T_g, for all the mixtures are about 25 °C.

Planar-oriented films of all copolymers and mixtures studied in this work are characterized by a selective light reflection in the IR and visible spectral regions (Fig. 1). First of all, it should be noted that introduction of the AO dopant leads only to a small shift of the selective light reflection wavelength to a long-wavelength spectral region. This effect is associated with the nonmesomorphic character of AO molecules which violate to some extent the orientational order in the mixtures, leading to a small untwisting cholesteric helical structure.

Now let us consider the temperature dependencies for all the mixtures. For copolymers I and III and the corresponding mixtures I and III at temperatures above about 60 °C we observed an increase in the selective light reflection wavelength during heating (Fig. 1). The dependences presented agree with the model speculations advanced in Refs. [19, 20, 21]. Near the clearing temperature, one may observe a slight increase in the pitch of the helix, and this increase is provided by a decrease in the orientational order parameter.

Another situation is observed for the menthone-containing copolymer II and mixture II, in which chiral side groups contain the two-ring rigid fragment. In this case the temperature coefficients of the dependences are negative for temperatures above about 60 °C. Usually, the negative values of the temperature coefficient were observed earlier for the cholesterol-containing copoly-

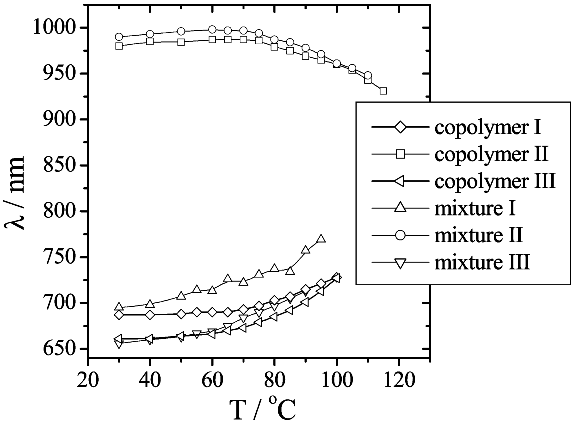


Fig. 1 Temperature dependences of the selective light reflection maximum wavelength for copolymers and mixtures

mers [22, 23, 24], and this behaviour is related to the fluctuations of smectic order in the N* mesophase (according to the X-ray data analysis). In the case studied, the broad outline is quite unusual. Our structural studies revealed the absence of any small-angle reflections in the corresponding X-ray patterns. This experimental evidence and the detailed studies of the phase behaviour of such copolymers performed in Ref. [11] suggests that chiral side units of copolymer II are nonsmectogenic. In our opinion this phenomenon can be explained by conformational changes of chiral side groups during temperature variation.

Photooptical behaviour of thin films of the mixtures

Let us consider some changes in the electronic spectra observed during visible and UV light irradiation of thin mixtures films obtained by casting them from chloroform solutions. The spectra of the thin films are characterized by two well-resolved maxima at 261 and 485 nm, corresponding to absorbance of phenylbenzoate groups of copolymer and AO, respectively (Fig. 2). The absorbance of chiral–photochromic benzilidenementhane-3-one fragments appears as a "shoulder" at wavelengths of about 300–320 nm [5, 10, 11]. It is important to note that shape of the AO absorbance peak is different from that in solution [25, 26]. It is probably explained by aggregation phenomena resulting in the formation of dimers and more complicated aggregates from AO molecules.

As seen from Fig. 2 the action of light leads to a small decrease in absorbance at wavelengths corresponding to $\pi\pi^*$ and $n\pi^*$ electronic transitions of chiral–photochromic bezilidenementhane-3-one copolymer units (300–320 nm). Most probably this effect indicates E–Z isomerization of these groups taking place in films of the mixture [11]. It is important to emphasize that chiral side groups do not absorb light in the visible region of the spectrum and that visible light irradiation ($\lambda > 450$ nm) leads to photoexcitation of only AO molecules. Nevertheless E–Z isomerization takes place in both cases (UV and visible light irradiation) and in the case of visible light this process apparently is due to energy transfer from dopant AO molecules to bezilidenementhane-3-one chiral side groups [15, 16]. The absorbance of dopant AO in the visible spectral region (400–500 nm) also decreases during the action of light, and can be explained by some side processes, such as photodegradation and photooxidation.

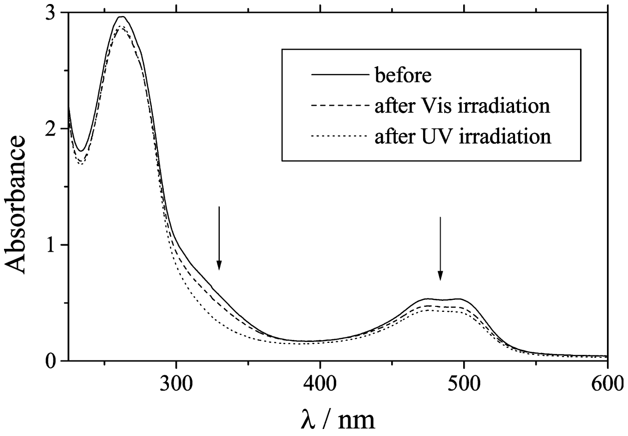


Fig. 2 Changes of absorbance spectra of the film of mixture I before irradiation, after 40-min visible light irradiation and after 5-min UV irradiation (365 nm). *Arrows* indicate changes in absorbance. The temperature of the sample was 25 °C

Photooptical behaviour of planar-oriented films of the mixtures

In the case of planar-oriented films of mixtures I and II the helix pitch of the supramolecular structure of the mixtures increases during irradiation and subsequent annealing (both at 100 °C) after the first 60–80 min of visible light irradiation. As already mentioned, helix untwisting is associated with a decrease of the helical twisting power of chiral–photochromic groups during their E–Z isomerization; however, the successive irradiation leads to very unusual behaviour: decreasing of the helix pitch. (Figs. 3, 4). It is important to note that irradiated films of mixtures I and II became partially insoluble after irradiation owing to cross-linking reactions in the films.

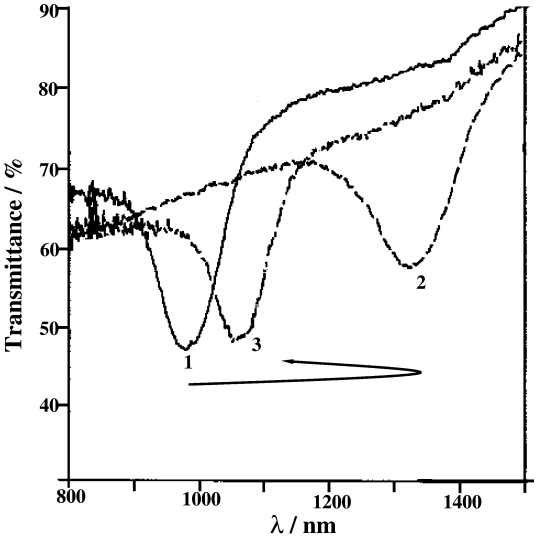


Fig. 3 Transmittance spectra of a planar-oriented film of mixture II before irradiation (*1*) and after 80-min (*2*) and 240-min (*3*) visible light ($\lambda > 450$ nm) irradiation at 100 °C

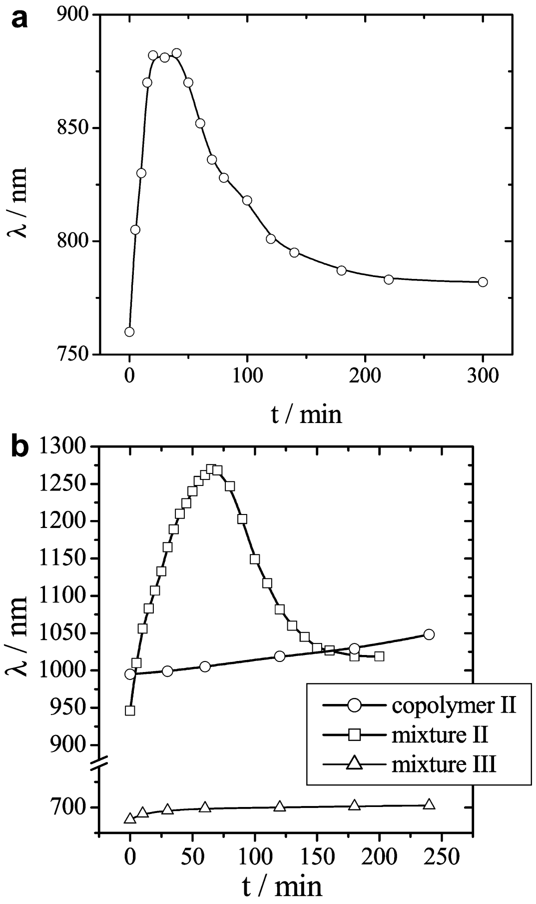


Fig. 4 Kinetics of the selective light reflection wavelength changes during visible light ($\lambda > 450$ nm) irradiation for **a** mixture I and **b** copolymer II and mixtures II and III. The temperature of all the samples was 100 °C; after each irradiation cycle (usually 10 min) the films of the mixture were annealed at 100 °C for 20–30 min

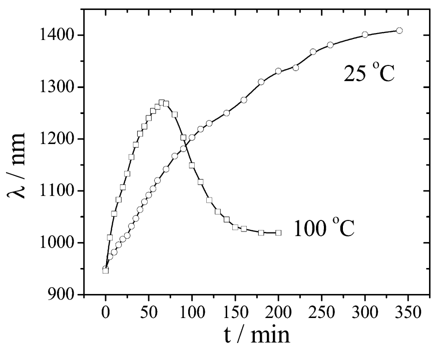


Fig. 5 Kinetics of the selective light reflection wavelength changes during visible light ($\lambda > 450$ nm) irradiation for mixture II at different temperatures. In both cases after each cycle of irradiation, samples were annealed at 100 °C

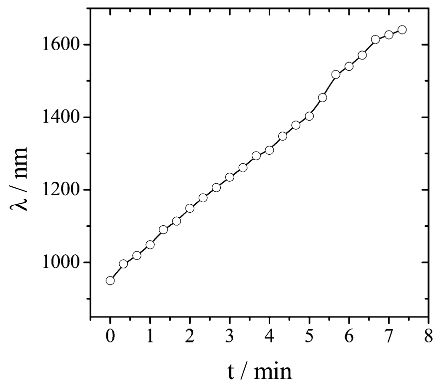


Fig. 6 Kinetics of the selective light reflection wavelength changes during UV light (365 nm) irradiation of mixture II. The temperature of the sample was 100 °C

In the case of "model" mixture III and copolymer II without AO dopant the spectral changes are negligible (Fig. 4b). In other words, helix untwisting and successive twisting are related to the chemical processes involving AO molecules together with bezilidenementhane-3-one chiral side groups.

The temperature of the samples during the action of light plays a key role in untwisting–twisting effects. Irradiation and annealing of the films near T_g do not lead to any spectral changes. After irradiation near T_g followed by annealing at high temperatures (about 100 °C) helix untwisting takes place (Fig. 5) but a reverse-shift selective light reflection peak (helix twisting) does not occur. The rate of the process in such a case is considerably lower that explained by a decrease of the diffusion rate of AO molecules and chiral–photochromic groups near T_g (for E–Z isomerization close contact of an AO molecule and a chiral group must be realized for the energy-transfer process).

The unusual effect of the helix twisting was also not observed during irradiation with UV light (Fig. 6). In this case direct photoexcitation of bezilidenementhane-3-one chiral side groups takes place with only negligible participation of AO molecules. That is why the rate of the shift of the selective light reflection peak is more than 1 order of magnitude higher in the case of UV light. Prolonged action of UV light leads to the disappearance of the selective light reflection peak. The same behaviour was observed for copolymers I and II without AO dopant as described before [6, 11]. For mixtures I and II visible light irradiation does not lead to destruction of the selective light reflection peak, but, in contrast to the previously mentioned case, fixes the helical supramolecular structure owing to photo-cross-linking.

Let us consider some possible photochemical reactions in the mixtures under consideration. The helix untwisting observed in mixtures during visible light irradiation is most probably explained by energy transfer from the triplet excited state of AO molecules to bezilidenementhane-3-one chiral side groups followed by their E–Z isomerization.

Photoinduced cross-linking of films of the mixtures is associated with the occurrence of one or several side photoprocesses. These processes preferably involved bezilidenementhane-3-one chiral side groups and AO molecules. Photocycloaddition (C=C+C=C) and Paterno–Buchi (C=C+C=O) reactions are almost improbable owing to the presence of noticeable steric hindrance [15, 16]. That is why we can expect that in the films Norrish type I or II [27, 28] photoreactions involving the ketone fragment of bezilidenementhane-3-one chiral side groups take place. Free radicals forming during these reactions can react intensively with neighbouring side groups of copolymers and form in such a way the three-dimensional network. The great difference in the behaviour of systems under the action of UV and visible light can be explained by the principal difference in the mechanisms of chromophore photoexcitation. During direct photoexcitation by UV light E–Z isomerization can occur through the singlet state $S_{n\pi^*}$ [15]. The presence of AO as a sensitizer can lead to a change of the mechanism to a triplet one [27]. In this case the reaction involves a triplet state $T_{\pi\pi^*}$ with much longer lifetime and, therefore, a higher probability of side chemical processes is realized. Unfortunately, the study of mixtures of the films before and after irradiation using IR spectroscopy did not allow us to make any conclusions about the mechanisms of photoreaction and photoproducts because spectral changes were negligible even in the case of mixtures of chiral–photochromic homopolymer (100% of bezilidenementhane-3-one chiral side groups) with AO.

Let us emphasize that a similar effect of helix twisting does not take place in cholesteric mixtures containing low molar mass cinnamoyl dopant as the chiral–photochromic component [28]. The photo-cross-linking process in this case was also absent and the films remained soluble even after prolonged irradiation. This clearly demonstrates that bezilidenementhane-3-one chiral groups are chemically linked to a polymer backbone and can form a three-dimensional network.

After prolonged irradiation using visible light performed at low temperatures (when polymer chains are almost immovable) fixation of the helical supramolecular structure owing to the cross-linking occurred (Fig. 5). The helix twisting effect is possible only at relatively high temperatures (about 100 °C). Such peculiarities of the behaviour of the mixtures allow us to suppose that the effect of helix twisting can be associated with a possible network shrinking during photo-cross-linking accompanied by phase separation. During the possible phase separation process noncross-linked parts of the mixtures form a separate phase and the network undergoes shrinking with decrease of the helix pitch.

The increase of temperature results in destruction of aggregates formed by AO molecules. We found the reversible change of the shape of AO spectra upon heating (not shown), which indicates a change of the ratio between AO molecules in monomeric and aggregated states. Such processes may also be considered as a possible reason for the helix twisting effect at relatively high temperatures owing to changes or enhancement of side reactions.

Conclusion

In conclusion it should be notd that for experimental proof of the hypothesis presented here additional experiments should be performed, including a study of the morphology changes during the actions of light and temperature. Nevertheless, the phenomena observed in this work are very unusual and excellently demonstrate the very complicated character of photoprocesses occurring in organized media containing two different types of photoactive fragments.

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