ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 155 (2003) 3–19

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Light-responsive chiral photochromic liquid crystalline polymer systems

Valery Shibaev*, Alexey Bobrovsky, Natalia Boiko

Department of Chemistry, Moscow State University, Leninskie Gory, Moscow 119992, Russia

Received 10 September 2002; accepted 17 September 2002

Abstract

The authors reviewed their results obtained in recent years in the field of development of advanced optically controlled polymer systems based on photochromic cholesteric liquid crystalline (LC) polymers and their blends with each other and with low-molar-mass chiral and photochromic dopants. Recent advances in the research dealing with the design and study of photo-optical properties of photoresponsive LC polymers composed of nematogenic, chiral and one or two photochromic fragments incorporated in the same monomer units or entirely into the macromolecule as individual monomers are discussed. All polymer systems form cholesteric phase with a helical supramolecular structure. The light irradiation leads to the isomerization of one or two photochromic groups, which results in the variation in the helical twisting power of chiral fragments. This process is accompanied by dramatic changes in the supramolecular helical structure and optical properties of the LC polymer. This provides the possibility for controlling the pitch of helix, the rate of helix twisting and untwisting, spectral range, and the width of the selective light reflection. The photochromic LC systems offer new promising materials for reversible and irreversible colour data recording that can be used in optical memory systems (data storage), holography, colour projection techniques and give rise to a new generation of videodiscs, flat light guides and coatings with photocontrollable optical properties.

Keywords: Photochromic polymers; Chiral polymers; Liquid crystalline polymers; Light responsive polymers; Photochromic dopants

1. Introduction

Rapid development of various modern systems for recording, transfer, processing, and display of data, visualization of images, as well as miniaturization of the optical devices requires, both solving numerous technological problems and creating new materials capable of providing rapid and reliable response to the control signals transmitted by electromagnetic fields, particularly by the light and laser actions.

Among various inorganic and organic photoresponsive materials usually referred to as “smart or intelligent materials”, the photochromic liquid crystalline (LC) polymers systems are of indubitable interest [1–12]. All these polymers successfully combine the physico-chemical properties of macromolecular compounds (with their ability of forming films, fibers, elastomers), the mesomorphic properties of low-molar-mass liquid crystals and photosensitivity of chromophores, covalently incorporated into the polymer chain as the side groups.

The most simple molecular structure of such LC polymers consists of mesogenic (typically, nematogenic) and photochromic fragments chemically linked to the main chain (backbone) via flexible aliphatic (or hydroxyaliphatic) spacers with a variable length (Fig. 1). Such macromolecular nature of photochromic LC polymers has great advantages over polymer–dye-mixtures.

First of all, this concerns the solubility of dyes in polymer matrix; the maximum content of “host-dye” in the polymer–dye-mixtures in general does not exceed 1–5 mol%; a higher concentration of dyes leads to the phase separation of the mixture. The photochrome-containing copolymers are more stable due to the covalent bonds of dyes with LC “mother-matrix” and the content of photochromic monomer units may reach several tens of percentages.

In addition, a simple procedure of the preparation of such copolymers in the form of thin film (for example, via spin-coating) and easy handling present a special attraction from the practical point of view.

The pronounced ability of these compounds for self-organization and formation of various ordered supramolecular structures present a considerable interest from the standpoint the development of new “smart” materials with optically controlled supramolecular structure and physical properties (optical data storage, display technology, holography, etc.).

It should be pointed out that the photo-optical investigations associated with LC polymers were begun at the

---

* Corresponding author. Tel.: +7-95-9391189; fax: +7-95-9390174.
E-mail address: lcp@genebee.msu.su (V. Shibaev).

1010-6030/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S1010-6030(02)00364-7

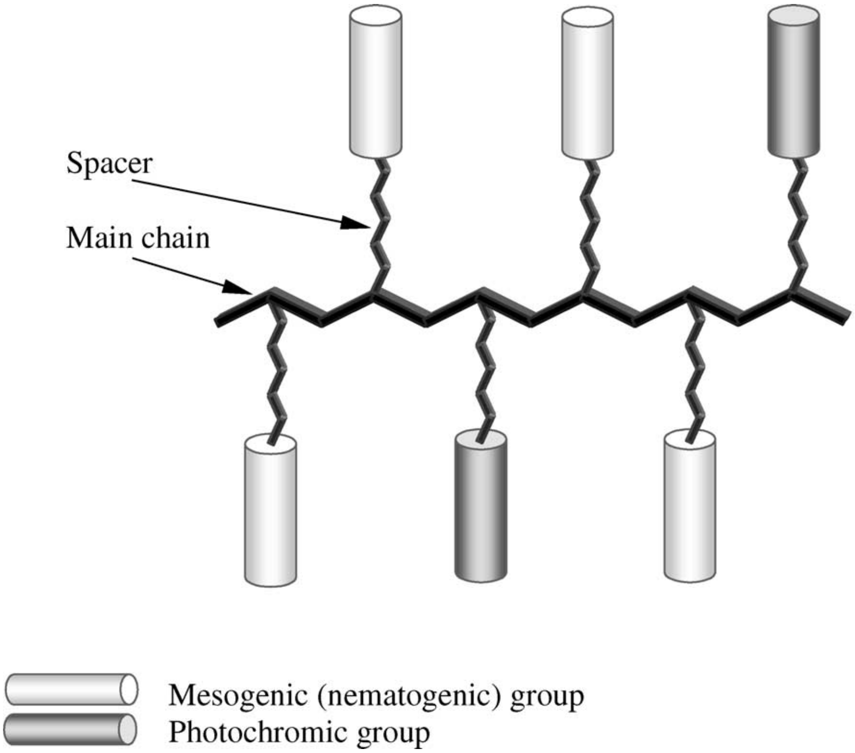


Fig. 1. Schematic representation of molecular structure of binary photochromic LC copolymer.

middle of the eighties and were namely performed on the base of binary photochromic LC copolymers forming nematic structure (Fig. 1). A key role determining the optical properties of these polymer belongs to the photoisomerizable side groups (azobenzene, spiropyran, cinnamatic acid fragments, etc.) which play the role of effective “switchers” capable of significantly changing their configuration and conformation under the polarized light action.

For instance, the photochromic groups of azobenzene-containing LC copolymers may undergo a reversible *trans–cis* (*E–Z*) isomerization due to the light irradiation with an appropriate wavelength. This leads to the photochemical configurational changes of azobenzene groups which are transformed from rigid-rode (mesogenic) shape to a nonmesogenic bent shape. As a result the supramolecular structure and the optical properties of polymer films are dramatically changed—the photochromic and (together with them) nematogenic groups are oriented so that their long axes would be perpendicular to the electric vector direction of the polarized light. In other words, the light irradiation effectively selects molecules by orientating them in a preset direction that causes the appearance of a considerable photoinduced birefringence ($\Delta n \sim 0.25$–0.30) [5,7,11,12] due to a cooperative character of the orientational process. This process is reversible, which allows these copolymers to be used as reversible optically active media for recording black-and-white images with controlled gray scale [3,4,7,11,12]. Detailed investigations into the mechanism and kinetics of photochemical and photo-optical processes in LC and amorphous binary photochromic (in particularly azo-containing polymers) have been repeatedly described in the literature [4,5,7,12] and they are beyond the consideration of this work.

In this paper, our attention is focused on more complex and sophisticated photochromic LC polymer systems forming cholesteric type of mesophase characterized by a helical supramolecular structure, which are a considerable interest for development of a novel family of promising photoactive materials for reversible and irreversible colour data recording.

The first publications devoted to the synthesis and study of photosensitive chiral LC polymers with photocontrolled helical supramolecular structure and selective light reflection wavelength were appeared recently, at the end of the 1990s. These pioneering investigations were carried out on the chiral photochromic LC copolymers based on benzylidene–menthanone derivatives by our group [13–15] and Philips research team [16,17] independently of one another.

In this paper, first of all, the main concept used as the basis for development of photoactive cholesteric LC polymers will be considered and after that the different possibilities of manipulation in their optical properties by means of light irradiation will be discussed. In so doing the main attention will be given to more complex ternary copolymers containing two different photoactive groups in their macromolecules and to photochromic mixtures of LC polymers with each other and with low-molar-mass chiral-photochromic dopants.

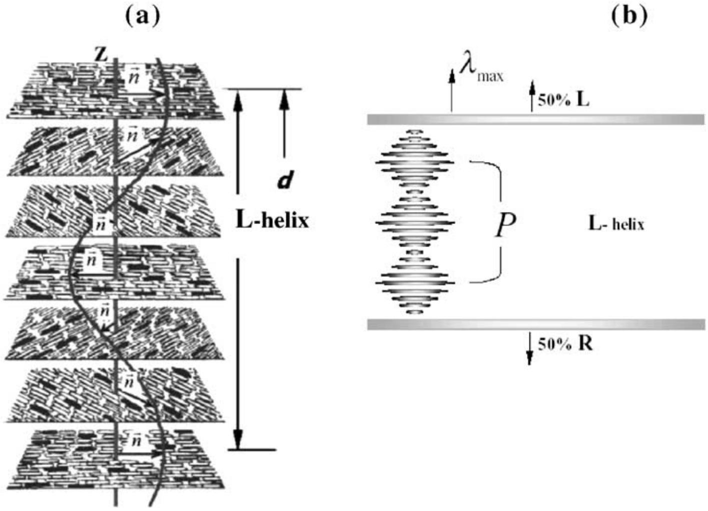


Fig. 2. Scheme showing (a) the arrangement of mesogenic groups and dopant molecules in cholesteric phase and (b) the planar texture of a sample confined between two glass plates. (P is the helix pitch; $\vec{n}$ is the director of liquid crystal; the helix axis Z is normal to the glass plates; L and R are left- and right-handed components of circularly polarized light).

2. Helical supramolecular structure of LC cholesteric copolymers and principle of photoregulation of their optical properties

The use of LC copolymers forming a cholesteric (or chiral nematic[1]) mesophase offers very interesting possibilities for development of smart materials with photoregulated optical properties.

It is well-known, that cholesteric mesophase is a mesophase with a helical supramolecular structure formed by chiral molecules or by doping the nematic host with chiral guest molecules in which the local director $\vec{n}$ processes around a single axis (Fig. 2a) [18]. For the normal incidences of a light beam upon a planarly oriented cholesteric texture (with the helix axis Z perpendicular to the layer), the helix pitch P is related to the wavelength of the maximum selective light reflection λ_{max} by a simple equation:

$$\lambda_{max} = \bar{n}P \qquad (1)$$

where $\bar{n}$ is the average refractive index of the LC polymer. It should be noted, that the structure repeats itself every half pitch ($d = P/2$) due to the equivalency of $\vec{n}$ and $-\vec{n}$.

In addition the helical structure is handed; one enantiomer will generate a left-handed helix (L), and the other enantiomer will produce a right-handed helix (R). If a cholesteric sample has L-helix, 50% of L-handed circularly-polarized light is reflected and 50% of R-handed circularly-polarized light is passed through a sample (Fig. 2b).

The side-chain LC polymers capable of forming cholesteric phase are usually obtained by the copolymerization of nematogenic and chiral (not necessarily mesogenic) monomers forming binary chiral LC copolymers (Fig. 3a).

Thus, a unique feature of the LC polymers forming cholesteric phase is the ability to selectively reflect light in the UV, visible, or IR spectral range, in accordance with the helix pitch.

The main parameter determining the helix pitch is called the helical twisting power β of an optically active dopant introduced either by mechanically mixing with the LC matrix composition or by chemically binding to the polymer macromolecule. The β value is inversely proportional to the helix pitch and is related to the chiral dopant concentration X by the equation:

$$\beta = \left(\frac{\mathrm{d}P^{-1}}{\mathrm{d}X}\right)_{X=0} = \bar{n}\left(\frac{\mathrm{d}\lambda_{max}^{-1}}{\mathrm{d}X}\right)_{X=0} \qquad (2)$$

The helical twisting power β of a chiral dopant depends on number of factors, including the interaction with the LC matrix, the temperature and the molecular structure and shape of the dopant molecule (or chiral fragment in the case of macromolecule).

Taking into account the features of photochromic and chiral LC polymers (Figs. 1 and 3), the original approach for the development of polymer cholesteric liquid crystals with photocontrolled helix pitch and λ_{max} were advanced [13,15–17].

The main principle of the development of such light-controllable LC polymers is based on the synthesis of photochromic copolymers whose macromolecules consist of mesogenic (as a rule, nematogenic) and combined chiral-photochromic groups which are chemically linked in the common monomer unit (Fig. 3b). In this case, mesogenic fragments are responsible for the formation of the nematic phase, chiral groups provide the twisting of the nematic phase and formation of helical supramolecular structure. Finally, photochromic fragments can easily change their molecular structure under the light irradiation.

---

[1] In the following presentation the chiral nematic phase and chiral nematic structure will be referred to as cholesteric phase and cholesteric structure, respectively.

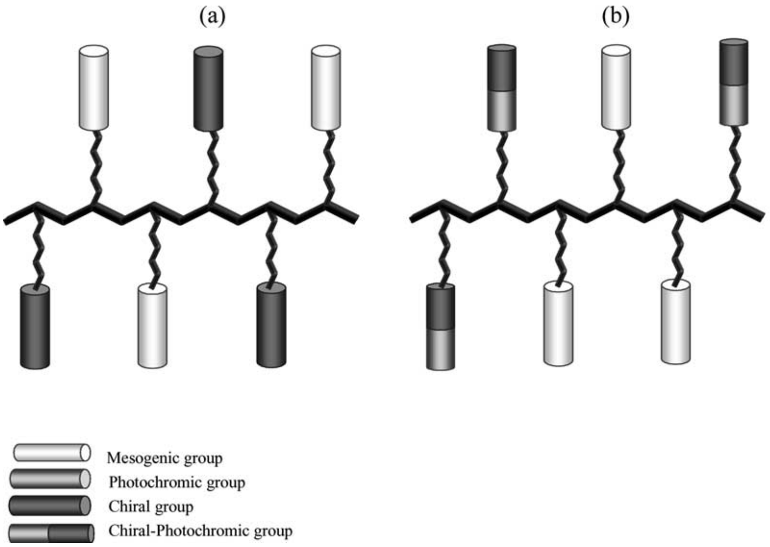


Fig. 3. Schematic representation of molecular structure of (a) chiral LC polymer and (b) chiral-photochromic LC polymer.

The light irradiation with a certain wavelength leads to the photoinduced transformations of the photochromic groups which (being directly bound to chiral fragments) affect both the configuration and shape of the side-chain group. This leads to a decrease both in the anisometry of chiral-photochromic group (Fig. 4) and the helical twisting power β of a given chiral group (see Eq. (2)). A decrease in β ($\beta_2 < \beta_1$) leads to the untwisting of the cholesteric helix which is accompanied by a shift in the selective light reflection maximum to longer wavelengths. Thus, using light irradiation as the external control factor, one may effectively modify the optical properties of polymer films by changing the local supramolecular helical structure.

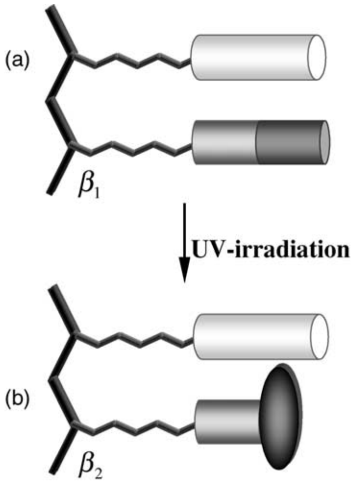


Fig. 4. Scheme illustrating the structure of a LC copolymer with combined chiral-photochromic side group (a) before, and (b) after a light irradiation. Helical twisting power $\beta_2 < \beta_1$.

3. Binary LC copolymers with combined chiral-photochromic monomer units

Some chemical formulae of the LC copolymers containing chiral and photochromic groups in the same monomer unit obtained by us and by Philips group are shown in Table 1. As is seen, copolymers **1–6** contain the same nematogenic groups while the molecular structure of photochromic groups were varied in a wide range. The number of photochromic copolymers containing photosensitive fragments such as double C=C and N=N bonds, and chiral menthanone and menthyl groups were used [10]. Taking into account a series existing publications devoted to the chiral-photochromic LC binary polymers [13–25] in this short review we will give only a few examples related to these systems and after that more complex chiral-photochromic LC polymers will be considered.

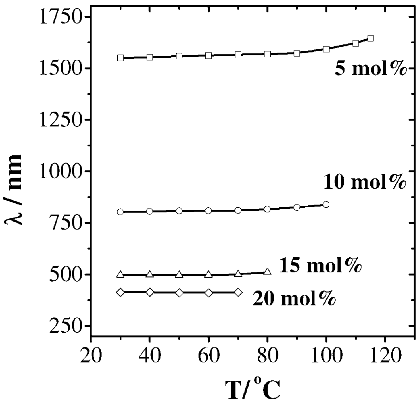
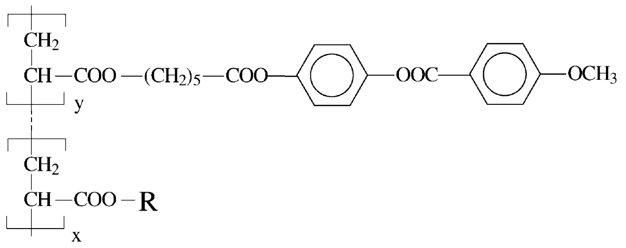
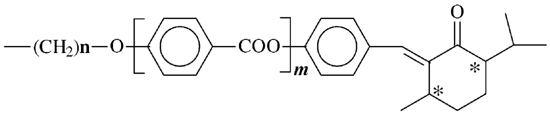
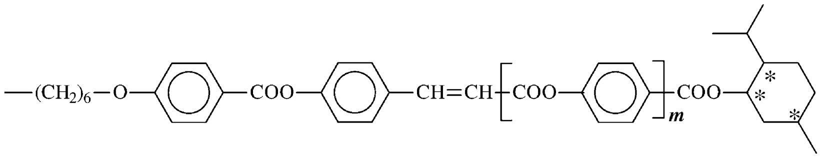
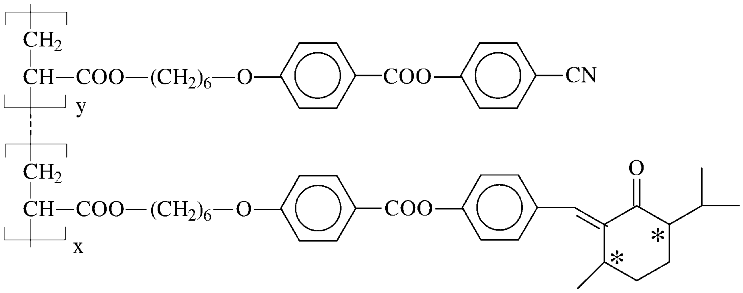


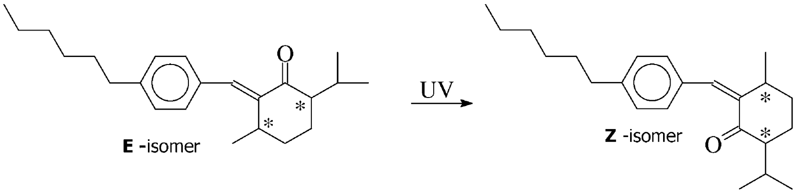
Fig. 5. Temperature dependencies of the maximum of selective light reflection for copolymers **2** (Table 1) with different content of chiral units [13,14].

Table 1
Molecular structure of combined chiral-photochromic LC copolymers

Polymer	*m*, *n*		References
			
R= 	$m = 0$, $n = 6$ $m = 0$, $n = 10$, $m = 1$, $n = 6$ $m = 2$, $n = 10$	**1** **2** **3** **4**	[13–15,19]
	$m = 0$ $m = 1$	**5** **6**	[17–21]
		**7**	[16]

The numbers (**1–6**) correspond to the appropriate copolymer.

As follows from [13–15,19] the copolymers **1–4** (Table 1) is characterized by the formation of the cholesteric phase in a wide temperature–concentration range and its planarly oriented films selectively reflect a circularly polarized light. Fig. 5 shows the typical plot of the selective light reflection peak wavelength versus temperature for a one series of copolymers films. These data clearly shows that monochromic films (quite stable up to 80–90 °C) reflecting visible and IR light can be obtained. Upon UV-irradiation followed by annealing of the samples the photochromic benzylidene–menthanone side groups of such copolymers are able to undergo the *E–Z* isomerization and the peak of the selective light reflection (λ_{max}) shifts to a longer wavelength region, that is, untwisting of helix takes place. In this case the *E–Z*-isomerization is responsible for an increase in the pitch of helix, and the twisting power β of *Z*-isomer is likely to be much lower. Irradiation induced variations in the helical twisting power β are associated with a strong change in anisometry of chiral-photochromic fragment (see Fig. 4). An intrinsic helical twisting power $\beta/\bar{n}$ (see Eqs. (1) and (2)) of *E*-isomer of menthanone-containing group is changed in the range of 13–17 μm^{-1}) (depending on the molecular structure of chiral side groups); but after irradiation this value is lowered by a factor at 10.



The rate photochemical *E–Z* isomerization process is strongly temperature-dependent: the greater the temperature at which the samples were irradiated, the higher the rate of untwisting (Fig. 6). These kinetic curves clearly show

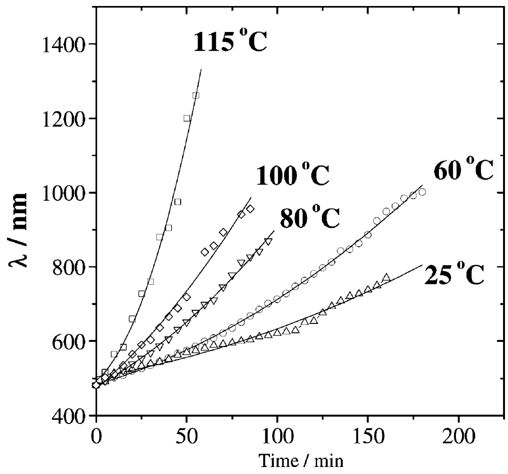


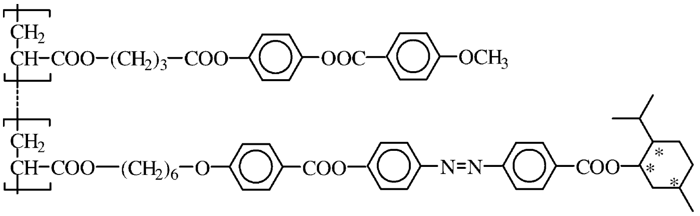
Fig. 6. Kinetics of the helix untwisting for copolymer **1** (Table 1) containing 15 mol% of chiral units irradiation at various temperatures. ($\lambda_{ir} = 313$ nm, power density of UV-irradiated 0.7 mW/cm^2).

how we can untwist the helix and change the colour of the polymer film. Moreover, the colour of the films can be fixed at any wavelength by cooling the samples below the glass transition temperature.

Using the mask (or test pattern), it is possible to change colour locally recording the colour image on the colour film. This phenomenon opens up a new way to record coloured data and to store it on the coloured background. Fig. 7a shows the scheme of the information recording and an example of an image recorded on a film of copolymer **1**, containing 15 mol% of the chiral-photochromic units (Fig. 7b). It would be emphasized, that the image is very stable and can be kept for prolonged time during several years.

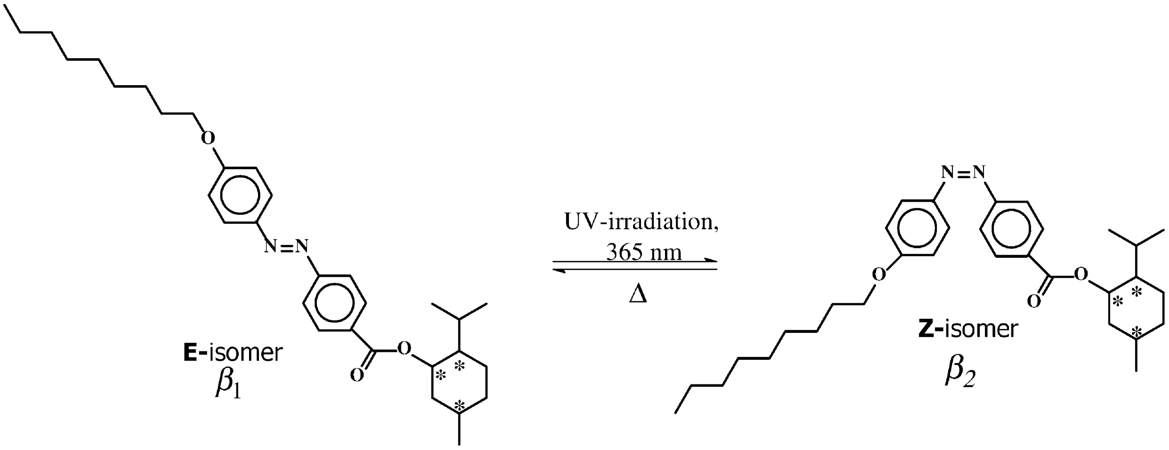
However, from the practical point of view, the series of copolymers **1–7** suffer from one drawback. They can be used only for irreversible recording because *E*–*Z* isomerization of chiral-photochromic benzylidene–menthanone (copolymers **1–4** and **7**, Table 1) as well as cinnamoyl fragments (copolymers **5** and **6**, Table 1) is irreversible.

This problem may be solved by synthesizing the other series of binary copolymers **8** containing azobenzene photochromic group capable of reversible light-induced isomerization. In our previous works, we used this chromophor for the synthesis of a series of azo-containing amorphous and LC copolymers forming reversible photosensitive materials [5,12]. Based on these data, we have obtained a new series of chiral-photochromic LC copolymers containing the same nematogenic group as well as photochromic azo-group and terminal chiral menthol fragment covalently linked into the same monomer unit:



8

After the UV-irradiation *E*–*Z*-isomerization of chiral-photochromic monomer units takes place and configuration and shape of the side group are drastically changed as is shown below:



In this case β_2 value becomes less than β_1 and region of selective reflection of light shifts to the red region. In other words, it means that the helical structure is untwisted. However, this process is completely reversible and heating of the sample leads to the twisting of the helix.

Fig. 8 shows the reversibility of the recording process. In each cycle the polymer film was irradiated during 30 min

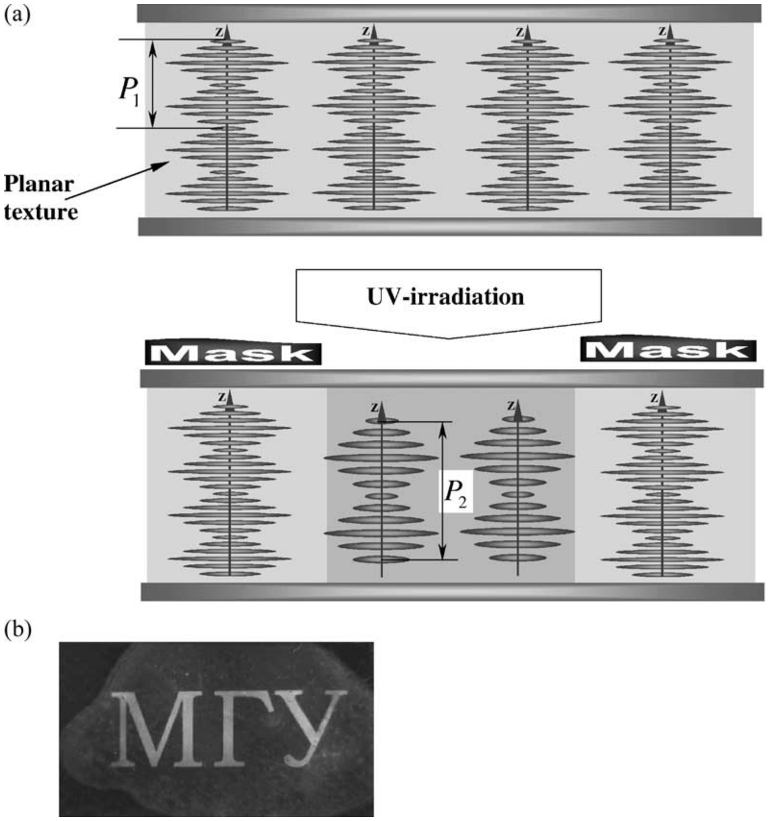


Fig. 7. (a) Sketch of the information recording on the planarly oriented polymeric LC film with the local pitch variation and (b) photo of the film with letters corresponding to the Russian abbreviation for Moscow State University (P_1 and P_2 are the pitches of the helix; $P_2 > P_1$; Z- is the axis of the helix).

by UV-irradiation at 90 °C. During this process the green colour of the film was transformed into the red one. Then the same film was heated during 20 min at the same temperature. The colour of the film was changed again from red to green. It means that one can perform the reversible changes of the recorded image without any marked loses of coloured characteristics in the repeated "recording–erasing" cycles.

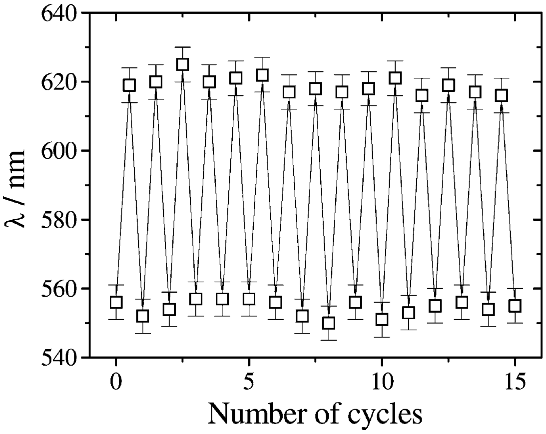


Fig. 8. Fatigue resistance properties of the film of LC copolymer **8** with 15 mol% of chiral units under the recording–erasing cycles.

From the viewpoint of the high fatigue resistance of the copolymer in the repeated recording–erasing cycles allow one to conclude that such polymers may be used as the materials for the reversible colour recording of optical information.

4. Multifunctional photochromic cholesteric LC copolymers

Combined chiral LC copolymers containing several different photosensitive groups in one and the same macromolecule could be of significant interest. Versions of the molecular design of such polymers are presented in Fig. 9. One may conclude that the "simplest" copolymer (from a synthesis viewpoint) should contain four types of monomer units including of one mesogenic, one chiral, and two photochromic groups (Fig. 9a). Such a copolymer may be obtained, for instance, by radical polymerization of four monomers with the appropriate functionalities. However, as far as we know, such copolymers are not described in literature. Light irradiation of a hypothetical copolymer might induce the photochemical reactions only in the photochromic groups, leaving the chiral fragments and the helical twisting power β unchanged. Therefore, it is difficult to expect that the optical properties of such a copolymer will

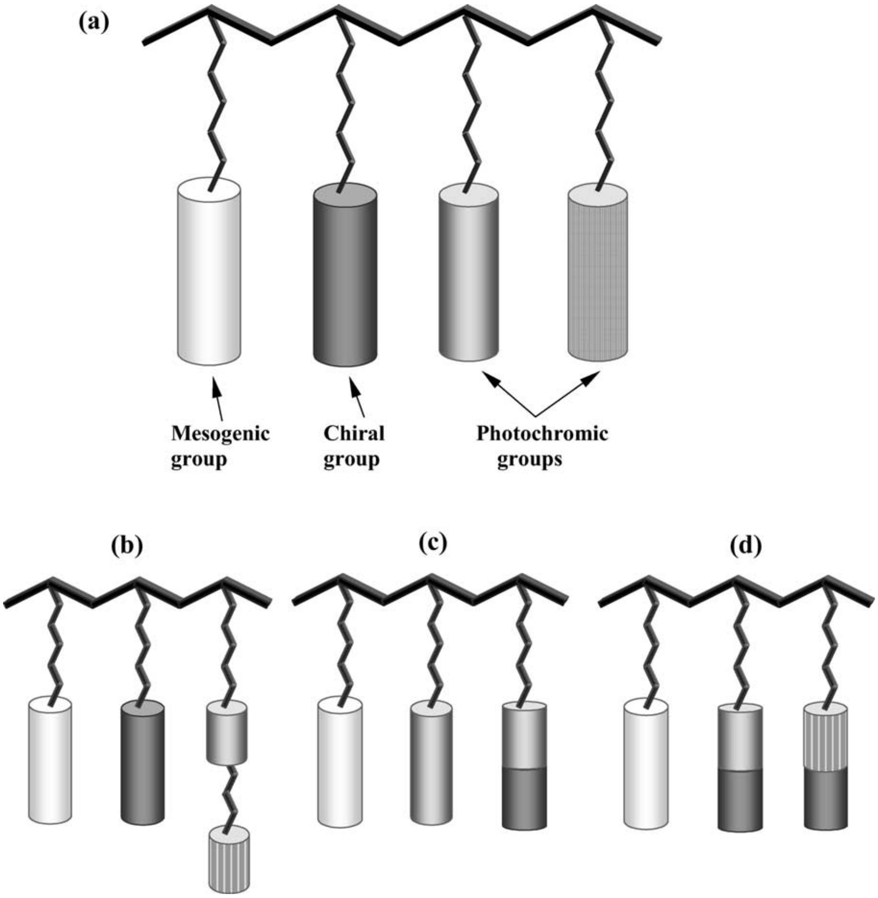


Fig. 9. Design of photochromic LC polymers with different molecular architecture.

be essentially changed because the helical twisting power of the chiral fragments might remain the same during irradiation. It seems likely that the same situation will occur for the molecular structure shown in Fig. 9b.

In this case, the copolymers with the molecular structure shown in Fig. 9c and d, appear to be better candidates for photoregulation. Hence, one (Fig. 9c) or two (Fig. 9d) chiral centers are covalently linked with photochromic groups. Using light of the appropriate wavelength one can separately stimulate the photochemical reactions in each photochrome. As the latter ones are chemically connected with chiral groups, the helical twisting power of each group is changed. All side photochromic and chiral groups shown in Fig. 9 look like rigid rods, i.e. they have a mesogenic shape. However, this requirement is not necessary. An important point is that a liquid crystalline phase should be retained.

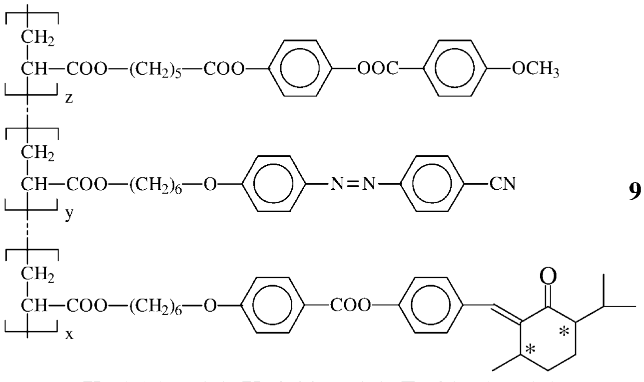
As a result, the unique possibility arises that each photochrome will respond to a certain wavelength of light irradiation. The photoinduced chemical transformations will lead to changes in helical twisting power of both chiral groups, and the helical supramolecular structure will be modified. The development and design of such complicated multifunctional polymer systems allows the preparation of novel materials with fascinating optical properties. Let us consider few examples of multifunctional LC copolymers obtained by us.

4.1. Ternary copolymers containing photosensitive and combined chiral-photochromic side groups

The existence of two different types of chromophores in a single macromolecule is of considerable interest for the creation of the new promising multifunctional materials and for manipulation of their optical properties (Fig. 9). Despite obvious difficulties related to the combination of two photochemical and a series of photo-optical processes, in the same materials, any approach to their synthesis is of considerable interest from academic and technological view points for the development of unique multifunctional polymeric materials.

For this purpose, we have synthesized a series of ternary copolymers consisting of nematogenic groups, chiral fragments and two different photosensitive azobenzene- and benzylidene–menthanone-containing groups, incorporated into side chains of macromolecules as individual monomer units (copolymer **9**) or combined chiral-photochromic units (see below copolymer **10**).

The structural formula of the first series of the ternary copolymers **9** is shown below:



9

X=5-15 mol%, **Y**=0.20 mol%, **Z**=65-75 mol%.

To reveal the specific properties of photo-optical behaviour of the ternary copolymer **9** the photochemical processes in their dilute solutions were analyzed.

Fig. 10 presents the absorption spectra of dichloroethane solution of ternary copolymer **9** containing 15 mol% of chiral side units. This spectrum shows two principal peaks: a long-wavelength peak ($\lambda_{max} = 365$ nm) corresponds to the π–π^* electron transition of cyanoazobenzene groups whereas a short-wavelength peak at $\lambda_{max} = 262$ nm corresponds to the π–π^* electron transition of mesogenic phenylbenzoate units The peak associated with the absorption of benzylidene-*p*-menthanone fragments appears only as a “shoulder” at 290–325 nm [26].

The UV-irradiation leads to significant changes in the absorption spectra of the copolymers (Fig. 10). Depending on the wavelength of the excitation light λ_{ir}, the character of these changes appears to be somewhat different. At $\lambda_{ir} = 365$ nm, one observes a marked decrease in the absorption peak associated with the π–π^* electron transition of the cyanoazobenzene groups (Fig. 10a), whereas, at $\lambda_{ir} = 313$ nm, changes in the “shoulder” at 290–325 nm are observed (Fig. 10b).

In other words, when dilute solutions of copolymers are irradiated with a wavelength of 365 nm, benzylidene-*p*-menthanone groups experience almost no *E*–*Z* isomerization; isomerization is observed only for azobenzene groups. At $\lambda_{ir} = 313$ nm, both groups undergo isomerization. Similar dependencies are observed for thin films of the copolymers prepared by evaporation of solvent from their dichloroethane solutions.

The *E*–*Z* isomerization of azobenzene groups is thermally and photochemically reversible: under the irradiation of the copolymers with a visible light, a reversible increase in absorption peak at $\lambda_{max} = 365$ nm is observed. One may conclude that isomerization of various photochromic groups may be controlled by varying the wavelength of incident light beam; in the case of azobenzene groups, one may also change the direction of the whole process. Let us note that chiral photochromic groups are irreversibly transformed to the *Z*-form. However, in the case of cyanoazobenzene chromophores, the *E*–*Z* isomerization is fully reversible.

Irradiation and subsequent annealing of planarly oriented films of copolymers shift the selective light reflection peak to the long-wavelength region (Fig. 11). As was shown earlier for copolymers with benzylidene-*p*-menthanone groups,

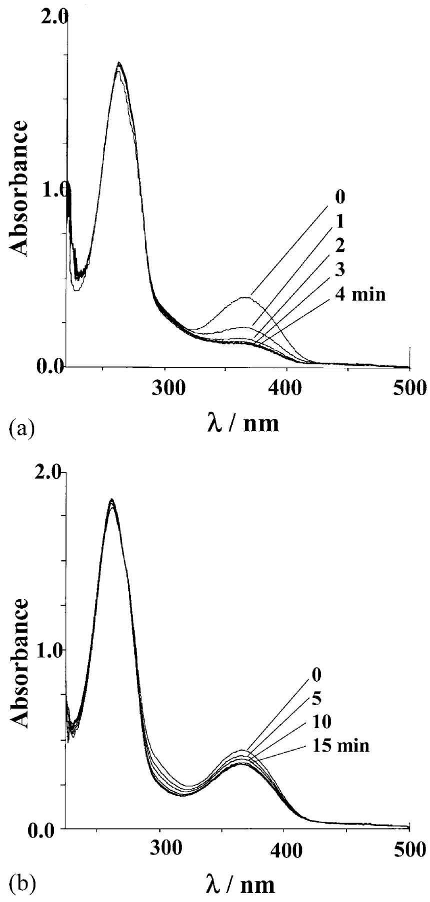


Fig. 10. Changes of the absorbance spectra for dichloroethane solution of copolymer **9** containing 15 mol% of combined chiral-photochromic units during UV-irradiation with light of different wavelength: (a) 365 nm and (b) 313 nm. Irradiation time is shown in figure.

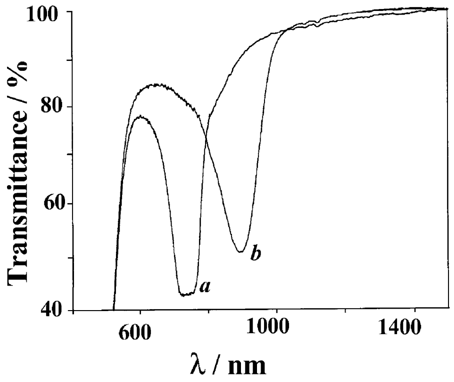


Fig. 11. Transmittance spectra of the copolymer **9** with 10 mol% of the chiral-photochromic units (a) before and (b) after a 75 min of UV-irradiation at 100 °C with $\lambda_{ir} = 365$ nm.

this effect is associated with the *E*–*Z* isomerization of menthanone-containing chiral photochromic groups, which is accompanied by a dramatic decrease in their twisting power. It is interesting to note that helix untwisting is likely to be induced by UV-irradiation with both wavelengths (313 and 365 nm). In a relatively 'thick' film of copolymer, benzylidene-*p*-menthanone groups are likely to be capable of a marked absorption even at a wavelength of 365 nm.

Hence, the effect of UV light on planarly oriented films of copolymers may locally change the helix pitch and correspondingly, the selective light reflection maximum. It is very important to stress, that the *E*–*Z* isomerization process is irreversible and the colour (or coloured image) can be fixed at any λ_{max} after termination of UV-irradiation.

At the same time the irradiation of the same film by the visible polarized light (Ar laser: 514 nm) induces birefringence due to photoorientation of only the azobenzene groups not affecting the benzylidene-*p*-menthanone fragments: no helix untwisting was observed. At the same time these copolymer films can be used for the holographic image recording. A simple holographic grating was recorded using the radiation of an Ar laser ($\lambda = 514$ nm). In this case, the appearance of the photoinduced birefringence which grow parallel to the diffraction efficiency has been observed (Fig. 12). This process is completely reversible and the image can be erased by heating of the sample.

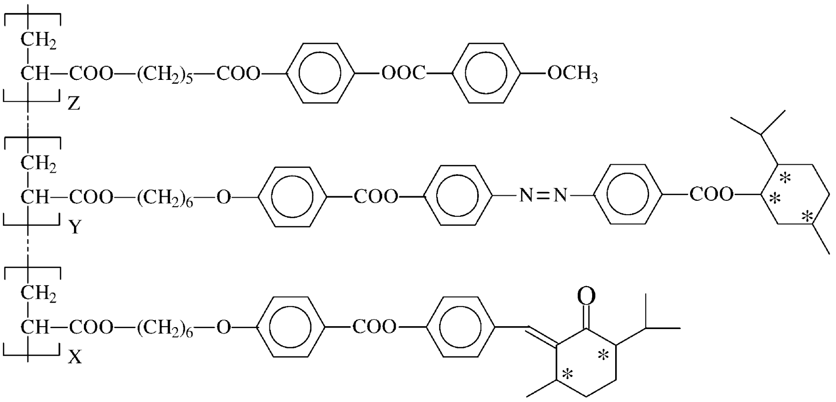
In such a way, a dual photochromism of ternary copolymers allows one to record optical information of "two types" on the same sample. Firstly, by varying the helix pitch and λ_{max} due to the short-wavelength light irradiation. And secondly, due to photoinduced birefringence using polarised light at wavelength more than 400 nm. It means that we can record and erase the images both separately and together.

The variation of the ratio between the *E*- and *Z*-isomers by irradiation also allows one to smoothly change not only the optical properties but, probably, rheological properties of the system due to a disordering effect of *Z*-isomeric form, which should decrease the viscosity of copolymers.

A high optical density of the synthesised copolymers opens wide possibilities for the preparation of planarly oriented films with a high gradient of helix pitch along the sample. Examination of such multifunctional chiral photochromic cholesteric copolymers is interesting not only from the viewpoint of optical data recording; investigation of, at least, two competing photochemical processes taking place in such system presents an independent interest.

4.2. Ternary copolymers containing two different combined chiral-photochromic side groups

The second series of the ternary copolymers **10** includes the compounds with the same nematogenic fragment (as in the copolymers of the series **9**) and two chiral-photochromic monomer units containing azo-menthol and benzylidene-*p*-menthanone groups [27]:



10

X=5mol%, Y=5 mol%, Z=90 mol%

This copolymer displays cholesteric phase over a wide temperature range between $T_g = 25\,^{\circ}$C and $T_{cl} = 123\,^{\circ}$C.

Planarly oriented copolymer films are characterized by selective light reflection in near IR spectral region ($\lambda_{max} \sim 940$ nm). Upon irradiation with UV ($\lambda_{ir} = 365$ nm) and visible light ($\lambda_{ir} > 450$), such films experience untwisting of the cholesteric helix and a shift in the selective light reflection wavelength to long-wavelength region (Figs. 13 and 14). Let us emphasize that, upon light irradiation with $\lambda_{ir} = 365$ nm, a shift in the selective light reflection peak is irreversible; at the same time, irradiation with visible light leads to reversible changes in λ_{max}. In this case, annealing of the sample at temperatures above $\sim 50\,^{\circ}$C provides for the recovery of the selective light reflection wavelength to its initial position (Fig. 14).

This behaviour suggests the occurrence of the *E*–*Z* isomerization of benzylidene-*p*-menthanone groups under the action of UV light and photoisomerization of azobenzene groups only under irradiation with visible light. In both cases, *E*–*Z* isomerization decreases the helical twisting power of chiral groups due to the lower anisometry of their *Z*-isomer. Under UV-irradiation, one may hardly exclude the possible photoisomerization of azobenzene fragments but the films annealed after light irradiation with $\lambda_{ir} = 365$ nm show no back process of helix twisting even at short irradiation times. This behaviour is likely to be related to the fact

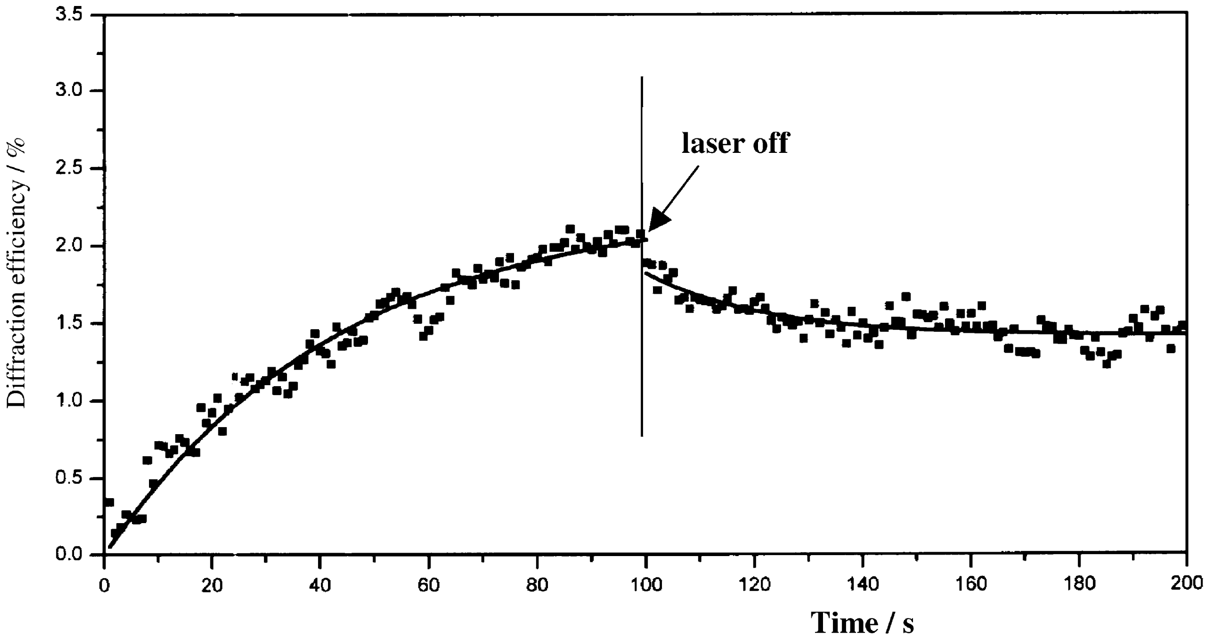


Fig. 12. First-order diffraction efficiency growth during holographic recording on copolymer **9** containing 15 mol% of chiral-photochromic units (orthogonal polarizations, Ar laser: 514 nm).

that isomerization of benzylidene-*p*-menthanone groups leads to a more pronounced decrease in helix twisting power as compared with that of azobenzene fragments. Under given experimental conditions and light irradiation with $\lambda_{ir} = 365$ nm, only irreversible changes in helix pitch related to the isomerization of only benzylidene-*p*-menthanone groups were observed.

By providing photoinduced changes in the selective light reflection wavelength, irradiation with visible light allows one to perform repeated “data recording–erasing” cycles. As follows from Fig. 15, fatigue resistance of the copolymer is rather high, although one may observe a minor systematic shift in the selective light reflection wavelength to a long-wavelength region.

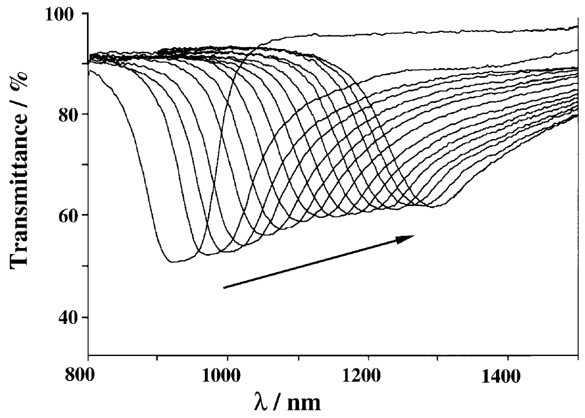


Fig. 13. Changes of transmittance spectra of planarly-oriented films of copolymer **10** during UV-irradiation ($\lambda_{ir} = 365$ nm); spectra were recorded each 10 min of irradiation, $T_{ir} = 100\,°C$.

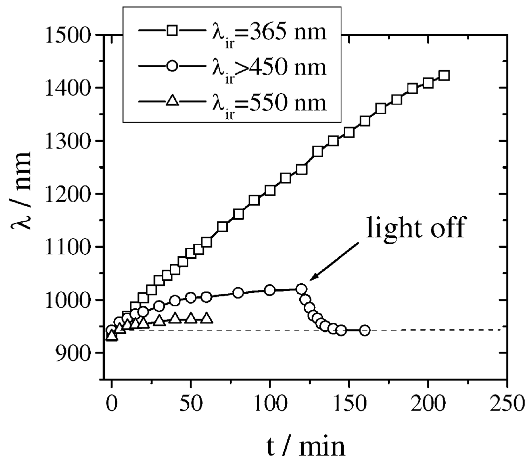


Fig. 14. Selective light reflection wavelength growth during irradiation of copolymer **10** film with light of different wavelength. Temperature of the sample 80 °C.

One may conclude that copolymerization of a nematogenic monomer with the two different combined photosensitive chiral monomers makes it possible to obtain a new class of multifunctional polymers with different “responses” to light irradiation with different wavelength. These copolymers may be used both for reversible and irreversible recording of optical information.

5. Photoresponsive LC polymer mixtures

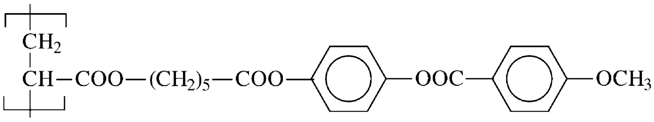
The considerable opportunity of controlling the supramolecular structure of cholesteric polymer systems opens up the use of the mixtures of LC polymers with low-molar-mass chiral-photochromic dopants and photoresponsive blends based on chiral and photochromic LC polymers [28–33].

5.1. Photosensitive mixtures based on LC polymers and low-molar-mass chiral-photochromic dopants

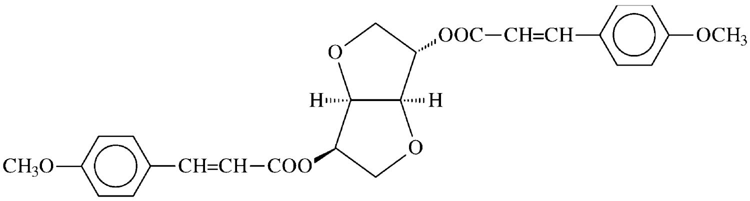
Mixtures of nematogenic polymers with chiral-photochromic dopants having a different (left or right) twisting sign offer an interesting opportunity for photoregulation of optical properties of LC polymeric systems. Such mixtures allow one to obtain materials with variable directions of change in the photoinduced helix pitch. Two types of these systems are considered below.

The first mixture **I** is composed of nematogenic homopolymer responsible for the development of the nematic phase and two low-molar-mass chiral-photochromic dopants which are capable of irreversible and reversible photoisomerization, respectively (Fig. 16a). The structural formulae of the corresponding compounds as shown below [29].

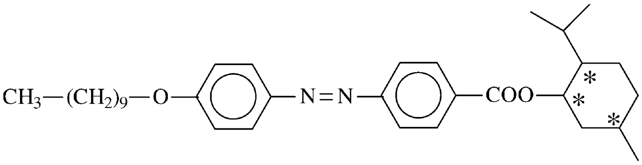
Mixture **I**:



11
(94mol%)



R
(4mol%)

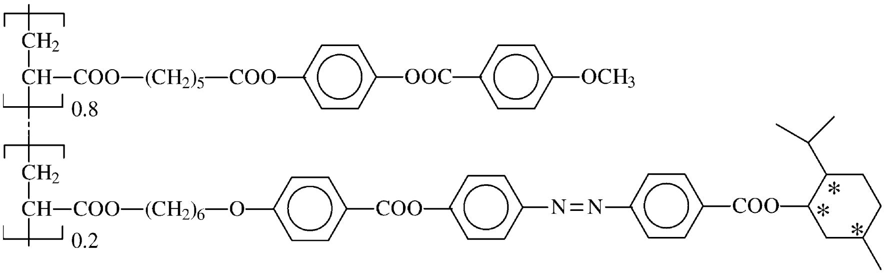


L
(2mol%)

Note that dopant **R** is a right-handed conformer; in other words, it is able to develop cholesteric helix with right twisting direction [32] while, in contrary, the second dopant **L** is a left-handed conformer [28]. The composition of the mixture is selected so that the twisting direction of this ternary mixture is controlled by enantiometric excess of dopant **R**, that is, the mixture is right-handed. The concentrations of the both dopants are very small, so that the mixture **I** shows a homogeneous one-phase cholesteric structure with a $T_{cl} = 93–95\,^{\circ}C$.

The second mixture **II** is composed of the left-handed cholesteric copolymer **12** containing nematogenic phenylbenzoate groups, and chiral menthol and photochromic azobenzene groups as well as dopant **R**:

Mixture **II**:



12
(97mol%)

+ Dopant **R** (3mol%)

Mixture **II** is also able to produce a cholesteric mesophase with a $T_{cl} = 102–103\,^{\circ}C$. The composition of this mixture is selected so that the twisting direction is left; that is in this case, azobenzene-containing chiral photochromic groups dominate. For both mixtures the glass transition temperature is equal to about 25 °C.

UV absorption bands for the azobenzene chromophores of dopant **L** and azobenzene groups of copolymer **12** are located in the higher wavelength region ($\lambda_{max} = 367$ nm for dopant **L** and $\lambda_{max} = 339$ nm for copolymer **12** in dichloroethane solution) as compared with that of dopant **R** ($\lambda_{max} = 312$ nm in dichloroethane solution). Furthermore, azobenzene chromophores are characterized by the existence of a high-wavelength n–π^* electron transition at about 450 nm; upon irradiation with a wavelength coinciding with this absorption band, *E*–*Z* photoisomerization also takes

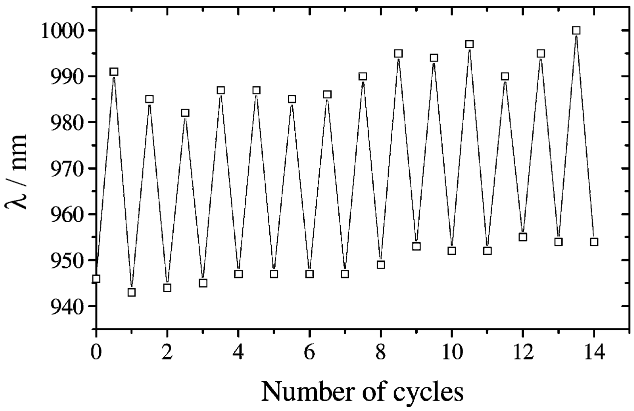


Fig. 15. Fatigue resistance properties of the copolymer **10** film under the recording–erasing conditions. In each cycle film of copolymer was irradiated during 30 min by light $\lambda_{\mathrm{ir}} > 450$ nm at 80 °C, then was annealed during 30 min at 100 °C.

place. Another important feature of cinnamoyl and azobenzene groups is that, in the case of dopant **L** isomerization of azobenzene fragments is thermally and photochemically reversible, while in the case of dopant **R** all light-induced changes are irreversible. Therefore, upon light irradiation with a wavelength coinciding with the UV absorption band of the dopant in enantiometric 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 contrast, should increase due to a decrease in helical twisting power. The above reasoning allows one to assume that, for mixture **I**, UV-irradiation should lead to the untwisting of the cholesteric helix whereas irradiation with visible light results in helix twisting.

The specific features of the photo-optical properties for mixture **I** are discussed below. UV-irradiation (365 nm) leads to untwisting of the cholesteric helix and a shift in the selective light reflection maximum to the high-wavelength spectral region whereas, upon irradiation with visible light (>450 nm), the selective light reflection maximum is shifted to the short-wavelength spectral region (Fig. 17a and b). Furthermore, upon irradiation with visible light, this shift in the selective light reflection maximum is much lower and is observed once the photostationary state is attained.

Under irradiation with visible light, the shift in the selective light reflection maximum is thermally reversible: upon annealing, this peak is shifted in the reverse direction (Fig. 18). It is interesting to note that even though, upon repeated recording–erasing cycles (Fig. 18), the amplitude of the changes of selective light reflection maximum remains almost unchanged. However, 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 **L** but also irreversible *E*–*Z* photoisomerization of cinnamoyl dopant **R** ($\{2+2\}$ photocyclization is less probable due to low concentration of dopant [32]).

In the case of mixture **II**, photo-optical behaviour appears to be quite different. Upon UV-irradiation and annealing, the selective light reflection maximum is shifted to the short-wavelength region whereas, in the case of irradiation with visible light, this maximum is shifted to the long-wavelength region (Fig. 19). As with mixture **I**, irradiation with visible light leads to a preferential photoisomerization of azobenzene groups whereas, upon UV-irradiation, photoisomerization of cinnamoyl groups of dopant **R** and azobenzene groups of copolymer **12** takes place. However, in the latter case, annealing leads to a reverse transformation from *Z*-isomers of azobenzene groups to *E*-form. The resultant shift in the selective light reflection maximum is controlled by the ratio between *E* and *Z*-isomers of dopant **R**. Upon irradiation with visible light, the amplitude of the

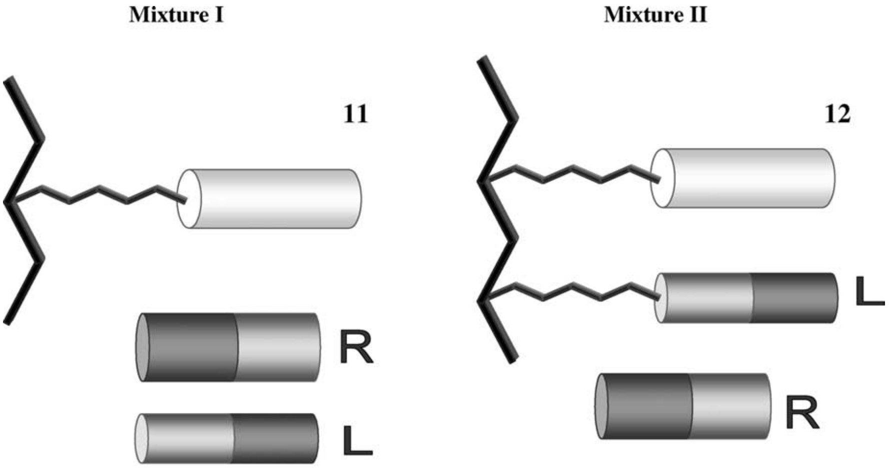


Fig. 16. Schematic representations of the two mixtures **I** and **II** consisting of nematogenic homopolymer **11** and chiral-photochromic copolymer **12** with right (**R**) and left (**L**)-handed low-molar-mass chiral-photochromic dopants.

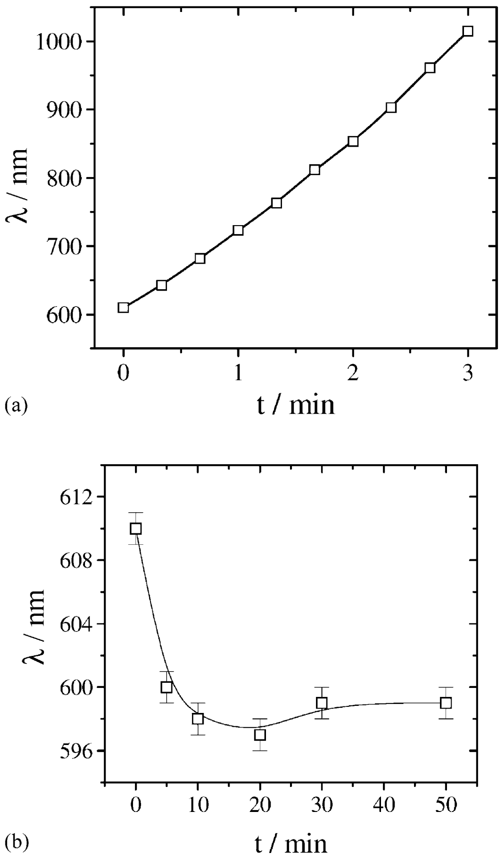


Fig. 17. Change of selective light reflection wavelength during (a) UV-irradiation (365 nm) and (b) visible light irradiation (>450 nm) for mixture **I**. Temperature of irradiated sample is 70 °C.

changes to the selective light reflection maximum is much higher than that in the case of mixture **I**; this trend is related to the much higher content of azobenzene chiral photochromic groups in mixture **II**.

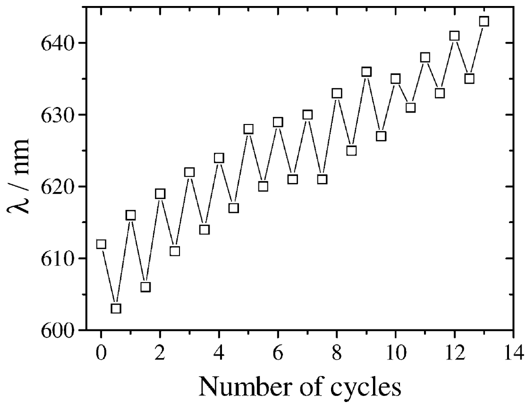


Fig. 18. Fatigue resistance properties of the mixture **I** film under the "recording–erasing" processes. In each cycle the film was irradiated during 20 min by light (>450 nm) at 70 °C, then the film was annealed during 20 min at the same temperature.

Let us emphasize the unique character of the above cholesteric polymer 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 for photo-optical control of the optical properties of polymer materials.

5.2. Photochromic immiscible blend of cholesteric copolymers

Study of polymer blends based on LC copolymers presents a challenging aspect of the modern physical chemistry of polymers. The preparation of compatible (miscible) and incompatible (immiscible) blends of cholesteric polymers offers new unique advantages for the optical properties of such materials. Let us briefly consider the results of our recent investigations [33] concerning a photochromic,

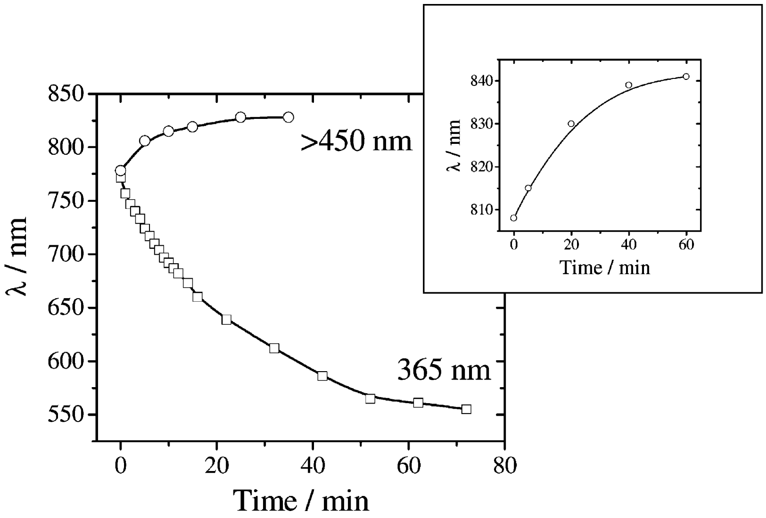
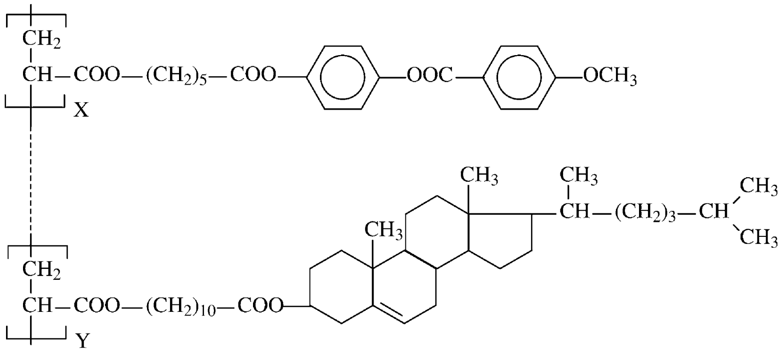
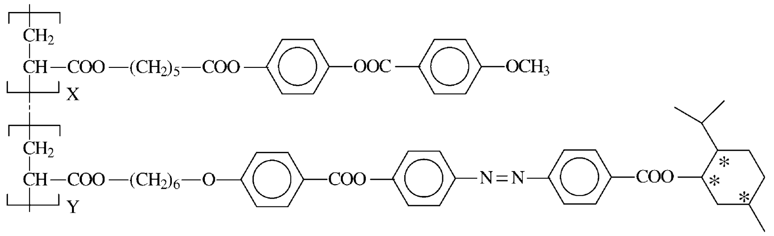


Fig. 19. Changing of selective light reflection wavelength during irradiation with light of different wavelengths for mixture **II** ($T = 90\,^{\circ}$C). Inset: the change of selective light reflection wavelength during irradiation with light of 550 nm at 80 °C. In the case of irradiation with light of 365 nm the sample was annealed after each cycle of light action during 20 min at 90 °C.

cholesteric blend containing two immiscible cholesteric side-chain acrylic copolymers **13** and **14**.



13



14

As follows from the above structural formula copolymer **13** contain nematogenic phenyl benzoate side groups and chiral cholesterol-containing units. Copolymer **14** is composed of the same nematogenic groups and contains chiral menthol-fragment with the double N=N bond. Both copolymers have the close molar masses and polydispersity. The polymer blend based on the copolymers taken in equal parts (1:1) was prepared by dissolving the copolymers in chloroform followed by solvent evaporation. The study of phase behaviour showed that a cholesteric phase is developed over a wide temperature range; the glass transition temperature of this mesophase in equal to about 25 °C and the T_{cl} lies within a temperature interval of 115–124 °C.

Let us emphasize that this blend is characterized by a complete immiscibility between the initial components forming a typical two-phases system. As a result, planarly oriented film based on the above blend show the two well-pronounced peaks of selective light reflection coinciding with corresponding peaks of the initial components—copolymers **13** and **14**. The first peak is observed in the visible spectral region whereas the second peak is observed in the near IR spectral region (Fig. 20). This trend suggests that the individual helical structure of each of the components is preserved, and both components are fully immiscible. Note that the wavelengths corresponding to the selective light reflection maxima for all samples are almost independent of temperature.

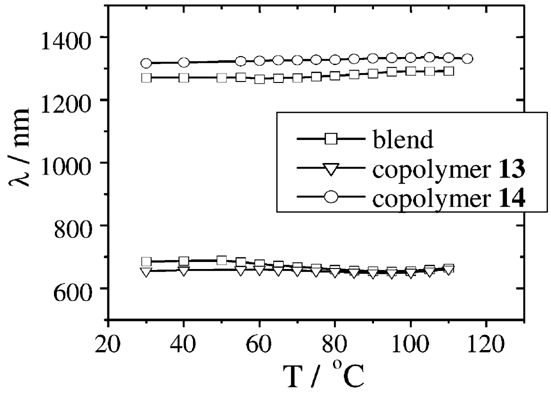


Fig. 20. Temperature dependencies of the wavelengths of selective light reflection for blend and corresponding copolymers **13** and **14**.

Under the action of UV-irradiation the long-wavelength peak and λ_{max} is shifted to higher wavelength whereas

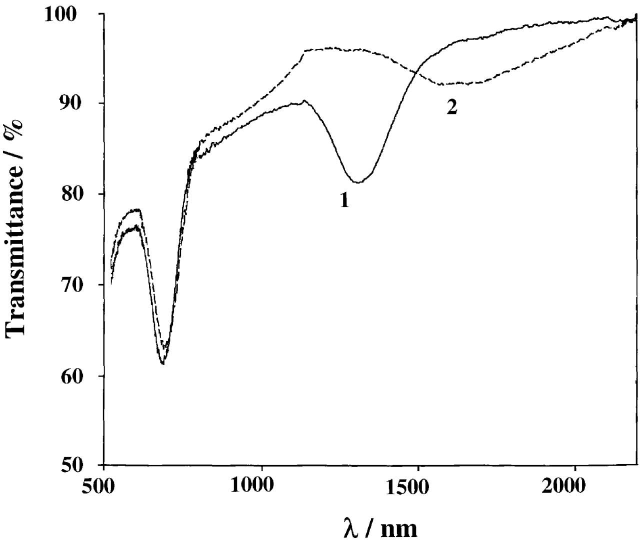


Fig. 21. Transmittance spectra of a planarly oriented films of blend (1) before and (2) after irradiation by UV light (365 nm at 70 °C) during 120 min. The spectra were recorded immediately after switching off light.

the second peak remains almost unchanged (Fig. 21). The sensitivity of the long-wavelength selective light reflection peak to the UV-irradiation indicates that the phase with the corresponding selective light reflection peak in the near IR-spectral region corresponds to photochromic copolymer **14**. Upon light irradiation, the *E*–*Z* photoisomerization of azobenzene photosensitive chiral side groups takes place and this process is accompanied by a concomitant decrease in anisometry and helix twisting power. At the same time the selective light reflection peak located in the visible spectral region remains unchanged.

In addition, more detailed investigations of photo-optical processes showed that the helix untwisting is also accompanied by a well-pronounced widening of the selective light reflection peak (Fig. 21) due to a marked gradient in the light irradiation doses in film and different ratio between the formed *E*- and *Z*-isomers in the blend. Another feature is related to the kinetic of untwisting the cholesteric helix.

The rate of helix untwisting appears to be much lower as compared with the initial photosensitive copolymer **14** (Fig. 22). This behaviours is likely to by related to the fact that, due to the existence of the two phases, the planar cholesteric texture of the blend is capable of a more pronounce light scattering. Therefore, the fraction of light required for the activation of photoisomerization appears to be somewhat lower.

It should be pointed out that photoisomerization and, hence, helix untwisting is thermally reversible process. After annealing of the blend above glass transition temperature the selective light reflection peak comes back to its initial position. On the other hand, upon fast cooling of the blend to room temperature, one may "freeze" the helical supramolecular structure and preserve this structure for a long period of time.

Thus, the cholesteric blend, obtained on the base of the two chiral copolymers is characterized by unique optical properties: as compared with the cholesteric materials, the above blend shows two selective reflection peaks, and the position of one of the above peaks may be changed under the action of light. Notwithstanding the fact that the above phenomenon may also be expected for multiplayer structures based on cholesteric films of various polymers, the approach considered here offers a much simpler solution for the preparation of the polymer systems with the above photo-optical properties.

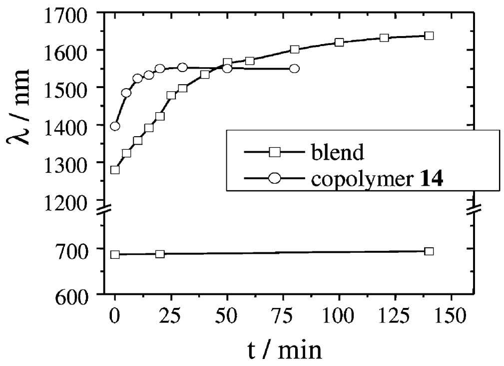


Fig. 22. Changes of the selective light reflection wavelength during UV-irradiation (365 nm) of blend and copolymer **14** at 70 °C. The spectral measurements were made immediately after each cycle of irradiation.

6. Conclusions

This brief review summarizes our results obtained in recent years in the field of development of advanced optically controlled polymer systems based on photochromic cholesteric LC polymers, and their blends with low-molar-mass chiral and photochromic dopants acting as the specific switchers. Interest in photochromic LC polymers is related to by reversible (or irreversible) changes in the optical properties and colour; such materials appear to be very attractive and fascinating. All side-chain LC polymers containing mesogenic and photochromic groups or mesogenic and chiral-photochromic groups, are structurally and functionally integrated systems that show simultaneously liquid crystalline, chiral, and photochromic properties. The main principal underlying the photoinduced control of the optical properties of such copolymers is provided by the photoisomerization of chiral-photochromic fragments, which is accompanied by changes in their anisometry and helix twisting power. In turn variation of the helical twisting power of the chiral fragments is also accompanied by sharp changes in the supramolecular helical structure and the optical properties of polymer film.

By properties selecting the binary copolymer composition and preparing blends of the cholesteric copolymers with low-molar-mass chiral-photochromic dopants, it is possible to obtain materials with different characters of the light-induced transformations. In more complex multifunctional polymer systems containing at least two different photochromes (ternary LC copolymers, photochromic LC mixtures) light irradiation can lead to a dual photochromism which allows one to record the optical information of the two types on one sample: first, by varying the helix pitch due to, for example short-wavelength light irradiation, and second, due to a photoinduced birefringence using, for example polarized light of the visible range of the spectrum.

The feasibility to fix the local changes in the molecular and supramolecular structure induced by the light irradiation opens wide ways for the development of new polymeric materials of new types with photomodulated supramolecular structure and controlled local optical properties: birefringence, refractive index, selective light reflection, colour characteristics, etc. Macromolecular nature of photochromic LC polymers offers fascinating advantages for the creation of solid glasses, thin films and coatings with desired and photoregulated optical properties—spectrum band filters, efficient polarizers, retarders, phase plates, and compensators. Optical storage can be provided by freezing LC director into an aligned state due to the photopolymerization of the selected reactive photochromic monomers leading to the cross-linked samples. All these directions of research deal with the development of advanced polymer-based optical data storage systems in both black–white and colour versions for optics, optoelectronics, holography, etc.

Presently by a rapid progress in the investigations related to the development of field-responsive polymers and other polymer-based "smart" materials is evident. It should be noted that high expectations concerning the practical application of such materials are not always justified because the polymer systems are characterized by a rather slow response to external factors, which is related to the slow rates of relaxation processes in polymers. On the other hand, the use of the blend compositions of polymers with low-molar-mass dopants, oligomers, and lyotropic LC systems and gels gives some benefits against an excessive scepticism with respect to the operational speed of the systems based on these materials. The search for new practical applications not requiring "instantaneous" response would favour a further progress in the development of new polymeric smart materials.

Acknowledgements

This work was supported by Russian Foundation of Fundamental Research (Grant-02-03-33048) and the Scientific Program "The Russian University".

References

[1] C.B. McArdle (Ed.), Side-Chain Liquid Crystal Polymers, Blackie, London, 1989.
[2] C.B. McArdle (Ed.), Applied Photochromic Polymer Systems, Blackie, London, 1989.
[3] V.P. Shibaev, S.V. Belyaev, Polym. Sci. USSR 42 (1990) 2384.
[4] V.P. Shibaev (Ed.), Polymers as Electrooptical and Photo-optical Active Media, Springer, Heidelberg/New York, 1996.
[5] V.P. Shibaev, S.G. Kostromin, S.A. Ivanov, Polym. Sci., Ser. A 39 (1997) 36.
[6] V.P. Shibaev, Int. J. Polym. Mater. 45 (2000) 169.
[7] T. Fuhrmann, J. Wendorff, Int. J. Polym. Mater. 45 (2000) 621.
[8] D. Broer, J. van Haaren, P. van de Witte, C. Bastiaansen, Macromol. Symp. 154 (2000) 1.
[9] V.P. Shibaev, A.Yu. Bobrovsky, N.I. Boiko, Macromol. Symp. 174 (2001) 333.
[10] V.P. Shibaev, A.Yu. Bobrovsky, N.I. Boiko, Polym. Preprints 43 (2002) 143.
[11] S.A. Ivanov, I.A. Yakovlev, S.G. Kostromin, V.P. Shibaev, L. Lasker, J. Stumpe, D. Kreysig, Macromol. Chem. Rapid Commun. 12 (1991) 709.
[12] V.P. Shibaev, A.Yu. Bobrovsky, N.I. Boiko, Polym. Sci., Ser. C 42 (2000) 103.
[13] A.Yu. Bobrovsky, N.I. Boiko, V.P. Shibaev, Liq. Cryst. 25 (1998) 679.
[14] A.Yu. Bobrovsky, N.I. Boiko, V.P. Shibaev, Polym. Sci., Ser. A 40 (1998) 232.
[15] A.Yu. Bobrovsky, N.I. Boiko, V.P. Shibaev, Liq. Cryst. 26 (1999) 1749.
[16] P. van de Witte, J.C. Galan, J. Lub, Liq. Cryst. 24 (1998) 819.
[17] M. Brehmer, L. Lub, P. van de Witte, Adv. Mater. 10 (1998) 1438.
[18] D. Demus, J. Goodby, G. Grey, H. Spiess, V. Vill (Eds), Handbook of Liquid Crystals, Wiley, New York, 1998.
[19] A.Yu. Bobrovsky, N.I. Boiko, V.P. Shibaev, Adv. Mater. 12 (2000) 1180.
[20] A.Yu. Bobrovsky, N.I. Boiko, V.P. Shibaev, K. Schaumburg, Polym. Sci., Ser. A 41 (1999) 107.
[21] E. Mena, P. van de Witte, J. Lub, Liq. Cryst. 27 (2000) 929.
[22] A.Yu. Bobrovsky, N.I. Boiko, V.P. Shibaev, J. Springer, Liq. Cryst. 28 (2001) 919.
[23] V.P. Shibaev, A.Yu. Bobrovsky, N.I. Boiko, K. Schaumburg, Polym. Int. 49 (2000) 931.
[24] A.Yu. Bobrovsky, N.I. Boiko, V.P. Shibaev, Polym. Sci., Ser. A 43 (2001) 1040.
[25] N.I. Boiko, A.Yu. Bobrovsky, V.P. Shibaev, Mol. Cryst. Liq. Cryst. 332 (1999) 173.
[26] A.Yu. Bobrovsky, N.I. Boiko, V.P. Shibaev, J. Mater. Chem. 10 (2000) 173.
[27] A.Yu. Bobrovsky, N.I. Boiko, V.P. Shibaev, Chem. Mater. 13 (2001) 1998.
[28] A.Yu. Bobrovsky, N.I. Boiko, V.P. Shibaev, Adv. Mater. 11 (1999) 1025.
[29] A.Yu. Bobrovsky, N.I. Boiko, V.P. Shibaev, K. Schaumburg, Macromol. Chem. Phys. 202 (2001) 2895.
[30] A.Yu. Bobrovsky, N.I. Boiko, V.P. Shibaev, Adv. Funct. Mater. 12 (2002) 367.
[31] A.Yu. Bobrovsky, N.I. Boiko, V.P. Shibaev, M.A. Kalik, M.M. Krayushkin, J. Mater. Chem. 11 (2001) 2004.
[32] A.Yu. Bobrovsky, N.I. Boiko, V.P. Shibaev, Mol. Cryst. Liq. Cryst. 363 (2001) 35.
[33] A.Yu. Bobrovsky, V.P. Shibaev, J. Mater. Chem. 12 (2002) 1284.