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New Types of Multifunctional Liquid Crystalline Photochromic Copolymers for Optical Data Recording and Storage

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SUMMARY: A new family of multifunctional chiral-photochromic liquid crystalline (LC) copolymers containing mesogenic, chiral and photoactive groups were synthesized. The new principles of photo-regulation of the helical supramolecular structure and optical properties of the binary and ternary chiral-photochromic LC polymers based on the change of helical twisting power of the chiral-photochromic monomer units, the dual photochromism and photochemical spectral gap burning were developed. It was shown, that the introduction of small amount of low-molar-mass chiral-photochromic dopants in chiral LC copolymers having different helix signs followed by light irradiation permits one to twist or untwist the helical supramolecular structure. The synthesized polymers are shown to be promising candidates for colour data recording and storage.

Introduction

In recent years the main scientific and applied interest of modern material chemistry has been associated with the creation of *Smart Materials* capable of being highly sensitive to environmental influence and responding easily to external fields, in particular to light irradiation^1, 2)^.

Among the different types of polymers the chiral liquid-crystalline (LC) polymers (LCP) are of particular interest due to their helical supramolecular structure which predetermines the unique optical properties such as selective reflection of light, circular dichroism, anomalously high optical activity etc^3)^.

On the other hand it is well-known that the photochromic polymers containing photoactive groups (chromophors) can easily change their molecular structure under the effect of light irradiation^1)^.

Taking into account these specific features of both polymer groups we have decided to combine their peculiarities in one and the same polymer material to create new type of light controllable (or photoaddressable) chiral-photochromic LC polymers, whose molecular and supramolecular structure might be regulated by a light irradiation.

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About ten years ago we started with very simple chiral and photochromic binary LC copolymers consisting of mesogenic and chiral or photochromic groups (Fig. 1a and b). Chiral LC polymers could be used for creation of optical filters, coloured decorative and technical overcoatings and circular dichroic polarizers. On the base of photochromic LC polymers the laser addressable materials for black and white reversible recording were obtained. The results of these our studies were published in the books, several reviews and in a number of publications[1, 2, 4-7].

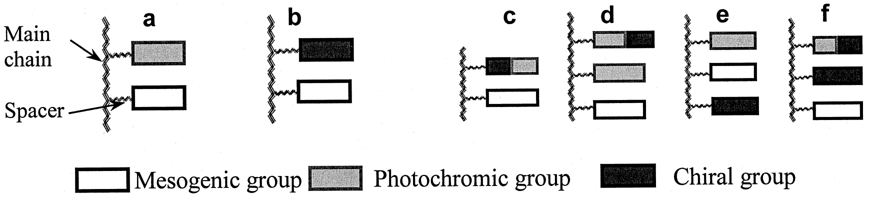


Figure 1. Schemes of the molecular structure of functional and multifunctional LC polymers: a) photochromic LCP; b) chiral LCP; c-f) chiral-photochromic LCP.

Two years ago our attention was focused on the more complex polymer systems, which were called multifunctional light responsive chiral-photochromic LCP. The macromolecules of these compounds consist of mesogenic (usually nematogenic), chiral and photochromic fragments, which can be combined in a single monomer unit (Fig. 1c) or can be incorporated into the different monomer units (Fig. 1 d-f). The great interest to these copolymers is dictated by the possibility to create a novel family of promising materials for coloured data reversible (and irreversible) recording and optical data storage for optics, optoelectronics, holography, coloured projection technique etc[8-11, 12-17, 18-24].

The main concept

It is well known, that main characteristic of the chiral nematic phase is the helical supramolecular structure, planar texture of which selectively reflects the incident light according to this equation[3]:

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

where P is the pitch of the helix, $\bar{n}$ is the average refractive index, and λ_{max} is the maximum of selective light reflection. The crucial factor determining the helix pitch is the helical twisting power β, described by

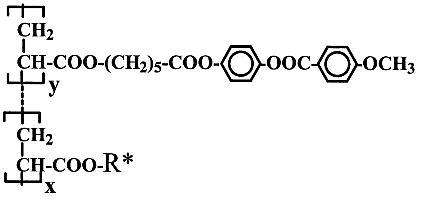
$$\beta=dP^{-1}/dX=\bar{n}(d\lambda_{max}^{-1}/dX)_{X=0}, \qquad (2)$$

where X is the concentration of the chiral fragments. In its turn the β-values depend on a number of factors, in particular, on the molecular constitution and the shape of the chiral fragment. In this connection it would be very attractive to use the light (for example, UV-irradiation) as a particular external field to regulate the β values of chiral groups and to control the helix pitch and optical properties of polymer films.

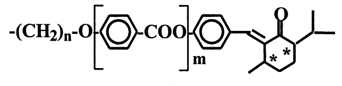
How we can realize this idea? In order to obtain photo-active, photo-addressable chiral LC copolymers, the chiral and photochromic fragments should be chemically combined in a single monomer unit. Light irradiation can induce the photochemical isomerization of chiral-photochromic groups, changing the configuration and shape of the chiral fragments together with their helical twisting power (HTP). This means that the helix pitch and optical properties should be changed under UV irradiation. In other words, changing the β values we can regulate the supramolecular structure and selective light reflection of polymer film exposed to the irradiation. Using this concept several series of the new binary and ternary chiral-photochromic copolymers (fig. 1c-f) have been synthesized and studied.

Binary chiral-photochromic copolymers

First of all let us consider a family of binary chiral-photochromic copolymers containing the same nematogenic monomer units and different chiral and photochromic groups combined in the second monomer unit[9, 12-17)]. Arabic numerals correspond to the molecular structure of the copolymers shown below:

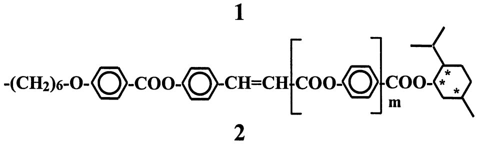


R=



n=6, 10
m=0, 1, 2

1



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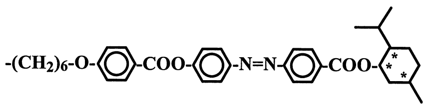

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All these copolymers satisfy to the following requirements: nematogenic monomer units are favourable to the nematic phase formation; chiral groups contribute to the twisting of the nematic phase and photochromic groups provide the photosensitivity to the copolymers.

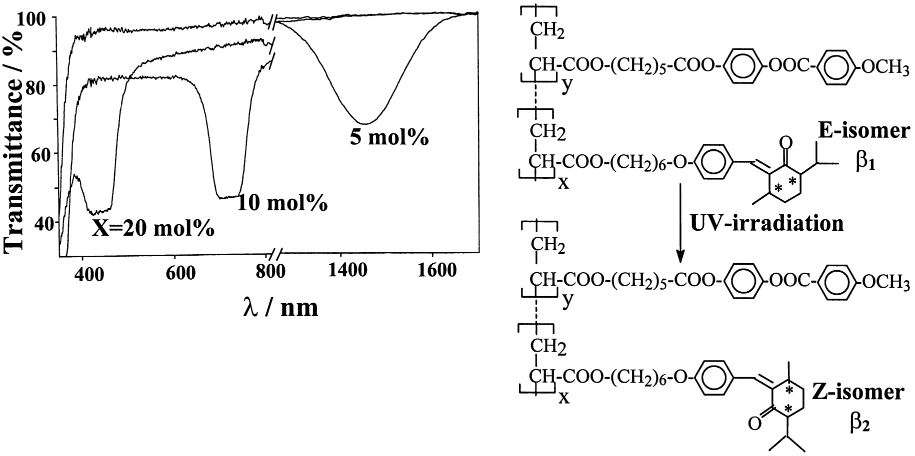


Figure 2. The transmittance spectra (corresponding to the maximum of selective light reflection) of chiral-photochromic LC copolymers of different composition and scheme of E-Z isomerization of chiral-photochromic fragments under UV irradiation.

Now let is consider the photochemical behaviour of the copolymers synthesized. Fig. 2 shows the selective light reflection of the first series of copolymers **1** containing the combined chiral-photochromic benzilidene-menthane-3-one fragments of the different compositions. Under UV irradiation these fragments undergo E-Z isomerization and their configuration and conformation are essentially changed. Helical twisting power β_2 of new Z-isomer becomes ten times less, then β_2 of the E-isomer[18].

The detailed photochemical studies clearly showed that helical supramolecular structure of the copolymers independently on the composition is untwisted after UV-irradiation[12, 13]. Kinetic investigations of the helix untwisting carried out at different temperatures demonstrated the significant influence of the temperature on the kinetics of the process (Fig. 3).

The higher temperature the higher is the rate of untwisting. These kinetic curves clearly show how we can untwist the helical supramolecular structure and change the colour of the polymer films. Using the mask 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

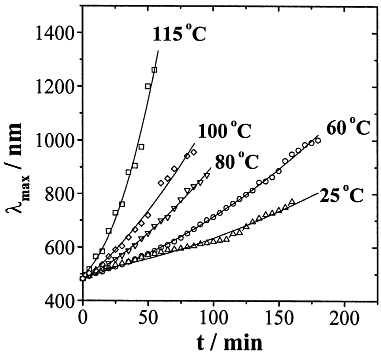


Figure 3. Kinetics of the helix untwisting for copolymer **1** (n=6, m=0, X=15 mol%) at different temperatures.

the coloured background. Scheme of the recording and an example of an image recorded on a planarly oriented film of copolymer **1** (n=6, m=0, X=15 mol%) are shown in Fig. 4. It would be emphasized, that the image is very stable and can be kept for prolonged time during several years.

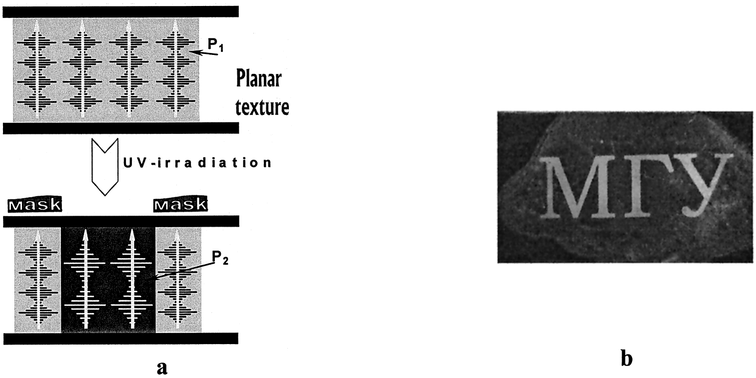
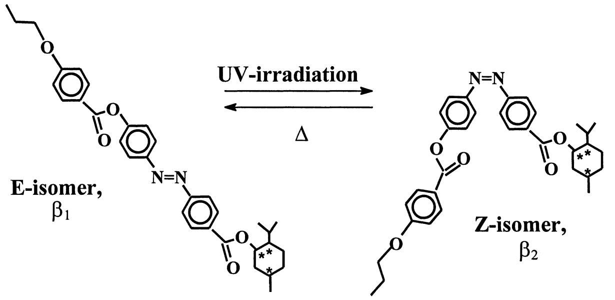


Figure 4. Sketch of the information recording on the planarly oriented polymeric film with the local pitch variation (a) and photo of the letters corresponding to the Russian abbreviation for Moscow State University (b) (P_1 and P_2 are the pitches of the helix; P_2>P_1).

However, from the practical point of view this copolymer has one essential disadvantage. This image can not be rewritten, because E-Z isomerization of chiral-photochromic benzilidenmenthanone fragment is irreversible.

This problem may be solved by synthesizing the other series of binary copolymers **3**, 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$^{2, 4-6, 9-11)}$. Based on these data we have obtained a new series of chiral-photochromic LC copolymers containing the same nematogenic group, photochromic azo-group and terminal chiral-menthol fragment (see copolymers **3**)$^{16, 17)}$. This family of copolymers, containing up to 20 mol% of chiral photochromic groups displays the chiral nematic phase over a wide temperature range between 25 and 115°C.

After the UV irradiation E-Z-isomerization of chiral-photochromic monomer units takes place and configuration and shape of the fragment are drastically changed as is shown below.



Simultaneously the β value becomes less ($\beta_1 > \beta_2$) and region of selective reflection of light λ_{max} 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. 5 shows the reversibility of the recording process. In each cycle the polymer film was irradiated during 30 min 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. This phenomenon demonstrates the high fatigue resistance of polymer film.

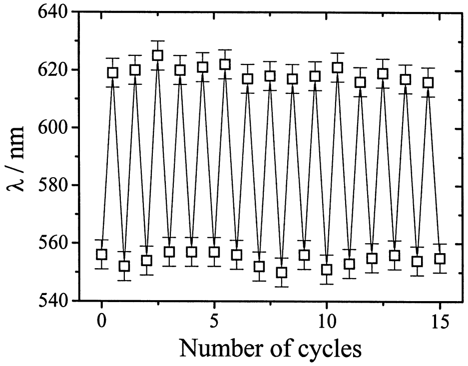
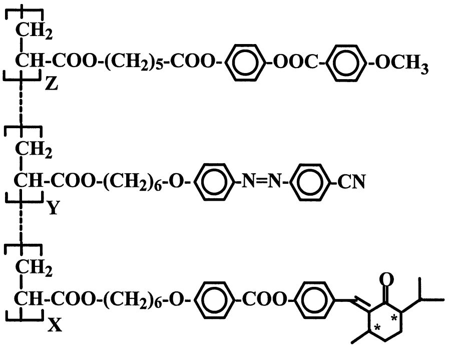


Figure 5. Fatigue resistance of LC copolymer **3** under the recording – erasing cycles.

Ternary chiral-photochromic LC copolymers displaying dual photochromism

The existence of two different chromophores in the single macromolecule is of considerable interest for the creation of the new promising multifunctional materials and for manipulation of their optical properties. For this purpose we have synthesized a series of ternary copolymers consisting of nematogenic groups, chiral fragments and two different photosensitive azobenzene- and benzilidenemethane-3-one-containing groups[19]. Let us briefly consider two examples of such copolymers. The structural formula of the first series of the ternary copolymers is shown below:



X=5-15 mol%
Y=20 mol%
X=65-75 mol%

4

All copolymers of this series, having the indicated composition display the chiral nematic phase[19].

Irradiation of the planarly oriented polymer films of the copolymers containing two different chromophores by light with the different wavelength is a very effective instrument for regulation of their optical properties. When polymer films are irradiated with λ_{ir} =366 nm the E-Z isomerization of both photochromic groups takes place. At λ_{ir}=313 nm the isomerization of benzilidenemethane-3-one groups predominantly occurs. However in both cases the peaks of selective light reflection λ_{max} shift to the red region (Fig. 6a).

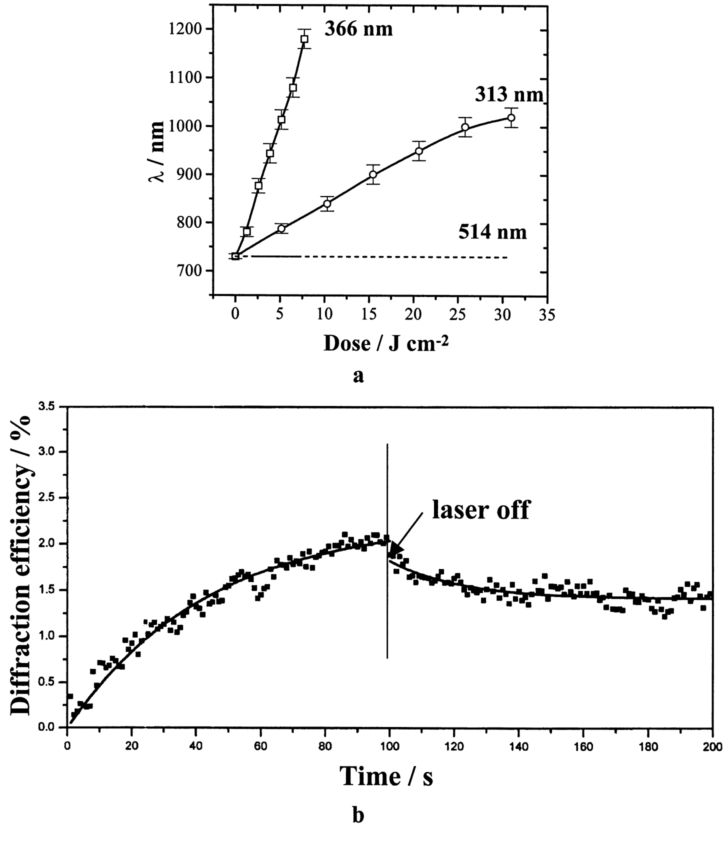


Figure 6. Change of selective light reflection wavelength (λ_{max}) during UV-irradiation of copolymer 4 (X=10 mol%, Y=20 mol%) by different wavelength (a) and first order diffraction efficiency growth during holographic recording by Ar laser (514 nm) (b).

It is very important to stress, that this process is irreversible and the colour (or coloured image) can be fixed at any λ_{max} value after termination of UV-irradiation. It is remarkable that the irradiation of the same film by the polarized light (Ar laser, 514 nm) induces birefringence due to photoorientation of only the azobenzene groups no affecting the benzilidenementhane-3-one fragments; no helix untwisting was observed (Fig. 6a). Preliminary data showed the appearance of the photoinduced birefringence, which is growing parallel to the diffraction efficiency (Fig. 6b). This process is completely reversible and an image can be erased by heating of the sample.

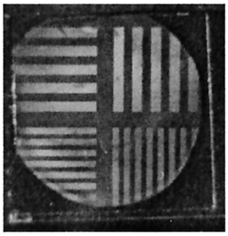
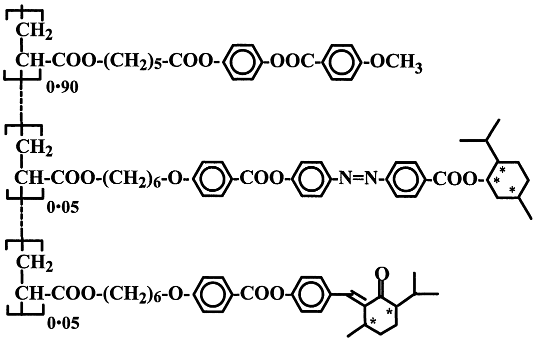


Figure 7. Microphoto of the film prepared from the copolymer **4** (15 mol% of chiral-photochromic units) exposed to UV-irradiation (366 nm) and demonstrated yellow pattern recorded through a test lattice on the blue background (here only black and white strips are seen)

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

The second series of the ternary copolymers **5** consists of the same nematogenic fragment (as in the copolymers of the series **4**) and two chiral-photochromic monomer units[20)]. Let us consider, as an example, the photo-optical behaviour of one of the copolymers synthesized (X=5 mol%, Y=5 mol%). This copolymer displays chiral nematic phase over a wide temperature range between 25 and 123 °C.

Fig. 8 shows the λ_{max} of polymer films as a function of irradiation time with the light of the different wavelengths. The initial film selectively reflects the light in the near IR region of the spectrum (λ_{max}~940 nm). UV (366 nm) and visible light (>450 nm) irradiation of such films leads to the helix untwisting and λ_{max} shifts to the longer wavelengths.



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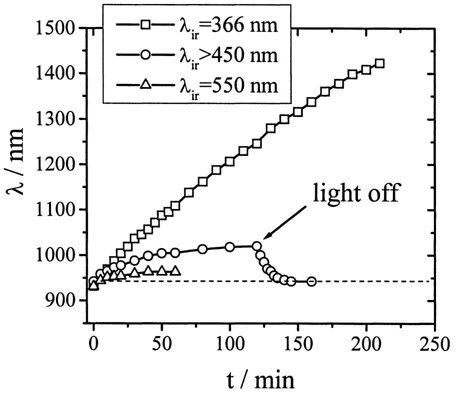


Figure 8. Time dependence of λ_{max} demonstrating the helix untwisting (λ_{max} growth) during the irradiation and the helix twisting after the light switching off.

It is important, that the peak shift (and helix untwisting) may be irreversible (λ_{ir}=366 nm) or reversible (λ_{ir}>450 nm). In the latter case, as is seen from Fig. 8, the λ_{max} shifts to the short wavelength region of spectrum after the light switching off (helix twisting).

Two above-mentioned series of copolymers clearly demonstrated that the ternary copolymers are really rather complicated compounds, nevertheless they are undoubtedly of a significant scientific and applied interest with respect to the development of unique multifunctional polymer photoactive materials.

Blends of chiral-photochromic low-molar-mass (LMM) dopants with chiral copolymers having opposite helix twisting sign

The considerable opportunity or controlling the supramolecular structure of copolymers opens up the use of the blends of chiral-photochromic LMM dopants with the chiral copolymers having a different twisting sign of the helix (Fig. 9).

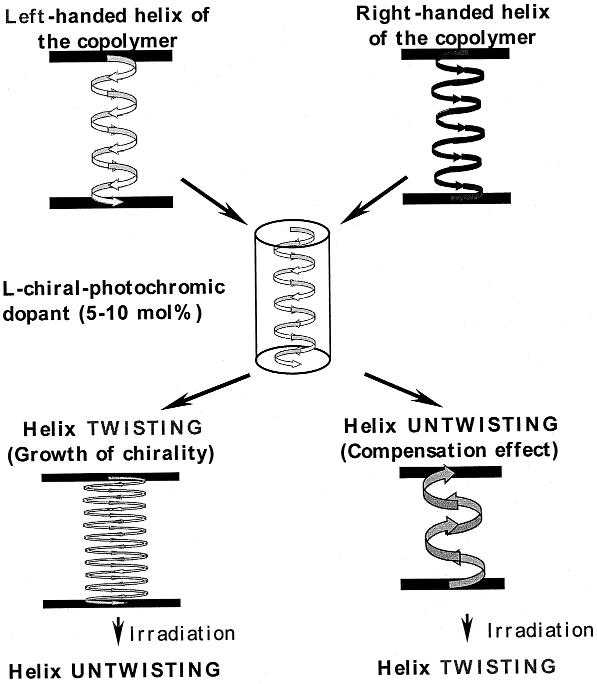
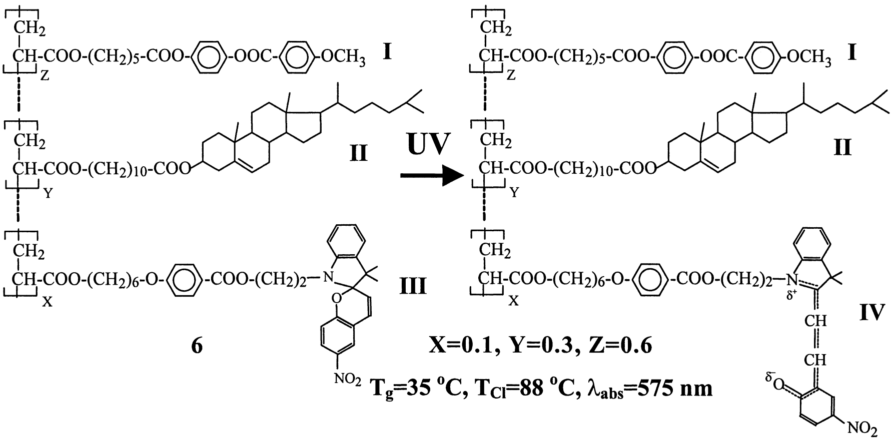


Figure 9. Schematic diagram showing the principle of the regulation of the helix twisting signs for the mixtures of the left- and right-handed copolymers with L-chiral-photochromic LMM dopant followed by UV-irradiation.

Using the L-chiral-photochromic dopant two mixtures with the left- and right-handed helical structures of copolymers can be prepared. Introduction of the L-dopant to the left-handed copolymer will increase the "chirality" of the mixture that leads to the helix twisting. However after irradiation the β value of the dopant decreases and the helix will be untwisted (Left part of Fig.9). The opposite situation will be observed in the second case. Introduction of the same L-dopant to the right-handed copolymer decreases the "chirality" due to the compensation effect, because the dopant and the copolymer have different signs of helix twisting. However after UV-irradiation of the mixture the β value of the dopant decreases and its compensation effect is suppressed due to the opposite helix twisting signs of the compounds. This is only the general concept. The detailed experimental data completely proving this idea have been recently published[8, 13)].

Optical data recording based on the reversible transition "selective reflection – absorption" in photochromic LC polymers

This approach is based on the synthesis of ternary copolymers (see formula of copolymers **6**) containing rather small amount of the photosensitive units **III** as well as the chiral (**II**) and nematogenic ones (**I**). The ratio between different fragments in the ternary copolymers **6** should be selected so, that the maximum selective light reflection of LC copolymer should coincide with the maximum light absorption of the photoinduced new isomer (merocyanine **IV**) formed during UV-irradiation as is shown below[21-24)]:



$X=0.1, Y=0.3, Z=0.6$

$T_g=35\ ^{\circ}C, T_{Cl}=88\ ^{\circ}C, \lambda_{abs}=575$ nm

The effect of UV-irradiation on a planarly-oriented copolymer **6** leads to dramatic changes in the transmission spectra. In the region of selective reflection of light (λ_{max}=540-620 nm) one may observe a well-pronounced absorption peak from the merocyanine form **IV** (λ_{abs}=575 nm), which is produced during the photoprocess (Fig. 10a, curve 2). Once the photostationary state is achieved, transmission of the test samples in this spectral region becomes almost zero (Fig. 10a, curve 3). The action of UV-irradiation also leads to essential changes in the circular dichroism (CD) spectrum (Fig. 10b, curves 1-3). Before irradiation the peak of CD was well-pronounced; after irradiation it completely disappears. Thus the irradiated regions of the copolymer film lost their selective light reflection ability in the spectral region of the absorption of the merocyanine form.

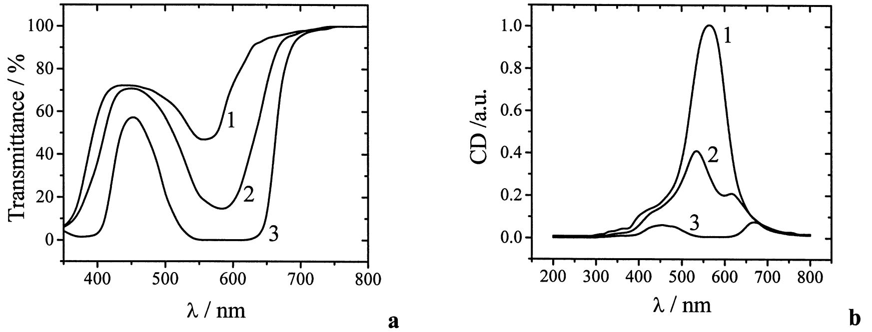


Figure 10. Transmittance (a) and circular dichroism (b) spectra during UV-irradiation (N_2 laser, 337 nm): 1-before irradiation, 2-after 30 s, 3-after achieving the photostationary state (~500s).

This phenomenon make it possible to use such copolymer for data recording. Fig. 11 shows a microphoto of the copolymer film after irradiation through the mask. The transparent white regions are non-irradiated zones, the dark regions correspond to the irradiated regions and contain the merocyanine form capable of a strong light absorption. In the reality they look like the dark pattern on the coloured background.

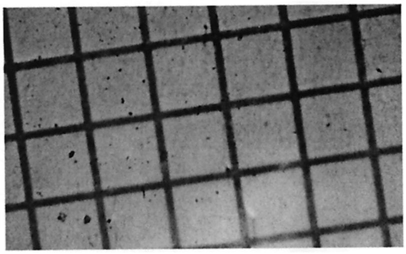


Figure 11. Optical microphoto showing cholesteric planar oriented film after UV-irradiation through the mask. Dark regions correspond to the irradiated zones (width of the dark lines – 25 μm).

Conclusion

All synthesized polymers are multifunctional LC copolymers which can be used as promising candidates for the preparation of new materials for storage of information, colour data recording, colour display technology, holography, colour projection systems and other applications.

Acnowledgments

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References

1. *Applied Photochromic Polymer Systems,* C. McArdle (Ed.), Blackie, Glasgow and London 1992
2. *Polymers as Electrooptical and Photooptical Active Media*, V. Shibaev (Ed.), Springer Verlag, Berlin-Heidelberg 1996
3. *Side Chain Liquid Crystal Polymers,* C. McArdle (Ed.), Blackie, London 1989
4. V. P. Shibaev, I. V. Yakovlev, S. G. Kostromin, S. A. Ivanov, T. I. Zverkova, *Polymer Science USSR.* **32**, 1478 (1990)
5. V. P. Shibaev, S. V. Belayev, *Polymer Science U.S.S.R.*, **32**, 2361 (1991) (in English)
6. V. P. Shibaev, *Intern. J. Polymeric Mater.* **45**, 307 (2000)
7. N. I. Boiko, V. P. Shibaev, *Intern. J. Polymeric Mater.* **45**, 533 (2000)
8. V. P. Shibaev, A. Yu. Bobrovsky, N. I. Boiko, *Polym. Int.* **49**, in press (2000)
9. V. P. Shibaev, A. Yu. Bobrovsky, N. I. Boiko, *Polymer Science, Ser. C*, in press (2000)
10. V. P. Shibaev, *Mol. Cryst. Liq. Cryst.* **243**, 201 (1994)
11. V. P. Shibaev, S. G. Kostromin, S. A. Ivanov, *Polymer Science, Ser. A.* **39**, 118 (1997)
12. A. Yu. Bobrovsky, N. I. Boiko, V. P. Shibaev, *Liq. Cryst.* **25**, 393 (1998)
13. A. Yu. Bobrovsky, N. I. Boiko, V. P. Shibaev, *Liq. Cryst.* **25**, 679 (1998)
14. A. Yu. Bobrovsky, N. I. Boiko, V. P. Shibaev, *Liq. Cryst.* **26**, 1749 (1999)
15. A. Yu. Bobrovsky, N. I. Boiko, V. P. Shibaev, K. Schaumburg, *Polymer Science. Ser. A.* **41**, 107 (1999)
16. A. Yu. Bobrovsky, N. I. Boiko, V. P. Shibaev, *Advanced Materials.* (accepted)
17. A. Yu. Bobrovsky, N. I. Boiko, V. P. Shibaev, *Liq. Cryst.* (in press)
18. S. N. Yarmolenko, L. A. Kutulya, V. V. Vashchenko, L. V. Chepeleva, *Liq. Cryst.* **16**, 877 (1994)
19. A. Yu. Bobrovsky, N. I. Boiko, V. P. Shibaev, *J. Mater.Chem.* **10**, 1075 (2000)
20. A. Yu. Bobrovsky, N. I. Boiko, V. P. Shibaev, *Chem. Mater.* (in press)
21. A. Yu. Bobrovsky, N. I. Boiko, V. P. Shibaev, *Advanced Materials.* **11**, 1025 (1999)
22. A. Yu. Bobrovsky, N. I. Boiko, V. P. Shibaev, *Liq. Cryst.* **27**, 57 (2000)
23. A. Yu. Bobrovsky, N. I. Boiko, V. P. Shibaev, *Liq. Cryst.* **27**, 219 (2000)
24. A. Yu. Bobrovsky, N. I. Boiko, V. P. Shibaev, *Polymer Science, Ser. A* **42**, 43 (2000)