

LIGHT-CONTROLLABLE MULTIFUNCTIONAL CHIRAL PHOTOCHROMIC LIQUID CRYSTAL COPOLYMERS FOR OPTICAL DATA RECORDING AND STORAGE

Valery P. Shibaev, Alexey Yu. Bobrovsky, Natalia I. Boiko

Chemistry Department,
Moscow State University
119899 Moscow, Russia

Introduction

The chiral photochromic liquid-crystalline (LC) copolymers with the helical supramolecular structure are of a significant interest, because their optical properties can be locally and effectively controlled by light irradiation.^{1,2} The principle of the creation of such polymers is based on the synthesis of multifunctional LC side chain copolymers consisting of nematogenic monomer units (favourable to the nematic phase formation), chiral fragments (contributed to the helical supramolecular structure formation) and photochromic groups provided the photosensitivity to the copolymers.^{3,4} Scheme of general molecular structure of such LC copolymers is shown in **Figure 1**.

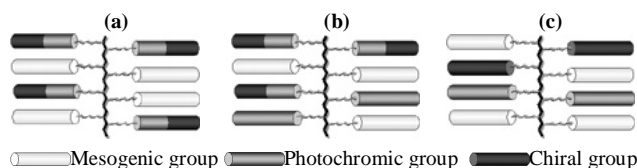


Figure 1. Schemes of molecular structure of multifunctional chiral photochromic LC copolymers

In this paper our attention is focused on the synthesis and study of a novel family of acrylic LC copolymers containing different mesogenic, chiral and photochromic groups sensitive to the light irradiation.

Experimental

Synthesis of polymers. All monomers were synthesized according to the procedures described in our papers.^{3,5,6} The chiral photochromic copolymers were prepared by radical copolymerisation of the corresponding monomers in benzene solutions at 60°C using as initiating agent azobisisobutyronitrile. All the synthesized copolymers were purified by repeated precipitation with methanol and dried under vacuum.

Instrumentation. Gel permeation chromatography (Knauer) was used to determine molecular masses and molecular mass distribution of samples with respect to polystyrene standards. Molecular masses were between 1×10^4 and 2×10^4 , polydispersity was change in the range of 2.0-3.2.

Phase transition temperatures of copolymers were studied by differential scanning calorimetry using a Mettler TA-400 thermal analyzer and a LOMO P-112 polarizing microscope. Selective light reflection of chiral polymers was studied with a Hitachi U-3400 UV-vis-IR spectrometer equipped with a Mettler EP-80 hot stage.

Photochemical and photooptical investigations were performed using a special optical set-up involving a DRSh-250 ultra-high pressure mercury lamp equipped with the filters selected the necessary bands of the linear radiation spectrum of the mercury lamp (313, 366 nm etc). The samples with planar texture were sandwiched between two flat glass plates and illuminated by the irradiation with a certain wavelength. During irradiation a constant temperature of the samples was maintained using a Mettler FP-80 hot stage.

Results and Discussion

The main conception of the work is based on incorporation of the "switchable" photochromic fragments into the chiral LC polymers forming helical supramolecular structure. This is the most readily achieved by the radical copolymerization of mesogenic, chiral and photochromic monomers leading to chiral photochromic LC copolymers (see **Figure 1**), forming the chiral nematic phase.^{2,3,4}

The main specific feature of the chiral nematic phase of LC copolymers is the helical supramolecular structure formed by the side

groups.⁷ For the normal incidence of a light beam upon a planar-oriented texture (with the helix axis perpendicular to the layer), the helix pitch P is related to the wavelength of the maximum selective light reflection by a simple equation

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

where \bar{n} is the average refractive index of the LC polymer. The crucial factor determining the helix pitch is the helical twisting power β , described by

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

where X is the concentration of the chiral fragments.

The value of β of a chiral fragment depend on a number of factors, including its interaction with the LC matrix, temperature, molecular constitution and shape (geometry) of the chiral fragment.

These factors serve a base for the development of light-controllable photochromic LC polymers forming chiral nematic phase. The photochromic switchable fragments play the key role in the photooptical behaviour of the planarly-oriented films of the copolymers. Irradiation of these films by the light with the definite wavelength causes the photoisomerization of photochromic groups accompanied by the change of their configuration and of the β value (**Figure 2**).

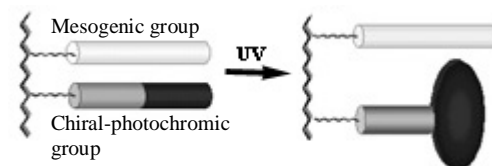


Figure 2. Schematic diagram illustrating the structure of a chiral-photochromic copolymer before and after UV irradiation.

As a result the supramolecular structure and optical properties in the irradiated zones of the polymeric films are drastically changed. Using this concept several series of the new binary and ternary chiral-photochromic copolymers have been synthesized and studied.

Binary chiral-photochromic LC copolymers. A series of binary chiral-photochromic copolymers containing the same nematogenic monomer units and different chiral and photochromic groups combined in the second monomer unit are shown in **Figure 2**:

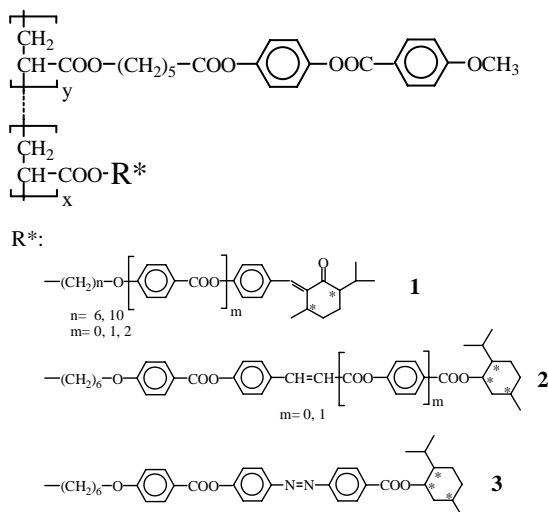


Figure 3. Structural formulae of the chiral photochromic copolymers.

Arabic numerals correspond to the molecular structure of the abovementioned copolymers. All these copolymers form the stable chiral nematic phase and display the selective light reflection over a wide range of the wavelength (500-1500 nm) depending on the concentration of the chiral monomer units. Under UV irradiation photochromic benzilidene-

menthane-3-one fragments undergo E-Z isomerization and their configuration and conformation are essentially changed. Helical twisting power β of new Z-isomer becomes ten times less, then β_1 of the E-isomer.

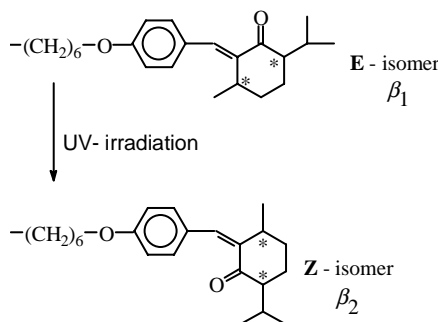


Figure 4. Isomerization of chiral-photochromic side groups of copolymers **1**.

As a result the λ_{max} shifts to longer wavelength after UV-irradiation i.e. the helix is untwisted (**Figure 5**).

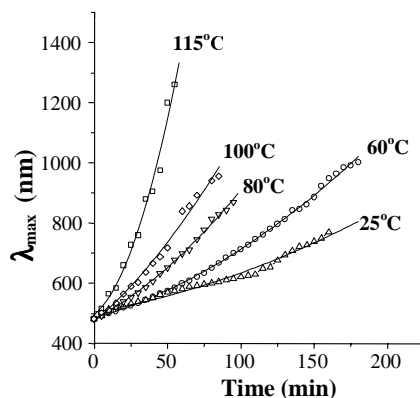


Figure 5: Kinetics of the helix untwisting for copolymer **1** ($n=6$, $m=0$) containing 15 mol% of chiral photochromic units at different temperatures.

Two series of copolymers **1** and **2** were used for irreversible recording of information because E-Z isomerization of their photochromic side groups is irreversible. Another type of "reversible materials" was obtained on the base of copolymers **3**, containing photochromic azo group and chiral menthol fragment. In this case the E-Z isomerization of azobenzene fragments is completely reversible: UV-irradiation leads to the untwisting of the helix and the successive heating of the sample causes the twisting of the helix (**Figure 6**).⁸

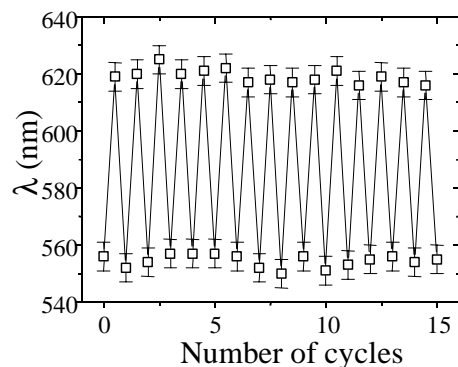
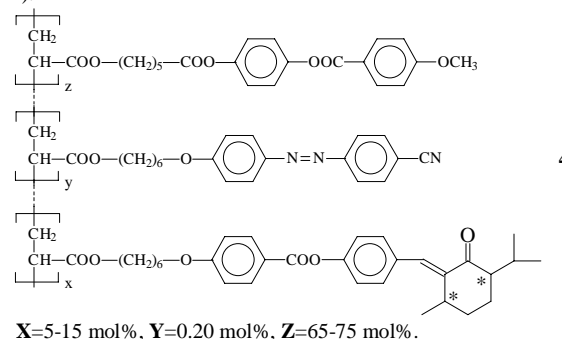


Figure 6. Fatigue resistance of LC copolymer **3** with 15 mol % of chiral photochromic units under the recording – erasing cycles.

Dual photochromism of ternary chiral-photochromic LC copolymers. The existence of two different 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. For this purpose a series of ternary acrylic copolymers of the different compositions consisting of nematogenic groups, chiral fragments and two different photosensitive azobenzene- and benzilidenemethane-3-one-containing groups were synthesized⁹ (**Figure 7**).



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

Figure 7. Molecular structure of ternary chiral photochromic LC copolymers.

These copolymers displaying chiral nematic phase possess the dual photochromism that allows us to record optical data of two types on the same sample: first, using the helix pitch (and λ_{max}) variation under the action of UV-irradiation and second, using the photoinduced birefringence caused by polarized light at wavelengths more than 400 nm.

Conclusion

A new family of multifunctional chiral photochromic LC copolymers has been synthesized and new principle of photoregulation of their optical properties based on the change of helical twisting power of chiral-photochromic fragments under light-irradiation has been developed. It was shown, that incorporation of two different photochromic groups in a single macromolecule allows one to realize the dual photochromism and to record information of two types on the same film – by varying the helix pitch and by inducing the birefringence. The polymers synthesized can be used as the promising candidates for creation of new materials for storage of information, color data recording, color display technology, holography and other applications.

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