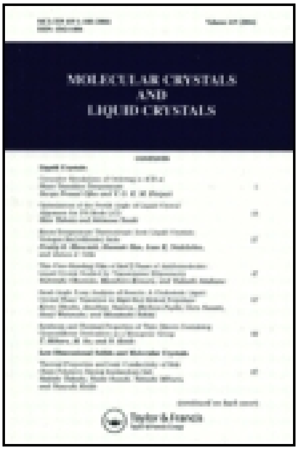

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New Principle of Optical Data Recording Based on Reversible Transition "Selective Reflection – Absorbance" in Photochromic Cholesteric Copolymers

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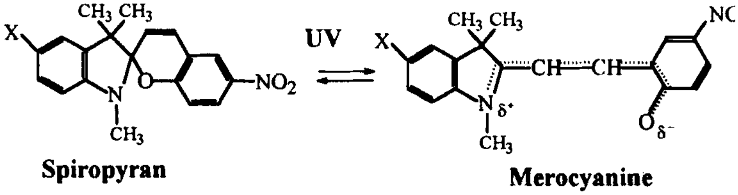
A new principle of information storage based on a realization of the reversible transition «selective reflection-absorbance» in photochromic liquid crystalline (LC) copolymers was suggested. For this purpose a new family of triple copolymers were synthesized by copolymerization of acrylic monomers, containing nematogenic (phenylbenzoate), chiral (cholesterol), and photochromic (spiropyran) fragments. Phase behaviour and optical properties of copolymers were studied. Isomerization of spiropyran groups and formation of merocyanine form under UV-irradiation (337 nm) of the polymer films was observed. It should be noted that the maximum of the absorbance of polymer films coincides with maximum of selective light reflection. As a result the disappearance of the selective light reflection in the irradiated regions of the films occurs. Scheme of the optical data recording and reading of information recorded on planarly oriented films of such copolymers was proposed.

Keywords: cholesteric copolymers; photochromic spiropyran-containing groups; optical photorecording

INTRODUCTION

Liquid-crystalline (LC) polymers containing photochromic side groups have attracted a great interest from the viewpoint of their application as unique materials for data recording and storage. Many publications were devoted to the comb-shaped LC polymers containing side-chain azobenzene groups[1-2]. At the present time, the appearance of photoinduced birefringence in the films of such polymers under the action of polarized light and possible application of such materials for data recording were studied in detail.

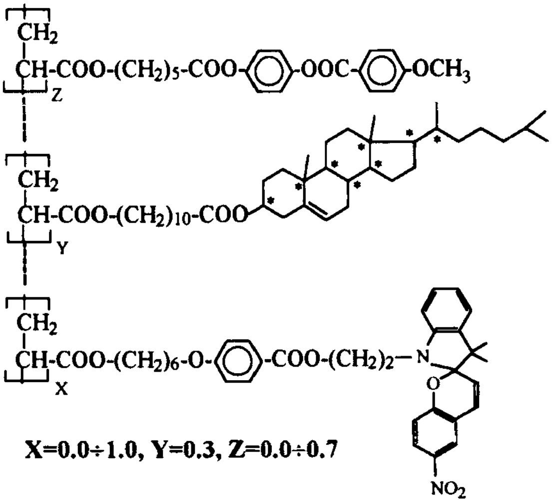
Another wide class of photochromic compounds involve derivatives of spiropyran and spirooxazine[1, 3-5]. These compounds are characterized by a marked photochromism. In this case UV irradiation of such compounds leads to the appearance of an intensive absorption peak in the visible spectral region (550-620 nm). The above mentioned changes are provided by the transition of spiro forms of such compounds to merocyanine form[1, 3, 4]:



This process is thermally and photochemically reversible. This fact allows one to use such compounds for repeated data recording and optical data storage.

Numerous works were devoted to the synthesis and study of photosensitive polymers containing spiropyran and spirooxazine side groups[1, 6-8]. However, one should note that, despite an active studying such polymer LC systems, no information concerning cholesteric phase (or chiral nematic) of polymers containing such photochromic groups is available. Combination of photochromic properties and helical supramolecular structure in the one and the same polymer system offers wide opportunities for varying optical properties of such materials under the action of external fields (electric and magnetic fields) and light irradiation. Furthermore, the presence of photosensitive units allow one to use such copolymers for reversible data recording at coloured (with selective light reflection) background.

In this work the following copolymers have been synthesized and studied:


I

II

III

X=0.0÷1.0, Y=0.3, Z=0.0÷0.7

As is seen these copolymers contain three different types of side groups: nematogenic phenylbenzoate groups (I), chiral cholesterol groups (II), and photochromic spiropyran groups (III). The presence of phenylbenzoate and cholesterol groups should provide the formation of chiral nematic mesophase[9], possessed a certain selective light reflection wavelength, whereas spiropyran groups are responsible for photochromic properties. Taking into account the above reasoning, the principal objective of this work is to characterise the features of photo-optical behaviour of photochromic chiral copolymers and to study the possibility of data recording using such systems.

EXPERIMENTAL

Nematogenic (I) chiral (II) and photochromic (III) monomers were synthesized according to the procedures described in[10-12].

The copolymers were synthesized by radical copolymerization of monomers in benzene solution at 60°C; AIBN was used as an initiating agent. Synthesized copolymers were purified by the repeated precipitation with methanol and dried in vacuum (Yields 70-90%).

IR spectra were recorded on a Bruker IFS-88 spectrophotometer using KBr pellets.

Relative molecular weight of copolymers was determined by gel permeation chromatography (GPC). GPC analysis was performed in THF on Knauer set up equipped with Ultrastyragel 8×300 mm column (Waters) having pore size 10^3 Å, detectors – RI Waters R-410 and UV spectrometer Knauer. Waters 19×300 mm column fulfilled with Ultrastyragel 10^3 Å was used for preparative GPC. The copolymers obtained have the following molecular mass characteristics: M_n=11000-18000, M_w/M_n=2.5-3.2[#].

Phase transitions were studied by differential scanning calorimetry (DSC) with a Mettler TA-4000 thermosystem at a scanning rate of 10 K/min. The polarising microscopic investigations were performed using a Mettler FP-800 central processor equipped with a hot stage Mettler FP-82 and control unit in conjunction with a Lomo R-112 polarising microscope. Selective light reflection of polymers was studied with a Hitachi U-3400 UV-Vis-IR spectrometer equipped with a Mettler FP-80 hot stage. The 20-μm-thick samples were sandwiched between the two flat glass plates. The thickness of the test samples was preset by Teflon spacers. Planar texture was obtained by shear deformation of the samples, which were heated to temperatures above glass transition temperature. Prior to tests, the test samples were annealed for 20-40 min.

CD spectra were recorded using spectropolarimeter “JASCO J-500C”.

Photochemical properties were studied with a special equipment using a N_2 laser (337 nm) “ILGI-503”. During illumination, the constant temperature of the test samples placed between two flat quartz plates was maintained using a Mettler FP-80 heating unit. The intensity of UV radiation was equal to 66.1 mW/cm^2 (as measured by “IMO-2N” intensity meter).

Photochemical properties of copolymers were studied by illuminating the 20-μm-thick films at 25 °C. After irradiation the absorption spectra were recorded.

[#] The mean degree of polymerization (~40) and large polydispersity implies a considerable content of low molar mass oligomers.

RESULTS AND DISCUSSION

Examination of the experimental data shows that, in a wide temperature range, the copolymers with relatively low dye units contents are able to produce chiral nematic phase (N*, see phase diagram on Figure 1a). Planar texture of these copolymers is characterized by selective reflection of circularly polarized light (minimum transmission corresponds to maximum of selective reflection of light) in a visible spectral region (λ_{max} = 540-620 nm, see Figure 1b and Figure 2, curve 1'), which is associated with the presence of left-handed helical supramolecular structure.

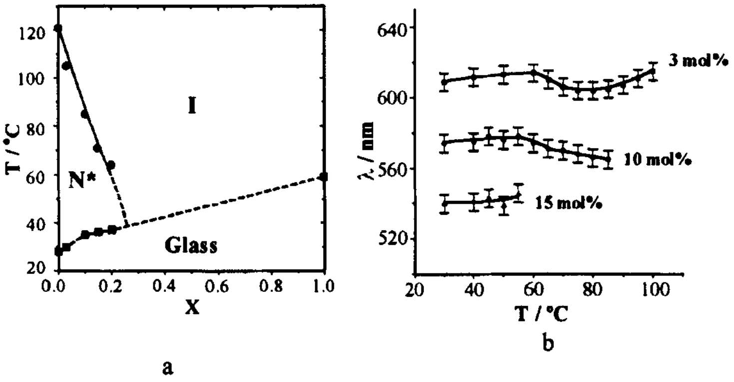


FIGURE 1. (a) Phase diagram for copolymers with different molar fraction (X) of spiropyran-containing units (I – isotropic melt, N* - chiral nematic phase, and "Glass" – glass state of copolymers). (b) Temperature dependence of selective light reflection wavelength (λ_{max}) for copolymers with different concentration of the dye units.

Note that λ_{max} and, correspondingly, helix pitch are almost independent of temperature, that is, the sample is monochromic in the whole temperature region of the existence of mesophase. On cooling below T_g, helical supramolecular structure of copolymers film is fixed in glassy state.

The effect of UV irradiation on planarly oriented film of polymers leads to dramatic changes in the corresponding transmission spectra (Figure 2, curves 2' and 3'). In the region of selective reflection, one may observe a well-pronounced absorption peak of merocyanine form (λ_{max} = 575 nm), which is produced during photoprocess (Figure 2, curve 2). Once photostationary state is achieved, transmission of the test samples in this spectral region becomes almost zero (Figure 2, curve 3').

As was mentioned earlier, planar oriented films of copolymers are characterized by selective light reflection of the left-handed circularly polarized light, and this fact is well seen in the spectra of circular dichroism (Fig. 2, curve 1). These spectra show an intensive peak, whose maximum coincides with maximum selective light reflection. The action of UV irradiation leads to essential changes in the CD spectrum (Figure 2, curves 2 and 3). Before irradiation, the peak of CD was well-pronounced; after radiation, it completely degenerates. The appearance of two poorly pronounced maxima of CD, instead of one intensive peak, is likely to be associated with the fact that the width of absorption band of the formed merocyanine form is somewhat smaller that the width of the band corresponding to the initial peak of CD. This phenomenon suggests that the irradiated regions of copolymer film lost their ability of selective light reflection in the spectral region of the absorption of merocyanine form.

These drastic light-induced changes in the optical properties make it possible to use such materials for data recording. The possible procedure of data recording and read-out is presented in Figure 3. After irradiation through the mask, read-out is performed by scanning the sample with light of a wavelength corresponding to the maximum of selective light reflection. When nonirradiated regions are scanned, selective light reflection of the left-handed circularly polarized light is observed; when the irradiated regions are scanned, almost complete light absorption takes place.

Figure 4 shows the microphoto of the copolymer film after irradiation through the mask. The transparent green regions are nonirradiated ones; the dark regions correspond to the irradiated regions and contain merocyanine form capable of a strong light absorption. They look like as the dark stripes on the colour background (Figure 4).

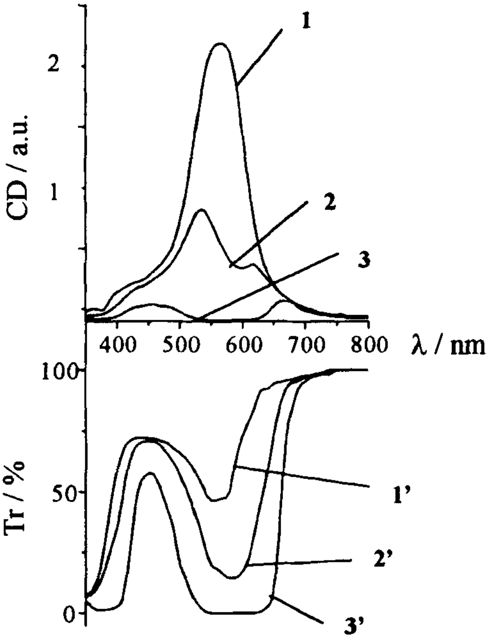


FIGURE 2. Circular dichroism (1-3) and transmittance (1'-3') spectra changes during the UV irradiation: 1) before irradiation; 2) after 30 sec of UV irradiation; 3) after achieving of the photostationary state (500 sec).

This process is thermally reversible. At 25°C, half-life of reverse reaction to spiropyran form of these copolymers is equal to about 15 h; however, this period is much longer than those of the earlier studied amorphous spiropyran polymers[1, 6-8]. In this case, LC order is likely to exert a stabilizing effect on merocyanine form. Rate of the reverse reaction may be strongly increased by the visible light irradiation.

Hence, in this work, we demonstrated an approach for the development of a new family of materials with controlled photo-optical characteristics. This approach is based on the introduction of some photosensitive units (in our case spiropyran) to the matrix of cholesteric copolymers. In this case, the ratio between different fragments in copolymers should be selected so that the maximum selective light reflection of cholesteric copolymers should coincide with the maximum light reflection of photoinduced new form (in our case merocyanine form) produced during UV irradiation.

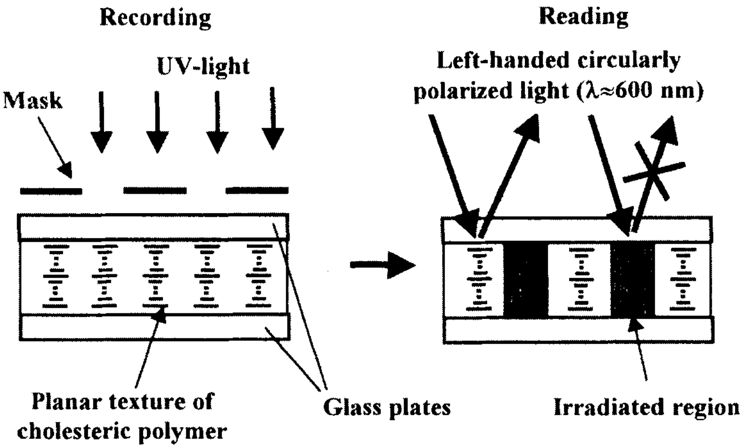


FIGURE 3. Principal scheme of the optical data recording on planarly oriented film of photochromic cholesteric copolymer (left part) and reading of information from the same film (right part).

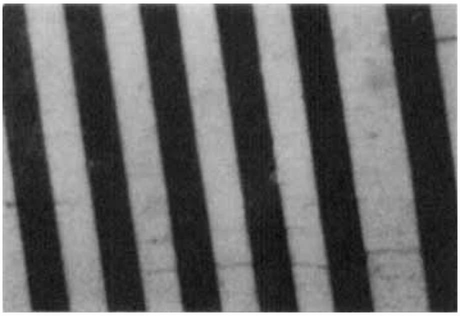


FIGURE 4. Optical microphoto showing cholesteric planar oriented film after UV irradiation through the mask. Dark regions correspond to the irradiated regions (width of dark line - 25μm).

See Color Plate XV at the back of this issue.

Acknowledgements

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