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A. Yu. Bobrovsky; N. I. Boiko; V. P. Shibaev

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Photosensitive cholesteric copolymers with spiropyran-containing side groups

I. Phase behaviour and photo-optical properties

A. YU. BOBROVSKY, N. I. BOIKO and V. P. SHIBAEV*

Faculty of Chemistry, Moscow State University, Leninskie gory, Moscow,
119899 Russia

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A number of terpolymers were synthesized by copolymerization of nematogenic, chiral and photochromic monomers with different contents of spiropyran photosensitive side groups. The synthesized copolymers possess selective light reflection in the visible region of the spectrum. Action of UV light on planarly-oriented films of the copolymers leads to the formation of the merocyanine form of the dye with a maximum of absorbance coinciding with the selective light reflection peak. The 'degeneration' of the selective light reflection is observed during this process. It was shown that such types of material can be used for reversible information storage; the principal scheme for the processes of optical data recording and reading is suggested.

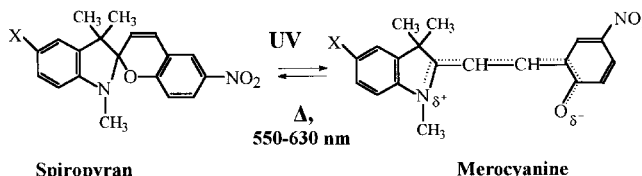
1. Introduction

Liquid crystalline (LC) polymers containing photochromic side groups have attracted great interest from the viewpoint of their application as unique materials for data recording and optical data storage. Many publications have been devoted to comb-shaped LC polymers containing azobenzene side groups [1–6]. The appearance of induced birefringence in films of such polymers under the action of polarized light, and the possible application of such materials for data recording, have been studied in detail.

Recently a number of publications concerning photosensitive cholesteric copolymers with variable pitch of the helix have appeared [7–10].

Another wide class of photochromic compounds involves derivatives of spiropyran and spiro-oxazine [11, 12]. These compounds are characterized by a marked photochromism. In this case, UV irradiation leads to the appearance of an intense absorption peak in the visible spectral region (550–630 nm) which is

explained by the transition of the spiro form of such compounds into the merocyanine form [11–13]:

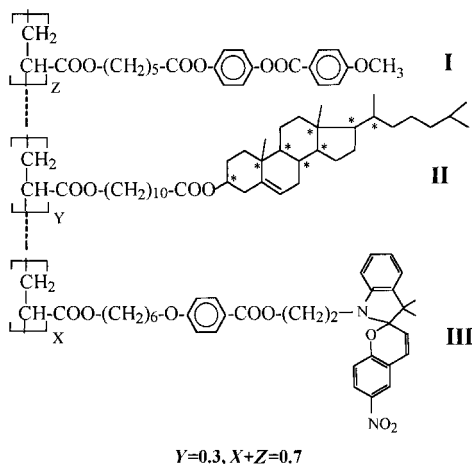


This process is thermally and photochemically reversible, allowing one to use such compounds in various devices for repeated data recording and optical data storage.

Numerous studies have been devoted to photosensitive polymers containing spiropyran and spiro-oxazine side groups [14]. However, one should note that, despite intensive studies of polymeric LC systems of this kind [14–17], no information concerning cholesteric polymers containing such photochromic groups is available. The combination of photochromic properties and a helical supramolecular structure in a united polymer system offers wide opportunities for varying the optical properties of such materials under the action of external fields (electric and magnetic) and light irradiation. Furthermore, the presence of photosensitive units allows one to use such copolymers for reversible data recording on a coloured (with selective light reflection) background.

* Author for correspondence
e-mail: lcp@libro.genebee.msu.su

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



As follows from the above formula, these copolymers contain three different types of side group: nematogenic phenyl benzoate groups (I), chiral cholesteryl-containing groups (II), and photochromic spiroopyran groups (III). The presence of phenyl benzoate and cholesteryl groups should provide for the development of a chiral nematic mesophase [18, 19] possessing the property of selective light reflection at a certain wavelength, whilst the spiroopyran groups are responsible for the photochromic properties. Taking into account the above reasoning, the principal objective of this work concerns the synthesis of photochromic chiral copolymers with different contents of spiroopyran units (III), and the study of their photo-optical behaviour, as well as of any manifestation of the possibility of using these copolymers for optical data recording.

2. Experimental

2.1. Synthesis of monomers

The following chemicals were used without further purification: dicyclohexylcarbodiimide (Fluka), *N,N*-dimethylaminopyridine (Fluka), 1'-(1-hydroxyethyl)-3',3'-dimethyl-6-nitro-spiro[2H-1-benzopyran-2,2'-indoline] (NIOPIK). 4-(6-Acryloyloxyhexyloxy)benzoic acid was prepared according to [20].

Cholesteryl-containing and nematogenic monomers were synthesized according to procedures described in [21, 22]. Figure 1 shows a schematic representation of the synthesis of the photochromic monomer.

2.1.1. Synthesis of the photochromic monomer

1'-(1-(4-(6-acryloyloxyhexyloxy)benzoyloxyethyl)-3',3'-dimethyl-6-nitro-spiro[2H-1-benzopyran-2,2'-indoline])

To a solution of 1.32 mmol of 1'-(1-hydroxyethyl)-3',3'-dimethyl-6-nitro-spiro[2H-1-benzopyran-2,2'-indoline] and 1.98 mmol of 4-(6-acryloyloxyhexyloxy)benzoic acid

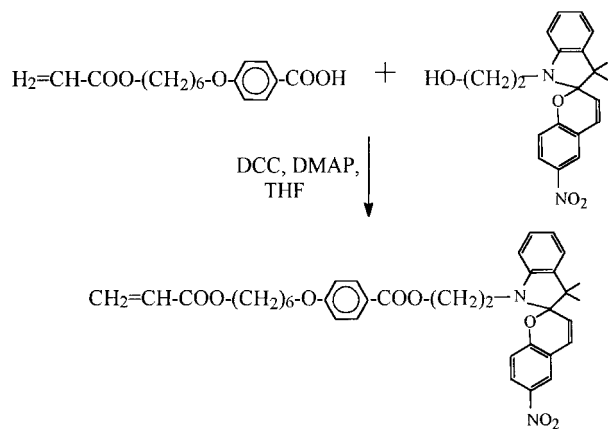


Figure 1. Scheme of synthesis for the photochromic acrylic monomer (DCC = dicyclohexylcarbodiimide, DMAP = *N,N*-dimethylaminopyridine, THF = tetrahydrofuran).

in 10 ml of purified THF, 0.20 mmol of *N,N*-dimethylaminopyridine was added. Then 1.98 mmol of dicyclohexylcarbodiimide were added and the resulting solution was stirred for 3 days. The precipitate was filtered off, washed with THF, and diethyl (50 ml) added to the filtrate. The ether layer was washed successively with water, 5% aqueous acetic acid, and finally with water until a pH of 7 was achieved. The ether extract was dried with anhydrous MgSO_4 . After removal of solvent the white crude product was purified by column chromatography (eluent toluene–ethyl acetate 10:1). Yield 56%, m.p. 90–93°C IR (cm^{-1}): 2944, 2888, 2864 (CH_2), 1716 (CO), 1645, 1635 (C=C), 1608, 1588 (C–C in Ar), 1514, 1336 (NO_2), 1265 (COC).

2.2. Polymerization

The copolymers were synthesized by radical copolymerization of the three monomers in benzene solution at 60°C; AIBN was used as initiating agent. All the synthesized copolymers were purified by repeated precipitation with methanol and dried in vacuum. Yields from the polymerization and molar mass characteristics of the copolymers are summarized in the table.

Table. Yields and molecular masses of homopolymers and dye-containing copolymers. *X*, *Y* and *Z* correspond to the concentrations of spiroopyran, cholesteryl and phenyl benzoate monomer units, respectively.

<i>X</i>	<i>Y</i>	<i>Z</i>	Yield/%	$M_n \times 10^{-3}$	M_w/M_n
0	0.30	0.70	80	8200	2.1
0.03	0.30	0.67	77	9500	2.5
0.10	0.30	0.60	88	7600	2.3
0.15	0.30	0.55	80	8100	2.9
0.20	0.30	0.50	72	6300	2.3
1.00	0	0	82	7200	2.8

2.3. Physical properties

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

Relative molecular masses of polymers were determined by gel permeation chromatography (GPC) using a GPC-2 Waters instrument equipped with an LC-100 column oven and a Data Modul-370 data station (table 1). Measurements were made using a UV detector, THF as solvent (1 ml min^{-1} , 25°C), a set of PL columns of 100, 500 and 10^3 \AA , and a calibration plot constructed with polystyrene standards.

Phase transitions in the copolymers were studied by differential scanning calorimetry (DSC) with a scanning rate of 10 K min^{-1} . All experiments were performed using a Mettler TA-400 thermal analyser and a LOMO P-112 polarization microscope. Selective light reflection from films of the chiral polymers was studied using a Hitachi U-3400 UV-Vis-IR spectrometer equipped with a Mettler FP-80 hot stage. The $20 \mu\text{m}$ thick samples were sandwiched between two flat glass plates. The thickness of the test samples was preset by Teflon spacers. Planar textures were obtained by shear deformation of samples heated to temperatures above the glass transition temperature. Prior to tests, samples were annealed for 20–40 min at appropriate temperatures.

X-ray diffraction analysis was carried out using a URS-55 instrument (Ni-filtered CuK_α -radiation, $\lambda = 1.54 \text{ \AA}$).

2.4. Photochemical properties

Photochemical properties were studied using specialized equipment and a N_2 laser (337 nm) ILGI-503. During irradiation, 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 66.1 mW cm^{-2} (measured by an IMO-2N intensity meter). The photochemical properties of the copolymers were studied by irradiation of the $20 \mu\text{m}$ thick films at different temperatures. After irradiation the absorption spectra were recorded.

3. Results and discussion

3.1. Phase behaviour and optical properties of the chiral photochromic copolymers

The terpolymers synthesized in our work contain a constant amount of cholesteryl-containing units ($Y = 30 \text{ mol \%}$); contents of spiropyran units varied from 0 to 20 mol %. With the homopolymer (100 mol % spiropyran) this allowed us to draw the full phase diagram in figure 2.

As shown in figure 2, copolymers with contents of spiropyran units less than 20 mol % form a chiral nematic (N^*) mesophase, increase in dye unit concentration leading to a dramatic decrease in the clearing temperature of the samples. As similar behaviour was observed

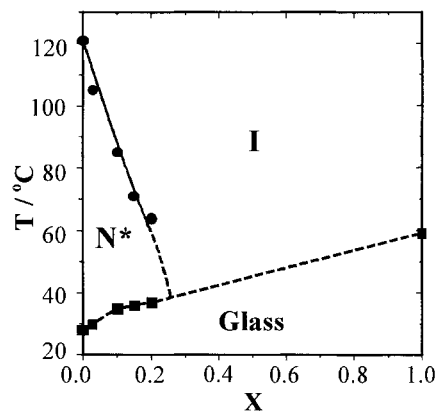


Figure 2. Phase diagram for copolymers with different molar fractions (X) of spiropyran-containing units.

earlier [16] for achiral spiropyran-containing copolymers and was associated with the poor longitudinal anisotropy of the spiropyran side groups and, as a result, their non-mesogenic character.

The formation of the N^* mesophase gives the appearance of selective light reflection for copolymers with spiropyran unit contents of 3–15 mol % (figure 3).†

First of all it is pointed out that an increase in the content of dye-containing groups leads to a noticeable shift of the selective light reflection to the short wavelength region of spectrum. This seems to be associated with the fact that the relative concentration of chiral units in comparison with phenyl benzoate nematogenic units is increasing, and that the dye units play a ‘passive’ role, i.e. do not take part in the formation of the helical supramolecular structure.

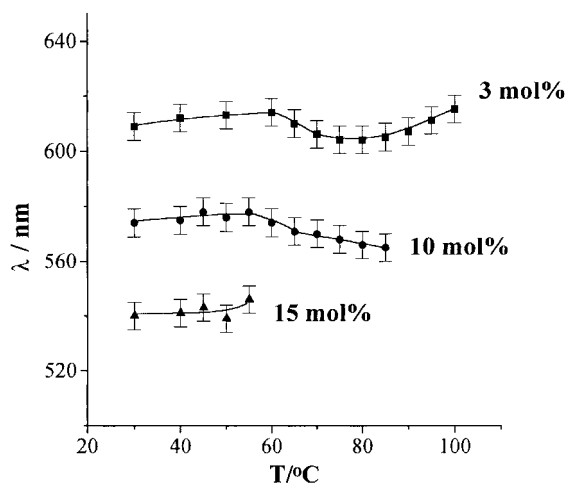


Figure 3. Temperature dependence of selective light reflection wavelength (λ_{max}) for copolymers with different concentrations of dye units.

† Selective light reflection from copolymers with $X = 20 \text{ mol \%}$ was very poor and we could not assess it due to texture defects.

As shown in figure 3, when the temperature decreases the selective reflection wavelength (λ_{max}) slightly increases or decreases, which is probably due to variations in growth of smectic order fluctuations. This phenomenon agrees with recently published data for thoroughly investigated cholesteric copolymers with chiral and nematogenic units of the same structure [18, 19, 21, 22]. In the present case the existence of 'smectic fluctuations' was confirmed by X-ray investigations: a small angle reflection was observed in the X-ray pattern of the copolymers, together with a diffuse halo in the wide angle region ($2\theta \sim 20^\circ$), as shown in figure 4.

3.2. The use of photochromic copolymers for optical data recording

In order to assess the possibilities of using the synthesized copolymers for optical data recording, we investigated in detail the photo-optical properties of the copolymer with 10 mol % of dye units, because in this case the selective light reflection peak ($\lambda_{\text{max}} = 585$ nm, figure 3) almost coincides with the absorbance peak of the merocyanine form ($\lambda_{\text{max}} = 575$ nm, figure 5) that is produced.

The effect of UV irradiation on the planar oriented film of polymer leads to dramatic changes in the corresponding transmission spectra (figure 5, transmittance minimum corresponds to a maximum of selective light reflection). In the region of selective reflection, one may observe a very pronounced absorption peak of the merocyanine form ($\lambda_{\text{max}} = 575$ nm), which is produced during the photoprocess. Once a photostationary state is achieved, transmission of the test samples in this spectral region becomes almost zero.

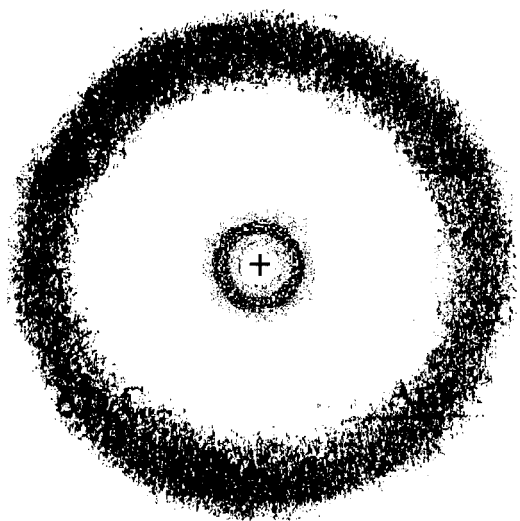


Figure 4. X-ray pattern obtained at 25°C for copolymer with 20 mol % of dye units.

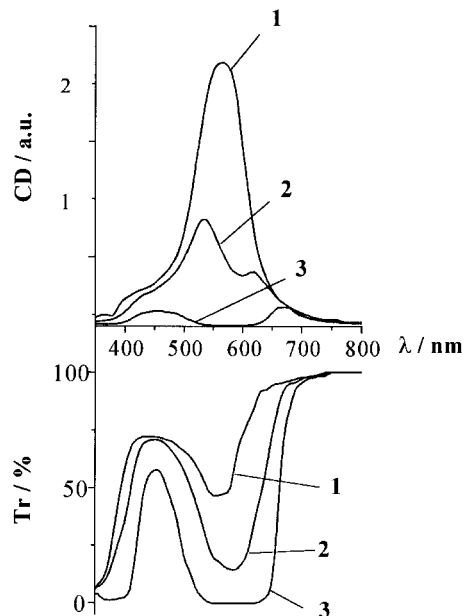


Figure 5. Circular dichroism (1–3) and transmittance (1–3) spectra of copolymer (10 mol % of dye groups) as a function of UV irradiation: (1) before irradiation; (2) after 30 s of UV irradiation; (3) after achieving a photostationary state (500 s).

As mentioned earlier, planar oriented films of copolymers are characterized by selective light reflection of left-handed circularly polarized light, and this fact is clearly seen in the circular dichroism spectrum (figure 5, curve 1). This spectrum shows an intense peak, whose maximum coincides with the maximum of selective light reflection. The action of UV irradiation leads to essential changes in the CD spectrum (figure 5, curves 2 and 3). Before irradiation, the CD peak was well-pronounced; after radiation, it completely degenerates. The appearance of two poorly pronounced maxima in the CD spectrum, instead of one intense peak, is likely to be associated with the fact that the width of the absorption band of the merocyanine form is somewhat smaller than the width of the band corresponding to the initial CD peak. This suggests that the irradiated regions of copolymer film have lost their property of selective light reflection in the spectral region of the absorption of the merocyanine form.

These drastic light-induced changes in the optical properties would make it possible to use such materials for data recording. The possible procedure for data recording and read-out is presented in figure 6.

After irradiation through the mask, read-out is performed by scanning the sample with light of a wavelength corresponding to the maximum of the selective light reflection. When non-irradiated regions are scanned, selective light reflection of the left-handed circularly

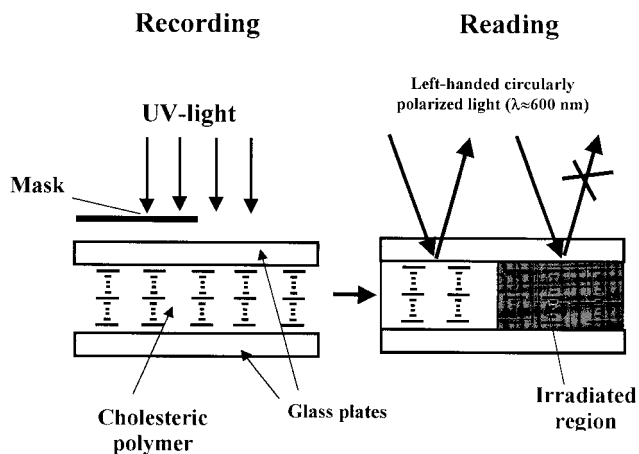


Figure 6. Principal scheme for optical data recording on a planar oriented film of photochromic cholesteric copolymer (left part) and for the reading of the information from the same film (right part).

polarized light is observed; when the radiated regions are scanned, almost complete light absorption takes place.

Figure 7 shows the microphotograph of a copolymer film after radiation through a mask. The transparent yellow–green bands are non-irradiated regions; the dark regions correspond to irradiated regions and contain the merocyanine form of the dye, capable of strong light absorption. They appear as dark stripes on a coloured background (figure 7).

It should be stressed that the suggested approach provides a high recording density due to the low mobility of the chemically bound side groups in the glassy state (the highest density values may be limited only by the

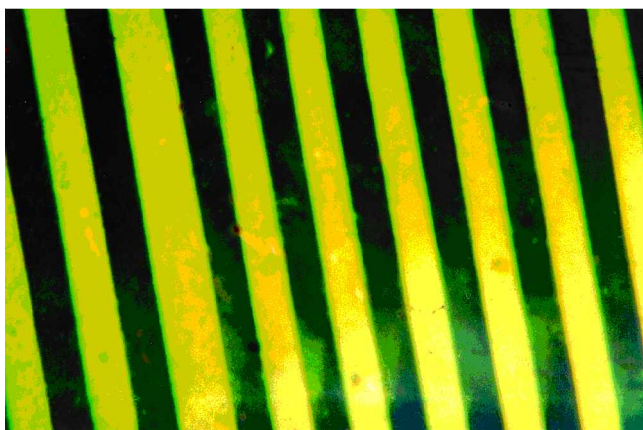


Figure 7. Optical microphotograph showing a cholesteric planar oriented film after UV irradiation through a mask. Copolymer with 10 mol % of spiropyran groups was used and the dark bands correspond to the irradiated regions.

scanning light wavelength). It must be pointed out that the given photoprocess is thermally reversible, and its kinetic features will be considered in a further publication.

In conclusion, analysis of the data concerning the photo-optical behaviour of the copolymers synthesized demonstrates the possibility of using such copolymers for reversible optical data recording.

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