

plating solution using a similar rinsing procedure. When gold is plated onto platinum at the second bimetal junction, plating is inefficient (presumably because hydrogen is evolved at the platinum electrode in the gold plating solution) before the cathode surface resembles bulk gold. The result is the loss of ca. 1 C of gold. Therefore, in order to make a symmetric tipped rod, an extra 1 C of gold must be applied to the second tip.

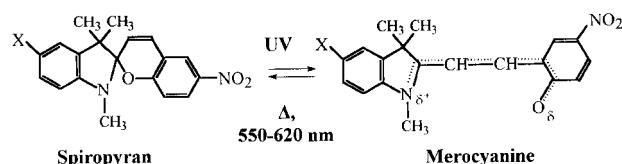
- [10] Some minor variation ($\pm 8\%$) in rod length was still observed due in part to "hot spots" in the sonicator bath, where agitation due to standing waves is particularly violent. This effect was minimized by using a sweep frequency sonicator (Crest Ultrasonics), which modulates the sonication frequency ± 1 kHz.
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- [26] Rods, suspended in ca. 2 mL hexane, were added to 2 mL of 1 mM 1-butaneisocyanide (BIC, Acros) and allowed to react for 18 h. During this time, the solution was shaken several times. The rods were collected and rinsed by 5 centrifugation/resuspension cycles with hexane, and then 1 cycle with ethanol. The rods were resuspended by sonicating briefly in ethanol. This suspension was added to 2 mL of 1 mM 2-mercaptoethylamine (MEA, Aldrich), and was allowed to react for 18 h. Isocyanide groups were displaced from gold by thiols, but not from platinum. The rods were washed and centrifuged with ethanol five times, then suspended in 10 mL of ethanol and purged with argon for 10 min. 5 mL ethanol containing 20 mg Rhodamine B isothiocyanate (Aldrich) was added, and the solution was stirred for 18 h under a positive pressure of Ar. The rods were rinsed and centrifuged 10 times with ethanol. A drop of the resuspended rods was placed on a quartz microscope slide, blotted with filter paper, and allowed to dry.

Photosensitive Cholesteric Copolymers with Spiropyran-Containing Side Groups: Novel Materials for Optical Data Recording**

By Alexey Yu. Bobrovsky, Natalia I. Boiko, and Valery P. Shibaev*

Liquid-crystalline (LC) polymers containing photochromic side groups have attracted great interest because of their potential application as unique materials for data recording and optical data storage. Many publications have been devoted to comb-shaped LC polymers containing side-chain azobenzene groups.^[1,2] The appearance of induced birefringence in the films of such polymers under the action of polarized light and possible applications of such materials for data recording have been studied in detail.

Another wide class of photochromic compounds involves derivatives of spiropyran and spirooxazine.^[1,3-5] These compounds are characterized by a marked photochromism. In this case, UV irradiation leads to the appearance of an intensive absorption peak in the visible spectral region (550–620 nm), which is explained by the transition of the spiro forms of such compounds to merocyanine forms, as shown in Scheme 1.^[1,3,4] This process is thermally and photochemically reversible, which allows one to use such compounds for repeated data recording and optical data storage.



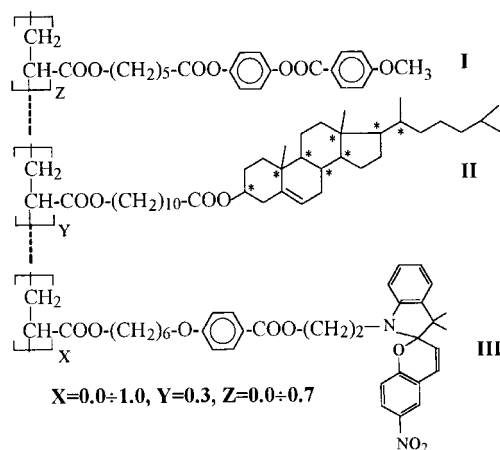
Scheme 1.

Numerous works have been devoted to photosensitive polymers containing spiropyran and spirooxazine side groups.^[1,6-8] However, one should note that, despite intensive study, no information concerning cholesteric polymers containing such photochromic groups is available. A combination of photochromic properties and helical supramolecular structure in the united 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 on colored backgrounds (with selective light reflection).

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The copolymers that have been synthesized and studied in this work are presented in Scheme 2. These copolymers contain three different types of side groups: nematogenic phenylbenzoate (I), chiral cholesterol-containing (II), and photochromic spiropyran (III). The presence of phenylbenzoate and cholesterol groups should permit the development of a chiral nematic mesophase,^[9] possessing the selective light reflection at a certain wavelength, whereas spiropyran groups are responsible for the photochromic properties. Taking into account the above reasoning, the principal objective of this work was the synthesis and study of photo-optical behavior in photochromic chiral copolymers and the possibility of usage of these copolymers for optical data recording.



Scheme 2.

Examination of the phase behavior of copolymers synthesized showed that the samples with relatively low dye contents are able to produce the chiral nematic phase (N*, Fig. 1) over a wide temperature range. The planar texture of these copolymers is characterized by selective reflection of circularly polarized light (minimum transmission corresponds to maximum selective reflection of light) in a visible spectral region ($\lambda_{\max} = 540\text{--}620$ nm; Fig. 2 and Fig. 3, curve 1'), which is associated with the presence of left-handed helical supramolecular structure. Note that

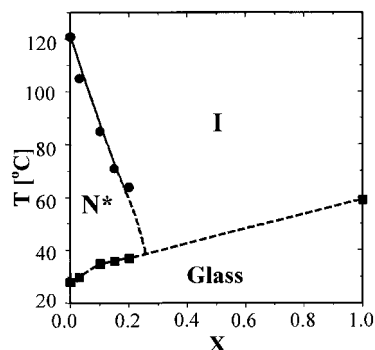


Fig. 1. Phase diagram for copolymers with different molar fraction (X) of spiropyran-containing units: I = isotropic melt, N* = chiral nematic phase, and Glass = glassy phase.

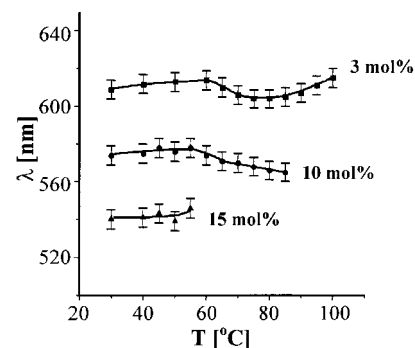


Fig. 2. Temperature dependence of selective light reflection wavelength (λ_{\max}) for copolymers with different concentrations of the dye units.

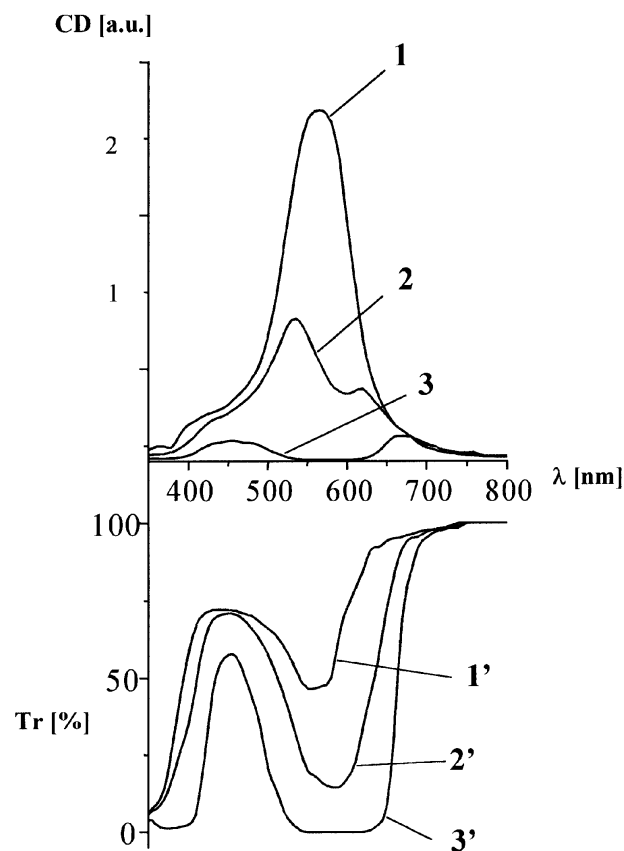


Fig. 3. Circular dichroism (CD; 1–3) and transmittance (Tr; 1'–3') spectra during the UV irradiation: 1) before radiation; 2) after 30 s; 3) after achieving the photostationary state (500 s).

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

The effect of UV irradiation on a planarly oriented polymer film leads to dramatic changes in the corresponding transmission spectra (Fig. 3, curves 2' and 3'). In the region of selective reflection, one may observe a well-pronounced absorption peak from the merocyanine form ($\lambda_{\max} = 575$ nm), which is produced during the photoprocess

(Fig. 1, curve 2). Once the photostationary state is achieved, transmission of the test samples in this spectral region becomes almost zero (Fig. 1, curve 3').

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

These drastic light-induced changes in the optical properties make it possible to use such materials for data recording. A possible procedure for data recording and read-out is presented in Fig. 4a. After irradiation through the mask, read-out is performed by scanning the sample with light of a wavelength corresponding to the maximum selective light reflection. When non-irradiated 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 4b shows a microphoto of the copolymer film after irradiation through the mask. The transparent green regions are non-irradiated ones; the dark regions correspond to the irradiated regions and contain the merocyanine form capable of a strong light absorption. They look like dark stripes on the colored background (Fig. 4b).

However, the back thermal process still remains an important problem. At 25 °C, the half-period of the back dark reaction of these copolymers to spiropyran form is equal to about 15 h; however, this period is much longer than those of the amorphous spiropyran polymers studied earlier.^[1,6-8] In this case, LC order is likely to exert a stabilizing effect on the merocyanine form.

Hence, in this work, we have demonstrated an approach to the development of a new family of materials with controlled photooptical characteristics. This approach is based on the introduction of 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, the merocyanine form) formed during UV irradiation.

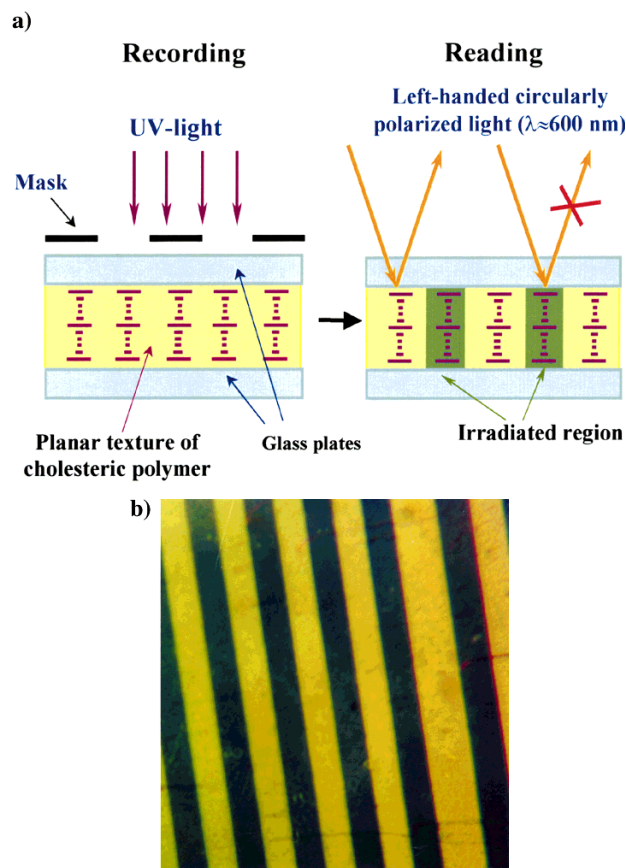


Fig. 4. a) Principle scheme of the optical data recording on planarly oriented film of photochromic cholesteric copolymer (left) and reading information from the same film (right). b) Optical micrograph showing cholesteric planar oriented film after UV irradiation through mask, dark regions correspond to the irradiated regions (width of dark line = 25 μm).

Experimental

Synthesis: Nematogenic phenylbenzoate (I) and cholesterol-containing (II) monomers were synthesized according to procedures described earlier [10,11].

Synthesis of photochromic monomer 1'-(1-(4-(6-acryloyloxyhex-1-yloxy)-benzoyloxyethyl)-3',3'-dimethyl-6-nitro-spiro [2H-1-benzopyran-2,2'-indoline]) (III) was carried out according to the following procedure.

To a solution of 1.32 mmol of 1'-(1-hydroxyethyl)-3',3'-dimethyl-6-nitro-spiro[2H-1-benzopyran-2,2'-indoline] (NIOPIK company, Russia) and 1.98 mmol of 4-(6-acryloyloxyhexa-1-yloxy)-benzoic acid [12] in 10 mL of purified THF was added 0.20 mmol of 4-(N,N'-dimethyl)aminopyridine. Then 1.98 mmol of dicyclohexylcarbodiimide was added and the resulting solution was stirred for 3 days. The precipitate formed was filtered, washed with THF, and diethyl ether (50 mL) was added to the filtrate. The solution was washed successively with water, a 5% solution of acetic acid, and finally with water until pH 7 was achieved. The ether extract was dried with anhydrous MgSO₄. After removal of the 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 (CH₂), 1716 (CO), 1645, 1635 (C=C), 1608, 1588 (C–C in Ar), 1514, 1336 (NO₂), 1265 (COC).

The copolymers were synthesized by radical copolymerization of three monomers in benzene solution at 60 °C; 2,2'-azobisisobutyronitrile (AIBN) was used as an initiating agent. Synthesized copolymers were purified by the repeated precipitation with methanol and dried in vacuum (yields 70–90%).

Characterization: IR spectra were recorded on a Bruker IFS-88 spectrophotometer using KBr pellets. Relative molecular mass of copolymers was determined by gel permeation chromatography (GPC). GPC analyses were carried out with a GPC-2 Waters instrument equipped with an LC-100 column oven and a Data Modul-370 data station. Measurements were made by

using a UV detector, THF as solvent (1 mL min⁻¹, 40 °C), a set of Polymer Laboratory columns of 10, 50 and 100 nm; and a calibration plot constructed with polystyrene standards. The copolymers obtained have the following molecular mass characteristics: $M_n = 7200\text{--}9500$, $M_w/M_n = 2.1\text{--}2.9$.

Investigations of Phase Behavior and Optical Properties: Phase transitions of the synthesized copolymers were studied by differential scanning calorimetry (DSC) with a scanning rate of 10 °C min⁻¹. All experiments were performed using a Mettler TA-400 thermal analyzer and a LOMO P-112 polarization 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 a JASCO J-500C spectropolarimeter.

Photo-optical Investigations: Photochemical properties were studied with ILGI-503 special equipment using a N₂ laser (337 nm). 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 was equal to 66.1 mW cm⁻².

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

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Efficient Polymerization of Aniline at Carbon Nanotube Electrodes**

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The possibility of high surface area electrodes with small dimensions has been realized in several applications: for example, for higher performance and miniaturization of

electrochemical devices.^[1] Conducting polymers have this potential owing to their porous morphology, but the electrochemical performance of polymer based electrodes has yet to be fully developed.^[2–4] Carbon nanotubes, which are macromolecular carbon structures, could fill this gap because of their nanosize dimensions, fibrous and inherently porous structure, and chemical stability.^[5,6] These structures are rolled up graphene sheets (cylinders) collected in the form of ropes (singlewalled nanotube ropes) or concentric Russian-dolls (multiwalled nanotubes). Nanotubes are mechanically and chemically robust and have unique electronic and transport properties depending on the way the carbon atoms are arranged in their cylindrical hexagonal honeycomb lattices.^[6] This material is being developed for applications ranging from microelectronic devices to high performance composites. Multiwalled carbon nanotubes have been made into electrodes recently and their electrochemical electron transfer characteristics have been demonstrated.^[7,8] The electrochemical performance of nanotubes is superior to conventional carbon structures and this behavior of the nanotubes is attributed to the dimensional-presence of topological defects in their lattices, which leads to higher local electron density.^[9] The previously reported construction of nanotube electrodes employed organic inert binders, which were in contact with the electrolytic medium employed. Herein we report experiments with nanotube electrodes constructed with whiskers of loosely packed multiwalled carbon nanotubes (arc-derived). This arrangement removes any ambiguity that might arise from the influence of inert binders on electrochemistry and provides a porous electrode.

We wish to report here the electrochemical oxidation of aniline and the behavior of polyaniline films formed on multiwalled carbon nanotube electrodes. The results suggest that polyaniline films on nanotubes are oxidized more readily and produce a higher current density during the anodic oxidation compared to conventional electrodes such as Pt. This is attributed to the unusual surface topology and relatively large surface area of the nanotube electrodes. The morphology of the polyaniline films formed on nanotube surfaces is granular and nanostructural.

Aniline (Aldrich) was distilled before use in the experiments. 1 M and 0.1 M H₂SO₄ were prepared from concentrated H₂SO₄ by suitable dilution. Carbon nanotubes were prepared by the well-established electric-arc method.^[5] Macroscopically discernable whiskers present in the arc deposit (which consist of aligned microbundles) were separated and these nanotube whiskers, of typical dimensions 0.15 cm long and 0.028 cm diameter, were used as electrodes by attaching them to the tips of copper wires with conductive paint. The copper wire was then reinforced in a plastic rod for rigidity. About 3 cm of the copper wire with the nanotube tip was left as a free end for immersing into the sulfuric acid solution. Only the nanotube ends made contact with the solution during experiments. A PAR 273 potentiostat/galvanostat was used for the electrochemical

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