Chiral Nematic Copolymers with Photoreversible and Irreversible Changing of Helical Supramolecular Structure Pitch

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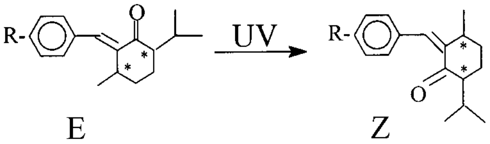
A new cholesteric copolymer consisting of nematogenic phenyl benzoate groups and two different types of photosensitive chiral groups, azobenzene- and benzilidene-*p*-menthan-3-one, was synthesized. Planarly oriented films of copolymer selectively reflect light in the near-infrared region of spectrum. It was shown that under UV irradiation (365 nm) irreversible untwisting of cholesteric helix takes place and selective light reflection maximum is shifted to the long-wavelength spectral region. This phenomenon is explained by the $E-Z$ isomerization of benzilidene-*p*-menthan-3-one chiral groups and the decrease of helix twisting power. On the contrary, under irradiation with visible light (>450 nm), a thermally reversible shift of selective light reflection peak was observed due to the $E-Z$ isomerization of azobenzene-containing chiral units. In both cases, cholesteric helix untwisting is explained by the decrease of the helix twisting power of chiral units during the photoisomerization process. As was demonstrated, such ternary copolymer containing chiral groups sensitive to the light of different wavelengths may be used for reversible as well as irreversible recording of optical information.

Introduction

The end of 20th century is characterized by an ever-growing interest in the preparation of new materials for data recording and storage. This interest has been triggered by remarkable progress in the development of information technologies and various means for information processing and imaging. This trend has generated numerous publications devoted to the preparation of photosensitive polymer materials and liquid crystals with a rapid photoinduced response.[1−18]

In 1998, the number of works led to the development of a new approach for the preparation of liquid-crystalline (LC) chiral nematic polymer materials with photocontrolled helix pitch and selective light reflection wavelength.[10−15] The polymers studied in our works contain nematogenic (phenylbenzoate) and chiral photochromic groups based on benzylidene-*p*-menthan-3-one. The latter compounds are able to experience light-induced irreversible $E-Z$ isomerization relative to the C=C bond:



This process is accompanied by a decrease in anisometry and helix-twisting power, which is defined according to the following relationship

$$\beta = \frac{dP^{-1}}{dx} = \bar{n}\left(\frac{d\lambda_{\max}^{-1}}{dx}\right)_{x=0}$$

where P is the pitch of chiral nematic helix, x is the mole fraction of chiral groups, $\bar{n}$ is the average refractive index, and $\lambda_{\max}$ is the wavelength of selective reflection of light. As was demonstrated, helix twisting power of

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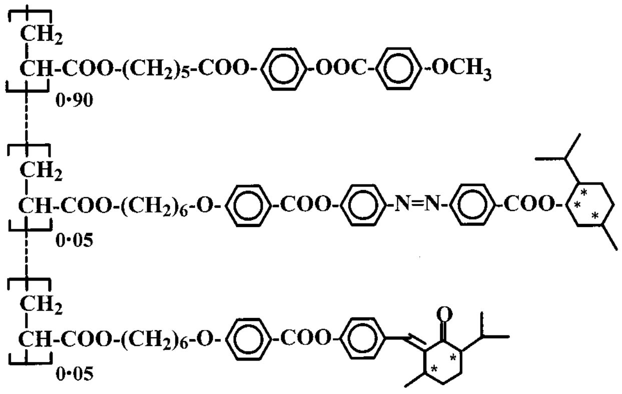
the Z-isomer of chiral photochromic groups is much lower; hence, under light irradiation, planarly oriented films of copolymers show a marked shift in selective light reflection wavelength to a longer wavelength spectral region.

As was shown, such polymers may be used for recording the colored optical information on the colored background. However, an irreversible character of the photoinduced process of benzylidene-*p*-menthan-3-one derivatives is considered to be an evident drawback. Hence, quite recently, we have synthesized and studied acrylic copolymers with chiral photochromic groups based on azobenzene.[16,17] In this case, the $E-Z$ photoisomerization is reversible, and this evidence allowed one to prepare the materials with photocontrolled helix pitch. We also demonstrated their high fatigue resistance, that is, the ability for repeated "recording–erasing" cycles.

In this work, we tried to widen the range of photosensitive cholesteric materials and to prepare the polymer in which changes in helix pitch (thermally reversible or irreversible character) are strongly controlled by the wavelength of incident light. To this end, using radical polymerization, we synthesized a new ternary copolymer that contains nematogenic phenylbenzoate side groups and two different types of chiral photochromic groups: benzylidene-*p*-menthan-3-one and azobenzene:



Such a copolymer structure is selected due to the following reasons: first, benzylidene-*p*-menthan-3-one and azobenzene groups absorb light in somewhat different spectral regions and absorption region of benzylidene-*p*-menthan-3-one chromophores is located in a shorter wavelength region; second, even though both groups are able to experience the $E-Z$ photoisomerization, the character of this process is different. As was mentioned earlier, isomerization of benzylidene-*p*-menthan-3-one fragments is irreversible, whereas for azobenzene groups, this process is thermally and photochemically reversible. This difference allows one to initiate photoisomerization of either benzylidene-*p*-menthan-3-one or azobenzene groups by selecting the wavelength of incident light (λ_{ir}); in other words, irradiation with short-wavelength UV light should lead to a preferential $E-Z$ isomerization of benzylidene-*p*-menthan-3-one groups and to an irreversible untwisting of cholesteric helix, whereas irradiation with visible light should initiate a reversible isomerization of only azobenzene groups and, correspondingly, leads to a reversible shift in the selective light reflection wavelength. (Earlier, we studied the ternary copolymers with benzylidene-*p*-menthan-3-one and achiral cyanobenzene side groups and demonstrated the possibility of selective control of the type of photoisomerizable groups by selecting λ_{ir}.[18])

The main advantage of such material is the combination of two different photosensitive side groups in one copolymer. It provides the possibility for using this "combined" material for reversible and irreversible optical data recording with highly photovariable optical properties.

The above evidence defines the principal objective of this work, which is related to studying the specific features of photooptical behavior of the copolymer and investigating the possibilities of reversible and irreversible recording of optical information on such materials.

Experimental Section

Synthesis. Phenyl benzoate and menthone- and menthyl-containing monomers were synthesized according to the procedures described in refs 14, 17, 19, respectively.

The copolymer was synthesized by radical copolymerization of monomers in benzene solution at 60 °C; AIBN was used as an initiating agent. The synthesized copolymer was purified by the repeated precipitation with methanol and dried in a vacuum.

Characterization. Relative molecular mass of copolymer 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, 40 °C), a set of PL columns of 100, 500, and 10^3 Å, and a calibration plot constructed with polystyrene standards. The copolymer obtained has the following molecular mass characteristics: $M_n = 19\,000$, $M_w/M_n = 2.5$.

Investigations of Phase Behavior and Optical Properties. Phase transitions of the copolymer were studied by differential scanning calorimetry (DSC) with a scanning rate of 10 °C/min. All experiments were performed using a Mettler TA-400 thermal analyzer and a LOMO P-112 polarization microscope. Selective light reflection of copolymer and mixture films 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. A planar texture was obtained by shear deformation of the samples, which were heated to temperatures above glass transition. Prior to the tests, the test samples were annealed for 20–40 min.

Photooptical Investigations. Photochemical properties investigations were studied using a special instrument[12] equipped with a DRSh-250 ultrahigh-pressure mercury lamp. Using filters, light with wavelengths 365, >450, and ~550 nm was selected. To prevent heating of the samples due to IR irradiation of the lamp, a water filter was used. To obtain plane-parallel light beam, quartz lens was used. During irradiation, the constant temperature of the test samples was maintained using a Mettler FP-80 heating unit. The intensity of light was equal to 1.9×10^{-8} Es·s^{-1}·cm^{-2} (for light of 365 nm, as measured actinometrically[20]), the intensity of visible light ($\lambda_{ir} > 450$ nm and $\lambda_{ir} \sim 550$ nm) was equal ~8.0 mW·cm^{-2} (for $\lambda_{ir} > 450$ nm) and ~0.7 mW·cm^{-2} (for $\lambda_{ir} \sim 550$ nm), as measured by an IMO-2N intensity meter.

Photochemical properties of copolymer were studied by illuminating the 20-ìm-thick films. Immediately after irradia-

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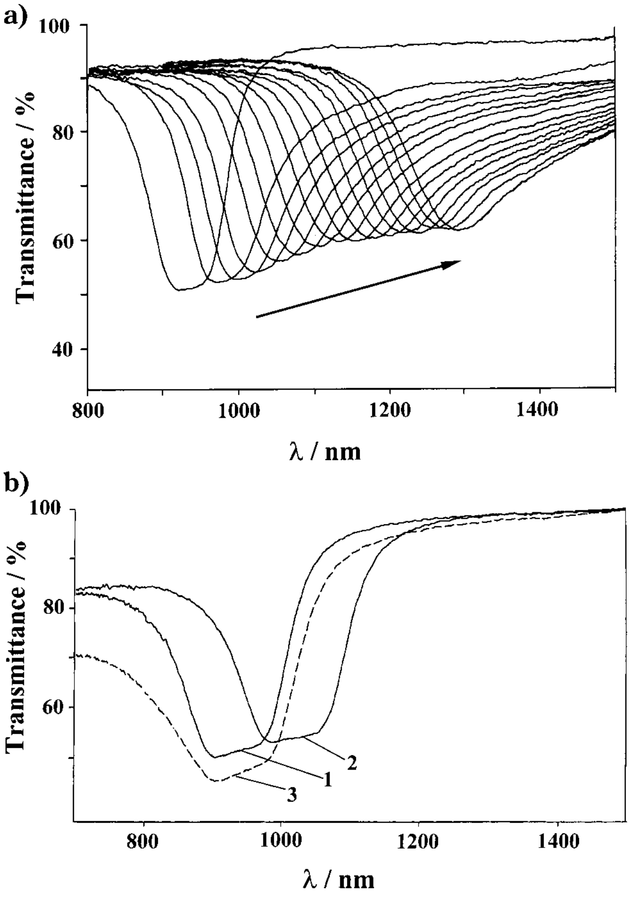

Figure 1. Changes of transmittance spectra of planarly oriented films of copolymer during irradiation with light λ_{ir} = 365 nm (a) and $\lambda_{ir} > 450$ nm (b). (a) Spectra were recorded every 10 min of UV irradiation, temperature of the sample 100 °C. (b) Spectrum 1 was recorded before irradiation; 2, after 60 min of irradiation at 80 °C; 3, after annealing during 20 min at 80 °C.

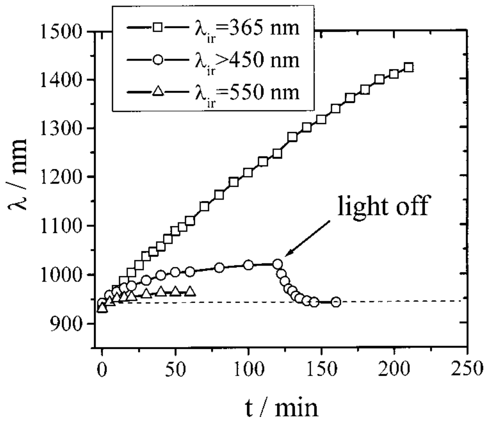

Figure 2. Selective light reflection wavelength growth during irradiation of copolymer film with light of different wavelength. Temperature of the sample was 80 °C. It should be pointed out that the selective light reflection peak shift is irreversible after irradiation by light of 365 nm. In the case of light with $\lambda_{ir} > 450$ nm or ~550 nm spectral changes are reversible: annealing of the film leads to back shift of the peak to the short wavelength region of the spectrum (the case $\lambda_{ir} > 450$ nm is shown).

tion absorbance or transmittance spectra were recorded using Hitachi U-3400 UV–vis–IR spectrometer.

Result and Discussion

According to the data of polarizing optical microscopy, the synthesized copolymer is able to produce chiral nematic phase N* with an isotropization temperature of 122–123 °C and glass transition temperature of about 25 °C. Planarly oriented films of copolymer are characterized by selective light reflection in the near-IR spectral region (λ_{max} ~940 nm). Upon irradiation with UV (λ_{ir} = 365 nm) and visible light ($\lambda_{ir} > 450$ nm and λ_{ir} ~550 nm), such films experience untwisting of cholesteric helix and shift in selective light reflection wavelength to long-wavelength region (Figures 1 and 2). Let us emphasize that, upon light irradiation with λ_{ir} = 365 nm, a shift in selective light reflection peak is irreversible; at the same time, irradiation with visible light leads to reversible changes in λ_{max}. In this case, annealing at temperatures above ~50 °C provides the recovery of selective light reflection wavelength to its initial position (Figures 1b and 2).

This behavior suggests the occurrence of the *E*–*Z* isomerization of benzylidene-*p*-menthan-3-one groups under the action of UV light and photoisomerization of only azobenzene groups under irradiation with visible light. In both cases, *E*–*Z* isomerization decreases helix twisting power of chiral groups due to a lower anisometry of their *Z*-isomer.[10–17] (Before irradiation, the helical-twisting power of benzilidene-*p*-menthan-3-one and azobenzene groups calculated for phenylbenzoate matrix is 16.9 ± 1.1 μm^{-1} and 18.5 ± 2.1 μm^{-1}, respectively.[14,17]) Under the action of UV irradiation, one may hardly exclude a possible occurrence of photoisomerization of azobenzene fragments but the films annealed after light irradiation with λ_{ir} = 365 nm show no back process of helix twisting even at short irradiation times. This behavior is likely to be related to the fact that isomerization of benzylidene-*p*-menthan-3-one groups leads to a more pronounced decrease in helix-twisting power as compared with that of azobenzene fragments. Hence, seemingly, under real experimental conditions and light irradiation with λ_{ir} = 365 nm, we observed only irreversible changes in helix pitch related to isomerization of only benzylidene-*p*-menthan-3-one groups.

Let us emphasize that, upon annealing and irradiation with visible light, the reversible shift in selective light reflection wavelength is accompanied by the distortion of planar texture and appearance of light scattering as evidenced by a wider selective light reflection peak (Figure 1b). This phenomenon was observed for the copolymers containing azobenzene chiral photochromic groups.[14,15] Prolonged annealing (several hours) or shear deformation allows one to eliminate the above undesirable effects, and this fact favors a *complete* recovery of the profile of selective light reflection peak.

The rate of helix untwisting is markedly controlled by temperature (Figures 3 and 4). The character of temperature dependences is different. Upon irradiation with UV light, with increasing the temperature, the rate of helix untwisting increases. This increase is related to the fact that, as was shown earlier,[12,13] the limiting stage of helix untwisting is the diffusion of isomerized benzylidenementhanone groups in the film.

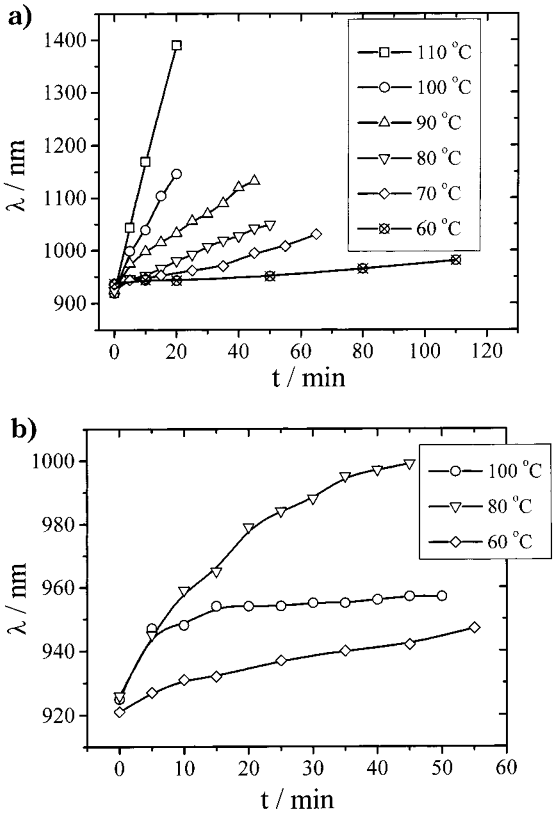

Figure 3. Changes of selective light reflection wavelength during irradiation (λ_{ir} = 365 nm (a) and λ_{ir} > 450 nm (b)) at different temperatures (shown in figure).

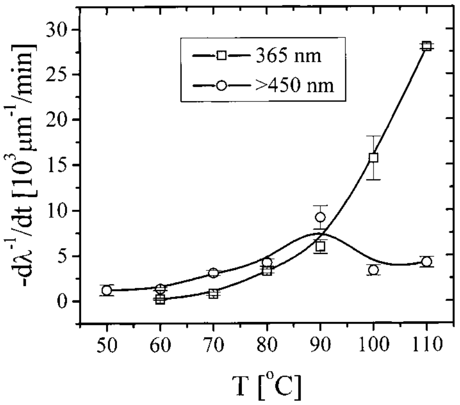

Figure 4. Temperature dependencies of the changing rate of reciprocal wavelength of selective light reflection during light action.

Under irradiation with λ_{ir} > 450 nm, the character of the temperature dependence is somewhat different: as temperature is increased, initially, the rate increases and then decreases (Figure 4). This behavior is related to the fact that, in the case of azobenzene groups, interplay between the two processes is observed: forward photoinduced $E-Z$ isomerization and back thermal $Z-E$ isomerization. In this case, the rate of the $Z-E$ process increases with increasing the temperature.[16,17] As a result, at temperatures below 80 °C, due to the high viscosity of the system, the rate of this process is low; at temperatures above 90 °C, this rate decreases due to an increase in the rate of the back-thermal process.

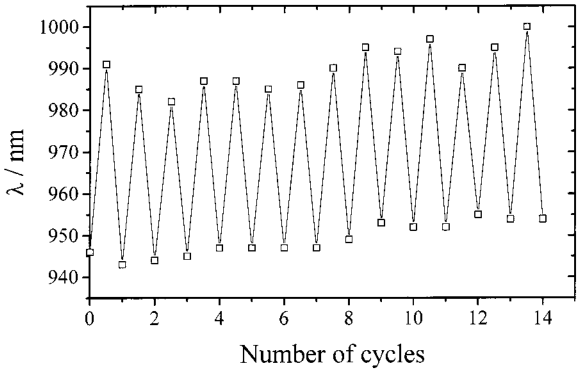

Figure 5. Fatigue resistance properties of the copolymer film under the recording − erasing conditions. In each cycle film of copolymer was irradiated during 30 min by light λ_{ir} > 450 nm at 80 °C, then was annealed during 30 min at 100 °C.

To provide photoinduced changes in the selective light reflection wavelength, irradiation with visible light allows one to perform repeated "data recording−erasing" cycles. As follows from Figure 5, fatigue resistance of the copolymer is rather high. Let us note that, as follows from Figure 5, despite a high fatigue resistance of the copolymer, upon repeated "recording−erasing" cycles, one may observe a minor systematic shift in selective light reflection wavelength to a long-wavelength region. Taking into account the fact that benzylidene-*p*-menthan-3-one groups do not absorb at λ_{ir} > 450 nm,[14] the origin of such unusual behavior is still open to speculation.

Hence, one may conclude that copolymerization of nematogenic monomer with the two different photosensitive chiral monomers makes it possible to obtain a new class of multifunctional polymers with different "response" to light irradiation with different wavelength. The synthesized copolymer clearly demonstrates this possibility and may be used both for reversible and irreversible recording of optical information.

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