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Mixture of cholesteric copolymer with dithienylethene photochromic dopant: a new material combining optical properties of cholesterics with photochromism

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The phase behaviour and optical properties of the mixture based on cholesteric copolymer with 6 wt% of a photochromic dithienylethene dopant was studied. It was shown that planarly-oriented films of the mixture possess a selective light reflection in the visible region of the spectrum ($\lambda_{\max} \sim 600$ nm). UV irradiation of the mixture film leads to the appearance of an intense absorbance peak in the spectral range coinciding with the selective reflection band. This process is associated with the photocyclization of dopant and the "degeneration" of the selective light reflection. The photoinduced coloured form of dopant is thermally stable, but subsequent irradiation of the film by visible light (633 nm) induces a back decoloration process.

For the first time the influence of temperature on the rates of forward and back photoprocesses in such polymeric liquid crystalline films was studied.

The potential for the use of such a type of material for reversible data recording and storage was demonstrated.

1. Introduction

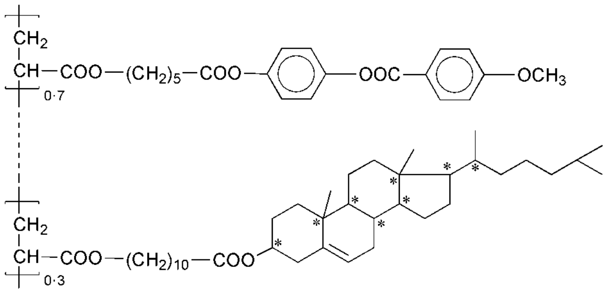
In recent years there has been an ever growing interest in photochromic polymer compounds, and this tendency is related to the wide possibilities of their application as active elements for various optical devices, as materials for data recording and storage, holography, *etc.*[1–7]

In our last publications we demonstrated the possibilities of the combination of optical properties of cholesteric liquid-crystalline (LC) polymers with photochromism for the development of materials for colored recording of optical information.[5–7] In these works, we described the synthesis of ternary copolymers containing, in addition to nematogenic phenyl benzoate (**I**) and optically active chiral side groups (**II**), photochromic units which are derivatives of spiropyran (**III**). The presence of units **I** provides a possible development of a LC phase; chiral cholesterol-containing side groups **II** are responsible for "twisting" of the nematic phase and cholesteric (chiral nematic) mesophase formation; finally, spiropyran groups impart photochromic properties to copolymers.

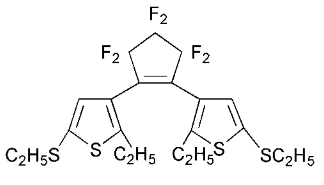
In this case, the ratio between monomer units was selected so that the selective light reflection band should coincide with the absorption peak of the photoinduced merocyanine form of spiropyran-containing units **III** caused by UV irradiation of polymer film. As was shown, this approach allows one to develop materials in which, under light irradiation, selective light reflection peaks in the spectral region of the absorption of the photoinduced form are "burnt off". However, spiropyran fragments used as photosensitive groups show some drawbacks such as low fatigue resistance[8] and thermal instability of the photoinduced form (even at room temperature, one may observe the back transition to the initial spiropyran form[7,9,10]).

Hence, in this work, we studied a mixture composed of binary cholesteric copolymer and low-molecular-mass photochromic dopant of the dithienylethene family.

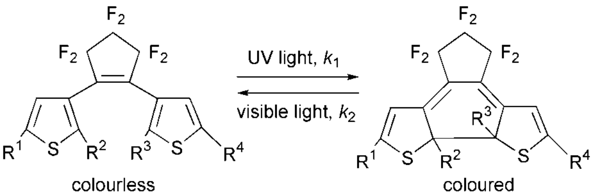
As compared with ternary copolymers synthesized and studied,[5–7] this binary copolymer is composed of the same units **I** and **II** and is able to produce the chiral nematic phase with clearing temperature $T_{cl} = 119–121\,°C$ and glass transition temperature $T_g \sim 25\,°C$.



This copolymer was used as a LC optically active "matrix" into which low-molecular-mass photochromic dopant 1,2-bis(2-ethyl-5-ethylthio-3-thienyl)hexafluorocyclopentene was introduced:



As is known, such compounds show a well-pronounced photochromism: UV irradiation is accompanied by photocyclization which leads to the formation of the coloured closed form of this compound:[11–15]



It is important to emphasise that this process is thermally irreversible whereas the action of visible light leads to the back process, that is, cycle opening.[11–15] Dithienylethenes are characterised by high quantum yields of photocyclization and high fatigue resistance. From this viewpoint, these compounds offer unique opportunities for the development of new photochromic materials.

Introduction of the photochromic low-molecular-mass dopant to the polymer LC matrix allows one to anticipate the development of polymeric material which happily combines the optical properties of copolymer with photochromism of the low-molecular-mass dopant.

To this end, in this work, a mixture of copolymer with 6 mol% of dopant was prepared, photo-optical properties and kinetic features of photo-optical behaviour were studied, possible applications of the as-prepared composition as a material for data recording and storage were considered.

2. Experimental section

2.1. Synthesis and mixture preparation

Cholesteric copolymer was synthesised by the radical copolymerization of the corresponding acrylic monomers according to the procedures described in ref. 16. Synthesis of photochromic dopant 1,2-bis(2-ethyl-5-ethylthio-3-thienyl)hexafluorocyclopentene is presented in ref. 17.

The mixture was prepared by dissolving copolymer and dopant in chloroform followed by solvent evaporation at 60 °C. The mixture was then dried under vacuum at 120 °C for two hours.

2.2. Physical properties

Phase transitions of the synthesised copolymer and mixture 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 polarisation microscope. Selective light reflection of the films of chiral 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. A planar texture was obtained by shear deformation of the samples, which were heated to temperature 5 degrees below the N*–I transition temperature followed by ~20 min of annealing at the same temperature. Prior to tests, the test samples were annealed for 20–40 min at appropriate temperatures.

X-Ray diffraction analysis was carried out using an URS-55 instrument (Ni-filtered CuK$_\alpha$-radiation, $\lambda = 1.54$ Å).

2.3. Photo-optical investigations

Photochemical investigations were performed using a special instrument[18] equipped with a DRSh-250 ultra-high pressure mercury lamp and HeNe laser (633 nm). Using a filter, the 313 nm band of the linear radiation spectrum of a mercury lamp was selected. To prevent heating of the samples due to IR irradiation of the lamp, a water filter was used. To obtain a plane-parallel light beam, a quartz lens was used. During irradiation, the constant temperature of the test samples was maintained using a Mettler FP-80 heating unit. The intensities of UV irradiation were determined actinometrically[19] and were equal to 1.0×10^{-9} einstein s^{-1} cm^{-2} (1.3 mW cm^{-2}). The intensity of HeNe laser was equal to 1.3 mW cm^{-2} (as measured by IMO-2N intensity meter)

Photochemical properties of the mixture were studied by irradiation of the 20 μm-thick films at different temperatures. After irradiation the absorption spectra were recorded.

3. Results and discussion

3.1. Phase behaviour and optical properties of cholesteric copolymer and mixtures with a photochromic dopant

First let us briefly discuss the phase behaviour and optical properties of cholesteric copolymer and its mixture with 6 mol% of a photochromic dopant. The initial copolymer and the mixture with low-molar-mass dopant form a chiral nematic phase. The clearing temperature of the mixture is 98–100 °C, that is by ~20 °C lower than for the initial copolymer. Such a decrease in thermostability is explained by low anisometry of the dopant molecules and, as a consequence, by their nonmesogenic character.

It is well-known[20,21] that planarly-oriented films of cholesteric materials selectively reflect light, the wavelength ($\lambda_{\max}$) of which is determined by the pitch of the cholesteric helix (P) according to eqn. (1):

$$\lambda_{\max} = nP, \qquad (1)$$

where n is the average refractive index.

The prepared mixture easily forms a planar texture which is characterised by the selective light reflection of $\lambda_{\max}$ ~620 nm at room temperature.

3.2. Photo-optical properties of the films of the mixture

Let us consider the photo-optical properties of planarly-oriented films prepared from the mixture. UV irradiation with light of 313 nm leads to the appearance of the intense absorbance peak with a maximum at 576 nm (Fig. 1a) that suggests formation of a coloured closed form of dopant. Note that the coloured form is thermally stable (at least at temperatures below 150 °C). Nevertheless, back transformation into an open form can be easily carried out by irradiation with visible light (for example, by using HeNe laser, Fig. 1b). It should be pointed out, that even after prolonged visible light irradiation the full recovery of initial optical density is not observed (Figs. 1b, 2). This phenomenon is related to the occurrence of a secondary irreversible photoprocess. At the same time during UV and visible light irradiation we did not observe any loss or deformation of planar texture (as follows from polarising optical microscopy observations).

It is important to note, that we selected copolymer composition in such a way, that the absorbance peak of the closed form strongly coincides with the selective light reflection band (Fig. 1). This allows us to observe the selective light reflection "degeneration" during UV irradiation, due to strong absorbance of the photoinduced closed form of dopant in this region of the spectrum. As was shown earlier,[5–7] selective light reflection "degeneration" of locally irradiated areas of polymer films provides a possibility to realise optical data recording with high contrast (especially in the case of using as a reading beam left-circularly polarised light with wavelength coinciding with a selective reflection maximum). This effect is clearly seen from circular dichroism (CD) spectra of planarly-oriented mixture films (Fig. 3). Before UV irradiation the mixture film possesses a high value of CD in the spectral range

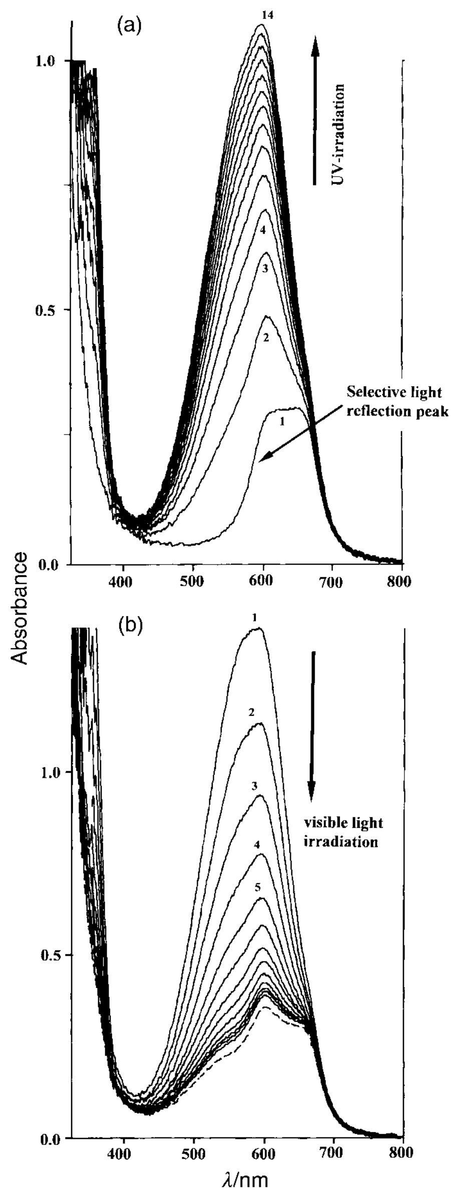


Fig. 1 (a) Spectral changes in absorbance during UV irradiation (313 nm) for the film of the mixture. The initial spectrum before irradiation is shown (1); spectra 2–14 were recorded after each 1 min; (b) spectral changes during the back process induced by visible light (633 nm) irradiation, spectra were recorded every 2 min, the dashed line corresponds to the steady state. (Film thickness 20 μm, temperature 20 °C.)

corresponding to the selective light reflection band, whereas during UV irradiation a noticeable decrease of CD is observed.

In this work, the influence of temperature on the rates of forward and back photoprocesses in a polymeric liquid crystalline matrix was studied for the first time for a substance of this type. For this purpose, plots of absorption *versus* time were plotted using the first order kinetics' coordinates (Fig. 4). We estimated the rate constants of forward (k_1) and back (k_2) processes using the above dependences and the following equation of the first-order kinetics:

$$\ln(A_\infty - A_t) \times (A_\infty - A_0)^{-1} = -k_1 t \qquad (2)$$

where A_0, A_t and A_∞ are the absorbance at 576 nm at time $t = 0$, current time t and $t \rightarrow \infty$, respectively.

In the case of the forward photocyclization process a small deviation from linear character of dependences is observed (Fig. 4a), *i.e.* in this case first-order kinetics can not be applied for precise calculation of rate constants. Nevertheless, we can estimate the rate of the forward process also by using only the

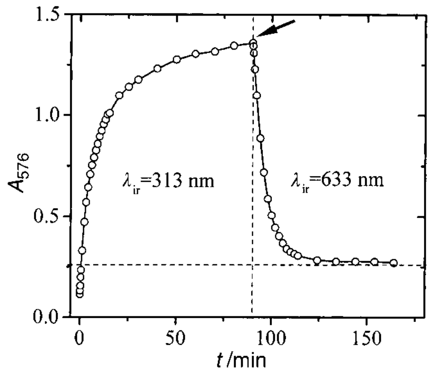


Fig. 2 Absorbance growth for the mixture during UV irradiation (313 nm) and subsequent decrease during irradiation by visible light (HeNe laser, 633 nm). Film thickness 20 μm, temperature 20 °C. (The arrow shows the UV-irradiation switching off and the visible light switching on.)

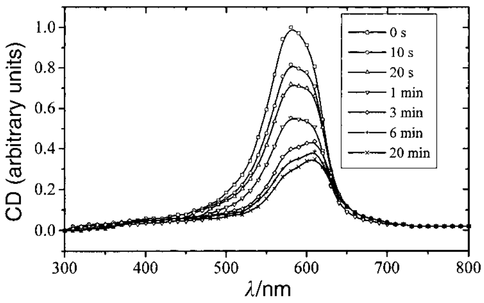


Fig. 3 Changes of circular dichroism spectra during UV irradiation of the planarly-oriented film of the mixture (T=20 °C). Irradiation time is shown in the figure.

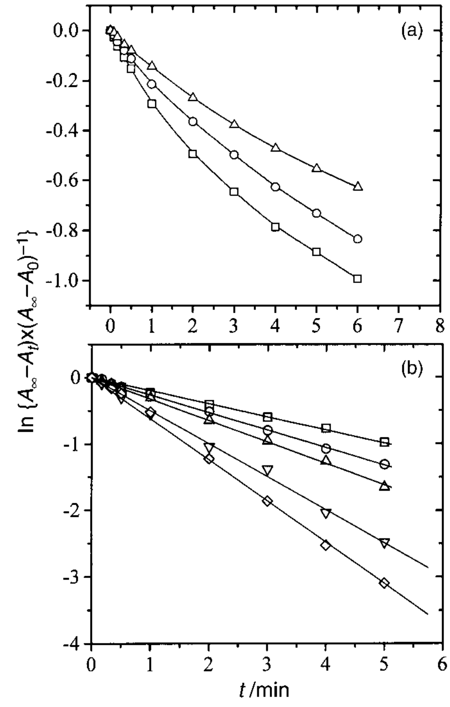


Fig. 4 First order plots for absorbance changes during UV (a) and visible light irradiation of the mixture (b) at different temperatures. Before measurements in case (b) films of the mixture were irradiated by UV light (313 nm) during 10 min. For (a) △ = 120 °C, ○ = 80 °C, □ = 20 °C. For (b) □ = 20 °C, ○ = 40 °C, △ = 60 °C, ▽ = 80 °C, ◇ = 100 °C.

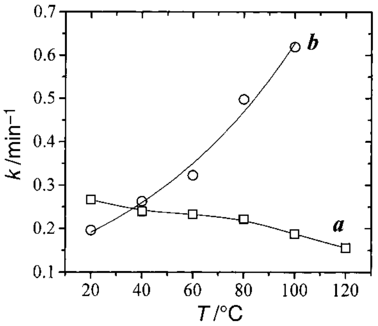


Fig. 5 Temperature dependence of the rate constant of photocyclization k_1 (a) and decoloration k_2 (b) processes during UV and visible light irradiation of the mixture, respectively. Rate constant k_1 was calculated from the slopes of initial parts of dependences in Fig. 4(a).

initial parts of the kinetic curves for calculating apparent constant values (Fig. 5). The origin of these deviations for the forward process is still open to speculation. In contrast, in the case of the back (cycle opening) process, dependences are close to linear (Fig. 4b).

As is seen from temperature dependences presented in Fig. 5, the rate constant of the forward process slightly decreases, and the rate constant of the back process rapidly increases when temperature grows. Probably, these effects are associated with an increase of molecular steric volume of dopant during the cycle opening (back) process. That is why the rate of cycle opening should be to a great extent controlled by free volume and viscosity of the polymer matrix. It is well known that temperature growth leads to increase of polymer free volume[22,23] and to a viscosity decrease. These phenomena can influence the rate constant of the back process induced in our case by a HeNe laser.

The extreme temperature dependence of decoloration rate (Fig. 5) allows us to consider the mixtures of this type as optically addressable materials for information recording and for non-destructive information reading. In this case "reading" of optical information by the laser with low intensity at low temperature can be possible, whereas at high temperature (in our case 80–100 °C) information erasing using visible light can be realized with high speed.

A very important parameter of materials for reversible information recording is their fatigue resistance, *i.e.* stability of material during repeated "recording–erasing" cycles. As clearly seen from Fig. 6, a change in mixture optical properties is observed after 20–30 repeated "recording–erasing" cycles. This effect is accompanied by an irreversible side photoprocess already discussed in this paper, which occurs in the mixture (Figs. 1b, 2).

In a number of works,[11,12] stable photochromic substances of similar structure with high fatigue resistance (capable of realizing up to 10^4 "recording–erasing" cycles) were synthesized. That is why this disadvantage can be excluded by varying the chemical structure of the photochromic dopant. The main goal of *this* work is only to demonstrate the principal possibility for creating new photochromic material on the base of polymeric cholesteric and dithienylethene photochromic dopant. In future it would be very expedient to link photochromic groups chemically to the main chain of the copolymer and to synthesize in such a way a new type of ternary copolymers. It would give the possibility of variation of composition and photo-optical properties of such materials. Now this work is in progress.

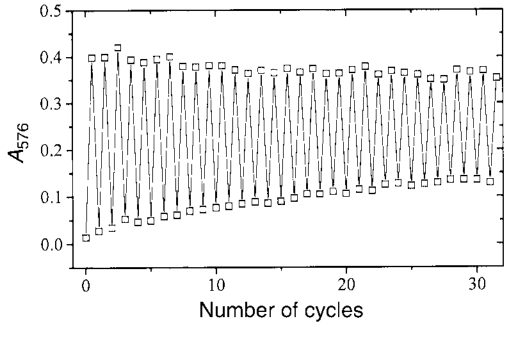


Fig. 6 Fatigue resistance properties of the mixture under the recording–erasing conditions. In each cycle a film of the mixture was irradiated during 5 min by UV light (313 nm) at 90 °C, then was irradiated during 10 min by visible light (633 nm) at the same temperature.

In conclusion it should be stressed, that mixtures of dithienylethene photochromic dopant with cholesteric copolymers were shown to be new promising materials combining photochromic properties of dopant and unique optical properties of cholesterics. Such mixtures can be used for reversible coloured optical information recording and long-term storage.

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