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Photosensitive cholesteric copolymers with spiropyran-containing side groups
II. Kinetic features of the photo- and thermo-chromic processes

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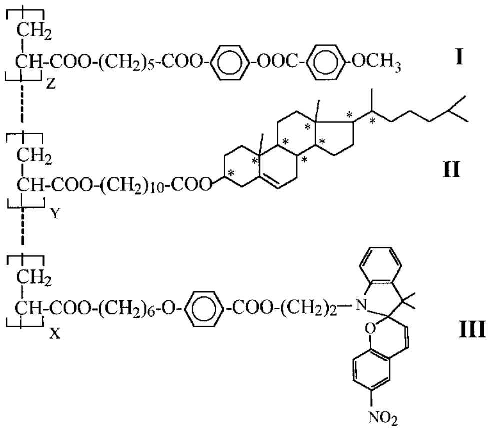
Kinetic features of the photo- and thermo-chromic behaviour of new cholesteric triple copolymers with photosensitive spiropyran-containing side groups are considered. The kinetics of the back thermal process at different temperatures have been studied; activation energies for this process for the copolymers with different contents of the dye units have been obtained. The photochromic homopolymer and copolymers with a low content of dye units are shown to possess maximum values of the activation energy.

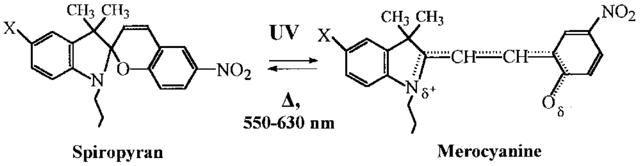
1. Introduction

In our previous papers [1, 2], a new principle for information storage based on a reversible 'selective reflection–absorbance' transition in photochromic liquid crystalline (LC) copolymers was advanced. We had synthesized a new family of triple copolymers by copolymerization of a nematogenic (I), a chiral (II), and a photochromic (III) monomers. These copolymers have the structure given below and form the cholesteric (N*) phase over a wide temperature range, which depends on copolymer composition:



$Y = 0.3$, $X + Z = 0.7$

Planar oriented films of the copolymers with $X < 0.2$ ($Z > 0.5$) were capable of selectively reflecting left-handed circularly polarized light in the visible spectral region ($\lambda = 540$–620 nm). Isomerization of the spiropyran groups (III) and formation of the merocyanine form are induced by the action of UV light (337 nm) on the polymer films; the isomerization process is shown below:



Note that the maximum absorbance of polymer films coincides with the maximum of selective light reflection. As a result, the selective light reflection in the irradiated regions disappears.

However, kinetic features of the photo- and thermochromic behaviour of these copolymers were not investigated. Our work here is devoted to a detailed study of this quite complex problem.

2. Experimental

The spiropyran-containing, cholesteryl-containing and phenyl benzoate-containing acrylate monomers and the triple copolymers were synthesized and characterized as described in [1, 2]. The copolymers obtained had the following molecular mass characteristics: $\bar{M}_n = 6300$–9500, $\bar{M}_w / \bar{M}_n = 2.1$–$2.9$ [2].

Selective light reflection and absorbance spectra of the chiral polymers were studied using a Hitachi U-3400 UV-Vis-IR spectrometer equipped with a Mettler FP-80 hot stage. The 20 μm thick polymer 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 the samples

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heated to temperatures above the glass transition temperature. Prior to measurements, the test samples were annealed for 20–40 min.

Photochemical studies were made with special customized equipment using a N_2 ILGI-503 laser (337 nm). The intensity of UV radiation was 66.1 mW cm^{-2} (as measured by an IMO-2N intensity meter). The photochemical properties of the copolymers were examined by illuminating 20 μm thick films at different temperatures, and after irradiation, the absorption spectra were recorded.

3. Results and discussion

During irradiation of planar oriented films of the polymers, the absorption spectra were recorded at certain time intervals. The photo-optical effects are shown in figure 1(*a*); the action of the UV light leads to the appearance of an absorption peak with a maximum at $\lambda \sim 585$ nm. According to literature data [3–7], this peak corresponds to a highly conjugated merocyanine form of the dye-containing side groups.

It should be noted that annealing of the copolymers leads to the back conversion of the merocyanine form to the spiropyran from, figure 1(*b*); in other words, the isomeric transition between spiropyran and merocyanine forms is thermally reversible.

Let us consider in more detail the kinetics of these processes for copolymers with different contents of spiropyran units and for the photochromic homopolymer. For copolymers in the merocyanine form, analysis of the dependences of optical density on irradiation time (figure 2) and on annealing time (figure 3) for the back thermal process shows that these curves cannot be fully described by the equations of first order kinetics, and that parallel processes must be involved.

This deviation from first order kinetics is likely to be associated with the possible formation of dimers of the merocyanine form [7]. Nevertheless, we can estimate the rate constants *k* of the forward and back thermal processes using only (as done by other authors [5]) the initial parts of the kinetic curves (figures 2 and 3) and the following equation for first order kinetics in its integral form [8] (figure 4):

$$\ln(D_\infty - D_t) \times (D_\infty - D_0)^{-1} = -kt \qquad (1)$$

where D_0, D_t and D_∞ are the absorbance at 585 nm at time $t = 0$, current time t and $t \to \infty$, respectively.

The rate constant of the forward process (at a fixed laser power and at 25°C) which emerges is equal to about 0.03 s^{-1}. For some copolymers and the homopolymer ($X = 1.0$; $Y + Z = 0$), the table shows values of rate constants and half-life times for the back thermal process. As follows from the table, in this case the values of *k* are by about one order of magnitude lower than for the forward process. The half-life time of merocyanine for irradiated polymers at room temperature is about 15 h.

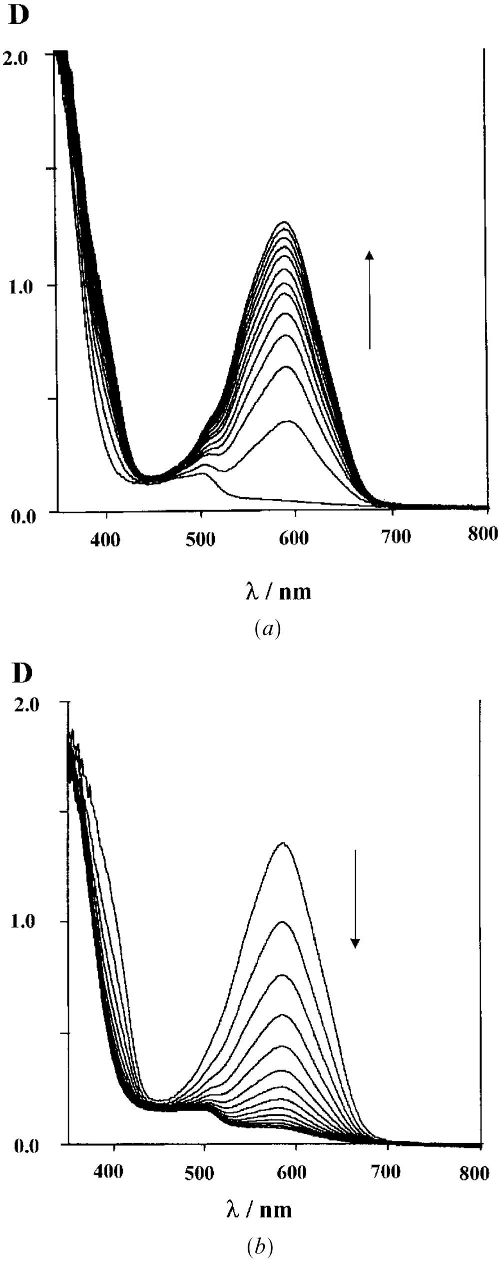


Figure 1. (*a*) Spectral changes in absorbance during UV irradiation of copolymer film with 15 mol% of spiropyran-containing units. Spectra were recorded every 5 s, at a temperature of 25°C; (*b*) spectral changes during the back thermal process at 45°C. Spectra were recorded every 200 s.

To calculate the activation energy E_A of the back process, the Arrhenius plot was constructed (figure 5). The activation energies were calculated from the slope of the dependences of bias angle. As shown in figure 6,

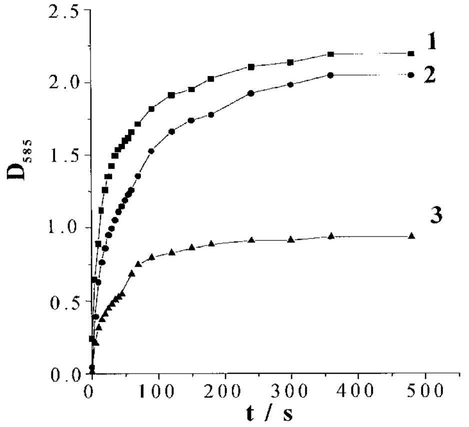
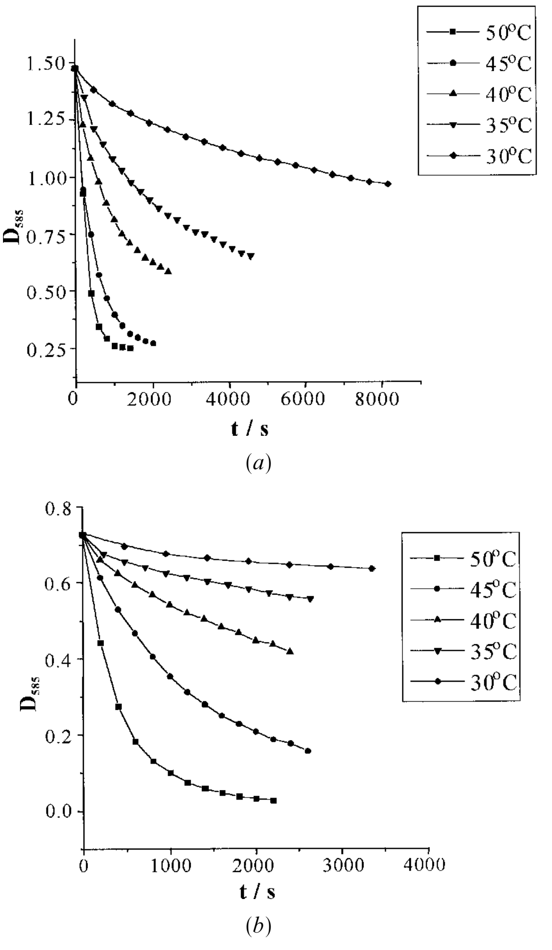


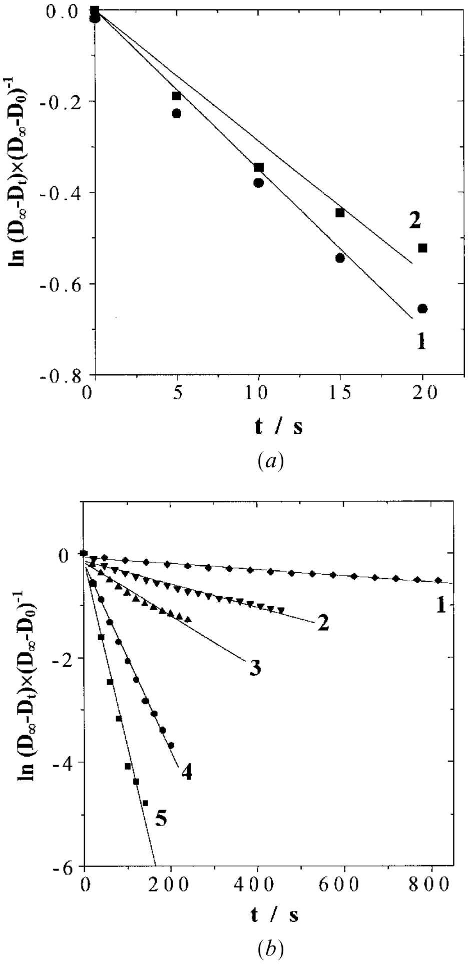
Figure 2. Kinetics of the increase in absorbance at $\lambda = 585$ nm for copolymers with 10 (1), and 15 (2) mol% of dye units and for the photochromic homopolymer (3). In the case of the homopolymer, the film was cast from dichloroethane solution.



(*a*)

(*b*)

Figure 3. Kinetics of the back thermal process at different temperatures (*a*) for the copolymer with 10 mol% of dye units, (*b*) for the photochromic homopolymer (*b*).



(*a*)

(*b*)

Figure 4. First order plots for: (*a*) the photochemical process at 25°C for copolymers with (1) $X = 10$ mol% ($k = 0.035 \pm 0.001\ \mathrm{s}^{-1}$), and (2) $X = 15$ mol% ($k = 0.029 \pm 0.002\ \mathrm{s}^{-1}$); (*b*) the back thermal process at different temperatures, (1) 30°C, (2) 35°C, (3) 40°C, (4) 45°C, (5) 50°C for the copolymer with $X = 10$ mol%.

as the content of spiropyran units in the copolymers is increased, the value of E_A first tend to decrease and then to increase.

This effect may be explained as follows. On the one hand, the activation energy of this process in the photochromic homopolymer is high, due to the stabilization of polar merocyanine groups by dipole–dipole interaction [9, 10]; in the case of the copolymers with a low concentration of photochromic groups, stabilization is possible due to the LC order [11, 12]. As a result of further increase in the concentration of photosensitive units, the orientational order of the system is diminished, but the concentration of dye units is not enough for the formation of merocyanine dimers. Hence, the activation energy of the thermal process decreases.

To prove the dimerization of the merocyanine form, the following experiment was performed. Copolymer

Table. Decolouration rate constants and half-life times for the coloured merocyanine form at different temperatures.

T/°C	$t_{1/2}$/s	$k\times10^3$/s^{-1}
Copolymer with 10 mol% of dye units		
30	11 500 (≈3.2 h)	0.06 ± 0.002
35	3140	0.22 ± 0.009
40	1350	0.51 ± 0.030
45	380	1.82 ± 0.050
50	190	3.60 ± 0.210
Copolymer with 20 mol% of dye units		
30	7670 (≈2.1 h)	0.09 ± 0.008
35	3000	0.23 ± 0.009
40	620	1.12 ± 0.02
45	430	1.46 ± 0.11
50	230	3.04 ± 0.42
Homopolymer[a]		
30	17 250 (≈4.8 h)	0.04 ± 0.005
35	6900	0.10 ± 0.007
40	3000	0.23 ± 0.009
45	1060	0.65 ± 0.010
50	280	2.50 ± 0.110

[a] $X=1.0$; $Y+Z=0$ (100 mol % of dye units)

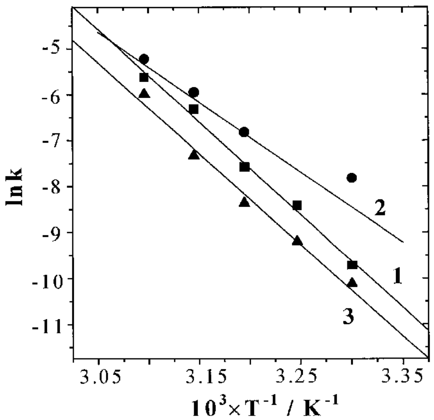


Figure 5. Arrhenius plot for the thermal isomerization of the merocyanine form of the copolymer with 10 (1) and 15 (2) mol % of dye units, and for the photochromic homopolymer (3).

film was irradiated at different temperatures: 25°C (glassy state) and 60°C (T_g + 25°C). As seen from the corresponding absorption spectra of the irradiated film (figure 7), in the case of the film irradiated at a temperature higher than T_g, the absorption maximum is shifted to the short wavelength spectral region as compared with the film irradiated in the glassy state. Furthermore, the peak obtained at 25°C has a short wavelength 'shoulder'. The above phenomena may be related to the difference in the concentration of the dimeric form of the dye units which absorbs in a shorter wavelength spectral region (in our case, λ_{max} = 568 nm) [3, 7, 9, 10].

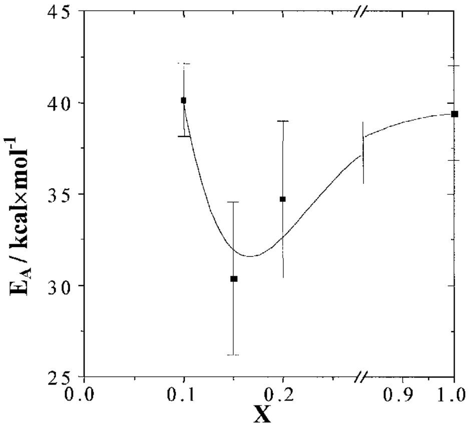


Figure 6. Activation energy of the back thermal process versus the mol content of dye units.

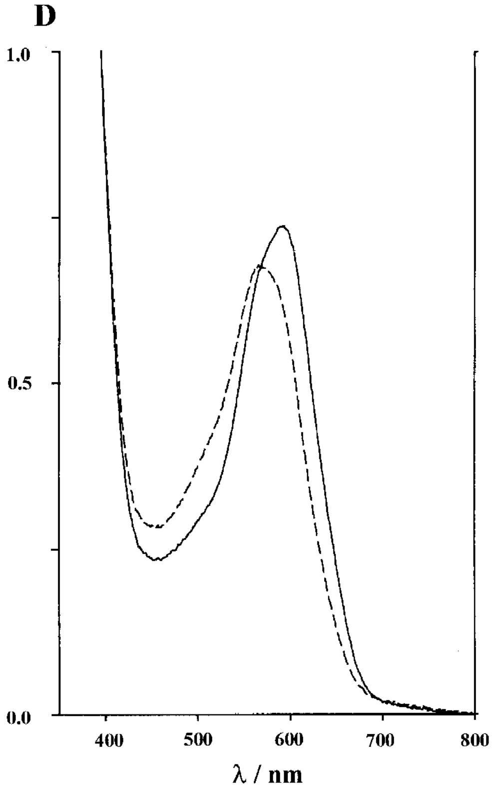


Figure 7. Absorption spectra of the merocyanine form after UV irradiation of the copolymer with 20 mol % of dye units in the glassy state at 25°C (solid line) and at 60°C (dashed line).

The irradiation of copolymers in the glassy state primarily leads to the formation of a monomeric form (λ_{max} = 595 nm), and this may be explained by a rather low probability of contact between two dye units in the merocyanine form. Quite a different situation is observed at temperatures above T_g: in this case side units are more mobile, and the probability of contact between two merocyanine units is much higher.

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