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Photo-optical properties of new combined chiral photochromic liquid crystalline copolymers

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For the first time, a series of cholesteric copolymers containing combined chiral photochromic side groups has been synthesized and the phase behaviour and optical properties of the copolymers have been characterized. Specific features of the photochemical and photo-optical behaviour of such systems were studied, and the quantum yields of the photo-induced process in solution and in the condensed state of the cholesteric copolymers were calculated. The selective light reflection wavelength was found to be controlled by the UV radiation. The synthesized polymers were shown to be promising candidates for colour data recording.

1. Introduction

At the present time, the synthesis and characterization of photochromic comb-shaped LC polymers containing azobenzene fragments are of great interest. The action of polarized light on films based on the above polymers leads to E–Z isomerization of the azo groups, which is accompanied by the directed orientation of side fragments and the appearance of photo-induced birefringence. Light-induced local and reversible changes in birefringence allow one to offer such polymers as advantageous materials for data recording and storage [1–7].

An alternative direction for the practical application of photochromic polymers involves the development of so-called 'commanding surfaces' [8–10]. The application of azobenzene-containing polymers as orientational films makes it possible to prepare a unique system due to the light-induced orientation of low molecular mass liquid crystal materials deposited onto the surface of such films.

As for chiral photochromic LC polymers, there are only few publications devoted to the synthesis and characterization of photochromic copolymers which are able to produce chiral nematic phases [11–14]. At the same time, these systems may be considered as promising materials for colour data recording due to the ability of chiral systems to change the parameters of their helical structure (pitch of helix) and values of the selective light reflection (λ_{max}) under the action of light.

Cholesteric cyclosiloxanes containing cholesteric and azobenzene units have been most fully studied [12, 13]. The action of polarized UV light on samples with a planar orientation leads to generation of the second and third orders of the selective light reflection. However, the principal disadvantages of such systems are associated with the fact that the light is adsorbed in the visible region, and this factor makes it difficult to study their photo-optical properties.

Cholesterol-containing copolymers with nematogenic units based on EE-bis-(benzylidene)cyclohexanone are free of the above drawbacks, and their description is given elsewhere [14]. The authors studied the possibility of E–Z isomerization and cross-linking in such systems. Under UV radiation, samples with planar orientation show 'degeneration' of the selective light reflection (λ_{max}). This behaviour is associated with the non-mesomorphic character of the Z-configuration of the nematogenic units which is produced as a result of the illumination of the test sample. Note that, in this case, photochromic properties are provided by the nematogenic 'matrix', and no light-induced changes in the pitch of the helix are observed.

At the same time, it seems interesting to combine photochromic and chiral fragments in one monomer unit. This combination would enable light-induced changes of both configuration of photochromic fragment and its so-called helical twisting power A, which can be expressed by the following relation:

$$A = \mathrm{d}P^{-1}/\mathrm{d}X \sim (\mathrm{d}\lambda_{max}^{-1}/\mathrm{d}X)_{X=0} \qquad (1)$$

where P is the pitch of the helix and X is the concentration of the chiral monomer units.

There are a few publications [15–17] devoted to low molecular mass mixed compositions in which a chiral dopant is able to experience photoisomerization, leading to changes in the pitch of the helix in the N* phase. The

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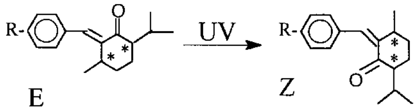
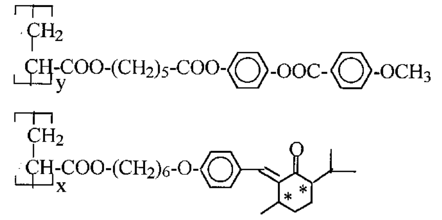
presence of the double (C=C) bond in the (-)-2-arylidene-*p*-menthan-3-one fragment of a chiral dopant allows light-induced changes in the configuration of the chiral fragment which are accompanied by concomitant variations in helix twisting power A as shown below ($A_E \gg A_Z$):



In previous work, we advanced a new approach to the synthesis of chiral photochromic polymers which involve chiral and photochromic fragments in the same monomer unit [18]. In this case, the above-mentioned dopant was used as a chiral photochromic fragment, which is capable of isomerization under the action of UV radiation. This fragment was used as a side group in acrylate copolymers containing chiral, but non-mesogenic 2-benzylidene-*p*-menthan-3-one and nematogenic phenyl benzoate groups:



In [18] a detailed description of the methods of synthesis of monomers and chiral photochromic copolymers was given, and their phase behaviour was considered. In this work, the principal attention focus was on studying the photochemical and photo-optical properties of the synthesized copolymers; this has unequivocally shown the fascinating advantages of their application for colour data recording.

2. Experimental

2.1. *Synthesis of monomers and polymers*

All monomers were synthesized according to the procedures described in [18, 19]. Figure 1 shows a schematic representation of the synthesis of the chiral monomer. The copolymers were synthesized by radical copolymerization of monomers in benzene solution at 60°C; AIBN was used as a initiating agent. All the synthesized copolymers were purified by repeated precipitation with methanol and dried in vacuum.

2.2. *Physical properties*

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

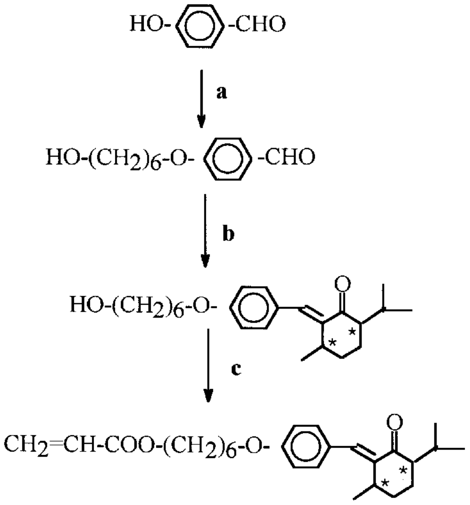


Figure 1. Synthetic scheme for the chiral monomer: (*a*) HO–$(CH_2)_6$–Br, acetone, K_2CO_3; (*b*) l-menthone, DMSO, KOH; (*c*) CH_2=CHCOCl, NEt_3, THF.

X-ray diffraction (XRD) analysis was carried out using a URS-55 instrument (Ni-filtered CuK_α radiation, $\lambda = 1{\cdot}54\,\mathrm{Å}$).

2.3. *Photochemical properties*

Photochemical properties were studied using a special set-up (figure 2) involving a DRSh-250 ultra-high pressure mercury lamp (1). Using filter (4), the 313 nm band of the linear emission spectrum was selected. To prevent heating of the samples due to IR radiation from the lamp, a water filter (3) was used. To obtain a plane-parallel light beam, the quartz lens (2) was used. During illumination, a constant temperature of the test samples

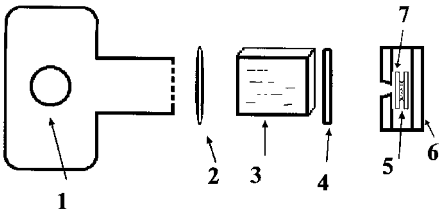


Figure 2. Scheme of the set-up used for the investigation of the photochemical behaviour of copolymer films: (1) high pressure Hg lamp DRSh-250, (2) quartz lens, (3) IR-filter, (4) filter (313 nm), (5) polymer sample, (6) heating state Mettler-FP-80, (7) quartz plates.

(5) placed between two flat quartz plates (7) was maintained using a Mettler FP-80 heating unit (6). The intensity of the UV radiation was determined actinometrically [20] and was equal to $2{\cdot}03\times10^{-9}$ Es s^{-1} cm^{-2} or 0·77 mW cm^{-2}.

In our studies of photochemical transformations in polymer solutions, *n*-octane and dichloroethane were used as solvents. Concentrations of the solutions were $1\text{–}5\times10^{-5}$ mol l^{-1}. For illumination, the solutions were placed in a 2 cm thick quartz cell. The process of isomerization was controlled by recording the absorption spectra of the illuminated solutions.

Photochemical properties of copolymers in the condensed state were studied by illuminating thick films (20 nm) at different temperatures. After a certain time of radiation, the samples were annealed at a temperature 30°C higher than the glass transition temperature. During annealing, the selective light reflection spectra were recorded. The samples were annealed until no changes in the selective light reflection wavelength were observed (usually, for about 40 min).

3. Results and discussion

3.1. *Phase behaviour and optical properties of chiral copolymers*

Figure 3 shows the phase diagram for the above copolymers. This diagram was constructed using data from polarization optical microscopy (DSC) and XRD. As follows from figure 3, copolymers containing less than 30 mol % of chiral units form a chiral nematic (N*) mesophase. Furthermore, at a relatively low (upto 15 mol %) content of chiral units in the copolymers, the chiral TDK* phase is formed and displays selective light reflection. As it is shown in [21], the achiral TDK phase is formed by a phenyl benzoate polymer with the local order typical of the crystal smectic K phase. The existence of chiral units in the copolymers leads to the twisting of this ordered phase, transforming it into the chiral phase (TDK*). Earlier, we described general features of the development of the TDK* phase (this phase was then referred to as N_B^* phase) in copolymers with non-mesomorphic chiral units [22]. The structure and properties of this phase are outside the scope of this work, and we only note that the TDK* phase is produced as a result of prolonged annealing (at least two weeks).

The occurrence of the chiral nematic mesophase over a relatively wide temperature–concentration region leads to selective reflection of the circularly polarized light. Figure 4 shows the temperature dependence of the selective light reflection wavelength for copolymers with different contents of chiral units. The profiles of the above dependences are typical of the N* mesophase, which is not 'complicated' by the elements of a layered structure. A slight untwisting of the helix with increasing temperature is associated with a decrease in the orientational order parameter *S*.

To estimate the helix twisting power of the new chiral photochromic component, λ_{max}^{-1} is plotted against the molar fraction of chiral units (at the reduced temperature $T=0{\cdot}95\ T_{cl}$) (figure 5). The helical twisting power *A* [23] was calculated from the slope of the initial portion of the line according to equation (1).

The calculated value of the helical twisting power was $15{\cdot}3\pm1{\cdot}3\ \mu m^{-1}$. This exceeds the values of *A* for cholesterol-containing units in corresponding copolymers [24, 25] and is comparable to those obtained for

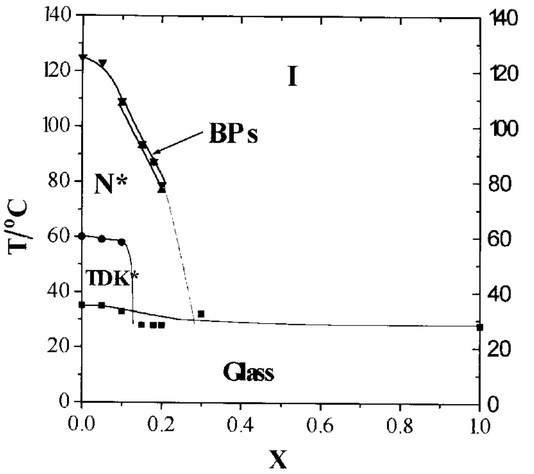


Figure 3. Phase diagram for the chiral photochromic copolymers (X: molar fraction of chiral units). BPs: blue phases, N*: chiral nematic phase, TDK*: chiral phase with local order typical of the crystal smectic K phase.

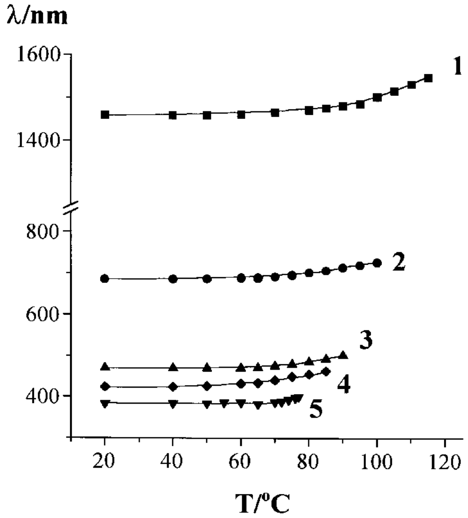


Figure 4. Temperature dependence of the maximum of selective light reflection for copolymers with 5(1), 10(2), 15(3), 18(4) and 20(5) mol % of chiral units.

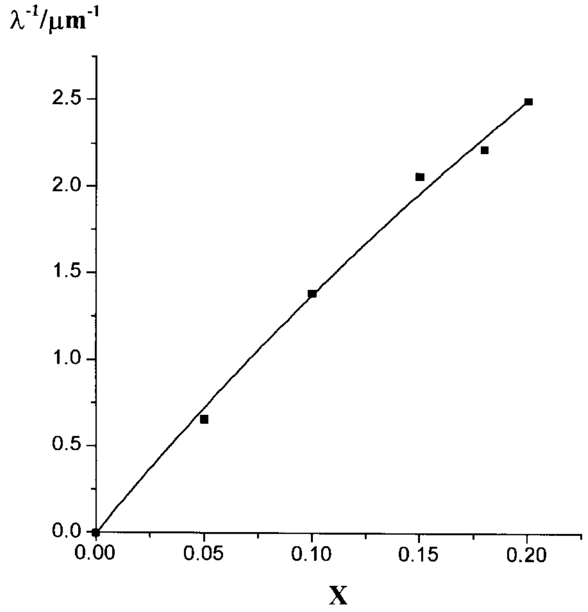


Figure 5. Dependence of λ_{max}^{-1} on the molar fraction of chiral units.

low molecular mass single-ring derivatives of menthone in the solutions of nematics [16, 26].

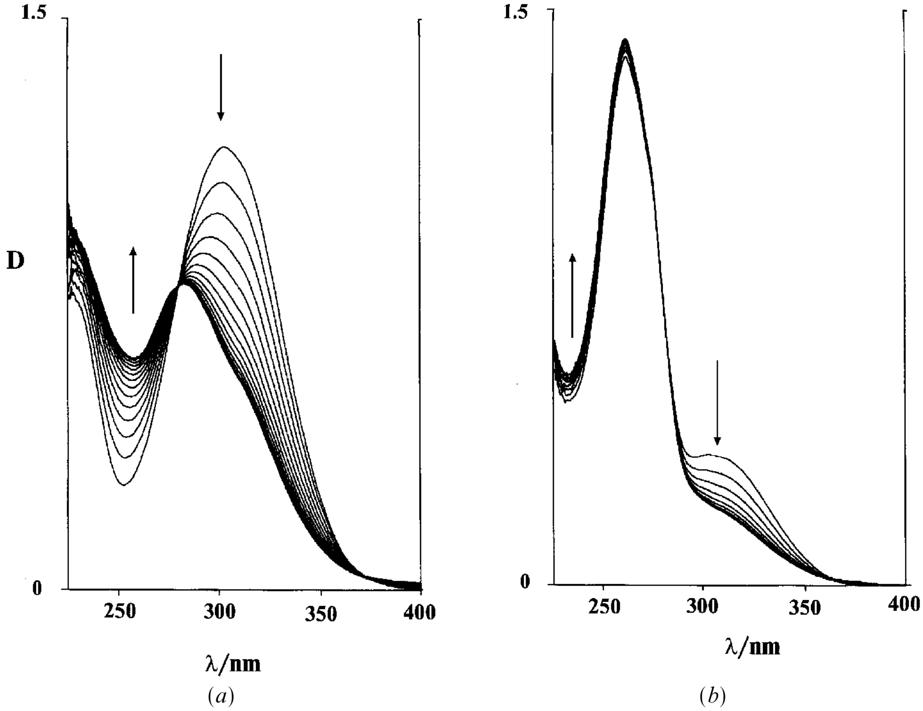
Hence, by varying the concentration of chiral photochromic component, one may prepare stable films with selective light reflection in the UV, visible, or IR spectral regions. On the other hand, the fact that the chiral fragment contains a double bond which is capable of E–Z isomerization offers a unique possibility to control the selective reflection wavelength using UV radiation.

3.2. *Photochemical behaviour of solutions of chiral photochromic homopolymer and copolymers*

In this work, we studied the photochemical behaviour of dilute solutions of the synthesized compounds containing the photosensitive benzylidenementhanone fragment. The solutions were illuminated during a fixed period of time (usually 5 min) and the absorption spectra were recorded.

Figure 6 shows the changes in the absorption spectra of solutions of the chiral homopolymer and one of the copolymers in dichloroethane solution under the action of UV radiation. As follows from figure 7, at a fixed wavelength (313 nm), the absorption of the solution decreases with time and after 100 min illumination achieves its constant value. This behaviour is associated with a lower extinction coefficient ε^{313} of the as-formed Z-isomer [16, 27]. The presence of a so-called isosbestic point [figure 6(*a*)] at $\lambda = 278$ nm according to [28] indicates the occurrence of only one photoprocess, that is, E–Z isomerization.

As follows from figures 6(*b*) and 7, in the case of the copolymer containing 30 mol % of chiral units, the optical density of the long wavelength ‘shoulder’ associated with the absorption of the chiral units decreases. The most intense absorption peak corresponding to



(*a*) (*b*)

Figure 6. Changes in the absorbance spectra of the chiral homopolymer (*a*) and the copolymer containing 30 mol % of chiral units (*b*) during UV irradiation (polymer solution in dichloroethane, $c = 4{\cdot}369 \times 10^{-5}$ mol l^{-1}; the interval between spectral recording was 5 min).

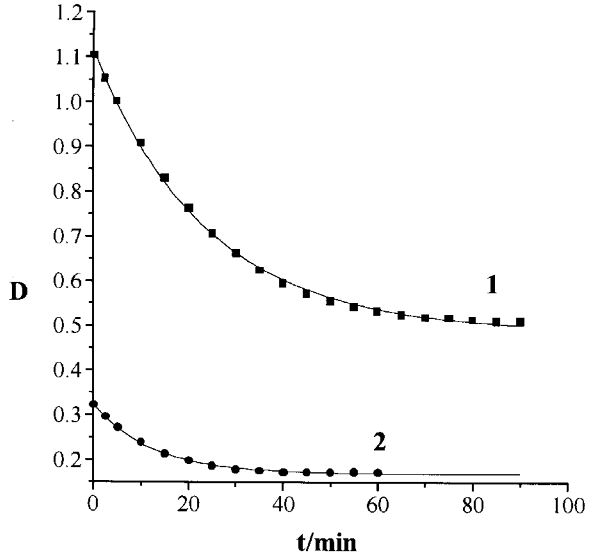


Figure 7. Change of the optical density D_{313} for solutions of the homopolymer (1) and the copolymer with 30 mol% of chiral units (2).

phenyl benzoate units ($\lambda_{max} = 263$ nm) remains unchanged. This fact indicates that the nematogenic groups of the polymer are not involved in the photochemical process.

Hence, the above experimental evidence confirms the occurrence of E–Z isomerization in the synthesized copolymers and that no secondary reactions take place. The corresponding spectra of the illuminated solutions exhibit no changes with time, that is, the back 'dark' process does not take place (at room temperature).

Attempts were made to estimate the quantum yield of the photoisomerization. According to [28], the quantum yield may be calculated as follows:

$$\varphi_E = -\frac{dn_E/dt}{I_{abs}} = -\frac{dc_E/dt}{I_{abs}}V \qquad (2)$$

where n_E and c_E stand for the molar content (mol) and concentration (mol l^{-1}) of E-isomer, respectively; I_{abs} is the intensity of the absorbed light per volume unit of the solution; V is the volume of the system.

It is known that $I_{abs} = I_0(1 - 10^{-D})$ and $c_E = D/\varepsilon_E^{313} l$, where D is the optical density of the solution at the initial moment of time (in other words, the optical density provided only by the presence of E-isomer); ε_E^{313} is the coefficient of extinction of E-isomer at a wavelength of 313 nm; l is the thickness of the measuring cell. Therefore, at the initial moment of time, the changes in the concentration of E-isomers may be written with a high accuracy as

$$\left(\frac{dc_E}{dt}\right)_{t\to 0} = \left(\frac{dD}{dt}\right)_{t\to 0} \frac{1}{\varepsilon_E^{313} l}. \qquad (3)$$

Substituting this expression into equation (2), we arrive at the following relationship:

$$\varphi_E = -\left(\frac{dD}{dt}\right)_{t\to 0} \frac{V}{I_0(1 - 10^{-D})\varepsilon_E^{313} l}. \qquad (4)$$

Using relationship (4), one may estimate the quantum yield of the direct E–Z process in the solutions studied. The results of our calculations are presented in table 1. The calculated values of the quantum yield correlate well with data obtained in earlier work [16, 27] devoted to low molar mass analogues.

3.3. *Photo-optical properties of the copolymers*

To reveal the general features of photochemical behaviour of the copolymers, 20 μm thick films were illuminated at different temperatures. For the films of copolymers illuminated at 25°C and not annealed at a temperature above T_g, the pitch of the helix remains unchanged. With increasing temperature, in the illuminated region of the test sample, the selective light reflection wavelength shifts.

As seen from figure 8, with increasing duration of illumination, the selective light reflection wavelength shifts to a longer wavelength region; that is untwisting of the helix takes place. Let us emphasize that the higher the temperature of illumination, the higher the intensity of this process. Note that the shift in the maximum of the selective light reflection peak is accompanied by its pronounced broadening (figure 9). Finally, this leads to its complete degeneration. Figure 10 shows a typical dependence of the half-width of the selective light reflection maximum $\Delta\lambda$ on the time of illumination. As is seen, even in the first minutes of illumination, there is a two-fold increase in $\Delta\lambda$, and then this value gradually increases.

The following speculations may be invoked to explain the broadening of the peak. The thickness of the test samples was 20 μm. At extinction coefficient

Table 1. Wavelengths of absorption maximum, extinction coefficients and quantum yields of E–Z isomerization for solution of the chiral materials under consideration (solvent: dichloroethane).

Polymers	λ_{max}	$\varepsilon_E^{max}/l\,mol^{-1}\,cm^{-1}$	$\varepsilon_E^{313}/l\,mol^{-1}\,cm^{-1}$	φ_E
Homopolymer	303	13 300	12 600	0·36
Copolymer with 30 mol% of the chiral units	262	15 800	12 300	0·33

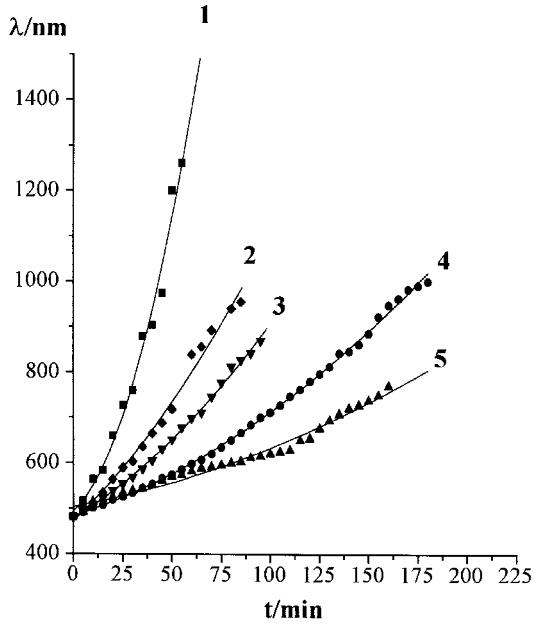


Figure 8. λ_{max} as a function of irradiation time for the copolymer with 15 mol % of chiral units. Temperature of irradiated sample: 115°C (1), 100°C (2), 80°C (3), 60°C (4) and 25°C (5).

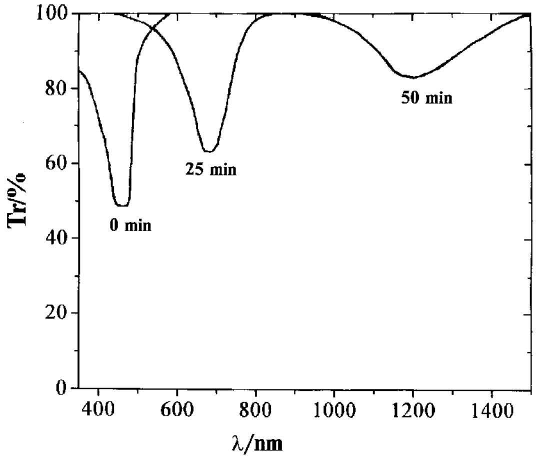


Figure 9. Change of the transmittance spectrum of the copolymer containing 15 mol % of chiral units at the irradiation temperature $T_{cl}+20$°C (the time of irradiation is indicated on the figure).

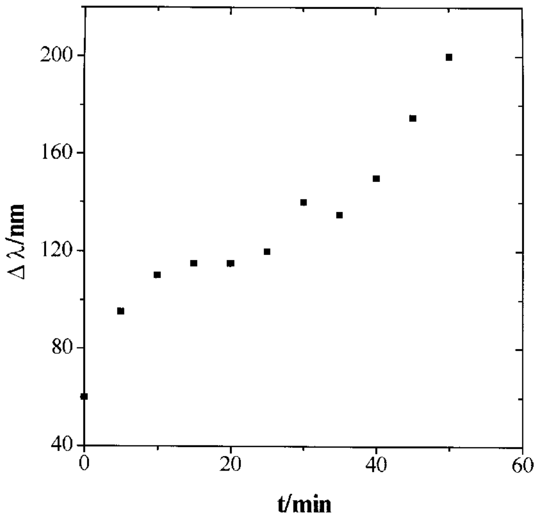


Figure 10. Half-width of the selective light reflection peak as a function of UV irradiation time for the copolymer with 15 mol % of chiral photochromic units at 130°C.

$\varepsilon_E^{313} \approx l\,10^5$ mol^{-1} cm^{-1}, the photochemical reaction proceeds in a very thin (about 1 μm) surface layer [28]. During illumination, even in the isotropic melt, thermal 'mixing' in the test samples is extremely low. This leads to the accumulation of a marked fraction of Z-isomer of the chiral side groups in the thin reaction layer. In the bulk, most of the chiral groups exist in the E-configuration. Annealing of the test samples is accompanied by the diffusion of macromolecules enriched with Z-isomer. Finally, noticeable fluctuations in the concentration of the Z-isomer in the sample was observed. As a result, the selective light reflection peak becomes more diffuse and then degenerates. Compositional inhomogeneity of the illuminated samples was the main reason why, in our experiments, we failed to fix the photostationary state in the copolymers.

The above photochemical studies of solutions allows one to conclude that the E–Z isomerization is responsible for an increase in the pitch of the helix (figure 8) and that the twisting power of the Z-isomer is likely to be much lower. For example, for low molecular mass analogues, the twisting power of Z-isomers is lower by an order of magnitude [26]. Radiation-induced variations in the helical twisting power of copolymers are associated with a strong change in the anisometry of the chiral fragment (figure 11). A decrease in anisometry of chiral molecules has a certain effect on the thermal stability of a mesophase, and, as a rule, the clearing temperature decreases (on average, by 10°C) after illumination for 2 h.

It seems interesting to estimate the efficiency of the photoprocess of the copolymers in different phase states by considering the above experimental evidence. To this end, we estimated the quantum yields of the photoprocess in films of the copolymers at different temperatures.

In the case studied, all incident light is absorbed by the sample. Therefore, $I_{abs}=I_0 S$ (I_0 is the intensity of the light source, S is the area of the illuminated surface). Hence, equation (2) may be written as:

$$\varphi_E = -\frac{dc_E/dt}{I_0} l, \qquad (5)$$

where l is the thickness of the test sample.

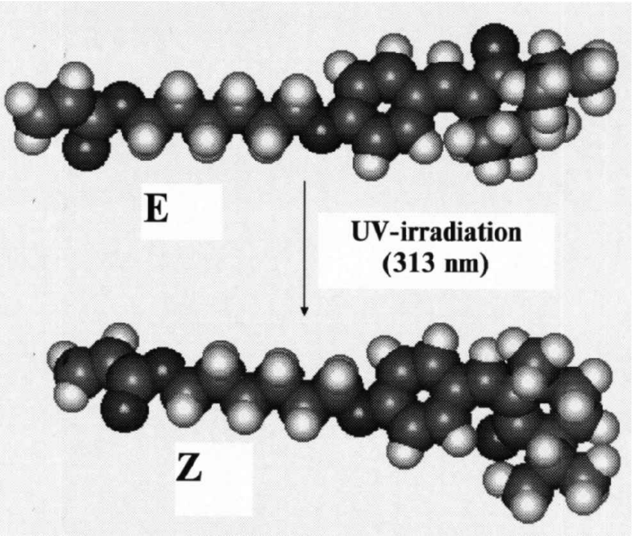


Figure 11. Molecular model showing change of anisometry of the (-)-2-arylidene-*p*-methan-3-one fragment during E–Z isomerization.

It seems necessary to relate the changes in the concentration of E-chiral units with the changes in the selective light reflection wavelength. According to the definition,

$$c_{\mathrm{E}}=\frac{n_{\mathrm{E}}}{V}=\frac{n_{\mathrm{E}}}{m/\rho}=\frac{n_{\mathrm{E}}}{n}\frac{\rho}{M}=X_{\mathrm{E}}\frac{\rho}{M} \tag{6}$$

$$\frac{\mathrm{d}c_{\mathrm{E}}}{\mathrm{d}t}=\frac{\mathrm{d}X_{\mathrm{E}}}{\mathrm{d}t}\frac{\rho}{M}. \tag{7}$$

Here, m stands for the mass of the test sample; M is the average molecular mass of the units in the copolymer; X_{E} is the molar fraction of chiral units in the E-configuration; ρ is the density of the copolymer; n_{E} is the content of chiral units before illumination (in moles); n is the total concentration of side units (in moles).

The molar content of chiral units may be easily estimated from the helical twisting power of E-isomer A_{E}:

$$X=\frac{\lambda_{\max}^{-1}}{A_{\mathrm{E}}}. \tag{8}$$

According to the published data [26], the helical twisting power of the Z-isomer is negligibly small as compared with that of the E-isomer. Therefore, at the initial moment of time,

$$\frac{\mathrm{d}X_{\mathrm{E}}}{\mathrm{d}t}=\frac{\mathrm{d}\lambda_{\max}^{-1}}{\mathrm{d}t}\frac{1}{A_{\mathrm{E}}}. \tag{9}$$

By substituting this expression into relationship (7), the following equation may be obtained:

$$\frac{\mathrm{d}c_{\mathrm{E}}}{\mathrm{d}t}=\frac{\mathrm{d}\lambda_{\max}^{-1}}{\mathrm{d}t}\frac{1}{A_{\mathrm{E}}}\frac{\rho}{M}. \tag{10}$$

The final equation for the quantum yield may be easily obtained by substitution of expression (10) into equation (5):

$$\varphi'_{\mathrm{E}}=(\varphi_{\mathrm{E}})_{t=0}=-\frac{\rho l}{MA_{\mathrm{E}}l_0}\left(\frac{\mathrm{d}\lambda_{\max}^{-1}}{\mathrm{d}t}\right)_{t=0} \tag{11}$$

For copolymers, the values of self-diffusion coefficients are low as compared with the rate constant of the photochemical process because, in the films studied, photoreaction primarily proceeds in the thin layer (about a 1 μm thick layer in the 20 μm thick film). It is important to mention that annealing is accompanied by changes in the pitch of helix. As a result of annealing, the concentration of the as-formed Z-isomer becomes the same across the whole thickness of the illuminated film.

Hence, one may conclude that the rate of isomerization is controlled by the diffusion of the reacted component. Therefore, the calculated values of the quantum yield are associated not only with the photochemical process but also they are primarily controlled by the self-diffusion coefficients. Nevertheless, using equation (11) and taking into accout the parameters of cofactors involved in this equation, the values of φ_{E} were calculated.

In the case studied, ρ is equal to 1 g cm^{-3}, $l=20$ μm, $A_{\mathrm{E}}=15{\cdot}3$ μm^{-1}, $M=412$ g mol^{-1} (mean molecular mass of the side units), $I_0=2{\cdot}03\times10^{-9}$ Es s^{-1} cm^{-2} = $1{\cdot}21\times10^{-7}$ Es min^{-1} cm^{-2} (intensity of UV radiation).

Table 2 shows the values of $(\mathrm{d}\lambda_{\max}^{-1}/\mathrm{d}t)_{t=0}$ and the apparent quantum yields for the copolymers containing 10 and 15 mol % of chiral units.

As is evident from table 2, in the films of the copolymers, the corresponding values of the quantum yield are lower than those in solution (table 1) by about one order of magnitude. This fact is associated with the higher viscosity of the copolymers in the condensed state.

Let us consider the effect of temperature on the rate of this process in more detail. With increasing temperature, a marked increase in rate of helix untwisting is observed, and the isotropic melt is characterized by the maximal values of the apparent quantum yield. Figure 12 shows the temperature dependence of the quantum yield for one of the copolymers in the temperature range covering the glassy state, LC state, and isotropic melt. The photochemical process of photoisomerization is likely to be affected by increasing temperature to a lesser extent, and the above increase in the rate of helix untwisting is associated with a dramatic decrease in the viscosity of polymer and an increase in the self-diffusion constants with increasing temperature. As the temperature increases, 'mixing' of the system is enhanced, and the efficiency of helix untwisting increases.

Table 2. Values of $(\mathrm{d}\lambda_{\max}^{-1}/\mathrm{d}t)_{t=0}$ and apparent quantum yield φ_E' for copolymers measured at different temperatures.

Chiral units content	Temperature of film irradiation/°C	$(\mathrm{d}\lambda_{\max}^{-1}/\mathrm{d}t)_{t=0}/\mu\mathrm{m}^{-1}\,\mathrm{min}^{-1}$	φ_E'
10 mol%	$T_{cl}+20=130$	−0·016	0·037
	60	−0·061	0·014
	25	−0·001	0·003
15 mol%	$T_{cl}+20=124$	−0·030	0·070
	100	−0·017	0·041
	80	−0·012	0·029
	60	−0·006	0·018
	25	−0·005	0·011

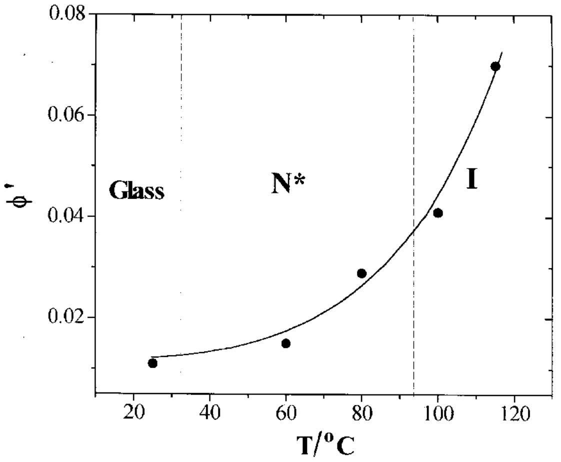


Figure 12. Dependence of apparent quantum yield on temperature for copolymer with 15 mol% chiral-photochromic units.

Problems concerning back processes are still unclear, but in this work we have shown that all systems do not experience a reversible thermal Z–E isomerization (at least, at temperatures below 120°C). Nevertheless, examination of the above experimental evidence allows us to conclude that the synthesized copolymers comprise unique and promising materials for colour data recording.

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