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Photosensitive cholesteric polymers with azobenzene-containing chiral groups and mixtures of cholesteric copolymer with chiral-photochromic dopants

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New chiral photochromic cholesteric comb-shaped acrylic copolymers and low molecular mass dopants containing azobenzene photosensitive fragments and chiral groups based on menthol and menthone were synthesized. For the copolymers and their mixtures with low molecular mass dopants, the phase behaviour and optical properties were studied. Under irradiation with UV and visible light, the untwisting of cholesteric helix takes place, and the selective light reflection maximum is shifted to the long wavelength spectral region. This shift is related to the *E–Z* isomerization of the azobenzene chiral groups. For the copolymers and mixtures of the cholesteric polymer with the menthyl-containing dopant, this process is thermally reversible. The specific features of the kinetics of the forward and the reverse thermal processes were characterized. It was demonstrated, that the copolymers and mixtures of the cholesteric copolymer with the menthyl-containing dopant may be used for coloured reversible recording of optical information. For such materials, their resistance with respect to the repeated 'recording–erasing' cycles was tested, and the fatigue resistance was shown to be rather high.

1. Introduction

After starting at the end of the 1980s, the number of the publications devoted to studies of photosensitive polymer liquid crystals has markedly increased [1–12]. This is related to the wide range of possibilities for their practical application as optically active media for the recording and storage of optical information, in holography, in the development of command surfaces, etc. In this connection, the combination of photochromic properties with a supramolecular structure and the unique optical properties of cholesteric liquid crystals seems to be very attractive.

In research performed by the Philips research group and in our laboratory, pioneering approaches in the development of polymer cholesteric liquid crystals with photocontrollable helical pitch and selective light reflection maximum have been advanced [13–17]. Upon UV irradiation, such materials are able to undergo the *E–Z* isomerization of chiral groups which is made possible by the presence of double C=C bonds in the side groups of the macromolecules. In turn, this process is accompanied by a decrease in the anisotropy and twisting power of the chiral groups; thus, the helical pitch and selective light reflection maximum are changed. Hence, light irradiation provides an effective method for controlling the supramolecular structure and optical properties of polymer films.

However, despite this, all the materials of this synthesized type show a marked drawback: the changes in the selective light reflection maximum are irreversible. This problem may be solved by synthesizing a copolymer which, in addition to chiral groups, contains photochromic groups capable of reversible light-induced rearrangements. As such photochromic units, one may use azobenzene groups which are widely acknowledged as promising groups for the preparation of reversible systems [1–12]. The second chiral component of the target copolymer may be provided by menthol derivatives which are known to be characterized by a high helical twisting power.

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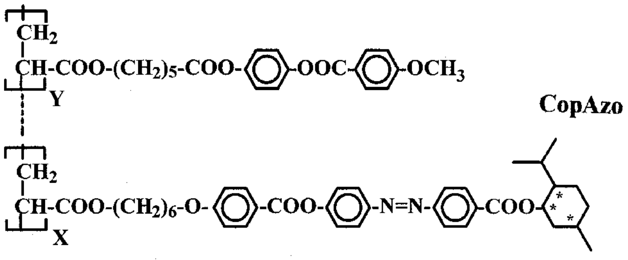
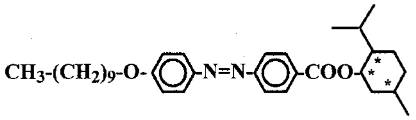
We have previously demonstrated the possibility of preparing a cholesteric material with a reversibly photocontrolled helical pitch using a blend of a chiral nematic copolymer with a low molar mass chiral dopant containing an aminoazobenzene fragment [18]. However, this dopant shows serious drawbacks. First, for this blend, the rate of the reverse thermal process is too high; second, fatigue resistance appears to be too low.

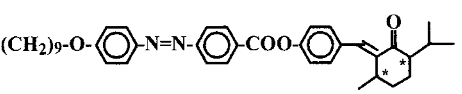
Taking into account these results, the objective of the present work involves the preparation of a binary copolymer CopAzo composed of the nematogenic fragment responsible for the formation of a nematic phase, and a chiral photochromic fragment composed of photochromic (azobenzene) and chiral (menthyl) groups;

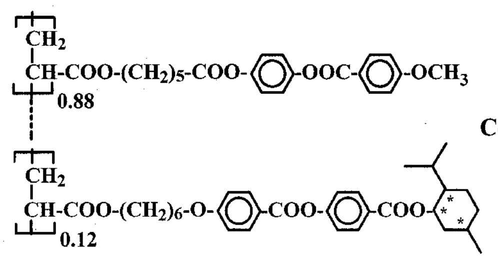

CopAzo

X=0.0-0.2; 1.0.

Preliminary data [19] demonstrated the possibility of the preparation of photosensitive reversible systems based on such copolymers and mixtures containing an azobenzene-based chiral dopant. In this work, we present the synthesis and characterization of specific kinetic features of the forward and back isomerization reactions and also, the kinetics of the shift of the selective light reflection maximum for cholesteric copolymers with azobenzene-containing chiral photochromic side groups (CopAzo). Furthermore, mixtures of the low molecular mass chiral photochromic dopants Azo and MtnAzo with a menthyl-containing copolymer CopMt were prepared:


Azo


MtnAzo


CopMt

We studied the mixtures of CopMt with Azo or AzoMtn containing 3 mol% of dopants. Dopant MtnAzo is structurally similar to the chiral photochromic side groups of the copolymers CopAzo, allowing one to carry out a comparative analysis of the kinetics of the photoprocesses for the 'pure' copolymers and for the mixtures of low molecular mass dopants with cholesteric polymer.

It should be noted that the dopant MtnAzo contains two photosensitive fragments capable of *E–Z* photoisomerization (double C=C and N=N bonds). This fact opens many possibilities for its application as a binary photochromic system. As is known from the literature, the photoisomerization of the azobenzene fragment with respect to the N=N bond is thermally and photochemically reversible. At the same time, isomerization of the benzylidenementhanone fragment with respect to the C=C bond is thermally irreversible. In other words, with the dopant MtnAzo, we have the unique possibility for studying the specific features of photoinduced rearrangements in systems with dual photochromism. This work is focused on a comparative analysis of the specific features of the photo-optical behaviour of these systems.

2. Experimental

2.1. *Synthesis of monomers and dopants*

The nematogenic monomer and the menthyl-containing non-photosensitive copolymer were synthesized according to procedures described in [20] and [21], respectively.

2.1.1. *Synthesis of the chiral-photochromic monomer l-menthyl 4-{4-[4-(6-acryloyloxyhex-1-yloxy)-phenylcarboxyloxy]phenylazo}benzoate (figure 1)*

4-Hydroxyazobenzoic acid was synthesized by a standard azo-coupling reaction [22] using 4-aminobenzoic acid.

2.1.1.1. *4-(4-Methoxycarbonyloxyphenylazo)benzoic acid, compound **1**, reaction (a).* The protection of the hydroxy group of 4-hydroxyazobenzoic acid was performed using a standard method [23]. 20.0 g (83 mmol) of 4-hydroxyazobenzoic acid was mixed with a solution of 8.3 g (206.6 mmol) of NaOH in 200 ml of water. The mixture was cooled in an ice–salt bath to 1–3°C and 7.7 ml (99.6 mmol) of methyl chloroformate was added dropwise over 3 h. The mixture was stirred for a further 2 h and hydrochloric acid was added until a pH of 5 was achieved. The resulting precipitate was filtered off and washed with water. After drying in vacuum over P_2O_5, the product was recrystallized from ethanol; yield 71% of a red crystalline powder. IR (cm^{-1}): 2960, 2850 (CH_2), 1764 (CO in $CH_3{-}O{-}COO{-}$), 1690 (CO in $-COOH$), 1603, 1501 (C−C in Ar).

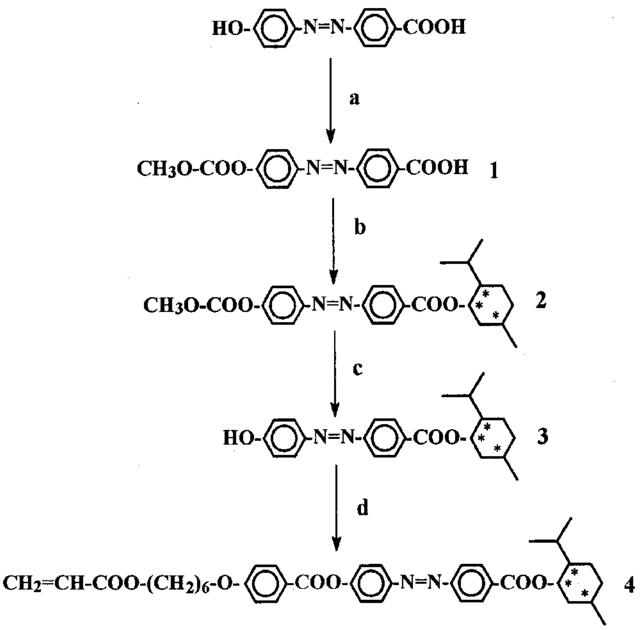


Figure 1. Synthesis of the chiral-photochromic monomer. (*a*) $CH_3O–COCl$, NaOH, H_2O; (*b*) (1) $SOCl_2$, (2) *l*-menthol, NEt_3, DMAP, THF; (*c*) NH_3, H_2O, EtOH; (*d*) $CH_2–CH–COO–(CH_2)_{10}–Ph–COOH$, DCC, DMAP, THF.

2.1.1.2. *l-Menthyl 4-(4-methoxycarbonyloxyphenylazo)benzoate, compound **2**, reaction (b).* (4-Methoxycarbonyloxyphenylazo)benzoic acid **1** (7.3 g, 24.3 mmol), thionyl chloride (20 ml), and a drop of dimethylformamide were added successively to a 200 ml round-bottom flask equipped with a reflux condenser and calcium chloride tube. The mixture was allowed to react for 24 h. The excess thionyl chloride was removed by evaporation, and the residue recrystallized from a toluene–hexane mixture (1:5): yield 7.5 g (96%) of 4-(4-methoxycarbonyloxyphenylazo)benzoyl chloride.

A solution of the acid chloride in THF was added dropwise to a solution of *l*-menthol (3.7 g, 23.4 mmol), triethylamine (4.1 ml, 28.1 mmol), and *N*,*N*′-dimethylaminopyridine (DMAP, 0.34 g, 2.8 mmol) in 25 ml of THF. The mixture was stirred for 3 days. Chloroform (100 ml) was added and the solution was washed with water. The chloroform extract was dried with anhydrous $MgSO_4$. After removal of the solvent, the red crude product was purified by column chromatography (eluent chloroform); yield 0.6 g (6%), red powder, m.p. 110–112°C. IR (cm^{-1}): 2960, 2890, 2870 (CH_2), 1766 (CO in $CH_3–O–COO–$), 1710 (CO in Ar–COO–), 1598, 1496 (C–C in Ar), 1270 (COC).

2.1.1.3. *l-Menthyl 4-(4-hydroxyphenylazo)benzoate, compound **3**, reaction (c).* Compound **2** (0.6 g, 1.4 mmol) was dissolved in 20 ml of ethanol, cooled in an ice bath, and a 25% aqueous solution of ammonia (10 ml) was added. The reaction was monitored by thin-layer chromatography; it was complete in 2 h. The solution was acidified with hydrochloric acid until weakly acidic, diluted with water, and extracted several times with chloroform (the total volume of the extract was about 100 ml). The extract was washed several times with water, dried over anhydrous $MgSO_4$, and the solvent evaporated. The product was purified by column chromatography (eluent chloroform); yield 0.38 g (71%) of a red powder. IR (cm^{-1}): 3350 (OH), 2960, 2890, 2870 (CH_2), 1712 (CO in Ar–COO–), 1598, 1504 (C–C in Ar).

2.1.1.4. *l-Menthyl 4-{4-[4-(6-acryloyloxyhex-1-yloxy)-phenylcarboxyloxy]phenylazo}benzoate, compound **4**, reaction (d).* 4-(6-Acryloyloxyalk-1-yloxy)benzoic acid (1.0 mmol) synthesized according to [24], phenol **3** (1.0 mmol), and DMAP (0.1 mmol) were dissolved in 1.5 ml of tetrahydrofuran. Dicyclohexylcarbodiimide (DCC) (1.2 mmol) was added and the resulting mixture stirred for 36 h. The reaction was monitored by TLC using a toluene–ethylacetate (10:1) mixture as eluent. The resulting precipitate was filtered off and washed with tetrahydrofuran; and chloroform (50 ml) was added to the filtrate. The solution was successively washed with water, a 5% solution of acetic acid, and finally with water until a pH of 7 was achieved. The chloroform extract was dried over anhydrous $MgSO_4$. The solvent was removed under vacuum, and the product purified by column chromatography using chloroform as eluent; yield 38% of a red crystalline powder, m.p. 95–97°C. IR (cm^{-1}): 2950, 2890, 2870 (CH_2), 1726 (CO in $CH_2=CH–COO–Alk$), 1710 (CO in Ar–COO–Ar′), 1644 (C=C), 1602, 1508 (C–C in Ar), 1272 (COC).

2.1.2. *Synthesis of the chiral-photochromic dopants*

2.1.2.1. *l-Menthyl 4-(4-dec-1-yloxyphenylazo)benzoate (Azo).* To a cooled solution of *l*-menthol (4.31 mmol), triethylamine (5.6 mmol) and DMAP (0.56 mmol) in 2 ml of distilled THF, was slowly added 4-(1-decyloxy)-phenylazobenzoyl chloride (4.31 mmol), synthesized by a procedure similar to that reported in [22]. The resulting mixture was stirred for 3 days. Chloroform (50 ml) was added and the solution was washed successively with water, a 5% solution of acetic acid, and finally with water until a pH of 7 was achieved. The chloroform extract was dried with anhydrous $MgSO_4$. After removal of the solvent, the red crude product was purified by column chromatography (eluent chloroform); yield 39% of a red powder, m.p. 78–79°C. IR (cm^{-1}): 2920, 2888, 2856 (CH_2), 1710 (CO), 1600, 1588 (C–C in Ar), 1256 (COC).

2.1.2.2. *4′[4-(4-Dec-1-yloxyphenylazo)benzoyloxy]-benzylidene-2-menthan-3-one (MtnAzo).* This was prepared using a similar method involving (−)-4-hydroxy-benzylidenementhan-3-one, synthesized according to [16]; yield 78% of a red powder, Cr 115–116 SmA 141–142 N* 180–181 I (°C). IR (cm^{-1}): 2980, 2920, 2856 (CH_2), 1730 (CO), 1680 (ketone C=O), 1600, 1500 (C–C in Ar), 1250 (COC).

2.2. *Synthesis of the polymers and preparation of mixtures*

The copolymers were synthesized by the radical copolymerization of solutions of the monomers in benzene at 60°C; AIBN was used as the initiator. All the synthesized copolymers were purified by repeated precipitation with methanol and dried under vacuum.

Mixtures of low molar mass dopants with the menthyl-containing copolymer were prepared by dissolving the copolymer and dopants together in dichloroethane, followed by solvent evaporation at 60°C. The mixtures were dried under vacuum at 120°C for 2 h.

2.3. *Physiochemical methods of investigation*

IR spectra were recorded using a Bruker WP-200 instrument in the range 4000–400 cm^{-1}. The samples were prepared as KBr pellets. In the case of oil-like substances, the compounds were applied as thin layers on a KBr plate.

The relative molecular weights of the copolymers were 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 using a UV detector, THF as solvent (1 ml min^{-1}, 40°C), and a set of PL columns of 100, 500 and 10^3 Å; a calibration plot was constructed with polystyrene standards. The copolymers obtained have the following molar mass characteristics: $M_n = 12\,000–15\,000$, $M_w/M_n = 2.1–3.1$.

The phase transitions exhibited by the copolymers were studied by differential scanning calorimetry (DSC) using a Perkin Elmer DSC-7 thermal analyser (a scanning rate of 10 K min^{-1}, and prior to the DSC measurement samples were annealed for one month at 45°C).

The polarizing microscope investigations were performed using a Mettler TA-400 thermal analyser and a LOMO P-112 polarizing microscope.

The selective light reflection of the chiral polymers was studied using a Hitachi U-3400 UV-Vis-IR spectrophotometer equipped with a Mettler FP-80 hot stage. Polymer samples with a thickness of 20 μm were sandwiched between two flat glass plates. Prior to tests, the polymer 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_α-radiation, $\lambda = 1.54$ Å).

2.4. *Photochemistry*

Photochemical investigations were performed using a special instrument [15] equipped with a DRSh-250 ultra high pressure mercury lamp and N_2 laser (337 nm). Using a filter, light with a maximum wavelength of 363 nm or > 450 nm was selected. To prevent the heating of the samples due to IR irradiation, 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 intensity of UV radiation was equal to 1.9×10^{-8} Es s^{-1} cm^{-2} (as measured actinometrically [25]); the intensity of visible light (> 450 nm) was equal to ~ 8.0 mW cm^{-1} (as measured by an IMO-2N intensity meter).

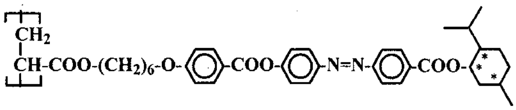
In our studies of photochemical transformations in solution, dichloroethane was used as the solvent; the concentrations of the solutions were $1–5 \times 10^{-5}$ mol l^{-1}. For illumination, the solutions were placed in a 2 cm thick quartz cell. The isomerization process was monitored by recording the absorption spectra of the illuminated solutions.

Photochemical properties of the mixtures and copolymers were studied by illuminating 20 μm thick films or thin films obtained by the casting of chloroform solutions followed by evaporation at 60°C. Immediately after irradiation, absorbance or transmittance spectra were recorded using the Hitachi U-3400 UV-Vis-IR spectrometer.

3. Results and discussion

3.1. *Phase behaviour and optical properties of copolymers CopAzo and mixtures of CopMt with 3 mol% Azo and 3 mol% MtnAzo*

First, let us briefly consider the phase behaviour of the CopAzo copolymers and mixtures of CopMt with either 3 mol % Azo or MtnAzo. The homopolymer of the chiral photochromic monomer (HomoAzo) is amorphous, and this is likely to be related to the presence of the bulky menthyl group preventing the formation of a liquid crystal phase;



HomoAzo

By comparison, all the copolymers containing less than 20 mol % of chiral photochromic groups and the mixtures of CopMt with 3 mol % of both the chiral photochromic dopants exhibit the cholesteric phase. We note that, as the content of the chiral photochromic groups is increased or as dopant Azo is added to the copolymer CopMt, the clearing temperature decreases (table 1). This behaviour is likely to be related to the effect of the bulky menthyl group. By comparison, the introduction of the dopant MtnAzo induces no changes in the thermal stability of the mesophase: in this case, the chiral dopant contains a long highly anisometric aromatic fragment.

All these copolymers and mixtures are characterized by selective light reflection in both visible and IR spectral regions (figure 2). We note that, in the case of the copolymers CopAzo, as the temperature is decreased, the selective light reflection maximum increases slightly, figure 2 (*a*); this trend is most pronounced for the copolymers with a high content of chiral groups. This behaviour has been observed also for menthyl-containing copolymers with a long three-ring aromatic fragment in the chiral side groups; this is associated with the presence of smectic order fluctuations in the copolymers [26, 27].

In the case of the mixtures of copolymer CopMt with Azo and MtnAzo, figure 2 (*b*), a quite different situation is observed: as the temperature is increased, an untwisting of the cholesteric helix is observed. In this case, on approaching the isotropization temperature, a principal role is attributed to a decrease in the orientational order parameter [28].

Using the approach proposed in [21], we calculated the twisting power β of the chiral photochromic groups in the copolymers. For the calculation of the twisting power of the chiral photochromic dopants in the mixtures, the following equation (1) was used:

$$\beta/n = \Delta\lambda_{\max}^{-1}/X \qquad (1)$$

where n is the average refractive index, $\Delta\lambda_{\max}$ is the difference between the selective light reflection wavelengths of the mixtures and copolymer and, X is the mole fraction of the chiral photochromic dopant. The values of β/n are summarized in table 2. We note that, in the case of the chiral photochromic units of the

Table 1. Thermal properties of copolymers and mixtures.

X/mol%	T_g/°C	T_{cl}/°C
Copolymers		
5	24	125
10	28	122
15	31	115
20	24	112
100 (HomoAzo)	57	amorphous
Copolymer CopMt	25	103
Mixtures		
CopMt with Azo	30	97
CopMt with MtnAzo	31	104

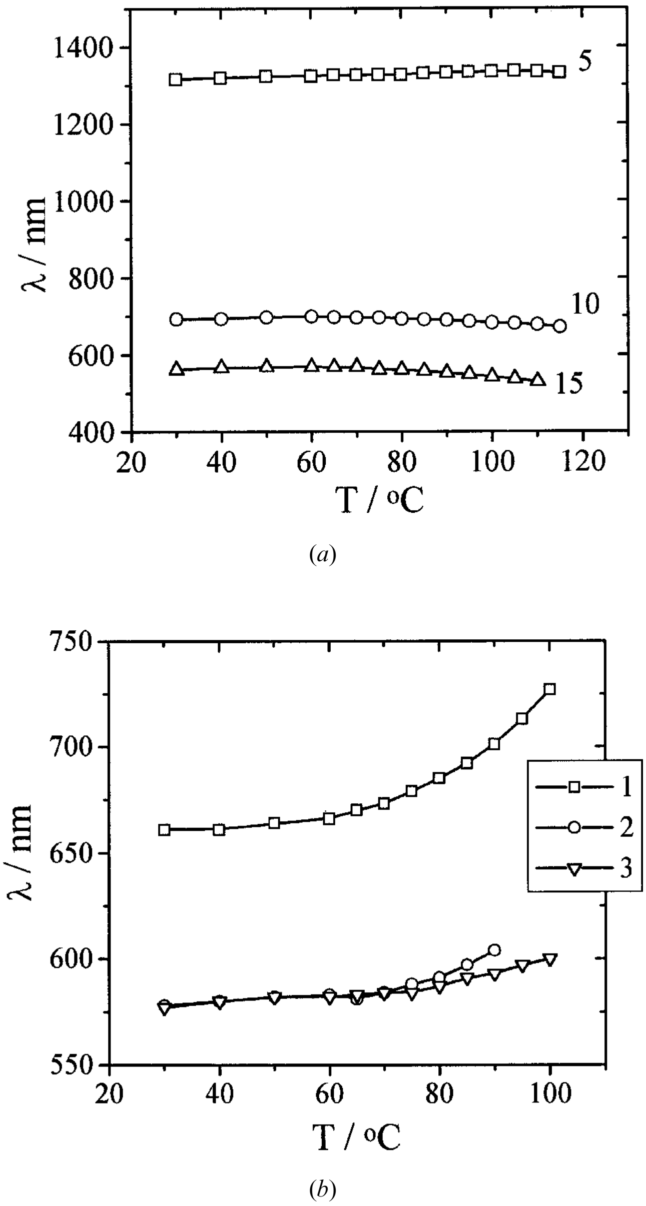


Figure 2. Temperature dependence of the selective light reflection wavelength: (*a*) for the azobenzene-containing copolymers CopAzo with differing content of chiral units (shown in mol%) and (*b*) for the menthyl-containing copolymer CopMt (1) and the mixtures with 3 mol% of the chiral-photochromic dopants Azo (2) and MtnAzo (3).

Table 2. Values of the helical twisting power β/n (at $T = 0.95T_{cl}$) of the chiral component for the chiral photochromic copolymers and mixtures.

Sample	$\beta/n/\mu m^{-1}$
Copolymers CopAzo	18.5 ± 2.1
Mixture CopMt with Azo	9.6 ± 2.0
Mixture CopMt with MtnAzo	8.6 ± 2.0

copolymers CopAzo, the twisting power is about two times higher than β/n of the low molecular mass dopants involved in the matrix of the cholesteric copolymer. To gain a deeper insight into the reasons of such behaviour, additional studies are now required.

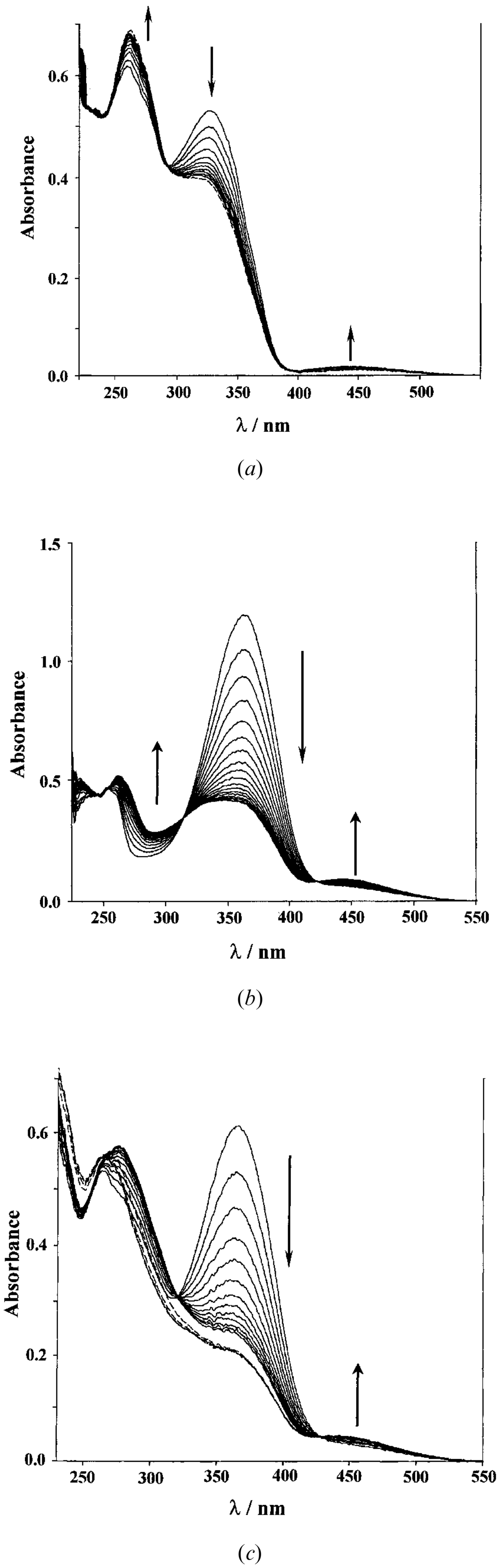
3.2. *Photochromic- and thermo-chromic properties of chiral-photochromic systems*

3.2.1. *Solutions of the chiral-photochromic homopolymer and dopants*

We now turn our attention to the photochemical behaviour of the synthesized compounds and their mixtures. Let us first consider in brief the photochemical transformations taking place in dilute solutions of the chiral photochromic homopolymer HomoAzo and the low molecular mass dopants in dichloroethane.

As follows from figures 3(*a–c*), upon UV irradiation dramatic spectral changes are observed, typical of the *E–Z* isomerization of the azobenzene group: specifically, the extinction coefficient of the π–π* electron transition decreases whereas, for the *n*–π* transition, this value slightly increases [29]. In this case, the existence of isosbestic points suggests that the chiral photochromic homopolymer and dopant Azo undergo a single photochemical process which is the isomerization with respect to the N=N bond [30]. For dopant Azo, the spectral changes are more pronounced as compared with those of the chiral photochromic homopolymer HomoAzo. This fact may be explained by the presence of the phenylbenzoate chromophore in the side groups of HomoAzo which shows no changes under irradiation (365 nm) and provides a marked contribution to the absorption spectrum. We note that this process is photochemically and thermally reversible, and the action of visible light leads to a back *Z–E* isomerization; even at room temperature, dark back isomerization is observed.

In the case of dopant MtnAzo, a somewhat different situation is observed: in the initial stage, the pattern of the spectral changes is quite similar to that described above, figure 3 (*c*), but as a result of prolonged irradiation (more than 20 min), more dramatic spectral changes are seen, and these are related to the changes in the absorption band of the benzylidenementhan-3-one fragment.



(*a*)

(*b*)

(*c*)

Figure 3. Changes of the absorbance spectra of solutions in dichloroethane: (*a*) of homopolymer HomoAzo ($c=7\times10^{-3}\,\mathrm{mg\,ml^{-1}}$); (*b*) of dopant Azo ($c=11.8\times10^{-3}\,\mathrm{mg\,ml^{-1}}$) and (*c*) of dopant MtnAzo ($c=5.5\times10^{-3}\,\mathrm{mg\,ml^{-1}}$), during UV irradiation (365 nm, $1.9\times10^{-8}\,\mathrm{Es\,s^{-1}\,cm^{-2}}$, 20°C). Spectra were recorded each 20 s (*a*) and 10 s (*b* and *c*) of irradiation. Dashed line in figure (*a*) corresponds to photostationary state; dashed lines in figure (*c*) correspond to 20, 40 and 60 min of UV irradiation.

The absence of isosbestic points suggests the occurrence of at least two processes. In the initial stages of light irradiation, primarily *E–Z* isomerization about the N=N bond takes place, and this is likely to be related to the high values of the extinction coefficient of the azobenzene chromophore at the light wavelength used (365 nm). The quantum yields of photoisomerization of azobenzene groups about the N=N bond and of the benzylidenementhan-3-one fragments about the C=C bond are comparable; in this case, the ratio between the extinction coefficients is of key importance [31, 32]. Once the first photostationary state related to the achievement of a certain ratio between *E* and *Z* isomers of the azobenzene fragments is attained, spectral changes associated with the isomerization of the benzylidenementhan-3-one fragment are seen. We note that, in this case, the back process only about the N=N bond is allowed; as a result, after the back process the initial spectral profile is incompletely recovered, which may be explained by the irreversible changes of the benzylidenementhan-3-one fragment.

3.2.2. *Thin films based on the chiral-photochromic homopolymer and copolymers*

Let us consider the spectral changes observed in thin films of the chiral photochromic homopolymer HomoAzo and copolymers CopAzo. As follows from figure 4, at a qualitative level the spectral changes are similar to those seen for solutions. However, we note firstly that, for the homopolymer and copolymer with 20 mol % of chiral photochromic groups, the maxima of the π–π* electron transitions are shifted to the low wavelength spectral region (329 and 339 nm for homopolymer and copolymer, respectively, compared with 367 nm in the case of their solutions in dichloroethane). Secondly, in this case, the irradiation-induced spectral changes are not so pronounced. Both phenomena are likely to be related to the aggregation of the azobenzene chromophores in the condensed phase [33–35]. On the one hand, as a result of the interaction of the chromophores, the absorption maximum is shifted; on the other hand, the occurrence of *E–Z* photoisomerization is prevented (to a certain extent).

We also studied the specific features of the kinetics of the back thermal process of the *E–Z* isomerization for the homopolymer HomoAzo and one of the copolymers (containing 15 mol % of chiral photochromic groups). To this end, the films of the UV-irradiated polymers were annealed at different temperatures, and the corresponding absorption spectra were recorded within certain periods of time. To calculate the rate constants of the back *E–Z* isomerization, the absorbance is plotted against time in the first order reaction coordinates, figure 5 (*a*):

$$\ln(D_\infty - D_t) \times (D_\infty - D_0)^{-1} = -kt \qquad (2)$$

where D_0, D_t, and D_∞ stand for the absorbances at wavelengths corresponding to the maxima at zero, at time *t*, and at infinite time, respectively.

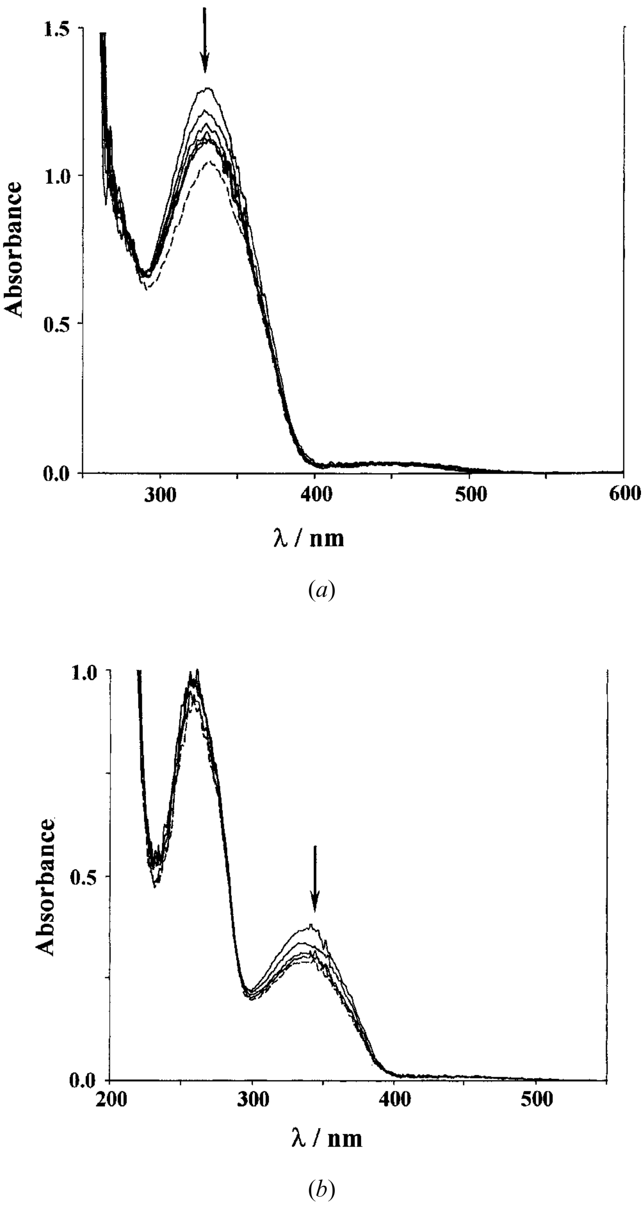
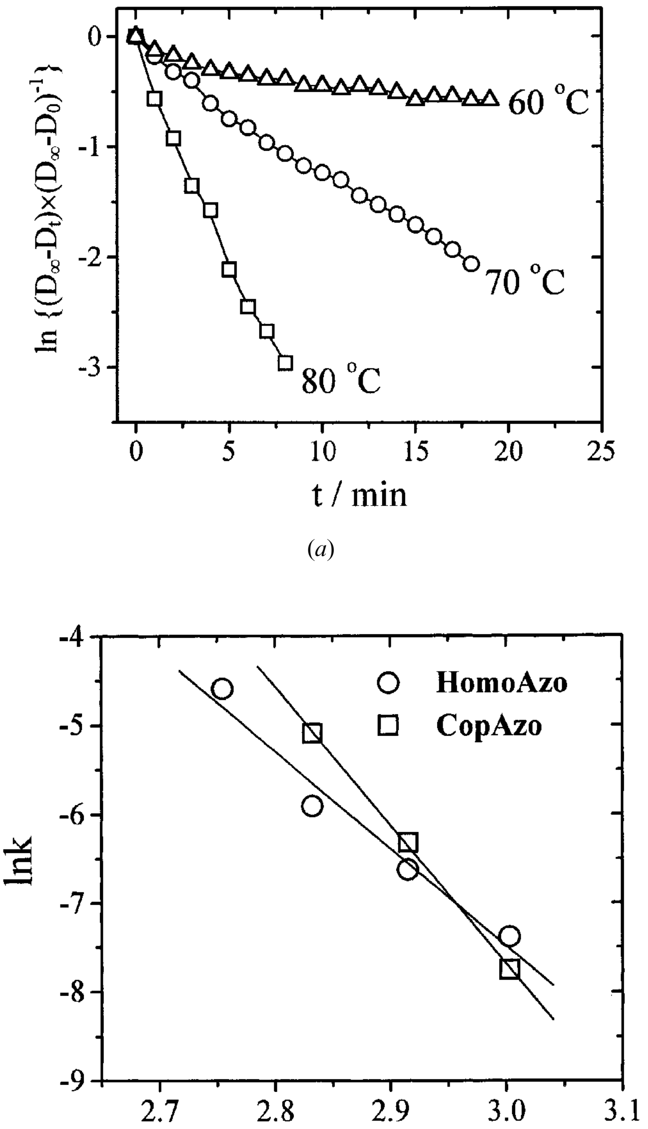


Figure 4. (*a*) Changes of absorbance spectra of the film of homopolymer HomoAzo during UV irradiation. Spectra were recorded each 1 min of irradiation; dashed line corresponds to 80 min of irradiation. (*b*) Changes of absorbance spectra of the film of copolymer CopAzo with 20 mol % of chiral units during UV irradiation. Spectra were recorded after 0, 1, 5, 10 and 40 min (dashed line) of irradiation. Temperature of irradiated samples in both cases 20°C.



(*a*)

(*b*)

Figure 5. (*a*) First order plots of *Z–E* thermal back process for a film of copolymer CopAzo with 15 mol % of chiral-photochromic units (obtained from $CHCl_3$ solution) at different temperatures (film was irradiated 10 min by UV laser 337 nm); (*b*) Arrhenius plot of thermal *Z–E* isomerization for the chiral-photochromic homopolymer HomoAzo and copolymer CopAzo with 15 mol % of chiral units

Table 3. Rate constants of the *Z–E* thermal process and the half-life time of the *Z*-isomer at different temperatures for the homopolymer HomoAzo and copolymer CopAzo with 15 mol % of chiral groups.

	Homopolymer HomoAzo		Copolymer CopAzo with 15 mol % of chiral groups	
T/°C	$t_{1/2}$/min	$k \times 10^3$/s^{-1}	$t_{1/2}$/min	$k \times 10^3$/s^{-1}
60	19	0.62	27	0.43
70	9	1.32	6.4	1.80
80	4.2	2.73	1.9	6.11
90	1.1	10.1	—[a]	—[a]

[a] At this temperature it was not possible to obtain kinetic data because the thermal back process was too fast.

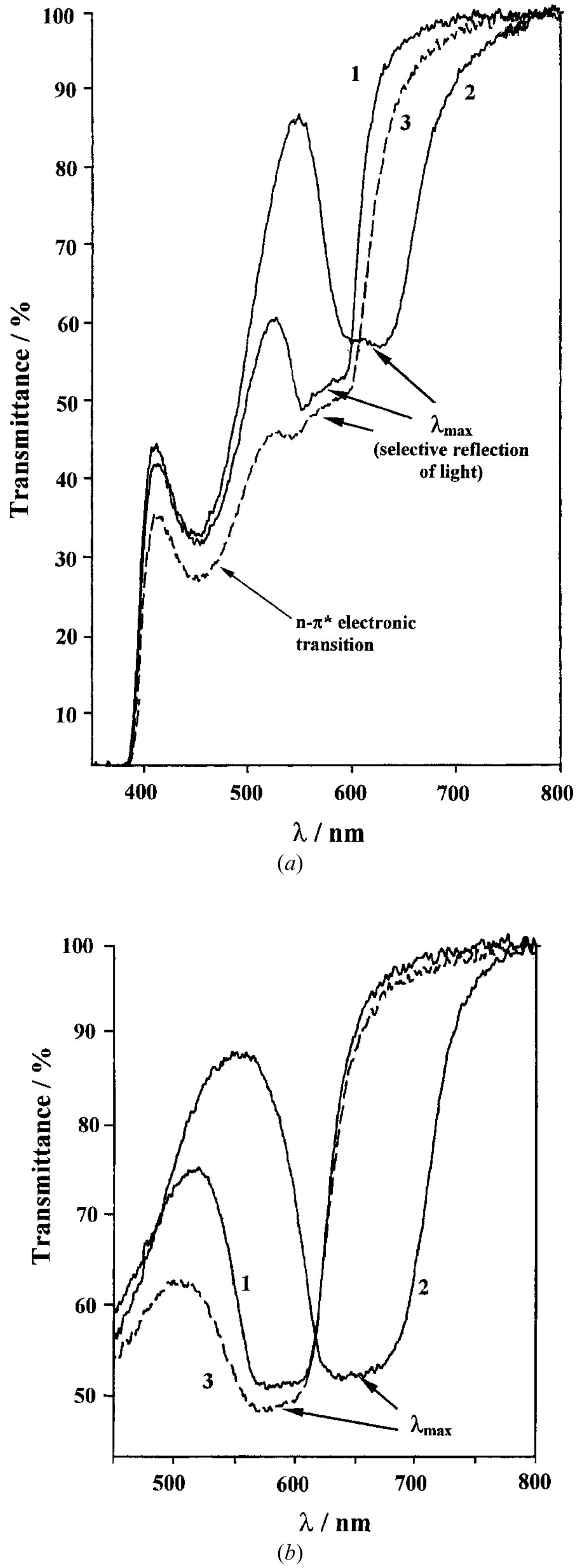
For the *Z*-isomer, the calculated values of the constant *k* and half-life times are summarized in table 3. We note that as the temperature is increased the back *Z–E* process is markedly accelerated. It is also interesting to mention that, for the homopolymer at temperatures above 60°C the rate of this process is lower than that for the copolymer. This trend is likely to be related to a higher viscosity of the homopolymer as compared with that of the copolymer, and this conclusion is supported by comparing the corresponding glass transition temperatures (table 1).

To calculate the activation energy of the thermal process, the temperature dependences of the isomerization rate constant are shown, figure 5 (*b*). For the homopolymer and copolymer, these values are equal to 88 and 130 kJ mol^{-1}, respectively; these values are typical for azobenzene derivatives [36].

3.3. *Specific features of the photo-optical behaviour of planar-oriented films of copolymers and mixtures*

In the case of the planar-oriented films of copolymers CopAzo and their mixtures, light irradiation leads to helix untwisting and a shift in the selective light reflection maximum to a higher wavelength spectral region, figures 6, 7 (*a*) and 8. Prior to irradiation, films of copolymer CopAzo and related mixtures show selective light reflection in the green spectral region. After UV irradiation, the selective light reflection maximum is shifted to the red spectral region, and figure 8 clearly shows a 'red' lattice on a green background. As was shown, these changes are related to the reduction in the anisotropy of the chiral photochromic fragment and, hence, to a decrease in its helix twisting power during the *E–Z* isomerization.

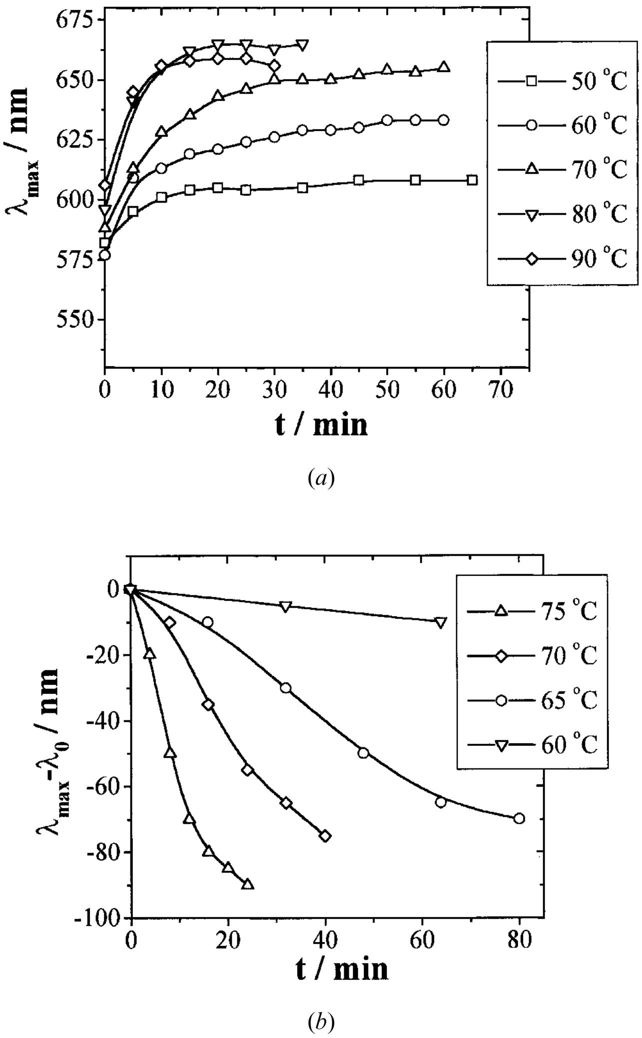
In the case of the copolymers CopAzo and the Azo-containing mixture, an obvious advantage of the above samples concerns their ability for reversible isomerization. For example, upon annealing the irradiated films at $T \geqslant 45$°C, the selective light reflection maximum is shifted to the short wavelength spectral region, figure 7 (*b*); that is, this process is completely thermally reversible. We note that, upon annealing the film, in addition to a complete recovery of the selective light reflection peak



(*a*)

(*b*)

Figure 6. Changes of transmittance spectra of planar-oriented films of (*a*) copolymer CopAzo and (*b*) mixture of Azo and CopMt: (1) before irradiation; (2) after 50 min of UV irradiation at 90°C; (3) after annealing for 15 min at 90°C.



(*a*)

(*b*)

Figure 7. Changes of the selective light reflection wavelength (*a*) during UV irradiation of mixture Azo+ CopMt and (*b*) during annealing of the same mixture irradiated previously (30 min at 80°C) at different temperatures (λ_0 = selective light reflection wavelength immediately after switching off light).

to its initial position, this peak also becomes broader, and light scattering in the short wavelength region appears, figures 6(*a*) and 6(*b*). In our opinion, the appearance of light scattering and the broadening of the peak are related to the distortion of the planar texture of the sample during thermal 'twisting' of the cholesteric helix. In this case, the effect is most pronounced for copolymer CopAzo, and is probably due to its higher viscosity as compared with that of the mixture containing the low molecular mass dopant. On the other hand, prolonged annealing or shear deformation allows one to eliminate the above undesired effects, and this fact favours a *complete* recovery of the profile of the selective light reflection peak.

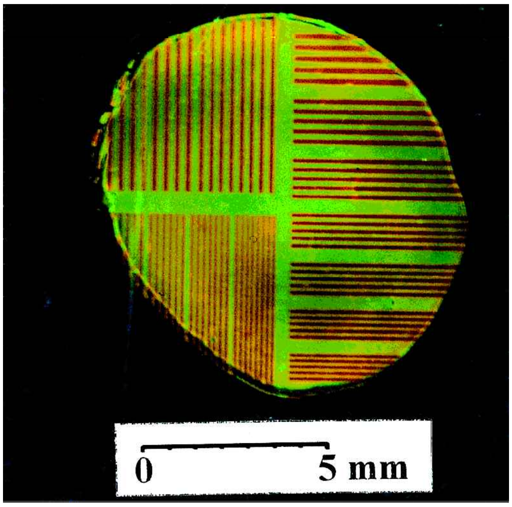
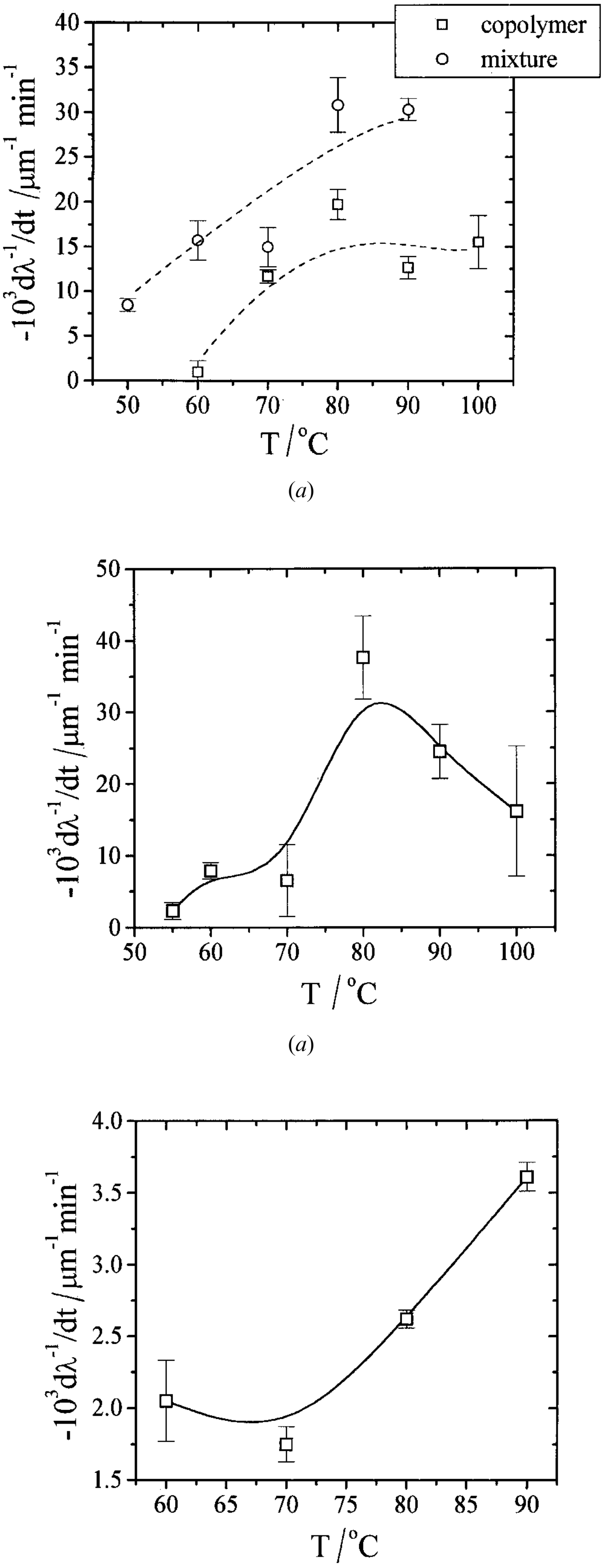


Figure 8. Photograph of the film prepared from the mixture Azo + CopMt exposed to UV irradiation for 20 min at 70°C through the mask. The red regions corresponding to the irradiated zones are clearly seen on the green background of the initial sample.

As follows from figure 7, the rates of the forward and back processes are markedly controlled by temperature; that is, these parameters are controlled by the viscosity of the system. On the other hand, at room temperature the films of the copolymer and mixture exist in a glassy state ($T_g \sim 25$°C). Hence, one may store the recorded optical information for rather long (at least, several months) periods of time.

Let us consider in more detail the temperature dependence of the initial helix untwisting rates for the copolymers and the Azo-containing mixture, figures 9(*a*) and 9(*b*). In the case of UV irradiation (365 nm), the rate of this process increases with increasing temperature, figure 9(*a*). Upon light irradiation with $\lambda > 450$ nm, initially the reaction rate increases; at temperatures above 80°C, the rate decreases.

The reasons for this difference in behaviour of the planar-oriented films of the copolymers upon irradiation with different wavelengths is likely to be related to the difference in the corresponding absorption coefficients (ε_λ). Taking into account the fact that $\varepsilon_{365} \gg \varepsilon_{450}$ (by more than 20 times), and that the photoprocess is localized in a thin surface layer, the limiting stage is provided by the



(*a*)

(*a*)

(*c*)

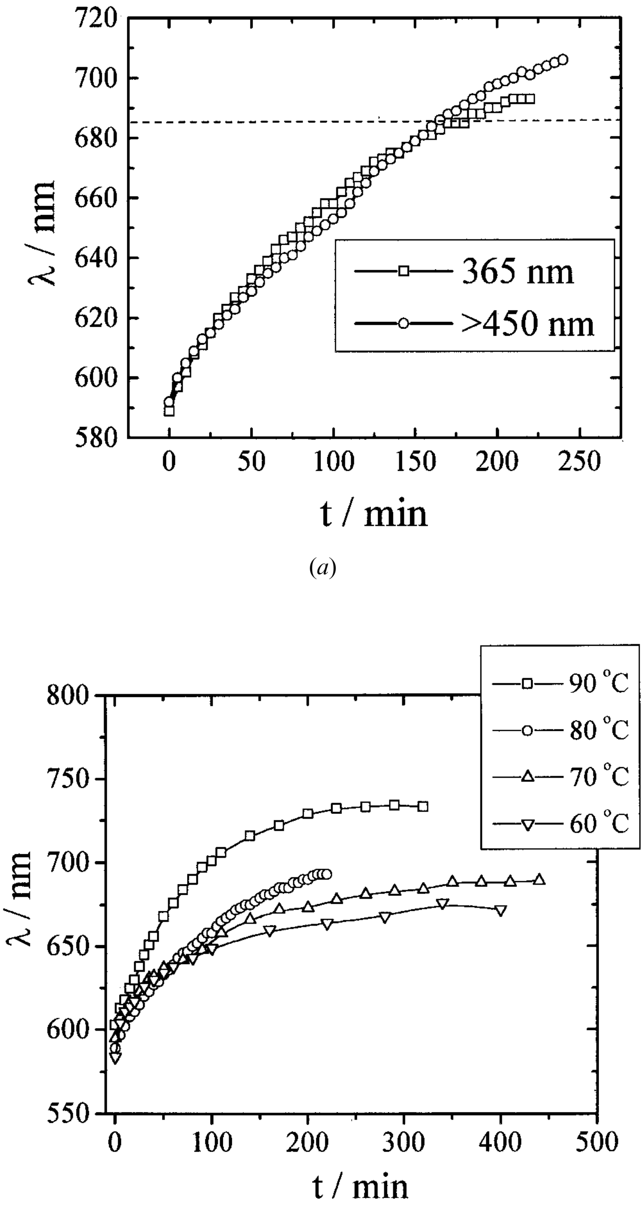
Figure 9. Temperature dependence of the rate of the reverse selective light reflection wavelength changing: (*a*) under UV light action (365 nm) for copolymer CopAzo with 15 mol% of chiral units and for mixture CopMt + Azo; (*b*) under visible light action (> 450 nm) for copolymer CopAzo with 15 mol% of chiral units; (*c*) for mixture CopMt + MtnAzo (365 nm).

diffusion of macromolecules enriched with Z-isomers of chiral photochromic groups across the whole film thickness. Evidently, as the temperature is increased, the diffusion constant increases. Hence, upon light irradiation with $\lambda = 365$ nm, the rate of this process increases monotonically with increasing temperature. This reasoning may be invoked to explain why, in the case of the mixture of CopMt with Azo, the helix untwisting rate is somewhat higher, figure 9 (*a*): the diffusion constant of the dopant is higher than the self-diffusion constants of copolymers CopAzo.

At $\lambda > 450$ nm, diffusion across the thickness of the film does not play any marked role. At temperatures below 80°C, the rate is limited by the process of the rotational relation of the mesogenic groups until an equilibrium value of the helical pitch is attained (this value is given by the ratio between E and Z isomeric forms of the chiral photochromic groups in the course of light irradiation). Upon further increase in the temperature, the rate of this process decreases due to a competing thermal back Z–E process whose rate increases with increasing temperature (table 3). As a result, the concentration of the Z-isomer decreases, and the selective light reflection wavelength decreases, figure 9 (*b*).

A quite different situation is observed for the mixture of CopMt with MtnAzo: UV irradiation or irradiation with visible light (> 450 nm) leads to *absolutely irreversible* changes in the helical pitch. Furthermore, this process is irreversible even at short exposure times. Seemingly, in contrast to the photochemical behaviour in dilute solutions, irradiation of this dopant in its mixture with CopMt leads only to the irreversible isomerization provided by the presence of the C=C double bond. The reasons for this unexpected behaviour are still unclear and require additional studies. In this case, one may hardly exclude the possible energy transfer from the azobenzene chromophore to benzylidenementhan-3-one. This effect may be more pronounced in the condensed phase with a higher viscosity than that of a dilute solution. It seems interesting to note that, in this case the amplitude of the shift in the selective light reflection peak is unexpectedly high: once the photostationary state is achieved, the selective light reflection wavelength exceeds that of initial copolymer CopMt (figure 10). This evidence implies that, in the case of the photostationary mixture of E- and Z-isomers of dopant MtnAzo, the twisting power has the opposite sign with respect to that of initial E-isomer.

In this case, firstly the rate of the photoprocess is an order of magnitude higher than that of the Azo–MtnAzo mixture and, secondly this value noticeably increases with increasing temperature, figure 9 (*c*). Both effects are related to the fact that dopant MtnAzo is characterized by higher values of the absorption coefficient at a wavelength of 365 nm as compared with those of the dopant Azo. Hence, one may expect that in the case of the MtnAzo–CopMt mixture the rate of the photo-induced untwisting of the cholesteric helix is noticeably limited by the diffusion of the dopant in the Z-form across the thickness of the film.



(*a*)

(*b*)

Figure 10. Kinetics of the selective light reflection wavelength growth for a film of the mixture CopMt + MtnAzo during irradiation with incident light of different wavelengths at 80°C (*a*) and at different temperatures (365 nm) (*b*). Dashed line in (*a*) corresponds to selective light reflection wavelength of copolymer CopMt at 80°C.

The above chiral photochromic materials based on CopAzo and dopant Azo show one important feature: high fatigue resistance. This phenomenon demonstrates the feasibility of repeated (cyclic) recording and erasing of optical information. As follows from figure 11, this allows one to perform reversible changes of the recorded image without any marked losses of the coloured characteristics in the repeated 'recording–erasing' cycles.

4. Conclusion

One may conclude that the synthesized menthyl-containing dopant and the chiral photochromic copolymer with photosensitive (azobenzene) and chiral (menthyl) fragments may be used for the preparation of cholesteric materials with a reversibly controllable helical pitch. High fatigue resistance to 'recording–erasing' cycles allows one to consider these materials as promising candidates for coloured recording and storage of optical information with possible multiple 're-recording'. The reasons for this unusual photo-optical behaviour seen for the mixture of the dopant MtnAzo with the cholesteric copolymer, namely, the absence of the back thermal process, are still unclear and warrant further study.

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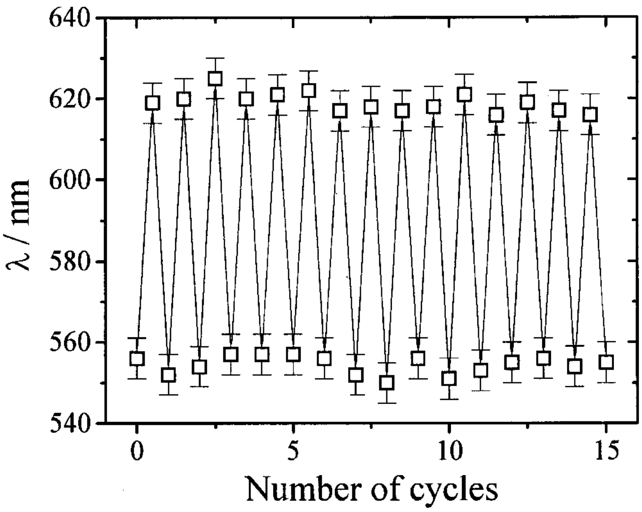

Figure 11. Fatigue resistance properties of the film of the copolymer CopAzo with 15 mol% of chiral units under recording–erasing conditions. In each cycle, the film was irradiated for 30 min by UV light at 90°C, then was annealed for 20 min at the same temperature.

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