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A new type of multifunctional material based on dual photochromism of ternary chiral photochromic liquid crystalline copolymers for optical data recording and storage

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An approach for the development of a new class of multifunctional photochromic liquid crystalline materials has been devised. Copolymerization of acrylic monomers allowed the preparation of ternary cholesteric copolymers containing nematogenic (phenyl benzoate), photochromic (azobenzene), and chiral photochromic side groups (benzylidene-*p*-menthanone). The phase behaviour and optical properties of such copolymers were studied. The synthesised copolymers are characterised by selective light reflection in the visible or IR spectral regions depending on the composition of the copolymers.

The photochemical and photooptical properties of the synthesised copolymers were studied. The character of the photochemical processes in the above copolymers was shown to be controlled by wavelength λ of incident light: as a result of light irradiation with $\lambda = 366$ nm, films or dilute solutions of copolymers experience *E–Z* photoisomerization of the azobenzene groups, whereas at $\lambda = 313$ nm, isomerization of both azobenzene and benzylidene-*p*-menthanone groups takes place.

The action of UV light on the plane oriented films of copolymers leads to the *E–Z* isomerization of the chiral photochromic groups, and this isomerization is accompanied by untwisting of the cholesteric helix and by a shift of the selective light reflection wavelength to a long wavelength spectral region.

On the other hand, irradiation of such films by polarised light with $\lambda = 514$ nm leads to the appearance of induced birefringence due to the existence of azobenzene groups which are capable of isomerization.

The synthesised copolymers were shown to constitute a new class of multifunctional materials for data recording and storage.

1 Introduction

In recent years, among scientific studies devoted to comb-shaped liquid-crystalline (LC) polymers, most interest is focused upon their possible application as new materials for data recording and storage, holography, *etc.* For such research, highly promising candidates are cholesteric polymers and their compositions with low molecular mass liquid crystals with a unique helical supramolecular structure. This supramolecular structure may be easily controlled by light irradiation, and this trend opens exceptionally wide possibilities for the preparation of so-called photo-addressed films with locally variable supramolecular structure and optical properties.[1–7]

Most studies related to synthesis and characterisation of photochromic LC polymer systems are focused on the derivatives of azobenzene.[8–25] This tendency is associated with a number of advantages offered by azobenzene compounds such as a high quantum yield of forward *E–Z* and back *Z–E* isomerization, relatively high stability and durability of polymer films as well as the possibility of multiple recording–erasing cycles, *etc.*

At the same time, despite numerous publications related to photosensitive systems based on various low molecular mass compounds, very little attention has been paid to polymer photochromic cholesterics.

In the work by Kreuzer *et al.*,[24,25] cholesteric cyclosiloxanes with azobenzene-containing nonchiral groups are described. As was shown, the effect of polarised light on the plane oriented films of such compounds leads to the deformation of the cholesteric helical structure and the generation of higher orders of selective light reflection.

As was reported in our recent communications[26–30] and in the publications of the research group at Philips,[31,32] there were synthesised copolymers in which photosensitive and chiral groups are united into a single chiral photochromic side fragment of comb-shaped cholesteric copolymers. This approach allowed preparation of photo-addressable materials whose helix pitch may be easily controlled by light irradiation *via* changes in the twisting power of the chiral photochromic fragments associated with changes in their configuration.

Combined LC copolymers containing both azobenzene and chiral photochromic groups are obviously also of interest. In this work, this approach was achieved for the first time by synthesising the ternary copolymers containing various monomer units, each of which plays a certain "functional role". Fig. 1 shows the schematic representation of a macromolecule of such a ternary copolymer.

The mesogenic groups (**1**) of the copolymer should provide the development of a LC phase. The side photochromic groups (**2**) containing, for example, fragments of well-known azo dyes[8–25] should experience light-induced *E–Z* isomerization which leads to the appearance of photoinduced birefringence. In this case, this process should be easily reversible (under the action of temperature or light of different wavelength or polarisation). Finally, multifunctionality necessitates the presence of combined chiral photochromic fragments (**3**) in one monomer unit which should provide the ability to form the cholesteric phase. In this case, irradiation with light of a different wavelength allows one to induce irreversible changes in the configuration of these units and to change their twisting power. As a result, one may control the pitch of the helix in the system and other parameters such as light transmission, viscosity, *etc.*

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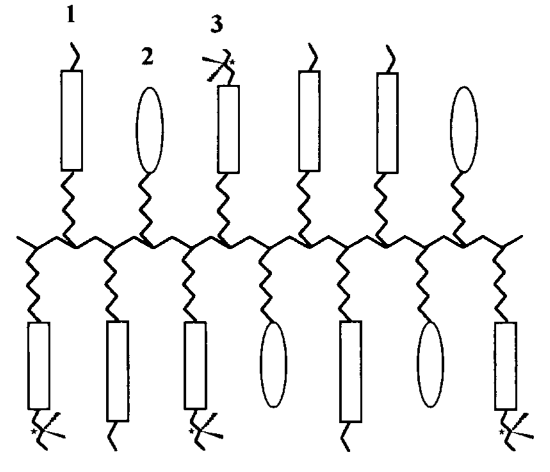

Fig. 1 Schematic representation of a terpolymer macromolecule designed as a multifunctional material.

Using this underlying principle for the development of multifunctional materials, certain comonomers satisfying the objective of this work were selected. Fig. 2 presents a structural formula of this ternary copolymer based on the above comonomers.

As follows from Fig. 2, methoxyphenylbenzoate groups (**1**) are responsible for the development of a nematic mesophase, and mesogenic cyanoazobenzene fragments do not disturb the mesophase.[33] Furthermore, let us emphasise that absorption bands of azobenzene groups lie in the visible and near-UV spectral region[8] whereas the whole absorption band corresponding to the benzylidene-*p*-menthanone fragments (**2**) is located in the UV spectral region.[26–30] Hence, by selecting the composition of the copolymer and the irradiation wavelength, one may control the type of process for varying the optical properties of polymer films such as birefringence or untwisting of the cholesteric helix. Despite obvious difficulties related to a simultaneous occurrence of the two individual or concurrent photochemical and photooptical processes, this approach undoubtedly presents a significant scientific and practically important advance with respect to the development of unique multifunctional polymer photosensitive materials.

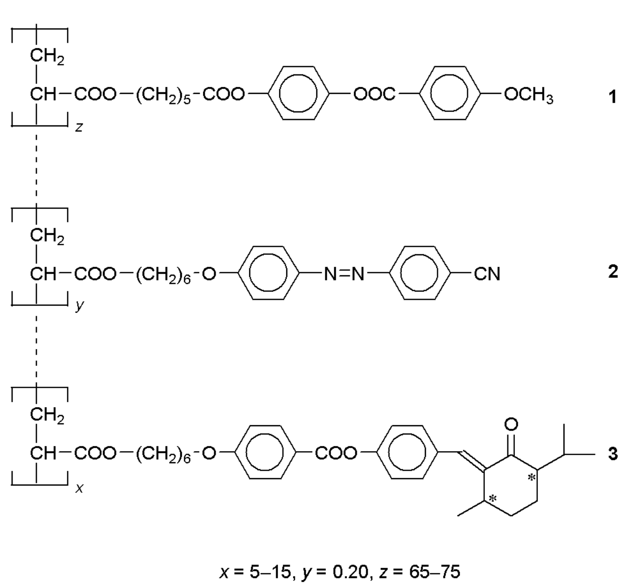

Fig. 2 Chemical structure of terpolymer satisfying the requirements of Fig. 1.

2 Experimental

2.1 Synthesis of copolymers

Methoxyphenyl benzoate monomer (**1**) was prepared according to the procedure described in ref. 34. The synthesis of chiral photochromic and azobenzene-containing acrylic monomers is described in ref. 30 and ref. 33, respectively.

All copolymers were obtained by radical polymerization of monomers using as initiating agent azobisisobutyronitrile (AIBN) in benzene solution at 60 °C. For example, 100 mg of chiral monomer and 1 mg (1 wt% of the monomer) of AIBN were placed in a glass ampoule and dissolved in 1 ml of dry benzene. The solution was purged with dry argon for 20 min and sealed. The ampoule was then kept at 60 °C for 30 hours; subsequently it was opened and the contents were poured into 15 ml of methanol. The precipitated solid was purified by repeated precipitation from chloroform into methanol and degassed under vacuum.

2.2 Physicochemical investigations

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

Selective light reflection of chiral polymers was studied with a Hitachi U-3400 UV-Vis-IR spectrophotometer equipped with a Mettler FP-80 hot stage. The polymer samples with a thickness of 20 μm were sandwiched between two flat glass plates. A planar texture was obtained by a shift deformation of the polymer film followed by a prolonged annealing at temperatures above the glass transition temperature (T_g). Prior to tests, the polymer samples were annealed for 20–40 min at appropriate temperatures.

The relative molecular masses 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 by using a UV detector, THF as solvent (1 ml min^{-1}, 40 °C), a set of PL columns of 100, 500 and 10^3 Å; and a calibration plot constructed with polystyrene standards. The copolymers obtained have the following molecular mass characteristics: $M_n = 7000–10000$, $M_w/M_n = 2.5–3.3$.

2.3 Photochemistry investigations

Photochemical properties investigations were performed using a special instrument[27] equipped with a DRSh-250 ultra-high pressure mercury lamp. Using filters, the 313 and 366 nm bands of the linear radiation spectrum of the mercury lamp were 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[35] and were equal to 1.0×10^{-9} einstein s^{-1} cm^{-2} ($\lambda_{irr} = 313$ nm) and 1.1×10^{-8} einstein s^{-1} cm^{-2} ($\lambda_{irr} = 366$ nm).†

The photochemical properties of the copolymers in the bulk were studied by illuminating 10 μm thick films at different temperatures. After a certain irradiation time, the samples were annealed at a temperature 30 °C higher than the glass transition temperature. During annealing, the spectra of selective light reflection were recorded. The samples were annealed until no changes in the selective light reflection wavelength were observed (usually, for about 40 min).

A possible recording of holographic images *via* isomerization

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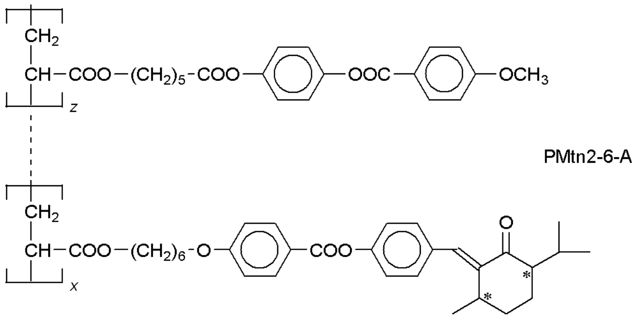
†1 einstein = 1 mole of photons.

of the azobenzene groups was studied on equipment whose detailed description is provided in ref. 36.

3 Results and discussion

3.1 Phase behaviour and optical properties of ternary chiral photochromic copolymers

In our previous work[30] we synthesized binary chiral photochromic copolymers (PMtn2-6-A) without any azobenzene side groups in contrast to the ternary copolymers studied in this work (in the abbreviations, the first digit corresponds to the number of benzene rings in the mesogenic fragment; the second digit stands for the length of the spacer).



PMtn2-6-A

Copolymers of this series are able to produce chiral nematic (N*) and ordered TDK phases (Table 1) which is characterised by the existence of local order of the SmK phase and by the absence of layered order.[37]

The introduction of 20 mol% of azobenzene side groups into the copolymer composition leads to the degeneration of the TDK* mesophase (Table 1) at any concentration of chiral photochromic units, even as low as 5 mol%. In this case, the clearing temperature and glass transition temperature remain almost unchanged.

Plane oriented films of the synthesised copolymers show a selective light reflection in the visible spectral region; the wavelength of the selective light reflection maximum depends on temperature (Fig. 3) and on the concentration of chiral units in the copolymers (Figs. 3 and 4).

By approximating the concentration dependence of the reciprocal of wavelength of selective light reflection maximum using eqn. (1),[38,39] the helical twisting power of chiral side units was calculated:

$$\lambda_{\max}{}^{-1} = AX/(1+BX) \qquad (1)$$

where B is the parameter describing the deviation from linearity of this plot. The calculated values of the helical twisting power A and parameter B for copolymers with (PMtn2-6-A-Azo) and without (PMtn2-6-A) azobenzene units are summarised in Table 2.

As follows from the data presented in Table 2, upon introduction of azobenzene units to the system, the twisting power of the chiral units slightly decreases whereas parameter B increases.

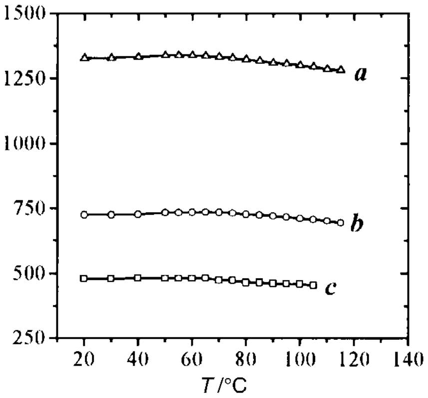


Fig. 3 Temperature dependence of selective light reflection wavelength ($\lambda_{\max}$) for copolymers with different concentrations of the chiral photochromic units: 5 (*a*), 10 (*b*) and 15 (*c*) mol%.

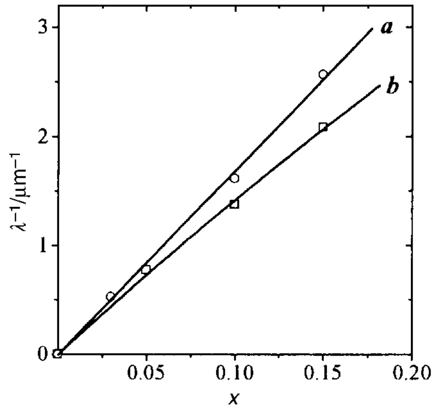


Fig. 4 Dependence of λ^{-1} on the molar fraction of chiral units (at $T=0.95T_{\mathrm{N^*-I}}$) for copolymers PMtn2-6-A (*a*) and PMtn2-6-Azo (*b*).

Table 2 Values of the helical twisting power (A) and parameter B for chiral photochromic copolymers of a different series

Copolymers	A/µm^{-1}	B
PMtn2-6-A	16.9±1.1	0.0±0.5
PMtn2-6-Azo	14.9±1.1	0.6±0.6

Both phenomena are likely to be related to an increased number of fluctuations of the smectic order in the copolymers. This trend is associated with the fact that the cyanoazobenzene-containing homopolymer forms a smectic mesophase.[34] Furthermore, as known from several publications devoted to copolymers and blended compositions of polymers containing alkoxy and cyano-substituted mesogenic side groups, these

Table 1 Phase behaviour and thermal properties of a series of chiral photochromic copolymers

Mole fraction of chiral units	Glass transition, T_g/°C	Phase transitions/°C[a]
PMtn2-6-A		
0.03	28	TDK*[b] 71 (7.4) N* 127 (1.0) I
0.10	30	TDK* 72 (0.9) N* 119 (1.2) I
0.15	31	N* 114 (1.2) I
PMtn2-6-Azo[c]		
0.05	30	N* 120 (0.8) I
0.10	33	N* 117 (0.9) I
0.15	29	N* 107 (1.0) I

[a] The values of enthalpies of phase transition in J g^{-1} are indicated in parentheses. [b] The structure of this unusual ordered phase was described in ref. 37. [c] All the copolymers of this series contain 20 mol% of cyanoazobenzene-containing units.

systems are able to develop an additional smectic order *via* donor–acceptor interactions.[40,41] In this case, phenyl benzoate groups may serve as electron donors, and cyanoazobenzene groups as electron acceptors.

Hence, the synthesised new ternary chiral photochromic copolymers are characterised by a helical supramolecular structure. This structure exists in a rather wide temperature range and is capable of selective light reflection in the visible and IR spectral regions.

3.2 Photochemical properties of ternary chiral photochromic copolymers in solution and thin films

To reveal the specific photooptical behaviour of ternary copolymers, let us first consider the photochemical processes carried out in dilute solutions: analysis of changes in electron spectra of solutions as induced by irradiation allows one to recognise easily the principal photochemical processes taking place in the system.

Fig. 5 presents the absorption spectra of a dichloroethane solution of ternary copolymers containing 15 mol % of chiral side units. As follows from Fig. 5, this spectrum shows two principal peaks: a long-wavelength peak ($\lambda_{max} = 365$ nm) corresponds to the π–π* electron transition of the cyanoazobenzene groups (**2**)[8–10] whereas a short-wavelength peak at $\lambda_{max} = 262$ nm corresponds to the π–π* electron transition of the mesogenic phenyl benzoate units (**1**)[27,33] (the long-wavelength peak at $\lambda = 420$–430 nm associated with the n–π* electron transition of the azobenzene groups is almost unseen due to a low extinction coefficient). The peak associated with the absorption of the benzylidene-*p*-menthanone fragments appears only as a 'shoulder' at 290–325 nm.[27,42,43]

The UV irradiation leads to significant changes in the absorption spectra of the copolymers (Figs. 5a and 5b). In this case, depending on the wavelength of the exciting light, the character of these changes appears to be somewhat different: at $\lambda_{irr} = 366$ nm, one may observe a marked decrease in the absorption peak associated with the π–π* electron transition of the cyanoazobenzene groups, whereas at $\lambda_{irr} = 313$ nm, changes in the 'shoulder' at 290–325 nm are observed (Figs. 5 and 6).

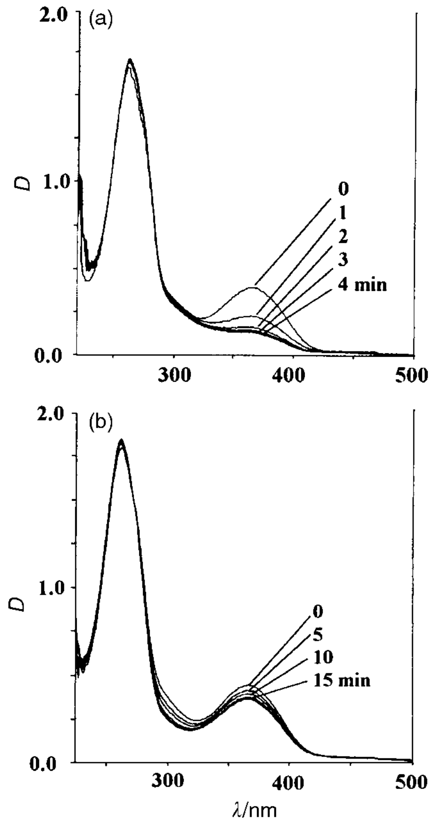


Fig. 5 Changes of the absorbance spectra for a dichloroethane solution of copolymer PMtn2-6-A-Azo containing 15 mol% of chiral units during UV-irradiation with light of different wavelengths: 366 nm (a) and 313 nm (b). Irradiation time is shown in the Figure.

In other words, when dilute solutions of copolymers are irradiated at a wavelength of 366 nm, the benzylidene-*p*-menthanone groups experience almost no *E*–*Z* isomerization; isomerization is observed only for azobenzene groups. At $\lambda_{irr} = 313$ nm, both groups undergo isomerization, and this conclusion is supported not only by changes in the absorption spectra but also by the corresponding kinetic dependencies of the absorption at different wavelengths (Fig. 6). Similar dependences are observed for thin films of the copolymers prepared by evaporation from their dichloroethane solutions (Fig. 6).

The *E*–*Z* isomerization of azobenzene groups is thermally and photochemically reversible: under irradiation of the solution with visible light, a reverse increase in the absorption peak at $\lambda_{max} = 365$ nm is observed (Fig. 7).

Taking into account the above speculations, one may conclude that isomerization of various photochromic groups may be controlled by varying the wavelength of the incident light beam; in the case of azobenzene groups, one may also change the direction of the whole process. Let us note that chiral photochromic groups are irreversibly transformed to the *Z*-form whereas, in the case of cyanoazobenzene chromophores, the *E*–*Z* isomerization is fully reversible.

We studied the kinetics of the back thermal process of the *Z*–*E* isomerization of azobenzene groups at different temperatures and for copolymers with different chiral group contents (Fig. 8). To this end, thin films of copolymers cast from dichloroethane solutions were light irradiated with

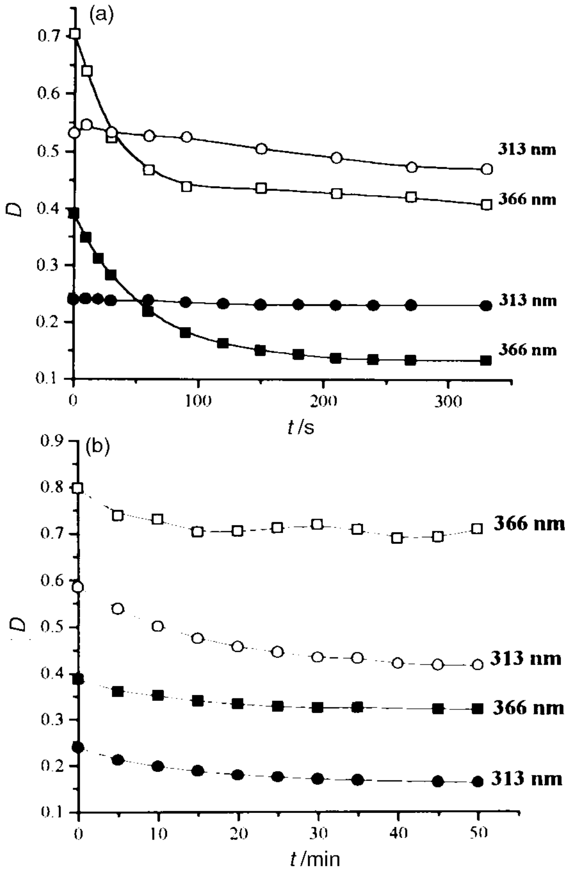


Fig. 6 Optical density changes for solution (solid symbols) and for film (obtained from dichloroethane solution, open symbols) of copolymer with 15 mol% chiral photochromic units during UV-irradiation with light of different wavelength: 366 nm (a) and 313 nm (b).

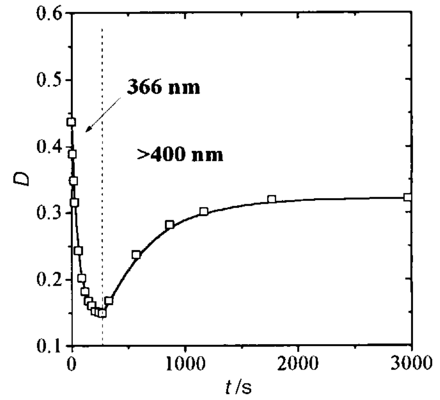


Fig. 7 Optical density changes for a dichloroethane solution of copolymer PMtn2-6-A-Azo containing 15 mol% of chiral units during UV-irradiation with light $\lambda_{irr} = 366$ nm followed by light with $\lambda_{irr} > 400$ nm.

$\lambda_{irr} = 366$ nm for 240 s; then, the corresponding absorption spectra were recorded as a function of the time of annealing at different temperatures. Finally, the plots of absorption *versus* time were constructed using the first order kinetic coordinates [eqn. (2), Fig. 8]:

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

where D_0, D_t and D_∞ are the absorbance at 366 nm at time zero, time t and infinite time, respectively.

To calculate the activation energies of this process, the semilogarithmic temperature dependences of isomerization rate were plotted (Fig. 9). The calculated values of activation energy are listed in Table 3. As follows from Table 3, these values are independent of the fraction of chiral side units and of isomer form (*E* or *Z*). However, it is interesting to note that, as the content of chiral side units is increased, the rate constants of thermal isomerization decrease (Fig. 9). This effect of the benzylidene-*p*-menthanone units on the kinetic reaction constants may be explained as follows. The nematic "matrix" of copolymers (being composed of rodlike molecules) should stabilise the *E*-form of cyanoazobenzene groups and should exert a destabilising effect on the *Z*-form. In turn, nonmesogenic benzylidene-*p*-menthanone groups violate a LC order and are likely to serve as specific defects. Hence, in a less ordered matrix with a high content of chiral units, the *Z*-form of cyanoazobenzene groups is more stable; as a result, the rate of the back process noticeably decreases.[44]

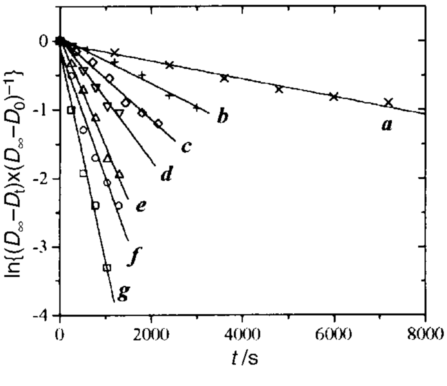


Fig. 8 First order plots of *Z*–*E* thermal back-isomerization for copolymer Mtn2-6-Azo with 15 mol% of chiral photochromic units at different temperatures: 30 °C (*a*), 35 °C (*b*), 40 °C (*c*), 45 °C (*d*), 50 °C (*e*), 55 °C (*f*) and 60 °C (*g*).

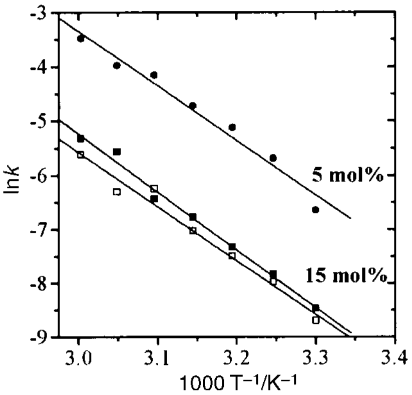


Fig. 9 Arrhenius plots for thermal *Z*–*E* isomerization for copolymers with different chiral group contents; in the case of 15 mol% the solid and open symbols correspond to polymer films before and after 50 min of UV irradiation (313 nm), respectively.

Table 3 Activation energies of back thermal *Z*–*E* isomerization process for ternary chiral photochromic copolymers

Mole fraction of chiral units	E_A/kcal mol^{-1}
0.05	21.31 ± 0.90
0.15 (before UV irradiation)	20.08 ± 1.50
0.15 (after UV irradiation)[a]	19.93 ± 1.35

[a] Before kinetic investigations the copolymer film was irradiated with UV light ($\lambda_{irr} = 313$ nm) for 30 min until a photostationary state was achieved.

3.3 Photochemical properties of plane oriented films of chiral photochromic copolymers

Irradiation of plane oriented films of copolymers and their subsequent annealing shifts the selective light reflection peak to a long-wavelength region (Figs. 10 and 11). As was shown earlier for copolymers with benzylidene-*p*-menthanone groups,[26–30] this effect is associated with the *E*–*Z* isomerization of menthone-containing chiral photochromic groups, which is accompanied by a dramatic decrease in their twisting power.

It is interesting to note that, as follows from Figs. 10 and 11, helix untwisting is likely to be induced by UV irradiation at both wavelengths (313 and 366 nm). In a relatively 'thick' film of copolymer, benzylidene-*p*-menthanone groups are likely to be capable of a marked absorption even at a wavelength of 366 nm.

In the case of $\lambda_{irr} = 313$ nm, the rate of this process is much lower (Fig. 11). This trend is related to the fact that, in this case, the photochemical reaction proceeds in a much thinner surface layer, and helix untwisting is markedly controlled by the diffusion of the formed *Z*-benzylidene-*p*-menthanone units along the whole thickness of the sample. Similar specific

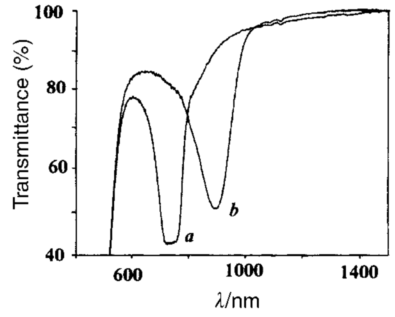


Fig. 10 Change of the transmittance spectrum of the copolymer with 10 mol% chiral photochromic units before (*a*) and after 75 min of UV irradiation (*b*). Irradiation temperature 100 °C, 366 nm.

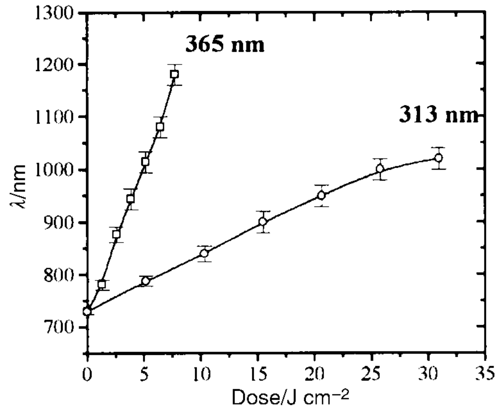


Fig. 11 Change of selective light reflection wavelength during UV irradiation of copolymer with 10 mol% chiral units at different wavelengths of incident UV light.

features of photooptical behaviour were also earlier observed in our studies for chiral photochromic copolymers.[27,30]

Hence, the effect of UV light on plane oriented films of copolymers may locally change the pitch of the helix and, consequently, the selective light reflection maximum. Fig. 12 shows examples of image recording on the thin films of copolymer containing 15 mol% of chiral photochromic monomer units.

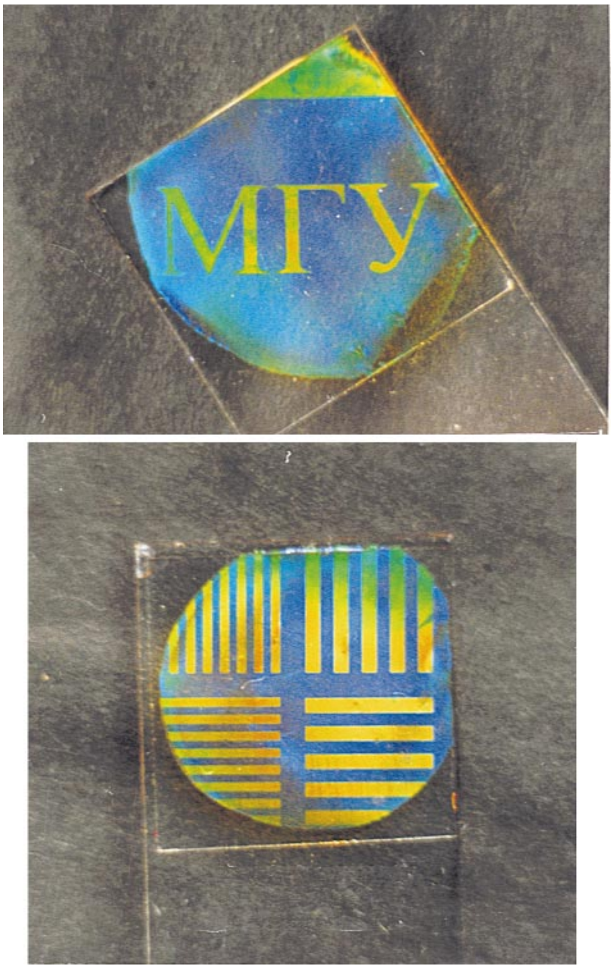


Fig. 12 Microphotos of the film prepared from the copolymer with 15 mol% of chiral photochromic units exposed to UV irradiation (366 nm, 15 min). In part (a) the characters (which are the Russian abbreviation for Moscow State University) corresponding to the irradiated zones are clearly seen on the blue background of the initial sample; part (b) demonstrates the coloured pattern obtained by UV irradiation through a test lattice.

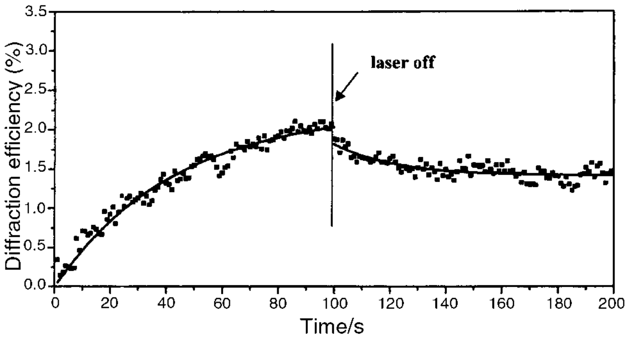


Fig. 13 First order diffraction efficiency growth during holographic recording (orthogonal polarizations, Ar laser, 514 nm, 143 mW cm^{-2}).

It seems interesting to study the possibilities of the induced birefringence due to photoisomerization of the azobenzene groups. Preliminary evidence demonstrating a significant possibility of holographic image recording on such copolymers was obtained (Fig. 13). For example, for holographic lattice recording, Ar laser irradiation (514 nm) was used; chiral photochromic groups do not absorb during this process and experience no isomerization. This conclusion was proved by annealing the irradiated copolymer films: no helix untwisting was observed.

4 Conclusion

Finally, one may conclude that the copolymers synthesised are unique multifunctional photosensitive materials, which have no analogs. These materials offer substantial advantages for coloured data recording on a coloured background.

Varying the ratio between the *E* and *Z*-isomers by UV irradiation allows one to change smoothly optical (wavelength at selective light reflection maximum) and, probably, rheological properties of the system (a disordering effect of the *Z*-isomer should decrease the viscosity of the copolymer). The possibilities of holographic recording due to photoinduced birefringence in the copolymers after UV-irradiation for different periods of time will be discussed in more detail in our forthcoming publications.

A dual photochromism of ternary copolymers of this class allows one to record optical information of 'two types' on one and the same sample: first, by varying the helix pitch (λ_{max}) due to short-wavelength light irradiation and, second, due to photoinduced birefringence (using polarised light with $\lambda \geqslant 400$ nm).

A high optical density of the synthesised copolymers opens wide possibilities for the preparation of plane oriented films with a high gradient of helix pitch along the sample.

Examination of such multifunctional chiral photochromic cholesteric copolymers is interesting not only from the viewpoint of optical information recording; investigation of, at least, two competing photochemical processes taking place in such system presents an independent interest.

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