

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

### Photochromism in mixtures of liquid crystalline chiral copolymers with a photosensitive chiral dopant

A. Yu. Bobrovsky

Online publication date: 06 August 2010

**To cite this Article** Bobrovsky, A. Yu.(1998) 'Photochromism in mixtures of liquid crystalline chiral copolymers with a photosensitive chiral dopant', *Liquid Crystals*, 25: 6, 679 – 687

**To link to this Article:** DOI: 10.1080/026782998205697

**URL:** <http://dx.doi.org/10.1080/026782998205697>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Photochromism in mixtures of liquid crystalline chiral copolymers with a photosensitive chiral dopant

A. YU. BOBROVSKY, N. I. BOIKO and V. P. SHIBAEV\*

Faculty of Chemistry, Moscow State University, Leninskie gory, Moscow 119899, Russia

(Received 20 May 1998; accepted 2 July 1998)

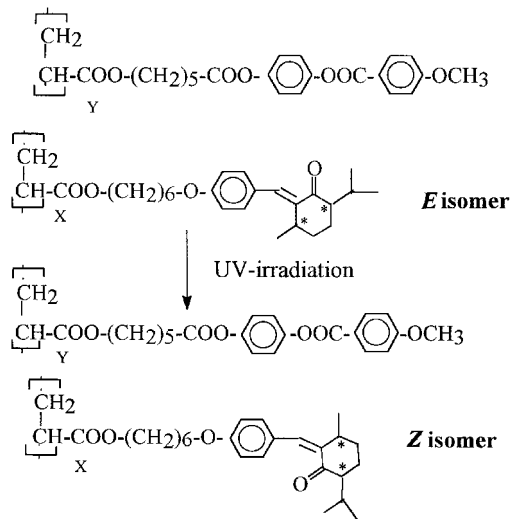
Mixtures of a photosensitive chiral dopant based on (–)-menthone with left-handed and right-handed cholesteric copolymers were prepared. The phase behaviour and optical properties of the mixtures prepared were studied. The action of UV radiation on planar oriented films of such systems was shown to induce dramatic changes in the maximum reflection wavelength as a result of *E*–*Z* isomerization of the dopant molecules. The kinetics of photoisomerization of such mixtures in solution and in the bulk were investigated at different temperatures. The above mixtures can be considered as promising and unprecedented materials for coloured data recording and storage.

## 1. Introduction

In recent years, photochromic polymer materials have attracted great interest. This interest is primarily associated with promising practical applications of such polymers for reversible optical data recording [1–3], for the preparation of command surfaces [4–8] and as non-linear optical media [9, 10]. In such cases, polymers containing fragments of azo dyes, which produce smectic or nematic mesophases, or amorphous polymers are of principal interest.

However, there have been a relatively limited number of publications devoted to the synthesis and study of photochromic polymers which are able to produce cholesteric mesophases [11–14]. Almost all publications of this kind report the results for comb-shaped copolymers, in which photosensitive fragments are provided by nematogenic fragments.

In our recent publications [15, 16], we have studied the phase behaviour and photo-optical properties of cholesteric copolymers containing methoxyphenyl benzoate and chiral benzylidene-*p*-menthane-3-one mesogenic groups, which are able to undergo *E*–*Z* isomerization induced by UV radiation.



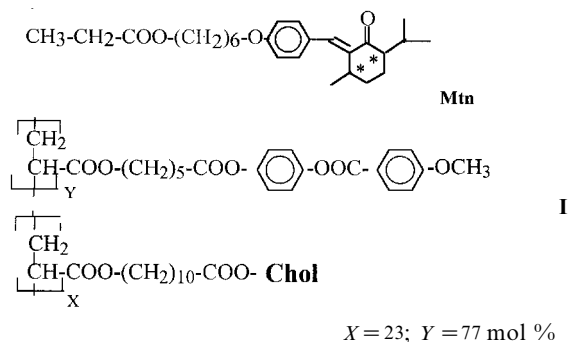
The twisting power *A* of the *Z* isomer of the chiral unit is much lower than the corresponding values of *A* for the *E*-isomer [15–17]. Therefore, as a result of isomerization in these copolymers, the selective light reflection wavelength is changed, and  $\lambda_{\max}$  shifts to a long wavelength region. The above results allow us to conclude that such copolymers are promising candidates for coloured photorecording and storage of information. However, the above copolymers suffer from a serious disadvantage, namely a marked radiation-induced

\* Author for correspondence.

broadening of the selective reflection wavelength band [15, 16]. This phenomenon is likely to be associated with the higher viscosity of polymers as compared with that of low molecular mass analogues and, consequently, with lower diffusion constants of the photochromic fragments, which affect the establishment of a photo-stationary state in the system and prevent the retention of a perfect planar texture throughout the whole volume of polymer.

*A priori*, one may assume that introduction of low molecular mass additive to a polymer, on the one hand will accelerate the attainment of equilibrium and, on the other hand will assist the 'self-healing' of the radiation-induced defects in the planar texture. In [18] we studied photorecording in the system based on a nematic homopolymer and a photosensitive chiral additive (dopant) containing the benzylidene-*p*-menthane-3-one fragment. However, a principal disadvantage of such mixtures is associated with their low stability: within one year, the above composition undergoes separation induced by crystallization of the chiral dopant. However, as shown in [19], when a cholesteric copolymer with its own helical structure is used as the polymer matrix, introduction of 10 mol % of chiral dopant to the copolymer provides complete miscibility between the components, and this system undergoes no phase separation.

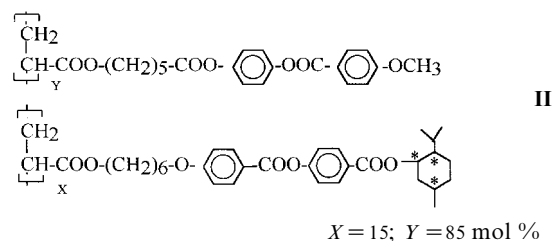
Taking into account the above reasons, in this work we studied the photo-optical properties of the mixture based on the low molecular mass chiral dopant **Mtn** and the cholesteric copolymer, which is characterized by the left-handed helical structure I:



Taking into account our previous publications [15, 16, 18], one may assume that, as a result of UV radiation, this mixture containing two left-handed components will undergo untwisting of the cholesteric helix; that is, the maximum selective reflection wavelength  $\lambda_{\max}$  will shift to the long wavelength region. On the other hand, it seemed interesting to study the case when UV radiation will lead to quite the reverse effect, such that  $\lambda_{\max}$  will shift to the short wavelength region.

To obtain such materials, we prepared the mixture of the above low molecular mass dopant **Mtn** with a chiral

nematic copolymer, which contains (+)-menthyl units and produces a right-handed supramolecular helical structure:



Therefore, the introduction of low molecular mass additives to photosensitive mixtures with cholesteric copolymers achieves three principal objectives:

- (1) Increase in the diffusion rate of the chiral photochromic component and, as a consequence, increase in the untwisting rate for this helix and attainment of photostationary equilibrium.
- (2) Provision of a homogeneous distribution of the chiral component in the mixture, allowing one to prevent broadening of the selective light reflection maximum induced by the UV radiation.
- (3) Investigation of the possibility of development of photosensitive materials in which the helix pitch may be either increased (mixture I) or decreased (mixture II) under the action of light.

## 2. Experimental

We synthesized the ester of propanoic acid and (-)-[4-(6-hydroxyhex-1-yloxy)benzylidene]menthane-3-one (**Mtn**) according to the procedures described in [15]. The structure of this compound was confirmed by IR,  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectroscopy; the optical rotation was measured ( $[\alpha]_{22}^D = -154.0^\circ$ ,  $[M]_{22}^D = -634^\circ$ ). The monomers for copolymerization were synthesized according to procedures described in [20, 21]. The copolymers were synthesized by radical copolymerization of the monomers in benzene solution at  $60^\circ\text{C}$ ; AIBN was used as an initiating agent. The copolymers synthesized were purified by repeated precipitation with methanol and dried in vacuum.

Phase transitions in the copolymers were studied by differential scanning calorimetry (DSC) using a Perkin Elmer DSC-7 thermal analyser at a scanning rate of  $10 \text{ K min}^{-1}$ . Before the DSC measurements, the test samples were annealed for one month at  $45^\circ\text{C}$ . The polarizing microscopic investigations were performed using a Mettler TA-400 thermal analyser and a LOMO P-112 polarizing microscope. Selective light reflection properties of the chiral mixtures were studied with a Hitachi U-3400 UV-vis-IR spectrophotometer equipped with a Mettler FP-80 hot stage. The samples of thickness

20  $\mu\text{m}$  were sandwiched between two flat quartz plates and annealed for 20–40 min.

In this work, X-ray analysis was performed using a URS-55 diffractometer (Ni-filtered  $\text{CuK}_\alpha$  radiation,  $\lambda = 1.54 \text{ \AA}$ ).

Photochemical studies were performed using a specially designed instrument equipped with a DRSh-250 mercury high-pressure lamp. (A detailed description and scheme of this instrument were reported in [16].) Using the filter, we identified the 313 nm band of linear lamp radiation. To prevent heating induced by IR radiation, a water filter was used; a quartz lens ensured a flat parallel light beam. Under radiation, a constant temperature of the samples was maintained using a Mettler FP-80 heating unit. The intensity of UV radiation was  $2.03 \times 10^{-9} \text{ Es s}^{-1} \times \text{cm}^{-2}$  or  $0.77 \text{ mW cm}^{-2}$ .

In our investigations, we used *n*-octane solutions of **Mtn**; the concentration was varied from  $1 \times 10^{-5}$  to  $5 \times 10^{-5} \text{ mol l}^{-1}$ . Irradiation was carried out using a quartz cell with a thickness of 2 cm; during radiation, the solution was stirred using a magnetic stirrer. Isomerization was monitored by recording absorption spectra of the irradiation solutions at certain time intervals.

### 3. Results and discussion

#### 3.1. Phase behaviour and optical properties of copolymers **I** and **II** containing low molecular mass dopant **Mtn**

Using the data from polarizing microscopy, DSC, and X-ray analysis, the types of mesophases and the temperatures and enthalpies of the phase transitions of the mixtures based on cholesterol-containing copolymer **I** with 10 mol% of **Mtn** were determined (table 1). Introduction of the chiral dopant does not change the phase sequence of the composition as compared with the initial copolymer. However, the clearing temperature decreases by  $30^\circ$ , and this decrease is associated with the non-mesomorphic nature of the dopant. The mixture of copolymer **II** (content of **Mtn** is 5 mol%) produces only a chiral  $\text{N}^*$  phase (table 1).

The existence of the chiral nematic mesophase in the mixtures over a relatively wide temperature interval primarily manifests itself in the appearance of selective reflection of circularly polarized light. Figure 1 shows the temperature dependences of the maximum selective light reflection wavelengths for menthyl-containing copolymer **II** and its mixture with **Mtn**. The profiles of both the above dependences are typical for a chiral nematic phase [15, 16, 20, 23, 24]. A slight helix untwisting near the clearing temperature is associated with a decrease in orientational order parameter *S*.

For cholesterol-containing copolymer **I** (figure 2), as the temperature is decreased, the maximum selective light reflection wavelength slightly decreases, and this phenomenon is caused by the appearance of smectic order fluctuations in the system. Such behaviour is typically observed for low molecular mass and polymer cholesterics [5, 6].

The presence of layer order fluctuations is proved by the X-ray analysis. In addition to an amorphous halo,

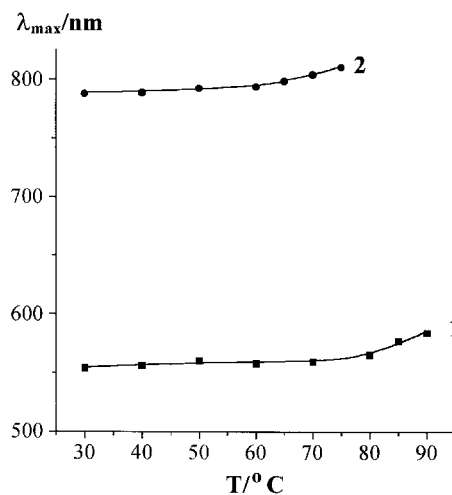


Figure 1. Temperature dependence of  $\lambda_{\text{max}}$  for copolymer **II** (1) and its mixture (2) with 5 mol% of **Mtn** dopant (mixture II).

Table 1. Phase behaviour and thermal properties of copolymers and mixtures.

Sample	Glass transition $T_g/^\circ\text{C}$	Phase transitions temperatures <sup>a</sup> / $^\circ\text{C}$
Left-handed copolymer <b>I</b>	21	TDK* <sup>b</sup> 49 (0.9) $\text{N}^*$ 117 (1.2) <b>I</b>
Mixture I (copolymer <b>I</b> + 10 mol% of <b>Mtn</b> )	18	TDK* 49 (1.4) $\text{N}^*$ 88 (–) <sup>c</sup> <b>I</b>
Right-handed copolymer <b>II</b>	25	$\text{N}^*$ 94 (1.0) <b>I</b>
Mixture II (copolymer <b>II</b> + 5 mol% of <b>Mtn</b> )	20	$\text{N}^*$ 82 (0.9) <b>I</b>

<sup>a</sup> The values of the enthalpies of phase transition are indicated in parentheses ( $\text{J g}^{-1}$ ).

<sup>b</sup> The structure of this unusual ordered phase was described in [22].

<sup>c</sup> Exothermic peak not clearly visible in the thermogram.

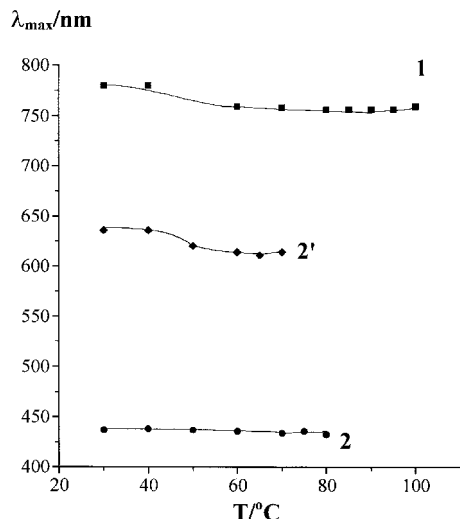


Figure 2. Temperature dependence of  $\lambda_{\max}$  for copolymer **I** (1) and its mixture with 10 mol % of **Mtn** dopant (mixture **I**) before (2) and after (2') irradiation.

the corresponding X-ray reflection pattern shows a diffuse small angle reflection with a low intensity (figure 3). Copolymer **I/Mtn** mixture (figure 2, curve 2) is monochromic, and the helix pitch is independent of temperature. In this case, as the temperature is decreased, the appearance of smectic fluctuations and an increase in order parameter  $S$  are likely to compensate each other. As follows from figures 1 and 2, in the case of mixture **I**, introduction of chiral dopant **Mtn** leads to an additional twisting of the system, whereas quite the reverse situation is observed for mixture **II**: the helix pitch increases. This behaviour may be rationalized by the fact that the dopant is left-handed. When this dopant is added to the left-handed copolymer **I**, the 'chirality' of the system increases, whereas its addition to right-handed copolymer **II** decreases its 'chirality'.

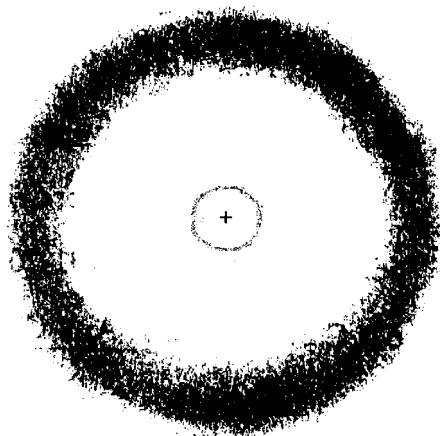


Figure 3. X-ray diffraction pattern of copolymer **I** at 22°C.

According to the following equation from [7],

$$A = \Delta \lambda_{\max}^{-1} / X \quad (1)$$

the twisting power  $A$  of the chiral dopant **Mtn** in cholesterol-containing copolymer may be calculated. In this case, it is equal to  $9.4 \mu\text{m}^{-1}$ , and this value is lower by a factor 1.5 than the corresponding value for the chiral units in menthone-containing copolymers [15, 16]. In our opinion, this difference is related to the presence of the above-mentioned smectic order fluctuations, which prevent helical twisting of mesogenic fragments in copolymers.

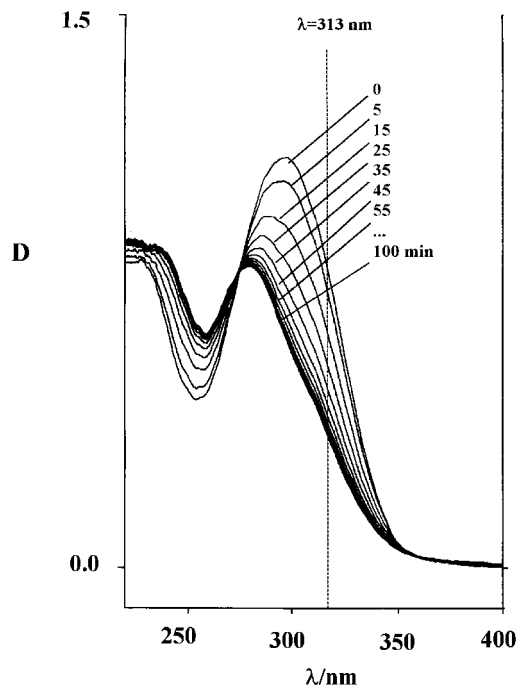
Thus, the above mixtures are materials with selective light reflection in the visible spectral region. Note that these mixtures are stable over time; the fact that they contain an unsaturated chiral compound offers a unique opportunity for controlling the maximum selective light reflection wavelength by UV irradiation. The results of our investigations of the photochemical processes occurring in solution and in the bulk (films) are discussed below.

### 3.2. Photochemical behaviour of chiral dopant **Mtn** in solution

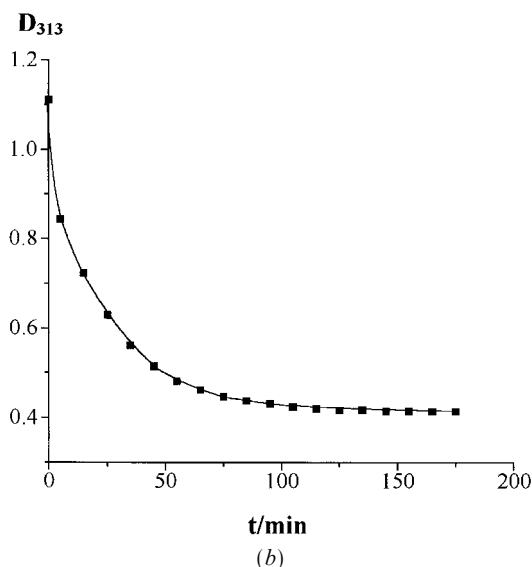
The **Mtn**-containing solutions were exposed to UV irradiation for a given period of time (usually 5 min), and the corresponding absorption spectra were recorded. Figure 4(a) shows the changes in the absorption spectra of **Mtn** dissolved in *n*-octane during UV irradiation. In this case, the principal absorption maximum corresponds to the  $\pi$ - $\pi^*$  electronic transition of the unsaturated benzylidenementhane-3-one fragment [28–30].

As follows from figure 4(b), the values of the optical density of the solution at the radiation wavelength (313 nm) decreases with time, and after 100 min exposure achieves a constant value. This phenomenon is related to the lower extinction coefficient ( $\epsilon_{313}$ ) of the *cis*-isomer formed [28, 29]. The existence of an isobestic point at  $\lambda = 287 \text{ nm}$ , figure 4(a), suggests the occurrence of only one photoprocess, that is *E*-*Z* isomerization [29, 30]. Note that the photochemical behaviour of the above solutions is similar to that of the chiral comb-shaped homopolymer containing side groups with identical chemical structure and of the menthone-containing copolymers [16].

Additional supporting evidence for the occurrence of *E*-*Z* isomerization in **Mtn**-containing solutions is provided by  $^1\text{H}$  NMR spectroscopy. Figures 5(a) and 5(b) show the spectra of the initial *E*-form and the mixture of isomers after achievement of a photostationary state. From the experimental data, we evaluated the approximate ratio between the components in the photostationary state to be 10 mol % of *E*-isomer and 90 mol % of *Z*-isomer.



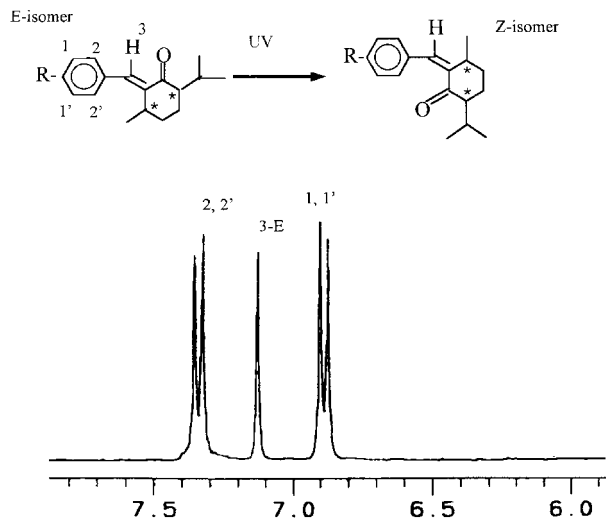
(a)



(b)

Figure 4. (a) Changes of the absorption spectra of **Mtn** in *n*-octane solution during UV irradiation (irradiation time is shown in the figure); (b) change in the optical density of the **Mtn** solution as a function of time ( $\lambda = 313$  nm  $D_{313}$ ) during UV irradiation.

The whole body of this experimental evidence suggests the occurrence of *E*-*Z* isomerization in the chiral photochromic dopant; no secondary reactions take place. The corresponding spectra of the irradiated solutions do not change with time, and therefore no back dark process occurs (at room temperature).



(a)

(b)

Figure 5. Part of the  $^1\text{H}$  NMR spectrum of **Mtn** before (a) and after (b) UV irradiation.

An effort was made to estimate the quantum yield of the photoisomerization. The calculations were carried out according to the equation derived in [16]:

$$\varphi_E = - \left( \frac{dD}{dt} \right)_{t \rightarrow 0} \frac{V}{I_0(1 - 10^{-D}) \epsilon^{313} l} \quad (2)$$

where  $I_0$  is the intensity of the incident light,  $V$  is the volume of the system,  $D$  is the optical density of the solution at the initial moment of time (in other words, the optical density associated with the presence of only *E*-isomer),  $\epsilon^{313}$  is the extinction coefficient of the *E*-isomer at a wavelength of 313 nm and  $l$  is the thickness of the cell.

Using equation (2), one may easily estimate the quantum yield of the forward process (*E* → *Z*) in the solutions studied. The results of our calculations are listed in table 2; for comparison, we also present the values of the quantum yield for the solutions of the menthone-containing homopolymer and copolymers

Table 2. Wavelength of the absorption maxima ( $\lambda_{\text{ads}}$ ), the extinction coefficient of the *E*-isomer at a wavelength of 313 nm and the quantum yield of *E*-*Z* isomerization of the **Mtn** dopant, as well as those of the chiral homopolymer and the copolymer containing 30 mol % of chiral units.

Sample	Solvent	$\lambda_{\text{ads}}/\text{nm}$	$\epsilon_{\text{E}}^{\text{max}}/\text{mol}^{-1} \text{cm}^{-1} \text{l}$	$\epsilon^{313}/\text{mol}^{-1} \text{cm}^{-1} \text{l}$	$\varphi_{\text{E}}$
<b>Mtn</b>	<i>n</i> -octane	297	16400	13300	0.34
Chiral homopolymer [16]	dichloroethane	303	13300	12600	0.36
Copolymer with 30 mol % of chiral units <sup>a</sup> [16]	dichloroethane	262	15800	12300	0.33

<sup>a</sup>The structure of the chiral photochromic copolymer is shown in the introduction.

with 30 mol % of chiral units [16]. The calculated values of the quantum yield are in good agreement with the data obtained for low molecular mass derivatives of menthone [28, 29].

### 3.3. Photo-optical properties of mixtures of chiral copolymers **I** and **II** with **Mtn**

To reveal the principal features of the photochemical behaviour of the above-mentioned mixtures, the 20  $\mu\text{m}$  thick films were exposed to UV radiation at room temperature. After a certain exposure time, the mixtures were annealed at a temperature exceeding the glass transition temperature  $T_{\text{g}}$  by  $\sim 30^\circ\text{C}$ .

Simultaneously, the corresponding selective light reflection spectra were recorded. For films irradiated at  $25^\circ\text{C}$  without further annealing at temperatures above  $T_{\text{g}}$ , no changes in the helix pitch were observed. As the temperature is increased, the maximum selective light reflection wavelength changes at the radiation-exposed point (figure 6). Under UV irradiation and with subsequent annealing of the mixture with cholesterol-containing copolymer **I**, the peak shifts to the long wavelength region. At the initial time, the test sample shows selective light reflection in the blue spectral region; as a result of irradiation and subsequent annealing, the value of  $\lambda_{\text{max}}$  shifts to the red spectral region (figure 7).

Figure 8 shows a microphotograph of the thin film prepared from a mixture of copolymer **I** with the dopant **Mtn** and the effect of exposure to UV irradiation. The initial film has a blue colour and after UV irradiation red spots are formed on the blue background. These red spots correspond to the irradiated regions having a helical supramolecular structure with a longer pitch of the helix.

In this case, the higher the temperature of UV radiation, the higher the intensity of this process (figure 9). Note that the shift of the selective light reflection peak is accompanied by no marked increase in its half-width as was observed for copolymers in [16]. In this case, the half-width of the peak remains almost unchanged until a photostationary state is attained. No degeneration of the peak is observed (figure 7).

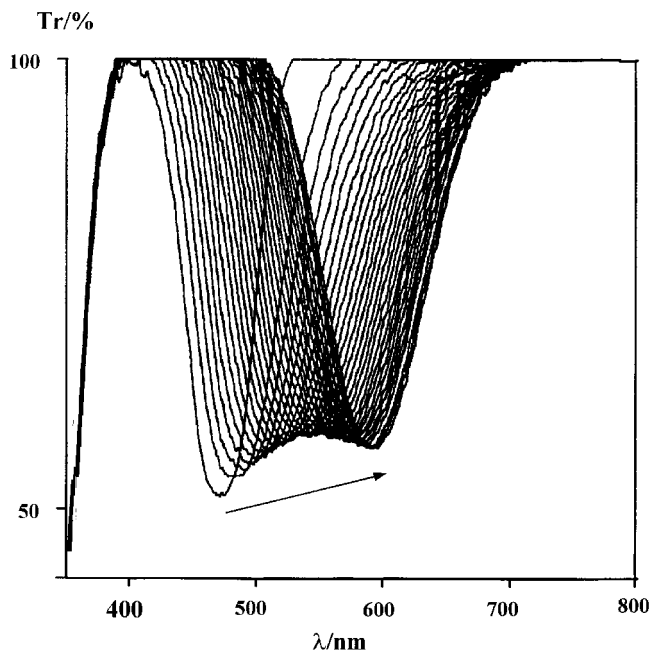


Figure 6. Kinetics of helix untwisting for the mixture of copolymer **I** with **Mtn**. The sample was irradiated for 125 min at  $25^\circ\text{C}$ , then annealed at  $60^\circ\text{C}$ ; the spectra were recorded at 2 min intervals after annealing. The arrow shows the direction of shift from the initial time of recording.

In the case of mixture **II** (menthyl-containing copolymer **II** and 5 mol % of **Mtn** dopant), the half-width of the peak also depends slightly on exposure time (figure 10). However we emphasize the principal feature of the photochromic behaviour of this system: the maximum shifts to the short wavelength region (figure 11). In this case UV irradiation of the mixture **II** leads to *E*-*Z* isomerization of the dopant and this means that helical twisting power of the dopant decreases, i.e. the influence of the dopant on the mixture is strongly suppressed. As a result, the helix starts to twist and the selective reflection of light is shifted to shorter wavelength. Figure 11 shows the time dependence of the helix twisting at two temperatures; at the higher temperature a shorter time of helix twisting is observed.

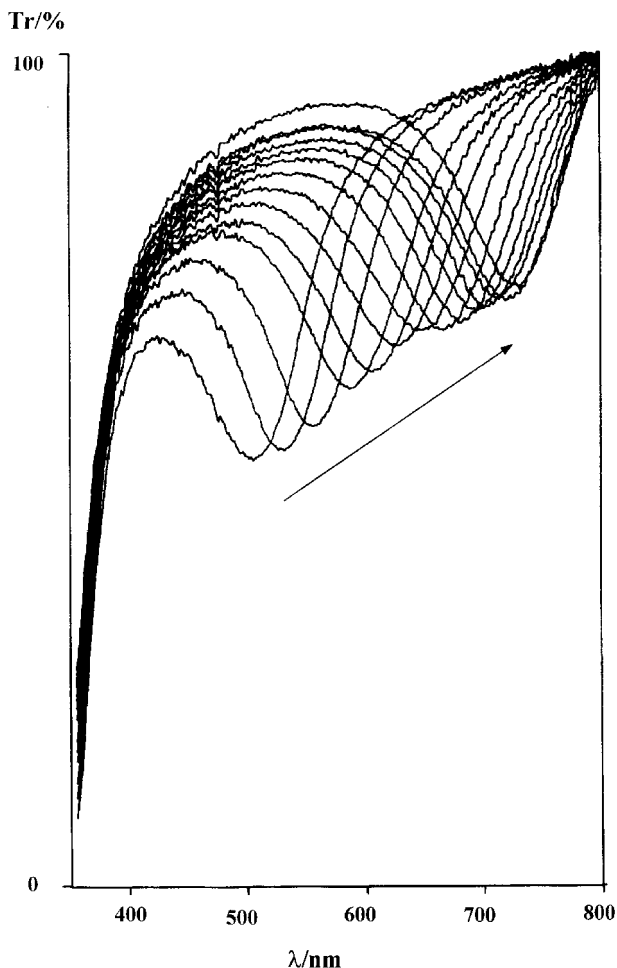


Figure 7. Change of transmission spectra of the mixture I (copolymer I and 10 mol % of **Mtn** dopant) during UV irradiation. Spectra were recorded at 5 min intervals after UV irradiation. The temperature of the irradiated sample was 60°C. The arrow shows the direction of shift of the peak of selective light reflection.

Thus, the introduction of left-handed dopant in the right-handed copolymer leads to untwisting of the helix and further UV irradiation leads to the twisting of the helix. In such a way we can regulate the supramolecular structure of cholesteric copolymers using UV irradiation.

Earlier, we assumed that the reason for an increase in helix pitch is provided by *E*-*Z* isomerization of chiral groups and the corresponding twisting power of the *Z*-isomer is much lower [16, 17]. For example, for unirradiation mixture I, the twisting power of the chiral dopant is equal to  $9.4\mu\text{m}^{-1}$ . In the case of the same mixture I, the helical twisting power of the photostationary mixture of *E* and *Z* isomers of **Mtn** is calculated through equation (1) and is equal to  $2.7\mu\text{m}^{-1}$  (figure 2, curve 2'). This marked change in helix twisting power is associated with a strong disturbance of the anisotropy of the chiral fragment.

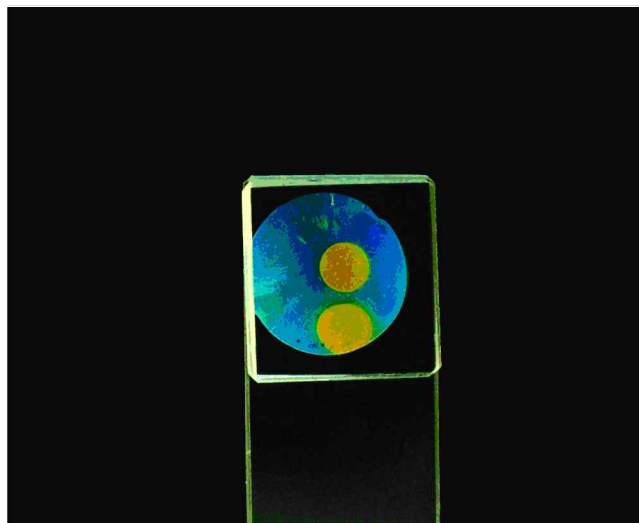


Figure 8. Microphotograph of a film prepared from mixture I on exposure to UV irradiation. The red spots corresponding to the irradiated zones are clearly seen on the blue background of the initial sample.

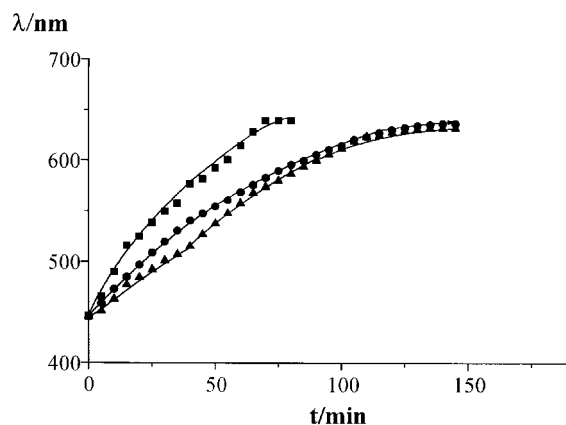


Figure 9. Untwisting of the helix for the mixture I (copolymer I + 10 mol % of **Mtn**) during UV irradiation at different temperatures: ■ 108°C; ● 60°C; ▲ 25°C.

A decreased anisotropy of the chiral molecules has an effect on thermal stability of mesophase. As in the case of copolymers under irradiation [16], the clearing temperature decreases (on average by 10°C) until the photostationary state is attained.

To estimate the efficiency of this photoprocess in films of the above mixtures, we calculated the values of the quantum yield at different temperatures. According to [16], the quantum yield may be easily obtained from changes in the maximum selective light reflection wavelength at the initial moment of time:

$$\varphi'_E = (\varphi_E)_{t=0} = - \frac{\rho l}{MAI_0} \left( \frac{d\lambda^{-1}}{dt} \right)_{t=0} \quad (3)$$



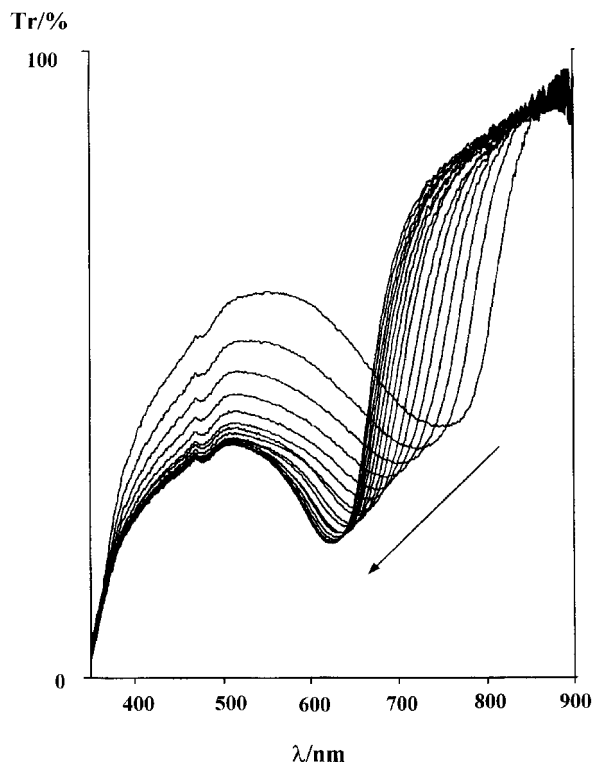


Figure 10. Change of transmission spectra of mixture II (copolymer II and 5 mol% of **Mtn** dopant) during UV irradiation. Spectra were recorded at 5 min intervals after UV irradiation. The temperature of the irradiated sample was 60°C. The arrow shows the direction of shift of the peak of selective light reflection.

Here  $M$  is the mean molecular mass of the copolymer units,  $\rho$  is the density of the copolymer,  $A$  is the twisting power of the chiral additive,  $I_0$  is the intensity of the incident light,  $\lambda$  is the maximum selective light reflection wavelength and  $l$  is the film thickness.

However, as was discussed in [16], the limiting stage of this process is the diffusion of the reacted component. Hence, the calculated quantum yields characterize self-

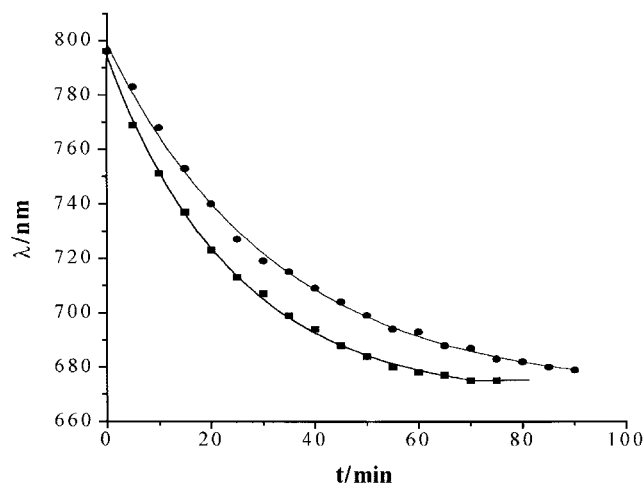


Figure 11. Change of the helix pitch of mixture II under UV irradiation at different temperatures: ● 25°C; ■ 60°C.

diffusion constants of the copolymers or the diffusion of the low molecular mass component in the polymer matrix rather than the elementary event of the photo-process. It seems evident that the diffusion constants of a chiral additive will be much higher than the self-diffusion constants of copolymers. Calculation of true quantum yields for media with high absorption in the absence of diffusive mixing presents a complicated mathematical problem [31–33].

Table 3 shows the values of  $(d\lambda^{-1}/dt)_{t=0}$  and apparent quantum yields for the copolymer with 10 mol% of menthone-containing chiral units [16] and for the mixture of cholesterol-containing and *d*-menthyl-containing copolymers I and II, respectively, with **Mtn** dopant (the content of photoactive component is 10 and 5 mol%, respectively).

As seen from table 3, the values of the quantum yields for films are lower by about one order of magnitude than those for solutions (table 1). This may be explained by the much higher viscosity and the low molecular

Table 3. Values of  $(d\lambda^{-1}/dt)_{t=0}$  and apparent quantum yields  $\phi'_E$  for the copolymer containing 10 mol% of chiral monomer units [16] and the mixtures I and II at different temperatures.

Sample	Irradiation temperature/°C	$\left(\frac{d\lambda^{-1}}{dt}\right)_{t=0} / \mu\text{m}^{-1} \text{min}^{-1}$	$\phi'_E$
Copolymer containing 10 mol% of chiral units	$T_{cl} + 20$	-0.0159	0.037
	60	-0.0614	0.014
	25	-0.00117	0.003
Mixture I (copolymer I + 10 mol% of <b>Mtn</b> )	$T_{cl} + 20$	-0.0202	0.074
	60	-0.0135	0.050
	25	-0.0116	0.042
Mixture II (copolymer II + 5 mol% of <b>Mtn</b> )	60	0.00778	0.028
	25	0.00615	0.023

mobility of these systems in the condensed state. On the other hand, comparing this evidence with the data for copolymer with 10 mol % of menthone-containing chiral units, one may conclude that, in the case of the mixtures I and II, the values of the quantum yields are several times higher (table 2). This difference is likely to be related to a marked difference between the values of the diffusion constants.

In conclusion we may stress that the above mixtures can be considered as universal coloured materials for coloured data recording and storage.

This research was supported by the Russian Foundation of Fundamental Research (Grant 96-03-33820), INTAS Project 96-922 and the International Soros Science Educational Program (Grant a98-2199).

### References

- [1] McARDLE, C. B. (editor), 1992, *Applied Photochromic Polymer Systems* (Blackie & Son Ltd).
- [2] SHIBAEV, V. P. (editor), 1996, *Polymers as Electrooptical and Photooptical Active Media* (Berlin, Heidelberg: Springer-Verlag), p. 37.
- [3] SHIBAEV, V. P., KOSTROMIN, S. G., and IVANOV, S. A., 1997, *Polym. Sci.*, **39**, 43.
- [4] CREAGH, L. T., and KMETZ, A. R., 1973, *Mol. Cryst. liq. Cryst.*, **24**, 59.
- [5] ICHIMURA, K., SUZUKI, Y., SEKI, T., HOSOKI, A., and AOKI, K., 1988, *Langmuir*, **4**, 1214.
- [6] ICHIMURA, K., SUZUKI, Y., TAKAHIRO, S., KAWANISHI, Y., and AOKI, K., 1989, *Macromol. Chem. rapid Commun.*, **10**, 5.
- [7] YANQUING, T., YANZHI, R., SUN, R., ZHAO, Y., TANG, X., HUANG, X., and XI, S., 1997, *Liq. Cryst.*, **22**, 177.
- [8] ICHIMURA, K., AKITA, Y., AKIYAMA, H., KUDO, K., and HAYASHI, Y., 1997, *Macromolecules*, **30**, 903.
- [9] MOHLMANN, G. R., and VORST, C. P. J. M., 1989, *Side Chain Liquid Crystal Polymers*, edited by C. B. McArdle (Glasgow: Blackie), p. 421.
- [10] WILLIAMS, D. J., 1987, *Nonlinear Optical Properties of Organic Molecules and Crystals*, edited by D. S. Chemla and J. Zyss, Vol. 1, p. 387.
- [11] KREUZER, F. H., 1996, *Polymers as Electrooptical and Photooptical Active Media*, edited by V. P. Shibaev (Berlin, Heidelberg: Springer-Verlag), p. 111.
- [12] PETRY, A., BRAUCHLE, CH., LEIGEBER, H., MILLER, A., WEITZEL, H.-P., and KREUZER, F.-H., 1993, *Liq. Cryst.*, **15**, 113.
- [13] GANGADHARA, K. H., 1995, *Macromolecules*, **28**, 806.
- [14] PINSL, J., BRAUCHLE, CH., and KREUZER, F.-H., 1987, *J. mol. Electron.*, **3**, 9.
- [15] BOBROVSKY, A. YU., BOIKO, N. I., and SHIBAEV, V. P., 1998, *Polym. Sci. Ser. A*, **40**, 232.
- [16] BOBROVSKY, A. YU., BOIKO, N. I., and SHIBAEV, V. P., 1998, *Liq. Cryst.*, **25**, (in press).
- [17] VINOGRADOV, V., KHIZHNYAK, A., KUTULYA, L., REZNIKOV, YU., and RESHETNYAK, V., 1990, *Mol. Cryst. liq. Cryst.*, **192**, 273.
- [18] BOIKO, N. I., KUTULYA, L. A., REZNIKOV, YU. A., SERGAN, T. A., and SHIBAEV, V. P., 1994, *Mol. Cryst. liq. Cryst.*, **251**, 311.
- [19] TROPSHA, E. G., 1987, PhD thesis, Moscow State University, Russia.
- [20] BOBROVSKY, A. YU., BOIKO, N. I., and SHIBAEV, V. P., 1997, *Polym. Sci. Ser. A*, **39**, 798.
- [21] BOIKO, N. I., 1988, PhD thesis, Moscow State University, Russia.
- [22] OSTROVSKII, B. I., SULIANOV, S. N., BOIKO, N. I., and SHIBAEV, V. P., 1998, *Liq. Cryst.*, **25**, 153.
- [23] LISETSKY, L., TIMAN, B., TISCHENKO, V., and POLOTI, T., 1977, *Solid State Phys.*, **19**, 3461 (in Russian).
- [24] BOBROVSKY, A. YU., BOIKO, N. I., and SHIBAEV, V. P., 1988, *Liq. Cryst.*, **24**, 489.
- [25] FREIDZON, YA. S., and SHIBAEV, V. P., 1993, *Liquid Crystal Polymers*, edited by N. A. Platé (New York: Plenum Press), p. 251.
- [26] SHIBAEV, V. P., and FREIDZON, YA. S., 1989, *Side Chain Liquid Crystal Polymers*, edited by C. B. McArdle (Glasgow: Blackie), p. 260.
- [27] ADAMS, J. E., and HAASE, W. E. L., 1971, *Mol. Cryst. liq. Cryst.*, **15**, 27.
- [28] YARMOLENKO, S. N., KUTULYA, L. A., VASHCHENKO, V. V., and CHEPELEVA, L. V., 1994, *Liq. Cryst.*, **16**, 877.
- [29] YARMOLENKO, S. N., CHEPELEVA, L. V., KUTULYA, L. A., VASHCHENKO, V. V., DRUSHLYAK, T. G., and PONOMAREV, O. A., 1995, *J. obsch. Chimii*, **65**, 145 (in Russian).
- [30] BEKKER, H. O. (editor), 1976, *Einführung in die Photochemie* (Berlin: VEV Deutscher Verlag der Wissenschaften).
- [31] SHEATS, J. R., DIAMOND, J. J., and SMITH, J. M., 1988, *J. phys. Chem.*, **92**, 4922.
- [32] MINAYLOV, V. V., VOROBIEV, A. KH., and GURMAN, V. S., 1995, *J. Photochem. Photobiol. A: Photochem.*, **87**, 67.
- [33] VOROBIEV, A. KH., 1994, *Modern Trends in Low Temperature Chemistry* (Moscow State University), p. 65.