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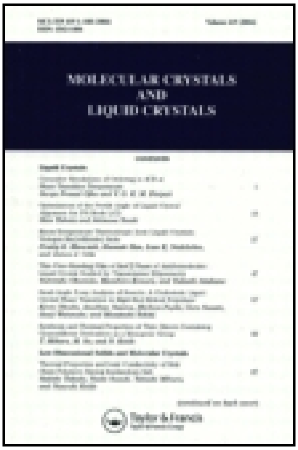

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New Chiral-Photochromic Dopant with Variable Helical Twisting Power and its use in Photosensitive Cholesteric Materials

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New Chiral-Photochromic Dopant with Variable Helical Twisting Power and its use in Photosensitive Cholesteric Materials

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A new photosensitive chiral dopant based on cinnamic acid and isosorbide was synthesised. UV light action leads to E-Z photoisomerization of the dopant about C=C double bond of cinnamoyl fragment. Mixtures of the dopant with nematic and cholestric polymers were studied. It was shown, that planarly-oriented films of mixtures possess a selective light reflection in ultraviolet, visible and infrared regions of spectrum depending on the dopant concentration. The helical twisting power of the chiral dopant was calculated. UV light action on mixture films leads to a shift of selective light reflection peak to the long wavelength region of spectrum, which is explained by photoisomerization and decrease of the helical twisting power of the dopant. Kinetics of the process of photoinduced untwisting of the cholesteric helix was studied. Advantages of the use of the synthesised dopant and of mixtures based on it were demonstrated in comparison to earlier studied chiral-photochromic materials for optical data recording and storage.

Keywords: photosensitive chiral dopant; chiral-photochromic cholesteric materials

INTRODUCTION

Low-molar-mass and polymer cholesteric liquid crystals attract a great attention of researchers owing to their unique optical properties (selective reflection of circularly polarized light, high optical activity, circular dichroism etc. [1]). The possibility for regulation of the pitch of the helix and, as a consequence, of selective

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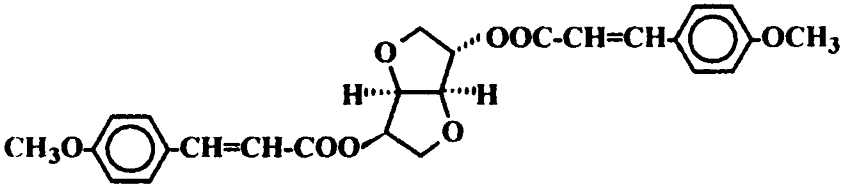
light reflection wavelength, under influence of different external factors (light, heat, mechanical field) makes such materials very perspective for optical data recording and storage [2–15].

Over last several years a number of publications devoted to low-molar-mass [4–8] and polymeric cholesteric liquid crystals with the pitch of the helix smoothly regulated under the light action have appeared [9–15]. It was shown, that cholesteric copolymers with photosensitive chiral side groups [10–14] and mixtures of cholesteric copolymers with chiral-photochromic dopants [15] can be used as optically active materials and, in particular, for optical data recording and storage. UV light irradiation of planarly-oriented films of these materials leads to E-Z photoisomerization of chiral-photochromic groups, that is accompanied by a decrease of the helical twisting power and a shift of the selective light reflection peak. In the case of polymeric photosensitive cholesteric liquid crystals there is a unique possibility for the local variation of the pitch of helix and of storage of recorded "information" for a prolonged time.

In spite of obvious progress, achieved in this field, the number of the effective photo-optical (or photochromic) polymeric materials with the photoregulated pitch of the helix is rather small and is mainly limited by some menthone derivatives [6, 9–15].

In the work [15] we demonstrated the advantages of mixtures of cholesteric copolymers and low-molar-mass photosensitive dopants in comparison with the copolymers having a similar chemical structure, in which both chiral-photochromic and nematogenic groups are chemically linked to polymer backbone. In the case of such mixtures we did not observed a widening of selective light reflection peak during UV irradiation of the films owing to their homogeneous planar structure caused by more "fast mixing" of low-molar-mass dopant with polymer matrix. In addition helix untwisting rate and virtual quantum yields of photoprocesses for the mixtures have been several times higher as compared with the pure copolymers [15].

The main objectives of this work is to synthesize a new family of chiral-photochromic dopants for cholesteric mixtures based on isosorbide and cinnamic acid:



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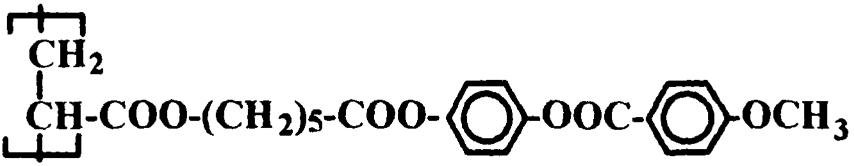
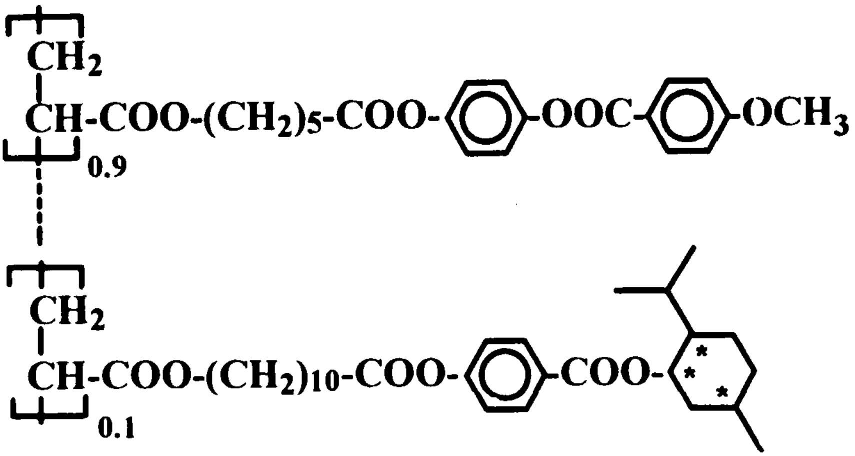
As seen from the chemical formula, this substance contains an optically active fragment based on isosorbide and two double C=C bonds capable of E-Z photoisomerization. The selection of cinnamoyl fragment as photosensitive group is explained by the fact that peculiarities of E-Z isomerization (including other possible processes in such substances) have been studied earlier [16–19]; moreover, it is well-known that isosorbide derivatives as chiral dopants in cholesteric mixtures have the greater values of the helical twisting power [20].

As for polymeric matrixes for this dopant we used nematogenic phenylbenzoate polyacrylate (mixtures of series **I**)



and *l*-menthyl-containing copolymer forming the chiral nematic phase with a left-handed cholesteric helix (mixtures of series **II**):



The main goals of this work are, firstly, the synthesis and investigation of photochemical behavior of the new chiral-photochromic dopant; secondly, the study of photo-optical properties of cholesteric mixtures of this dopant with polymeric substances aimed at their use for optical data recording and storage.

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EXPERIMENTAL PART

Synthesis

Menthyl-containing and nematogenic monomers were synthesized according to the procedures described in [21, 22].

The following chemicals were used without further purification: Dicyclohexylcarbodiimide (Fluka), N,N′-dimethylaminopyridine (Fluka), 4-methoxycinnamic acid (REAKHIM) and isosorbide (Lancaster Synthesis Ltd).

Synthesis of chiral-photochromic dopant 2,5-bis(4-methoxycinnamoyl)-1,4;3,6-dianhydro-D-sorbitol

To a solution of 3.42 mmoles of 1,4;3,6-dianhydro-D-sorbitol and 10.27 mmoles of 4-methoxycinnamic acid in 10 ml of purified absolute THF 1.03 mmoles of N,N′-dimethylaminopyridine was added. Then 10.27 mmoles of dicyclohexylcarbodiimide was added and the resulting solution was stirred for 3 days. The formed precipitate was filtered, washed with THF, and diethyl ether (50 ml) was added to a filtrate. The solution was washed successively with water, a 5% solution of acetic acid, and finally with water until pH 7 was achieved. The ether extract was dried with anhydrous $MgSO_4$. After removal of solvent the white crude product was purified by column chromatography (eluent-chloroform). Yield: 96 % m.p.: 170–173 °C. IR (cm^{-1}) 2936, 2884, 2856 (CH_2), 1706 (CO), 1634 (C=C), 1600, 1512 (C-C in Ar), 1254 (COC). UV (in dichloroethane): λ_{max}=312 nm, $\lg\varepsilon_{max}$=4.63.

Polymerization

The homo- and copolymer were synthesized by radical polymerization of appropriate monomers in benzene solution at 60°C; AIBN was used as an initiating agent. The synthesized polymers were purified by the repeated precipitation with methanol and dried in vacuum.

Physical Properties

IR spectra were recorded on a Bruker IFS-88 spectrophotometer using KBr pellets. Gel permeation chromatography (GPC) analysis was performed in THF on Knauer set up equipped with Ultrastyragel 8×300 mm column (Waters) having pore size 10^3 Å, detector – UV spectrometer Knauer. Waters 19×300 mm column fulfilled with Ultrastyragel 10^3 Å was used for preparative GPC.

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Phase transitions of the synthesized copolymers and mixtures were studied by differential scanning calorimetry (DSC) with a scanning rate of 10 K/min. All experiments were performed using a Mettler TA-400 thermal analyzer and a LOMO P-112 polarization microscope. Selective light reflection of the films of chiral polymers was studied with a Hitachi U-3400 UV-Vis-IR spectrometer equipped with a Mettler FP-80 hot stage. The 20-μm-thick samples were sandwiched between the two flat glass plates. The thickness of the test samples was preset by Teflon spacers. Planar texture was obtained by shear deformation of the samples, which were heated to temperatures above glass transition temperature. Prior to tests, the test 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).

Photo-optical Investigations

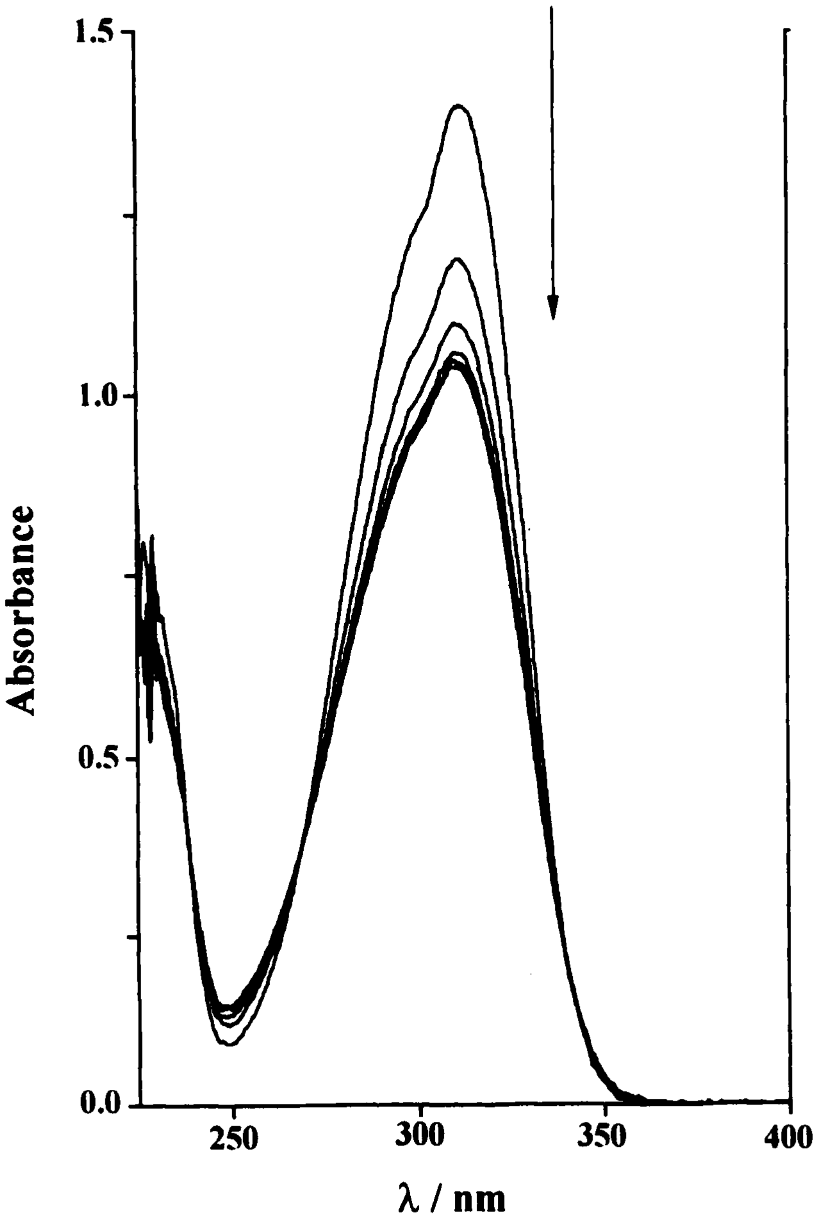
Photochemical investigations were performed using a special instrument [13] equipped with a DRSh-250 ultra-high pressure mercury lamp. Using filters, the 313 and 366 nm bands of linear radiation spectrum of mercury lamp were selected. To prevent heating of the samples due to IR irradiation of the lamp, water filter was used. To obtain plane-parallel light beam, 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 [23] and were equal to 1.0×10^{-9} Einstein$\times$s$^{-1}\times$cm^{-2} (λ_{ir}=313 nm) and 1.1×10^{-8} Einstein$\times$s$^{-1}\times$cm^{-2} (λ_{ir}=366 nm).

In our photochemical studies dichloroethane was used as solvents. Concentrations of the solution was 1.65×10^{-5} mol/L. For illumination, the solution was kept in a 2-cm-thick quartz cell. The process of isomerization was controlled by recording the absorption spectra of the illuminated solutions.

RESULTS AND DISCUSSION

Photochemical study of chiral-photochromic dopant in dilute solution

UV-light irradiation of the dilute solution of the chiral dopant in dichloroethane leads to the significant changes in the absorbance spectra (Figure 1a, b). A decrease of extinction coefficients corresponding to π-π^* and n-π^* electronic



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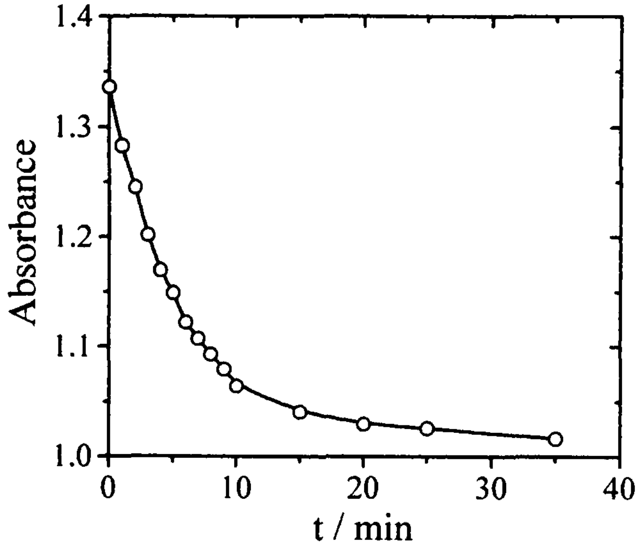

FIGURE 1 (a) Changes of absorbance spectra of dichloroethane solution of chiral-photochromic dopant during UV-irradiation (313 nm). Spectra were recorded each 5 min of irradiation; (b) absorbance decrease (at 313 nm) during UV irradiation

transitions of cinnamoyl chromophore is observed. It should be noted, that the spectral peaks corresponding to the above-mentioned electronic transitions practically fully overlap (Figure 1). Such spectral changes during UV irradiation provide evidence of E-Z photoisomerization of the chiral-photochromic dopant [16–18], as it is shown in Scheme 1.

In the course of phototransformations described above a noticeable decrease in chiral molecules anisometry occurs, which is more clearly seen from molecular models of the dopant (Figure 2). Using experimental data obtained earlier by several authors [6, 9–15] one can assume that these structural changes must have a marked influence on the helical twisting power of the chiral dopant.

Photo-optical properties of mixtures of chiral-photochromic dopants with nematogenic homopolymer (mixtures I) and cholesteric copolymer (mixtures II)

Until describing photo-optical properties of mixtures based on synthesized chiral-photochromic dopant, let us consider their phase behavior and optical properties.

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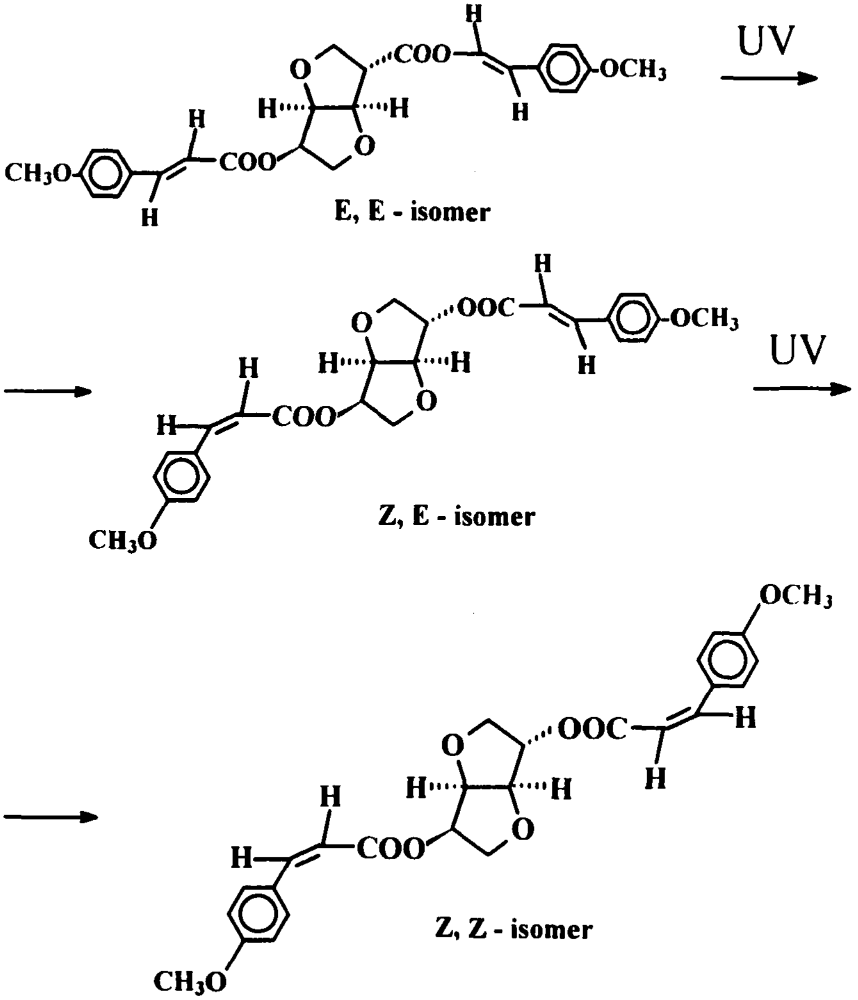

SCHEME 1 Schematic representation of E-Z photoisomerization process of chiral-photochromic dopant

All prepared mixtures with the chiral dopant concentration less then 10 mol% form the chiral nematic phase (N^*)*; as clearly seen from Figure 3, an increase of the chiral dopant content leads to a decrease in clearing temperature.

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* The prolonged annealing of the mixtures leads to the formation of ordered TDK^* phase with melting temperature about 60–65 °C; structure of this phase was studied in detail in [24, 25]. Nevertheless the formation of TDK^*phase does not affect on texture and optical properties of cholesteric mixtures, that is why we do not take into consideration an existence of this phase.

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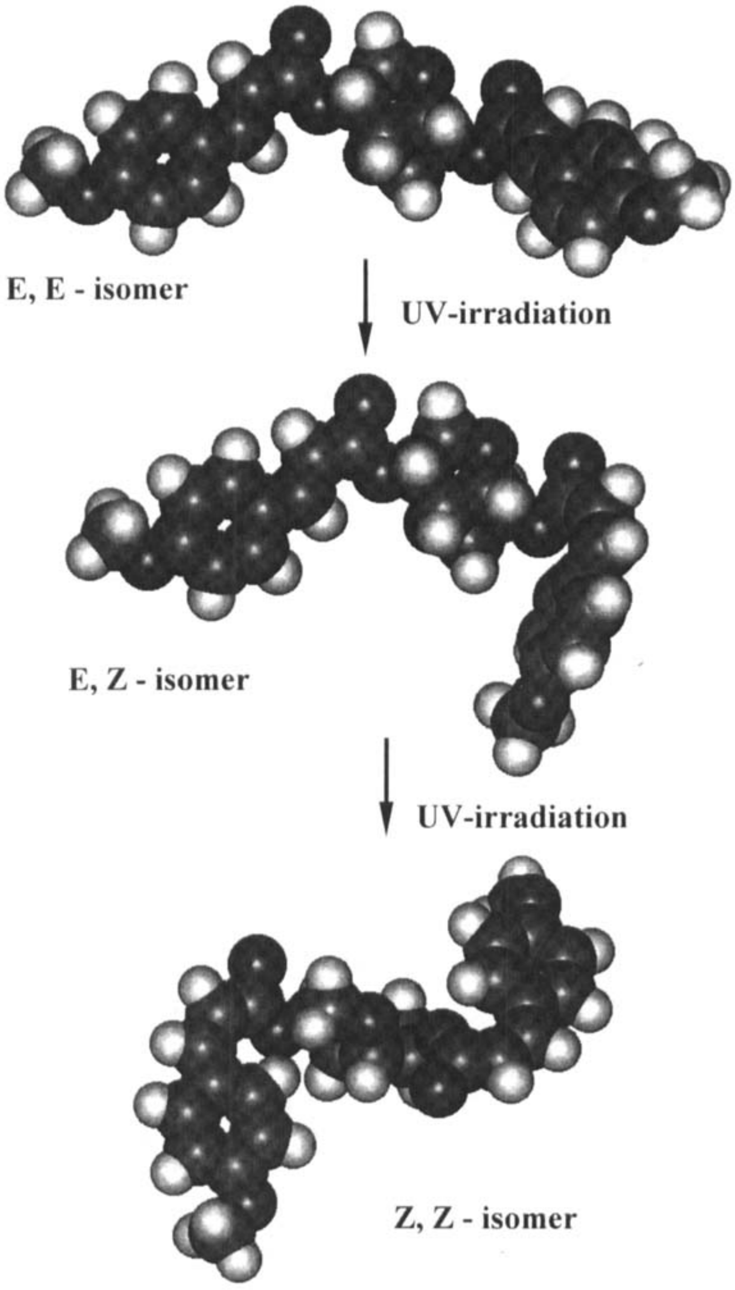

FIGURE 2 Schematic representation of molecular shape changes of chiral-photochromic dopant during UV-irradiation

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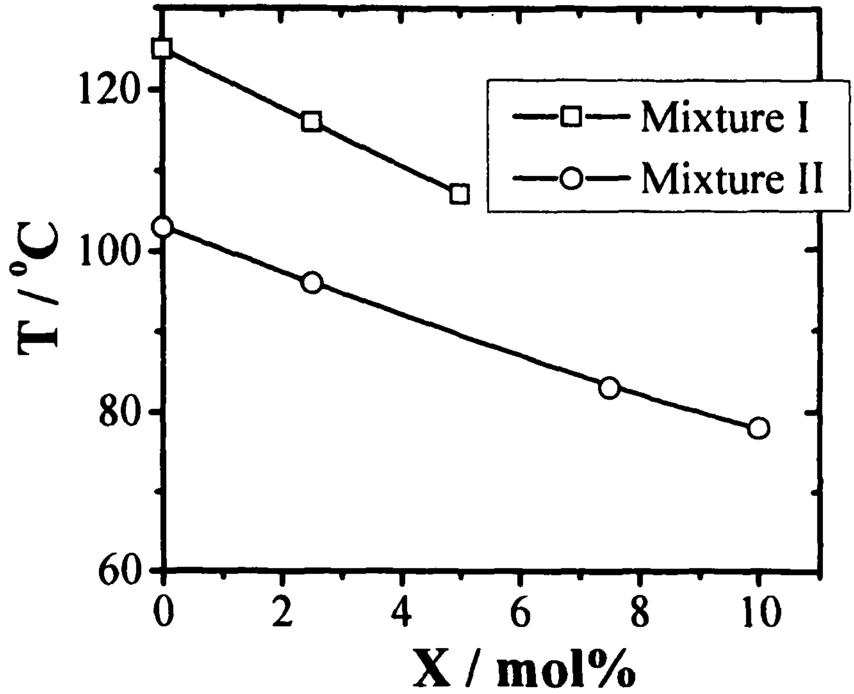

FIGURE 3 Dependence of clearing temperature on chiral dopant contents for cholesteric mixtures of series I and II

According to the DSC data all mixtures have approximately the same glass transition temperatures, equal to about 20 – 25°C.

As shown in Figure 4, planar texture of all mixtures selectively reflects the light with wavelength corresponding to the visible and infrared regions of the spectrum. The maximum of selective light reflection λ_{max} weakly depends on temperature.

In order to determine the handedness (sign) of cholesteric helix of the mixtures, the sandwich-like samples were prepared using the mixtures of series I and cholesterol-containing chiral nematic copolymers [26]. Cholesterol-containing copolymer composition was selected in such a way, so that the selective reflection bands of the mixtures and the copolymers would coincide [26]. The transmittance spectra analysis showed that in the case of mixtures I the transmittance in selective reflection band is about zero. As known from literature data [27, 28], cholesterol derivatives with the long alkyl substituents usually stimulate left-handed cholesteric helix formation. This fact allowed to conclude that in

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mixtures **I** the right-handed cholesteric helix is formed, in the mixtures **I**, i.e. the synthesized chiral dopant induces the right-handed cholesteric helix [29, 30].

A more complicated situation takes place in the case of mixtures of series **II** obtained by introduction of the chiral dopant in the left-handed cholesteric menthyl-containing copolymer (see Figure 4b). The introduction of 2.5 mol% of the dopant leads to the compensation of "chirality" of the mixture: helix untwisting is observed (as showed investigations of sandwich-like sample; the sense of helix in this case coincides with the helical sense of the initial copolymer used as a "matrix"). The mixtures with concentration of the dopant more then ~2.7 mol% of the chiral dopant form the right-handed helix (Figure 4b and 5).

In order to calculate the helical twisting power of the chiral-photochromic dopant, dependencies of the reciprocal wavelength of the selective light reflection on mole fraction of the chiral dopant were plotted (Figure 5). The helical twisting power was calculated from the slope of the dependencies of bias angle:

$$\beta = \bar{n}(d\lambda^{-1}/dX)_{X=0},$$

were $\bar{n}$ is the average refractive index, × is the mole fraction of the chiral dopant in mixture. The apparent helical twisting power $(\beta/\bar{n})$ of the chiral-photochromic dopant is equal to 44.9±2.4 μm^{-1} for mixtures of series **I** and 39.9±2.5 μm^{-1} for mixtures of series **II**. The $\beta/\bar{n}$ values obtained are actually 5–5.5 times higher than the helical twisting power of the chiral menthyl-containing side groups of the copolymer used as matrix for dopant introduction (7.9±0.1 μm^{-1}) [25]. It should be pointed out, that values of the helical twisting power are very high, that is why the introduction of only 3–5 mol% of the chiral dopant give us a possibility to obtain films with selective light reflection in the visible region of the spectrum.

Thus, the above-mentioned peculiarities of the optical properties of mixture of series **II** are explained by the fact, that the helical twisting power of the chiral-photochromic dopant is several times higher than the helical twisting power of menthyl-containing chiral side groups of copolymer.

UV-light irradiation of planarly-oriented films of the mixtures leads to a noticeable shift of selective light reflection peak to the long-wavelength region of the spectrum (Figures 6 and 7). This effect is explained by a decrease in anisomery of the chiral dopant molecules during E-Z isomerization process (Figure 2). It is important to underline that, as shown in Figure 6, during the photoinduced shift of the peak its widening does not occur; that is an advantage of the obtained mixtures, comparing to the previously studied photosensitive cholesteric copolymers [10–15].

It is very interesting that the rate of the selective light reflection shift in the case of the mixture **II** with 10 mol% of the dopant is higher (Figures 6, 7b). In

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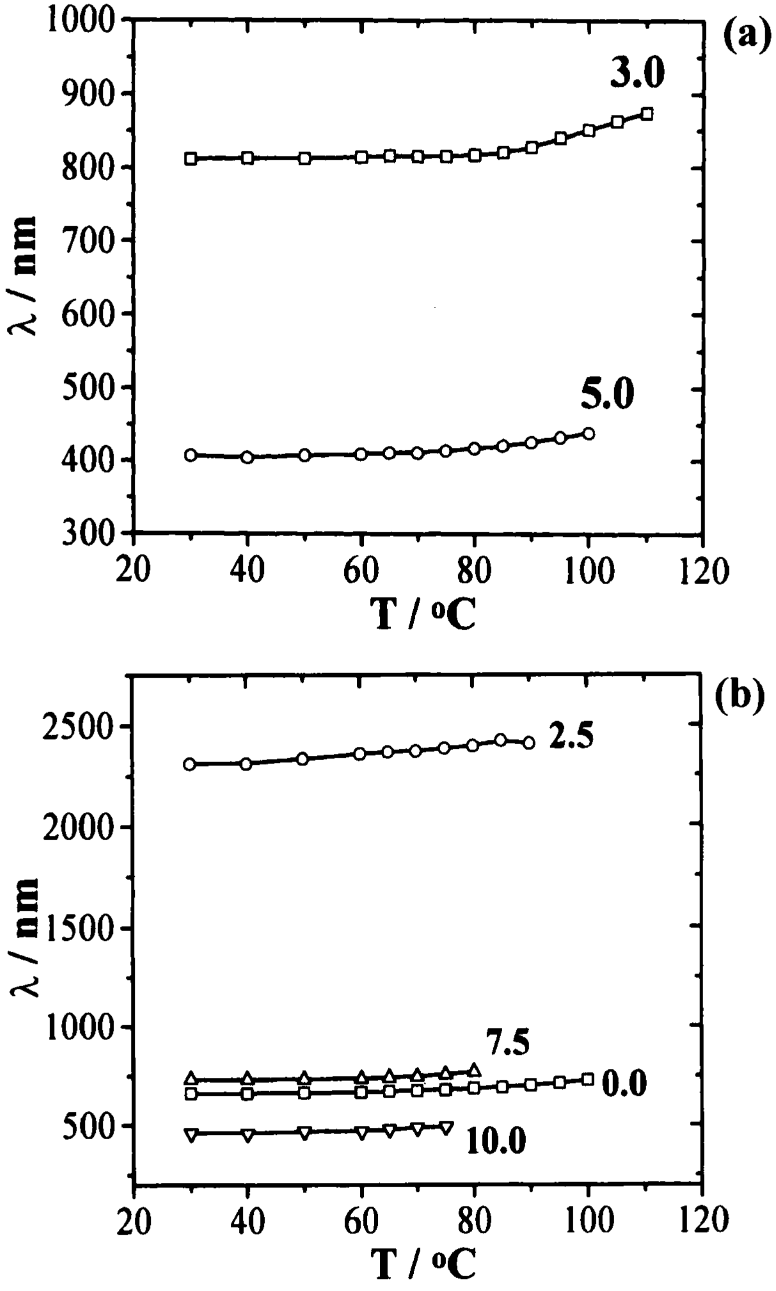

FIGURE 4 Temperature dependencies of selective light reflection maximum for mixtures of series **I** (a) and **II** (b) with different chiral-photochromic dopant content (shown in mol% in figure)

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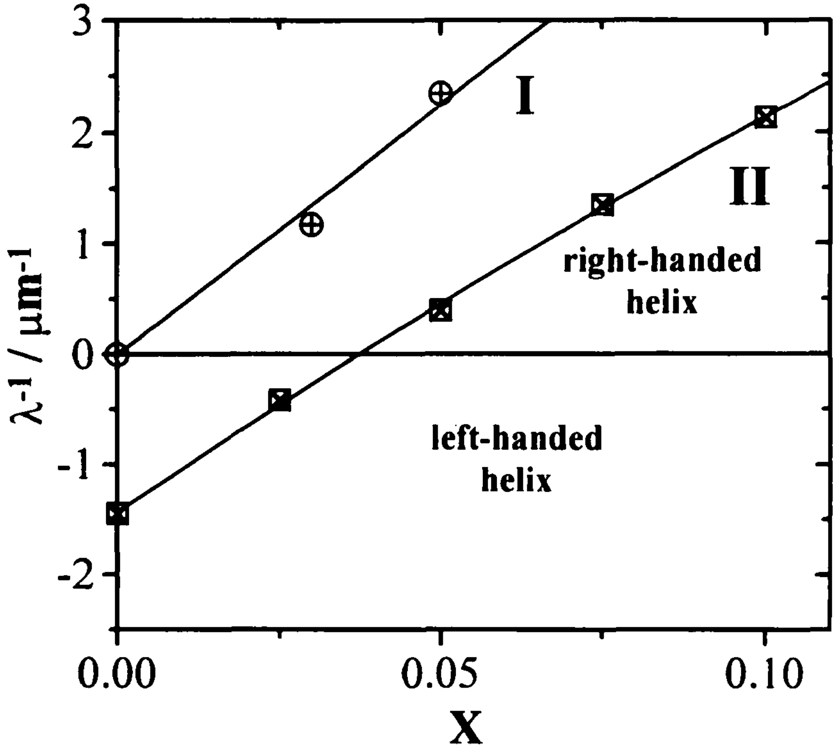

FIGURE 5 Dependence of the inverse selective light reflection wavelengths on molar fraction of chiral-photochromic dopant for mixtures of series I and II at temperature $T=0.95T_{cl}$; × is the mole fraction of chiral-photochromic dopant

the case of the mixtures **II**, a the right-handed dopant was introduced in the left-handed cholesteric matrix of menthyl-containing copolymer, that is why in this case the pitch of the helix is more sensitive to the helical twisting power decrease during UV irradiation.

Other interesting feature of the helix untwisting kinetics is connected with two-stage process. As clearly seen from Figure 7a, this process actually can be considered as consisted of the fast and slow steps. In our opinion, the first stage of helix untwisting is explained by E-Z isomerization, whereas the slow stage of the decrease in the helical twisting power may occur due to a possible {2+2} photocycloaddition of dopant's double bonds with formation of cyclobutane ring [16–19]. The dimers formation must lead to a supplementary decrease of the helical twisting power of the dopant, however the rate of this process is not high, as

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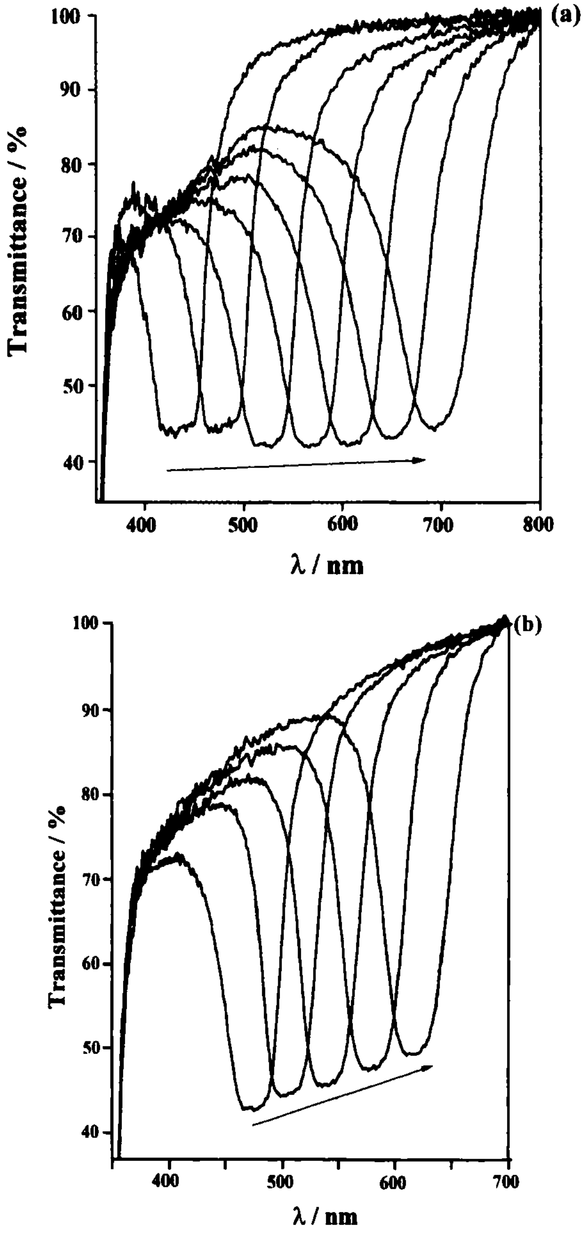

FIGURE 6 Transmittance spectra changes during UV irradiation (366 nm) of planarly-oriented film of mixture of series **I** (a) and **II** (b) with 5 and 10 mol% of chiral dopant, respectively. Spectra were recorded each 40 s (in the case a) and 20 s (b) of irradiation. Irradiation temperature was 90 °C (a) and 70 °C (b)

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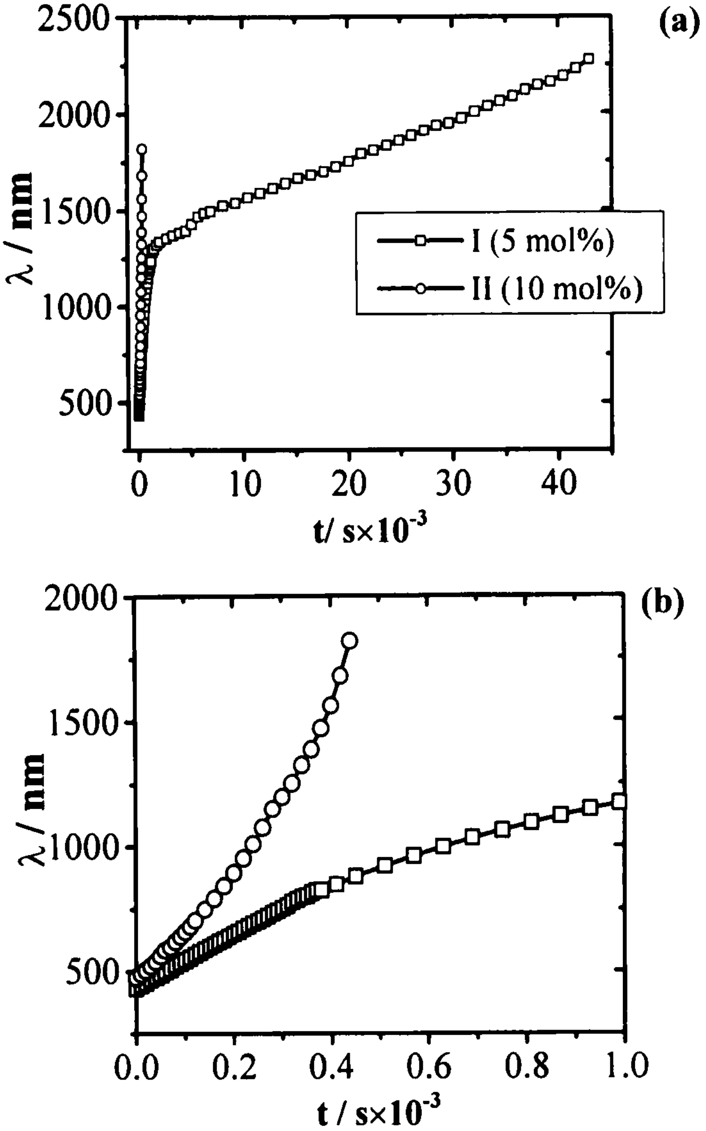

FIGURE 7 (a) Changes of selective light reflection wavelength of the films obtained on the base of mixtures of series **I** and **II** under UV irradiation (366 nm); (b) initial part of the plot (a)

it is controlled topochemically: a close contact of two C=C bonds is needed for this process [31]. The analysis of the mixtures irradiated during two hours by the gel permeation chromatography showed that the concentration of the chiral dopant dimers after irradiation is neglectably small.

The analysis of the obtained experimental data allows to conclude that the synthesized new chiral-photochromic dopant possesses a number of undoubtable merits, such as a large value of the helical twisting power, a good compatibility with liquid crystalline polymers. Under UV light irradiation on cholesteric mixtures containing this dopant no widening of the selective light reflection peak is observed, the rate of untwisting of cholesteric helix being high.

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