

Chiral Nematic Polymer Mixture Containing Crosslinker and Photosensitive Chiral Dopant: New Type of Materials with Tunable Photo-Optical Properties**

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A cholesteric mixture based on a menthyl-containing copolymer, photosensitive chiral dopant, mesogenic diacrylate, and photoinitiating agent has been prepared. The mixture shows a selective light reflection in the visible light spectral region. The action of UV irradiation (313 or 365 nm) on the planar-oriented films generates the occurrence of two parallel processes: *E/Z* (i.e., *cis-trans*) photoisomerization of the chiral dopant and photopolymerization of the diacrylate. The first process leads to the untwisting of the cholesteric helix and shifts the selective light-reflection maximum to the long-wavelength spectral region, whereas the second process leads to the development of a polymer network that fixes the helical supramolecular structure. As a result of a simultaneous occurrence of the two above-mentioned processes, the shift in the selective light-reflection maximum is thermally irreversible, even though the *Z/E* isomerization of the chiral dopant itself can be reversed by annealing. On irradiation with visible light (>450 nm), the dopant experiences the *E/Z* isomerization but photopolymerization is absent because the photoinitiator shows no absorption in this spectral region. In this case, the shift in the selective light-reflection maximum can be reversed to its initial value by annealing, whereby the original helix pitch is recovered. The kinetic features of helix untwisting at different temperatures and light wavelengths were studied. The experimental data obtained in this work allow one to conclude that the as-prepared mixture presents a new multifunctional material with “tunable” photo-optical properties and may be used for recording and storage of optical information.

1. Introduction

The rapidly growing flow of information in the modern world makes strict demands on the data carriers and, presently, the interest of most researchers is focused on materials with photocontrolled optical properties, such as liquid-crystalline (LC) polymers.^[1–7] The combination of LC order and photosensitive groups in the same material allows one to develop various types of photoswitchable devices based on liquid crystals.^[1,2,5,8–10]

Among the various LC systems, cholesteric or chiral nematic materials attract the utmost interest due to their unique helical supramolecular structure, which is capable of selective light reflection in a certain spectral region.^[2,11,12] The introduction of photosensitive groups to cholesteric polymers allowed the preparation of materials with a photocontrolled helix pitch and a selective light-reflection maximum.^[13–21]

The main principal underlying the photoinduced control of the optical properties of such materials is provided by the photoisomerization of chiral photochromic fragments, which is accompanied by changes in their anisotropy and helix twisting

power β . As is well known,^[22] β is directly related to the concentration of chiral component x and helix pitch P in the helical supramolecular structure, which is responsible for the selective light-reflection maximum λ_{\max} :

$$\beta = \frac{dP^{-1}}{dx} = \bar{n} \left(\frac{d\lambda_{\max}^{-1}}{dx} \right)_{x=0} \quad (1)$$

where \bar{n} is the average refractive index.

The efficiency of this approach has been convincingly proved,^[14–21] and allows one to control the optical properties of polymer films by irradiation, which causes helix untwisting due to a decrease in the anisotropy of the *Z*-isomer and a concomitant decrease in β . Furthermore, the direction of changes in helix pitch may be effectively controlled by using mixtures of low-molecular-mass photosensitive dopant with right- or left-twisted chiral copolymers. Thus, λ_{\max} can be shifted to a longer-wavelength or shorter-wavelength spectral region under light irradiation.^[17]

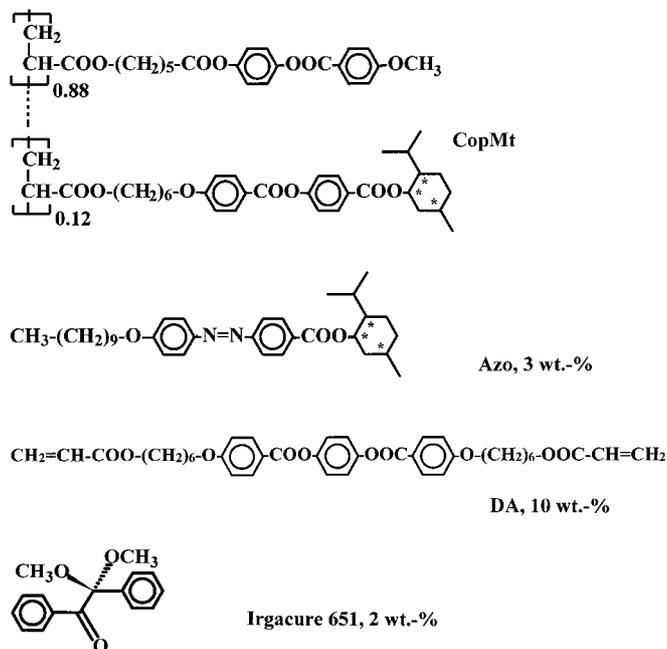
Finally, a concurrent introduction of two different photochromic groups, e.g., azobenzene and benzylidenemethanone, to macromolecules makes it possible to yield a selective reaction to the light from each of the groups. This finding allows one either to design the helical structure of the polymer (by varying the helix pitch and λ_{\max}), or to develop the photoinduced birefringence in the polymer film.^[23] All the above methods for controlling changes in optical properties deal with finished systems in which the properties are modified upon light irradiation.

At the same time, even better advantages in the development of polymers with controlled optical properties are offered

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by polymer mixtures with photopolymerized monomers, because a desired supramolecular structure in these materials is developed directly in the course of the synthesis of the finished products. The advantages of this approach have been vividly demonstrated.^[24–26] In this work, we studied the photo-optical behavior of the multicomponent mixture containing the cholesteric (chiral nematic) copolymer, **CopMt**, as a principal component, and the chiral photochromic dopant, **Azo**, as the functional photosensitive additive, as well as the mesogenic diacrylate, **DA**, as a crosslinker, and photoinitiating agent α -dimethoxybenzoin (Irgacure 651). Structures of the above are shown in Scheme 1).

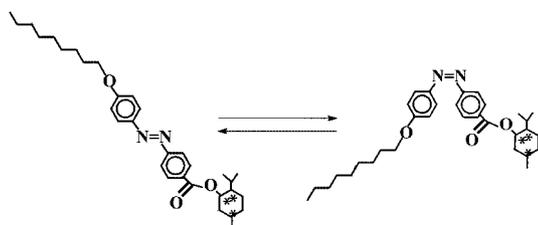


Scheme 1. Structures of the species used in the multicomponent mixture.

The appropriate choice of the above compounds makes it possible to take the advantages of a dual role of UV irradiation and combine the processes of the untwisting of the cholesteric helix via photoisomerization of **Azo** (Scheme 2) with a concurrent photopolymerization of **DA** in the system.

Under UV irradiation, the latter fragment should polymerize and form the network in which the helical structure, which is responsible for the optical properties of such multicomponent system, is fixed.

Furthermore, by varying the wavelength of light irradiation, one may control the ratio between the processes of photoisomerization and crosslinking. For example, on UV irradiation,



Scheme 2. E-Z isomerization process.

both processes of crosslinking and photoisomerization are induced (light absorption of the photoinitiating agent Irgacure 651 is observed only in the UV spectral region, and $\lambda_{\max} = 338$ nm in dichloroethane), however, on irradiation with visible light (>450 nm), only E/Z photoisomerization of **Azo** takes place.^[20,21,23]

To prevent the processes of phase segregation, only low concentrations of the low-molecular-mass components (dopant and photoinitiator) should be used. Furthermore, a similar concentration for the latter two compounds should enable one to compare the contributions of photoisomerization and photoinduced crosslinking.

The above observations offer new, fascinating advantages for studying the competing processes of photoisomerization and photoinduced crosslinking in the above systems, and the controlled design of the optical properties of LC polymers and related mixtures.

2. Results and Discussion

The mixture studied in this work is able to produce a chiral nematic (or cholesteric) phase with a clearing temperature of 98 °C and a glass-transition temperature of about 20 °C (as shown later by data from polarization optical microscopy and differential scanning calorimetry (DSC)).

The planar-oriented films of the studied mixture show the selective light reflection in the red spectral region (Fig. 1). One may also observe a marked difference in the character of the temperature dependencies of the selective light-reflection maximum, λ_{\max} , of the mixture and **CopMt**. As the temperature is increased, the copolymer experiences the untwisting of the cholesteric helix, which is related to a decrease in the orientational order parameter.^[27,28] In the case of the mixture, the character of the temperature dependence is far more complicated: as the temperature is increased from 80 °C up to the clearing temperature (T_{CI}), λ_{\max} increases, and this increase is likely to be related to a decrease in the order parameter. As the temperature is decreased below 70 °C, one may observe the process of helix untwisting, which is related to the development of smectic-order fluctuations as was earlier observed for some polymer cholesteric systems.^[29,30] The marked difference in the

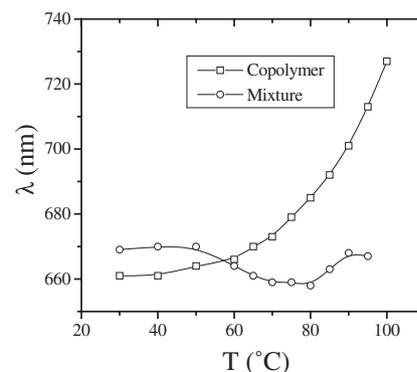


Fig. 1. Temperature dependencies of selective light reflection wavelengths for methyl-containing copolymer **CopMt** and for the mixture.

temperature dependencies of helix pitch between **CopMt** and its related mixture must be due to the addition of **DA**, as no changes in the character of the temperature dependence of λ_{\max} were observed^[21,31] on the introduction of **Azo** to **CopMt**. The dramatic effect of diacrylate is likely due to the fact that this component is smectogenic, because it forms the monotropic smectic phase.^[32]

On light irradiation at different wavelengths (313 nm, 365 nm, >450 nm, and ~550 nm), the cholesteric helix experiences untwisting, and the selective light-reflection maximum is shifted to the long-wavelength spectral region (Figs. 2 and 3). The above variations are associated with the *E/Z* photoisomerization of **Azo** and the reduction of anisotropy; as a result, β decreases and, according to Equation 1, the helix pitch increases (an increase in λ_{\max}). The rate and amplitude of the shift are markedly controlled by the wavelength of the incident light (Fig. 3). Maximum spectral changes are induced by light irradiation with a wavelength of 365 nm because it is this value of λ that is mostly close to the maximum of the π - π^* electron transition of the *E*-isomer of **Azo** ($\lambda_{\max} = 367$ nm).

Note that, on UV irradiation (in the case studied, 313 nm and 365 nm), the shift in the selective light-reflection maximum is thermally irreversible. This trend is related to the fact that the *E/Z* photoisomerization of **Azo** is accompanied by the

concurrent photopolymerization of **DA** and the formation of a network, which fixes the supramolecular helical cholesteric structure.^[33]

The occurrence of photopolymerization was proved by gel-permeation chromatography (GPC) data, and by the fact that the irradiated film was completely insoluble. In the case of the irradiated film, the chromatogram shows that the intensity of the peak corresponding to **DA** and photoinitiator becomes much lower (Fig. 4). All other peaks corresponding to **CopMt** and **Azo** remain almost unchanged; the only exception is the

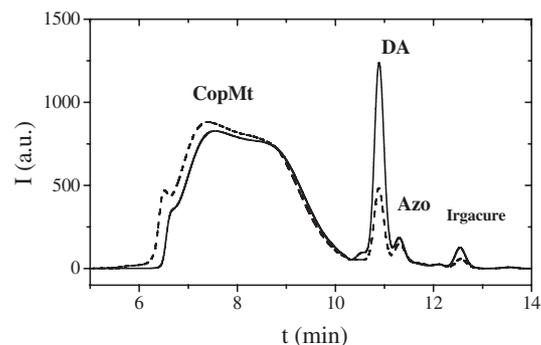


Fig. 4. Gel-permeation chromatography data for the mixture before (solid line) and after (dashed line) 40 min of UV irradiation ($\lambda = 365$ nm, $T = 70$ °C).

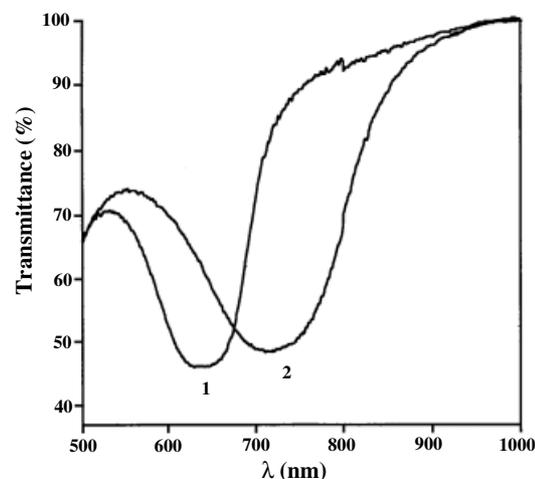


Fig. 2. Transmittance spectra of a planarly oriented film of the mixture: 1) before irradiation, 2) after 40 min of UV irradiation at 70 °C.

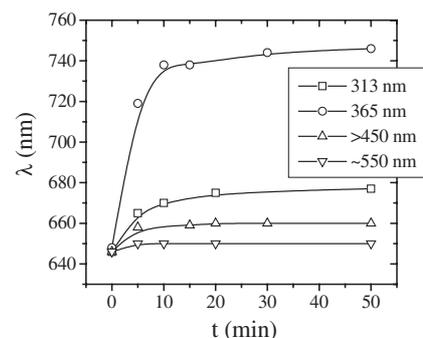


Fig. 3. Changes of the selective light-reflection wavelength during irradiation with light of different wavelengths at 80 °C.

peak seen in the region of the elution times of **CopMt**, which is slightly changed due to the appearance of a soluble high-molecular-mass fraction produced by photopolymerization. The formation of the high-molecular-mass fraction is likely to be related to the formation of a linear or weakly branched product of the photopolymerization of **DA**. The contribution of this process should be rather high because the probability of the reaction of the second double bond and the development of a three-dimensional network decreases due to a marked restriction in the mobility of a growing polymer chain in the polymer matrix in the course of photopolymerization.

The formation of the network is followed by quite an unorthodox phenomenon: as the temperature is increased above T_{Cl} , the selective light-reflection peak does not disappear completely (Figs. 5 and 6). This observation implies that, on photopolymerization the polymer network produced by **DA** fragments “remembers” the helical supramolecular structure. This phenomenon has also been observed previously.^[34–37] It seems interesting to note that, on cooling from isotropic melt, the irradiated regions quickly recover the selective light-reflection maximum whereas, in the non-irradiated regions, the confocal texture is developed. In other words, the fragments of helical structure that are preserved in the mixture, even at temperatures above T_{Cl} , favor the development of a well-pronounced planar texture; at the same time, on cooling of the non-irradiated regions, the isotropic phase is transformed to the non-oriented N^* phase (focal conics texture). This phenomenon may be used for the development of new materials for optical data recording. For example, one may advance the two ways of image recording on the mixture studied: one way involves the untwisting of the cholesteric helix and shift in λ_{\max} to the long-wavelength spectral region whereas another approach is pro-

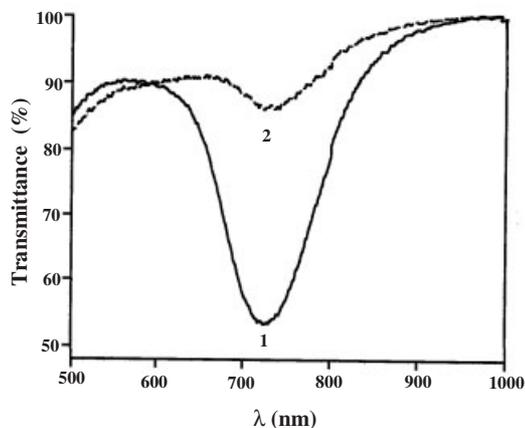


Fig. 5. Transmittance spectra of a planar-oriented film of the mixture after 40 min of UV irradiation ($\lambda=365$ nm) at different temperatures: 1) at 70 °C (N^* phase), 2) at 100 °C (isotropic phase).

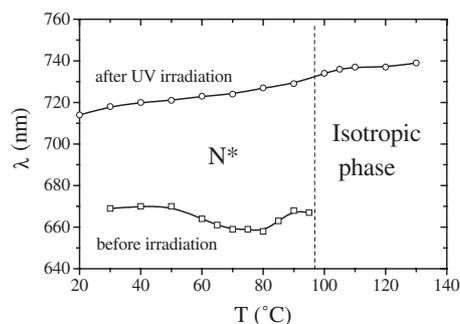


Fig. 6. Temperature dependencies of the selective light reflection wavelengths for the mixture before and after UV irradiation ($\lambda=365$ nm, $T=70$ °C, 40 min).

vided by the development of the network with a “memory” effect.

The network formation also leads to changes in the temperature dependence of the selective light-reflection maximum: after irradiation, as the temperature is increased λ_{\max} increases (Fig. 6), which is related to the thermal expansion of the system.^[32,38]

A quite different situation is observed on irradiation with wavelengths of >450 nm and ~ 550 nm; in these cases, the above spectral changes are reversible. Therefore, on annealing at temperatures above 40–50 °C, the selective light-reflection maximum returns to its initial position. This behavior implies that, in this case, only *E/Z* photoisomerization of **Azo** takes place and photopolymerization ceases.

We studied the effect of temperature on the kinetics of untwisting of a cholesteric helix upon irradiation (Figs. 7 and 8). On UV and visible light irradiation at different temperatures, the rate of the shift in the selective light-reflection maximum is controlled by temperature. For UV irradiation, the rate of this process monotonically increases with increasing temperature of the irradiated samples. On light irradiation with a wavelength of >450 nm, however, one may observe the maximum rate at a temperature of about 70 °C. The effect of the temperature on the kinetics of the system lies in the fact that, on UV irradiation,

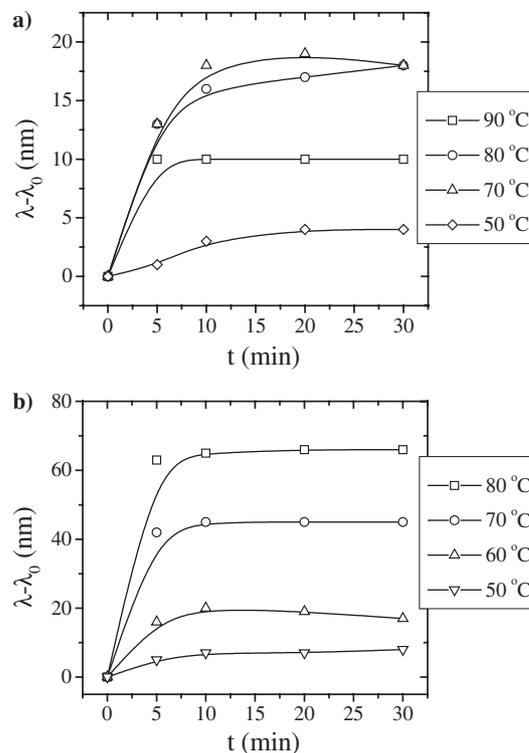


Fig. 7. Temperature dependence of the selective light-reflection wavelength during irradiation with light of different wavelengths: a) >450 nm, b) 365 nm.

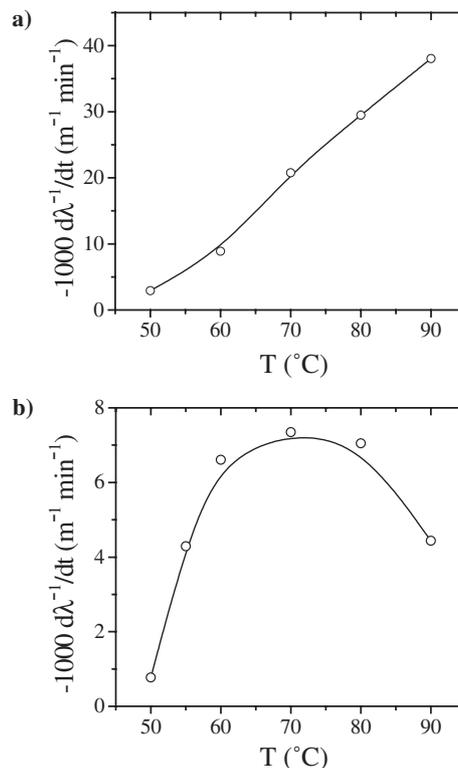


Fig. 8. The temperature dependence of the change of the reciprocal selective light-reflection wavelength with time during irradiation with light of different wavelengths: a) 365 nm, b) >450 nm.

a competition between the two processes takes place and, with increasing temperature, untwisting of the cholesteric helix proceeds at a higher rate and is accomplished before the three-dimensional network is formed by photopolymerization of **DA**.

In the case of irradiation with visible light (in the absence of photopolymerization of **DA**), the rate maximum is seen at about 70 °C. This behavior has been observed earlier^[21,31,39] and may be explained by the fact that in the system several competing processes occur: *E/Z* photoisomerization, back thermal *Z/E* isomerization, and helix untwisting. The contributions of these processes to the total rate of the process is different at different temperatures: at high temperatures, the helix untwisting rate decreases due to a high contribution from thermal back isomerization; at low temperatures, the rate of the shift in λ_{\max} is limited by the high viscosity of the medium.

On UV irradiation at temperatures below 40 °C, helix untwisting and shifts in the selective light-reflection maximum to the long-wavelength spectral region do not take place; however, one may observe the occurrence of photopolymerization of **DA**. Figure 9 presents the kinetic curves of untwisting of the cholesteric helix as a function of time for UV irradiation at 30 °C. As follows from Figure 9, on the 20 min irradiation, the polymer network produced by **DA** virtually prevents helix untwisting. Therefore, the UV irradiation of the planar-oriented films based on the mixture allows one to design their photo-optical properties.

To study the feasibility of repeated recording–erasing cycles, experiments on fatigue resistance of the mixture on irradiation with visible light and subsequent annealing were performed (Fig. 10). It can be seen from Figure 10 that the fatigue resistance of the as-treated mixture is rather high, which makes this system a promising material for the reversible recording of optical information.

3. Conclusions

From the results of the experiments conducted in our work, one may conclude that the cholesteric mixtures present new, promising materials that might find their application in modern information technologies. Figure 11 shows the possible modes of the photo-optical recording of optical information on cholesteric mixtures of a given type.

On masked UV irradiation of the planar-oriented film of the mixture, irreversible untwisting of the cholesteric helix takes place and the selective light-reflection maximum is shifted to the long-wavelength spectral region (Fig. 11a). Hence, UV irradiation allows one to control the photo-optical properties of the planar-oriented film of the mixture. Further irradiation of

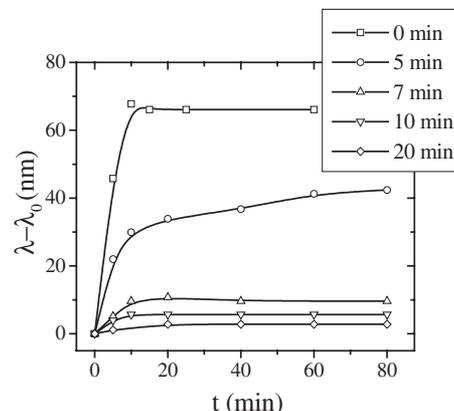


Fig. 9. Changes of selective light reflection wavelength during UV irradiation ($\lambda = 365 \text{ nm}$, $T = 70 \text{ }^\circ\text{C}$) after photo-crosslinking by irradiation at 30 °C with light of the same wavelength (time of irradiation at 30 °C is shown in the Figure).

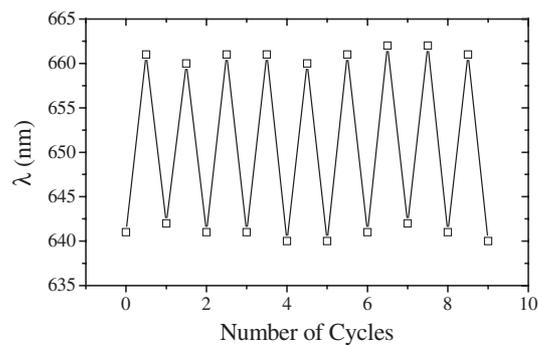


Fig. 10. Fatigue resistance properties of the mixture film under the recording–erasing conditions. In each cycle, the film of the copolymer was irradiated for 20 min with light ($\lambda_{\text{ir}} > 450 \text{ nm}$, $T = 80 \text{ }^\circ\text{C}$), and then annealed for 20 min at the same temperature.

the films at temperatures below 40 °C allows one to fix the recorded image due to the photopolymerization of **DA** in the whole sample. This approach makes it possible to use such mixtures for long-term storage of the recorded information.

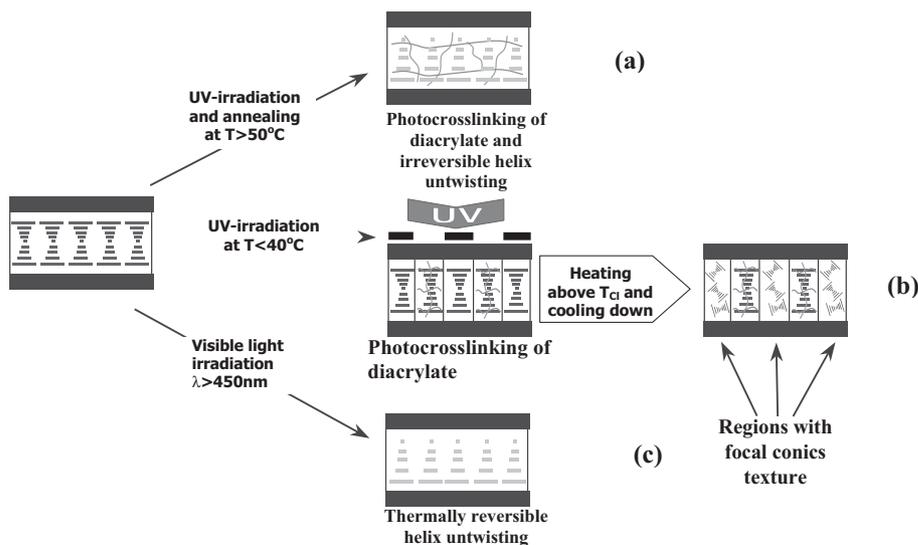


Fig. 11. Schematic representation of three possible ways of optical data recording using the cholesteric mixture prepared in this work.

Masked UV irradiation of the films at low temperatures (below 40 °C), followed by heating to temperatures above T_{CI} , and cooling down to ambient temperature allow one to perform an irreversible data recording (Fig. 11b). On cooling down to temperatures below T_{CI} , the irradiated regions show the recovery of the planar texture and selective light reflection whereas, in the non-irradiated regions, one may observe the development of the confocal structure that is capable of a marked light scattering.

Finally, an alternative method of data recording may be accomplished via the irradiation of films with visible light. In this case, this process is thermally reversible, and repeated recording-erasing cycles may be performed (Fig. 11c).

In our opinion, due to their multifunctional character, the above mixtures offer great advantages in their utilization as a photosensitive medium.

4. Experimental

Synthesis and Mixture Preparation: Procedures from the literature were used to synthesize **Azo** [20], phenyl benzoate [40] and menthyl-containing [41] monomers, and **DA** [42]. **CopMt** was synthesized by radical copolymerization of monomers in benzene solution at 60 °C; 2,2'-azobisisobutyronitrile was used as an initiating agent. The synthesized copolymer was purified by repeated precipitation with methanol and dried in vacuum. The copolymer obtained has the following molecular-mass characteristics: $M_n = 17000$, $M_w/M_n = 2.5$; the T_{CI} of **CopMt** is 105–106 °C, and the glass-transition temperature is about 25 °C. The mixture was prepared by dissolving **DA**, **Azo**, Irgacure 651 (Ciba-Geigy), and the thermal polymerization inhibitor di-*tert*-butylphenol in chloroform, followed by solvent evaporation at 60 °C. The mixture was then dried under vacuum at 120 °C for two hours. Before photopolymerization and the study of photo-optical behavior, the 20 μm thick samples of mixture were sandwiched between two flat glass plates. The thickness of the test samples was preset by Teflon spacers. A planar texture was obtained by shear deformation of the samples (by slight shift of the cover glass plate), which were heated to temperatures above the glass-transition temperature.

GPC analysis was carried out with a Knauer chromatograph using a Waters column (8 \times 300 mm) packed with a 1000 Å (7 μm) Ultrastayragel. Tetrahydrofuran was used as eluent, and a Knauer UV spectrophotometer was used as the detector. Phase transitions of the mixture were studied by DSC with a scanning rate of 10 °C min⁻¹. All experiments were performed using a Mettler TA-400 thermal analyzer and a LOMO P-112 polarization microscope. Selective light reflection of the **CopMt** and mixture films was studied with a Hitachi U-3400 UV-vis-IR spectrometer equipped with a Mettler FP-80 hot stage. Prior to tests, the test samples were annealed for 20–40 min.

Photo-Optical Investigations: Photo-optical properties were studied using a special instrument equipped with a DRSh-250 ultra-high pressure mercury lamp. Using filters, light with wavelengths 365 nm, >450 nm, and ~550 nm were selected. A water filter was used to prevent heating of the samples due to IR irradiation from the lamp. A quartz lens was used to obtain a plane-parallel light beam. During irradiation, the constant temperature of the test samples was maintained using a Mettler FP-80 heating unit. The intensity of light was equal to $1.1 \times 10^{-8} \text{ Ess}^{-1} \text{ cm}^{-2}$ (3.6 mW cm⁻²) for light of 365 nm, and $1.9 \times 10^{-9} \text{ Ess}^{-1} \text{ cm}^{-2}$ (0.7 mW cm⁻²) for light of 313 nm (as measured actinometrically [43]), the intensity of visible light ($\lambda_{ir} > 450 \text{ nm}$ and $\lambda_{ir} \sim 550 \text{ nm}$) was equal to $\sim 8.0 \text{ mW cm}^{-2}$ (for $\lambda_{ir} > 450 \text{ nm}$) and to $\sim 0.7 \text{ mW cm}^{-2}$ (for $\lambda_{ir} \sim 550 \text{ nm}$), as measured by a IMO-2N intensity meter. Photochemical properties of the mixture were studied by illuminating the 20 μm thick films. Immediately after irradiation, or after annealing, transmittance spectra were recorded using Hitachi U-3400 UV-vis-IR spectrometer.

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