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Cholesteric Polymer Guest−Host Mixture with Circularly Polarized Fluorescence: Two Ways for Phototuning of Polarization and Its Intensity

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A photosensitive fluorescent cholesteric guest−host mixture consisting of a nematic polyacrylate, a chiral, photochromic dopant sensitive to UV light, and a fluorescent dopant was prepared. The nematic polyacrylate contains 4-phenyl-4′-methoxybenzoate nematogenic side groups and photochromic 4-cyanoazobenzene side groups. The chiral-photochromic dopant formed by isosorbide and cinnamic acid is capable of E−Z photoisomerization and [2 + 2] photocycloaddition under light irradiation. The planarly oriented films possess a selective light reflection in the visible spectral region coinciding with the emission peak of the fluorescent dopant. The fluorescence emitted by the planarly oriented films of the mixture is strongly circularly polarized and characterized by a large value of the dissymmetry factor. At temperatures below glass transition (T_g) the polarized light action of an Ar^+ laser (488 nm) leads to the photoorientation of the azobenzene fragments resulting in a strong and reversible disruption of the selective reflection and a decrease of the dissymmetry factor of fluorescence. UV irradiation leads to E−Z isomerization and/or [2 + 2] cycloaddition of the chiral-photochromic dopant, causing an irreversible shift of the maximum of the dissymmetry factor to a long-wavelength spectral region under subsequent annealing at temperatures higher than T_g. Such multifunctional glass-forming guest−host mixtures combining photosensitive and fluorescent properties with the unique optical properties of cholesteric liquid crystals can be considered as promising material for optical data processing technologies and photonic applications.

Introduction

Unflagging interest in cholesteric liquid crystals is connected to their unique chiral structure and, on this basis, to their optical properties, such as optical rotation, selective reflection, and circular dichroism, etc.[1,2] Cholesteric materials with photovariable optical properties attract special attention due to their potential application for optical devices and optical data storage.[3−17] Different ways and approaches were elaborated in order to develop new types of low molar mass[3,5−10] or polymeric[11−17] cholesteric materials with photovariable helical pitch, allowing one to change the wavelength and intensity of selective reflection, etc.

A combination of the unique optical properties of cholesterics with the emission properties of fluorescent dyes dissolved in a small amount in a cholesteric matrix is a very promising feature widely studied in the past few years.[18−30]

When the wavelengths of selective reflection and fluorescence coincide,[18−23] the photonic band gap theory in direct analogy to the band gap theory of semiconductors has to be applied.[20] The cholesteric phase is considered as a one-dimensional photonic crystal in which the refractive index is regularly modulated along the helix axis due to the particular helical arrangement of the molecules. The result is that the propagation of light is suppressed for a particular range of wavelengths. Within the frame of this theory the wavelength interval for which no propagation is possible is called stop band. In the case of cholesteric mesophases the stop band is, in principle, another representation for the selective reflection band. The propagation of one of the circularly polarized components of the fluorescence light is suppressed within the stop band, whereas its handedness corresponds to that of the external light which is selectively reflected. Thus, a left-handed helix will emit a right-handed circularly polarized light and vice versa. The degree of circular polarization defined by eq 1 is high in this case.

$$g_e = 2(I_L - I_R)/(I_L + I_R) \tag{1}$$

where I_L and I_R are the intensities of the left- and right-handed circularly polarized light, respectively.

In our previous papers we have prepared and studied several new cholesteric materials with photocontrollable circularly polarized fluorescence.[31−33] Two main approaches, namely, photoregulation of helical pitch[31] and photobleaching of fluorescent dopant,[32,33] were explored for this purpose.

In the former case we prepared a mixture containing cholesteric cyclosiloxane, chiral-photochromic dopant based on cinnamic acid and different fluorescent dopants. UV irradiation of planarly oriented films of the prepared mixture leads to E−Z photoisomerization of chiral-photochromic dopant, a decrease of its helical twisting power, and a shift of selective reflection peak. This shift is accompanied by changing the emission intensity of the fluorescent dyes and the degree of circular polarization of the emitted light.

In the second approach we have used anthracene derivatives as photobleachable fluorescent dopants. In this case UV

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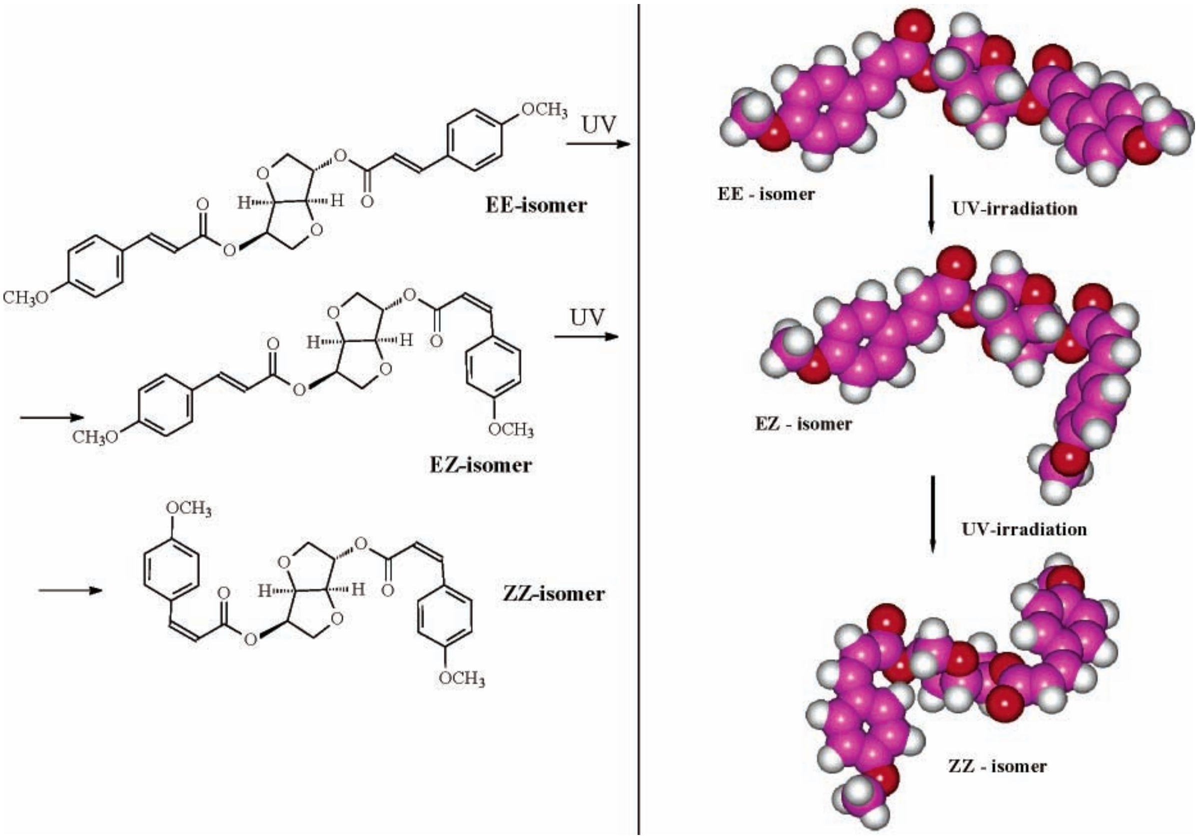
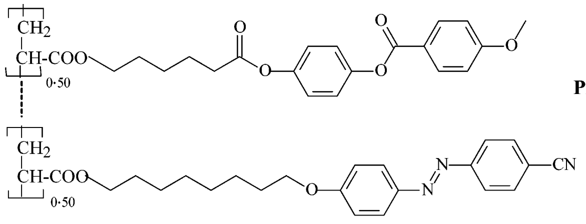
SCHEME 1: Schematic Representation of the Changes of the Molecular Shape of Chiral Cinnamic Ester Dopant Sorb during UV Irradiation



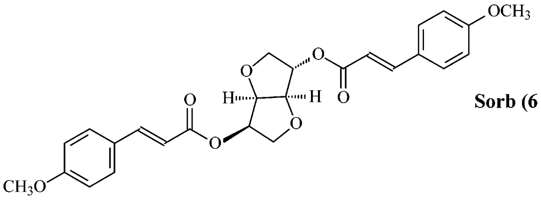
irradiation (365 nm) lead to a [4 + 4] photocycloaddition reaction of anthracene moieties, causing a strong decrease of the fluorescence intensity. The dissymmetry factor remains the same under the light action.

In the present paper for the first time the photoregulation of the emission properties of polymeric materials has been demonstrated by means of the photoorientation of azobenzene groups of a side-chain copolymer upon irradiation with linearly polarized visible light.

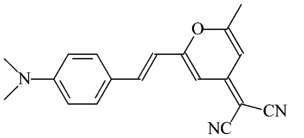
We prepared a mixture containing polyacrylate with phenylbenzoate and azobenzene side groups (**PAAzo8**), the photosensitive chiral dopant (**Sorb**), and the fluorescent dye (**DCM**):



PAAzo8



Sorb (6 wt%)



DCM (1 wt%)

As is seen the nematic polyacrylate consists of nematogenic phenylbenzoate groups and photochromic cyanoazobenzene side groups. The chiral-photochromic dopant **Sorb** contains the carbon−carbon double bond in the cinnamic ester capable of E−Z isomerization and {2 + 2} photocycloaddition upon light irradiation. The photoreactions of the chiral dopant **Sorb** reduce its anisometry and decrease the helical twisting power resulting in helix untwisting of cholesteric systems[34] (Scheme 1). The fluorescent dopant **DCM** is widely used in lasing and fluorescence research[18,19,31,33] and has emission in the visible spectral range with a maximum at ca. 590 nm.

The composition of mixtures was selected in such a way that planarly oriented films possess a selective reflection in the visible spectral region coinciding with the emission peak of the fluorescent dopants.

The main idea of this work is to combine two different possibilities for phototuning of the intensity and polarization of fluorescence by helix untwisting in cholesteric films due to UV light irradiation and photoorientation due to linearly polarized visible light action. In addition, we would like to study the photooptical processes occurring in planarly oriented films of the cholesteric polymeric guest−host system of different thicknesses and upon exposure with light of the different wavelengths and polarizations. Special attention will be paid to investigations of fluorescence changes upon irradiation, including the study of polarization of the emitted light.

Experimental Section

4-Cyano-4′-oxyazobenzene and 4-phenyl-4′-methoxybenzoate monomers were synthesized according to the procedures described in refs 35 and 36, respectively. The copolymer was synthesized by radical polymerization of monomers in benzene solution at 65 °C; azobis(isobutyronitrile) (AIBN) was used as an initiating agent. The synthesized polymer was purified by the repeated extraction of low-molar-mass substances with boiled ethanol and dried in a vacuum.

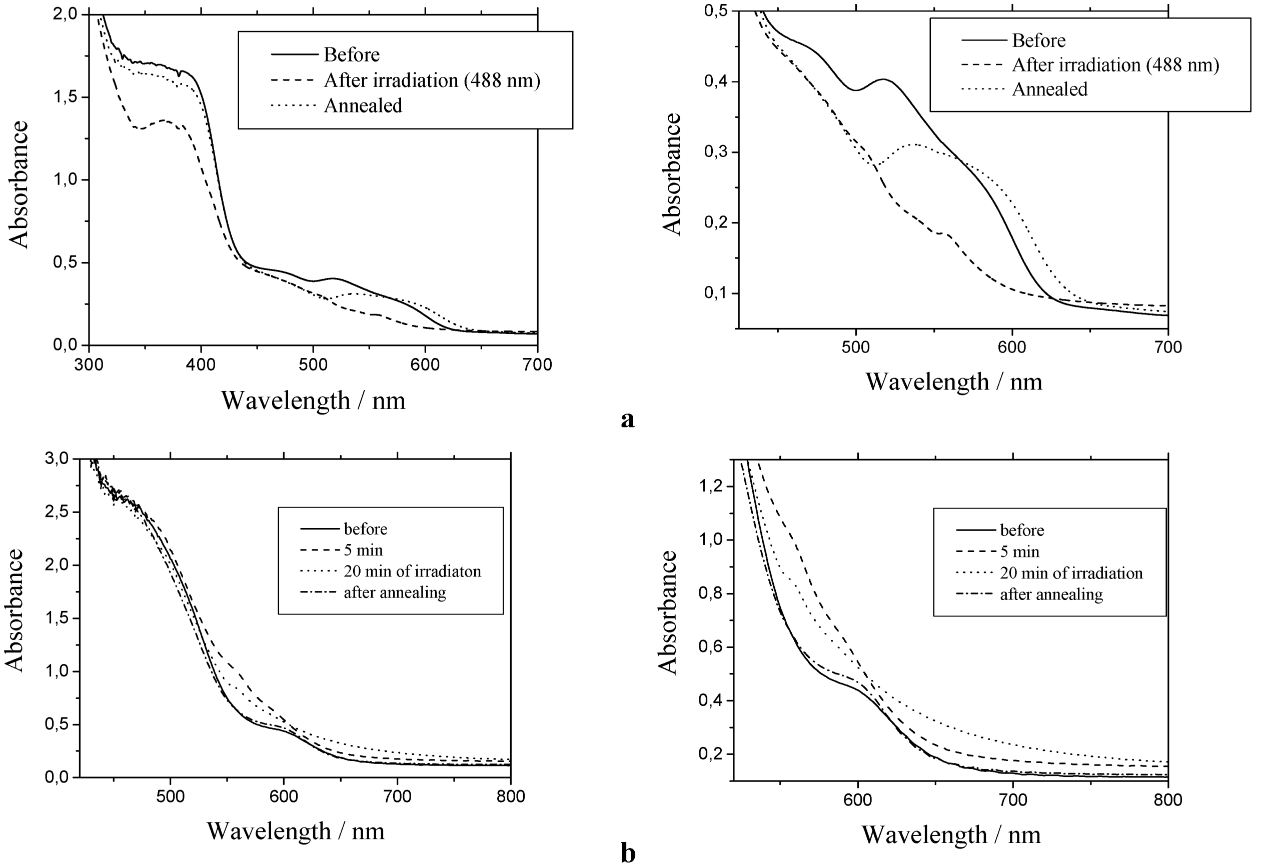


Figure 1. Absorbance spectra before and after 40 min of Ar$^+$ laser irradiation at 488 nm, (200 mW/cm^2) and after annealing at 85 °C: (a) thin spin-coated film (0.7 μm) and (b) thick film (11 μm). The right panels of a and b correspond to the magnified parts of the figures on the left side.

The phase transitions of the polymer and mixture were studied by differential scanning calorimetry (DSC) with a Perkin-Elmer DSC-7 thermal analyzer (a scanning rate of 10 K/min).

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

The nonpolarized UV and visible irradiation was performed with a setup of an XBO 150 W lamp, a water IR filter, and a metal interference filter (365 nm) at room temperature. The power density of the incident light was about 64 mW/cm^2. After irradiation the absorbance spectra were recorded using an UV−vis spectral photometer (Lambda 2, Perkin-Elmer).

Thin films were prepared by spin-coating technique using solutions in chloroform and between two polyimide-coated and unidirectionally rubbed glass plates. For drying, the spin-coated films were kept at room temperature during 1 day. Thickness of the films was measured using atomic force microscopy (AFM) by a Multi-Mode microscope with the NanoScope IIIa controller from Digital Instruments in contact mode.

The photoorientation experiments were performed using the linearly polarized beam of an Ar$^+$ laser (Innova 90/4 of Coherent, 488 nm). The intensity of the light was 200 mW/cm^2.

Circularly polarized fluorescence spectra were recorded using J&M diode-array spectrofluorimeter. Fluorescence spectra were recorded with the detection normal to the plane of the film. Circularly polarized fluorescence spectra were obtained analyzing the emitted light using a combination of a linear polarizer with a broad-band quarter-wave plate. Irradiation in all cases was performed at room temperature, but for helix untwisting experiments samples of mixture were annealed at 85 °C.

Results and Discussion

Spectral and Photooptical Properties of the Planarly Oriented Films of the Mixture. The developed mixture forms exclusively a cholesteric (chiral nematic) phase with a clearing temperature at 100−101 °C and a glass transition temperature of about 25 °C.

Figure 1 presents the absorption spectra of two films of the mixture with different thicknesses. The film with the relatively large thickness (11 μm) was prepared between two polyimide-coated and unidirectionally rubbed glass plates. The thin film (0.7 μm) was prepared by spin-coating using a concentrated solution of the mixture solution in chloroform. Both the thin and the thick films are characterized by the same planar texture with oily streaks, which is typical for a cholesteric phase.[1]

The thin film is characterized by a strong absorbance at $\lambda <$ 400 nm, corresponding to the $\pi-\pi^*$ electronic transition of the azobenzene group, and two small weakly pronounced peaks at ca. 470 nm, caused by the n$-\pi^*$ electronic transition of the azobenzene group and the **DCM** absorption, and at ca. 550 nm, which corresponds to the selective reflection (Figure 1a). With respect to the thickness, the thick film has very large absorbance even at wavelengths below 550 nm (Figure 1b) and the selective light reflection peak appears only as a long-wavelength “shoulder”.

The irradiation of the films with the linearly polarized light of an Ar$^+$ laser (488 nm) leads to a complete disruption of the peak of selective reflection (see dashed curves in Figure 1). This effect is explained by the orientation of the azobenzene groups in a plane perpendicular to the electric field vector of the light as it was well-described before.[4,5,37] Linearly polarized light is absorbed by all azobenzene groups with a transition moment

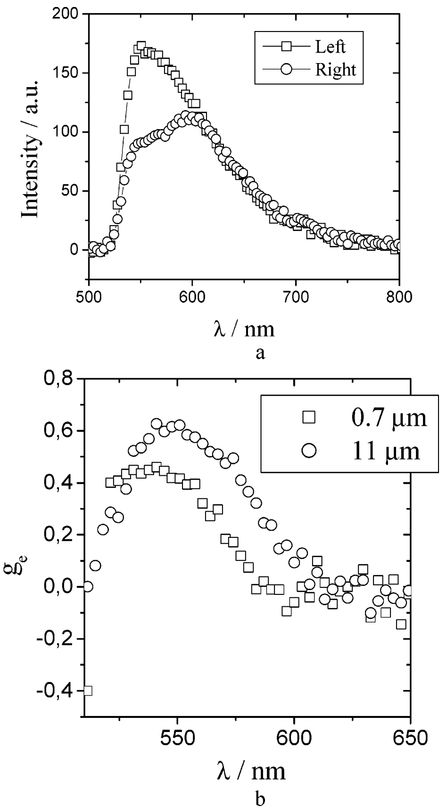


Figure 2. (a) Circularly polarized fluorescence spectra of the planarly oriented film excited at 495 nm. Intensities of the left- and right-handed circularly polarized light are shown by rectangular and circle symbols, respectively. (b) Dissymmetry factor of the fluorescence for films with different thicknesses.

lying along the electric field vector direction. The azobenzene fragments oriented perpendicular to the polarization plane are not excited and remain almost inactive. A great number of E−Z and Z−E photoisomerization cycles in the steady state of the photoisomerization induce a cooperative orientation of the azobenzene and all other mesogenic fragments to a plane perpendicular to the polarization direction. Such reorientation results in a disruption of the helical supramolecular structure of the planarly oriented cholesteric films, leading to a decrease of the intensity of the selective reflection. Before, a similar phenomenon was observed by Kreuzer et al.[5]

Annealing of the films at high temperatures corresponding to the chiral nematic phase recovers the peak of selective reflection (see dotted curves in Figure 1). But in the case of the thin film prepared by spin-coating the recovering process is accompanied by a small shift of the peak to the long wavelengths (Figure 1a), whereas in the case of the thick film placed between two glass plates the peak reappears in the same wavelength as that observed before irradiation (Figure 1b). Probably, this difference can be explained by photochemical side reactions of the chiral dopant **Sorb** sensitized by energy transfer or electron transfer by the azobenzene or the **DCM** unit, causing isomerization, cycloaddition, or photooxidation. These processes lead to a permanent small helix untwisting. Unfortunately, due to very low concentration of the chiral-photochromic dopant (6%) and the products of photoprocesses (less than 0.2% according to selective light reflection shift), it is impossible to determine the structure of substances formed during these photochemical side reactions.

Photoregulation of Fluorescent Properties of the Mixture Films. Planarly oriented films of the mixture are characterized by the strong circularly polarized fluorescence (Figure 2). [It is important to note that the fluorescence intensity of the **DCM** in the mixture under study is several orders of magnitude smaller than for systems without azobenzene. This effect of fluorescence quenching was observed recently[38,39] and could be the cause of electron transfer between azobenzene and **DCM** molecules.] Polarization of fluorescence was investigated for films of different thicknesses and provided by the above-mentioned suppression of the light propagation of one handedness in a particular range of wavelengths. The handedness of emitted light with lower intensity corresponds to the sense of helically supramolecular structure (right-handed in the case of the investigation).

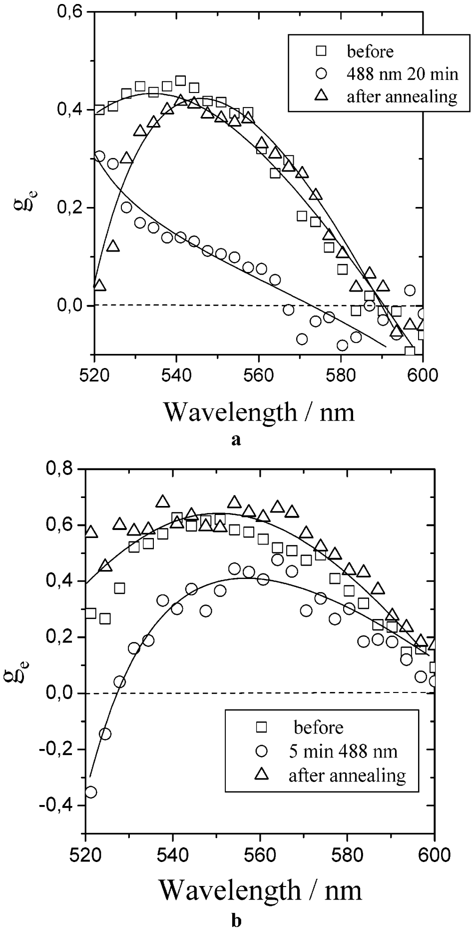


Figure 3. Dissymmetry factor of the fluorescence for the films with thicknesses of 0.7 (a) and 11 μm (b) before and after irradiation with 488 nm linearly polarized light (200 mW/cm^2).

The dependence of the dissymmetry factor on the emission wavelength for films of different thickness is presented in Figure 2b. As seen from the figure, the value of the dissymmetry factor is a little bit larger in the case of the thick film, that is, in relation to the decrease of the cholesteric film reflection with the decrease of their thickness.[2]

Irradiation of the thin film with linearly polarized Ar$^+$ laser light leads to a strong decrease of the dissymmetry factor (Figure 3a), whereas in the case of the thick film the changes are less pronounced (Figure. 3b). Probably, this difference can be explained by a stronger disruption of the cholesteric helical structure by a more perfect photoinduced reorientation of the azobenzene groups in the whole volume of the thin film compared to that with the thick one. The thick film has strong absorbance at the excitation wavelength at 488 nm (Figure 1) that results in a nonhomogeneous distribution of light intensity through the film: the light is absorbed mostly in a very thin

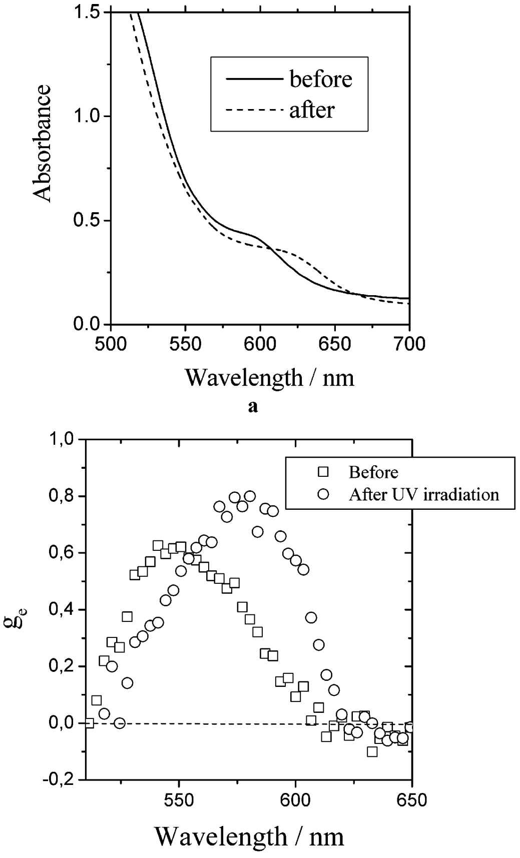


Figure 4. Absorbance spectra (a) and dissymmetry factor (b) before and after irradiation of a planarly aligned film by UV light (365 nm, 60 min) followed by annealing at 85 °C (during 1 h).

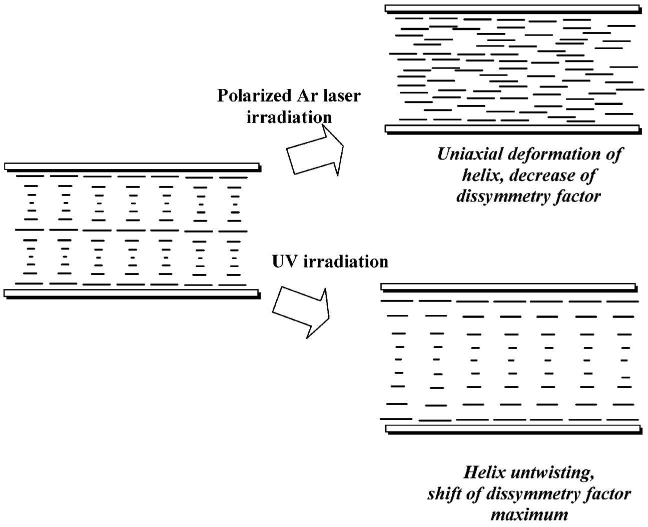
(about 1 μm) surface layer. Another factor predetermining the reorientation ability is the presence of the two glass plates in the case of the thick film with strong anchoring conditions due to the rubbed polyimide coating. These factors prevent the reorientation of the film.

The photoinduced changes of the dissymmetry factor are reversible: annealing of films at 85 °C recovers the initial value of dissymmetry (Figure 3). But in the case of the thin film the wavelength of the maximum of the dissymmetry factor is lightly shifted to longer wavelengths (Figure 3a). This is in accordance with the shift of selective reflection due to possible photochemical side reaction as discussed above (Figure 1a).

An additional possibility for photoregulating the fluorescence polarization is provided by the presence of the photoreactive C═C double bond of the chiral-cinnamic ester **Sorb**. UV irradiation causing photoisomerization and photocycloaddition followed by the annealing at 85 °C leads to a shift of the selective reflection peak to longer wavelengths (Figure 4a), and, as consequence, it results in similar changes of the dissymmetry factor spectrum (Figure 4b). This process is thermally and photochemically irreversible due to strong stability of photoproducts of the chiral-photoactive dopant.

In conclusion, to our best knowledge, for the first time two ways for the photomodulation of fluorescent properties combined in one dye-doped cholesteric polymer material are demonstrated. The first way is the cooperative photoorientation of the azobenzene fragments under the action of linearly polarized visible light, whereas the second one is helix untwisting due to photoisomerization or photocycloaddition of chiral biscinnamic ester dopant. Two main possibilities of the fluorescence manipulation are depicted in Scheme 2. The polarized light action of the Ar$^+$ laser (488 nm) leads to the photoorientation of azobenzene side groups, resulting in a strong and reversible disruption of the selective reflection peak and a decrease of the dissymmetry factor of fluorescence. UV irradiation causes E−Z photoisomerization and/or [2 + 2] photocycloaddition of chiral biscinnamic dopant, resulting in an irreversible shift of the maximum of the dissymmetry factor to long wavelengths. Such a multifunctional glass-forming mixture combining photosensitive and fluorescent properties with the unique optical properties of cholesteric liquid crystals can be considered as promising material for optical data processing technologies and photonic applications.

SCHEME 2: Representation of Two Mechanisms of Photomodulation of Fluorescence Polarization



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