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Alexey Bobrovsky[a][b]; Natalia Boiko[a]; Valery Shibaev[a]; Joachim Wendorff[b]
[a] Faculty of Chemistry, Moscow State University, Lenin Hills, Moscow 119899, Russia [b] Institut für Physikalische, Kern und Makromolekulare Chemie, Philipps Universität, Marburg, Germany

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Glass-forming cholesteric mixtures with photosensitive anthracene-containing fluorescent dopants

ALEXEY BOBROVSKY*†‡, NATALIA BOIKO†, VALERY SHIBAEV† and JOACHIM WENDORFF‡

†Faculty of Chemistry, Moscow State University, Lenin Hills, Moscow 119899, Russia
‡Institut für Physikalische, Kern und Makromolekulare Chemie, Philipps Universität, Marburg, Germany

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Three glass-forming cholesteric mixtures containing anthracene-based fluorescent dopants were prepared and studied. UV irradiation of films of planarly-oriented films of mixtures leads to photocyclization of the anthracene fragments and, consequently, to decreasing fluorescence intensity. The kinetics of this photoreaction were studied. It is shown that fluorescence of the anthracene groups for all mixtures is strongly circularly polarized and can be controlled by UV light irradiation. It was demonstrated that the cholesteric mixtures prepared can be considered as promising materials for optical data recording and storage.

1. Introduction

Recent developments in information processing and data storage technologies show that polymeric materials with fluorescent fragments or dopants are good candidates for application in these fields [1–5]. The interest in fluorescent materials markedly increased after the demonstration of the use of two-photon processes for optical data storage, which was first introduced by Rentzepis and co-workers [6–8] and subsequently by Webb *et al.* [9].

Cholesteric polymers or polymeric mixtures are another promising type of material, and have recently met with increasing interest in the area of optoelectronic applications due to their unique optical properties. These materials have some potential applications; for example, in light emitting diode devices and lasers [10–12]. The particular properties of interest arise from the helical arrangement of the molecules in the liquid crystalline state. The cholesteric mesophase is optically uniaxial and characterized by optical rotation dispersion and circular dichroism. A particular feature is the selective reflection in a given wavelength for circularly polarized light of a particular handedness [13]. For example, in the case of a left-handed helical structure of a cholesteric liquid crystal, left-handed circularly polarized light completely reflects whereas right-handed light passes easily through a film.

The combination of these optical effects with the emission, fluorescence or electroluminescence from chromophores incorporated in the matrix, results in a rather complicated and interesting optical behaviour [14–19]. One effect is that the emitted light is, at least to a certain extent, circularly polarized. This property is used to prepare light-emitting diodes serving as back illumination for liquid crystal displays.

When the wavelength of the selective reflection and fluorescence coincided [15–20] photonic band gap theory, in direct analogy to the band gap theory of semiconductors, has to be applied [19]. The cholesteric state is considered as a one-dimensional photonic crystal with a refractive index which 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 framework of this theory, the wavelength interval for which no propagation is possible is called the stop band. For the cholesteric mesophase, 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, its handedness corresponding to that of external light which is selectively reflected. A left-handed helix will thus emit a right-handed circularly polarized light and *vice versa*. The degree of circular polarization is high in this case. This effect can be exploited for light-emitting diodes serving, as was mentioned earlier, as back illumination for liquid crystal displays.

Furthermore, the photonic band gap approach is able to account for a sign reversal of the dissymmetry factor of emmission at the edge of the stop band. The density of state, for circularly polarized light having the same

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*Corresponding author. Email: bobrovsky@kharkan.ru

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handeness as the helix, is increased strongly with the consequence that the cholesteric material emits light with the same handeness as the helix. The high density of states at the edges of the stop band gives rise to very low group velocities of the fluorescent light, and to long life times of the corresponding states which in turn favours stimulated emission. Such properties have led to considerable activity in the study of cholesteric materials containing fluorescent dyes as resonators for mirrorless lasers [10–12, 19–21].

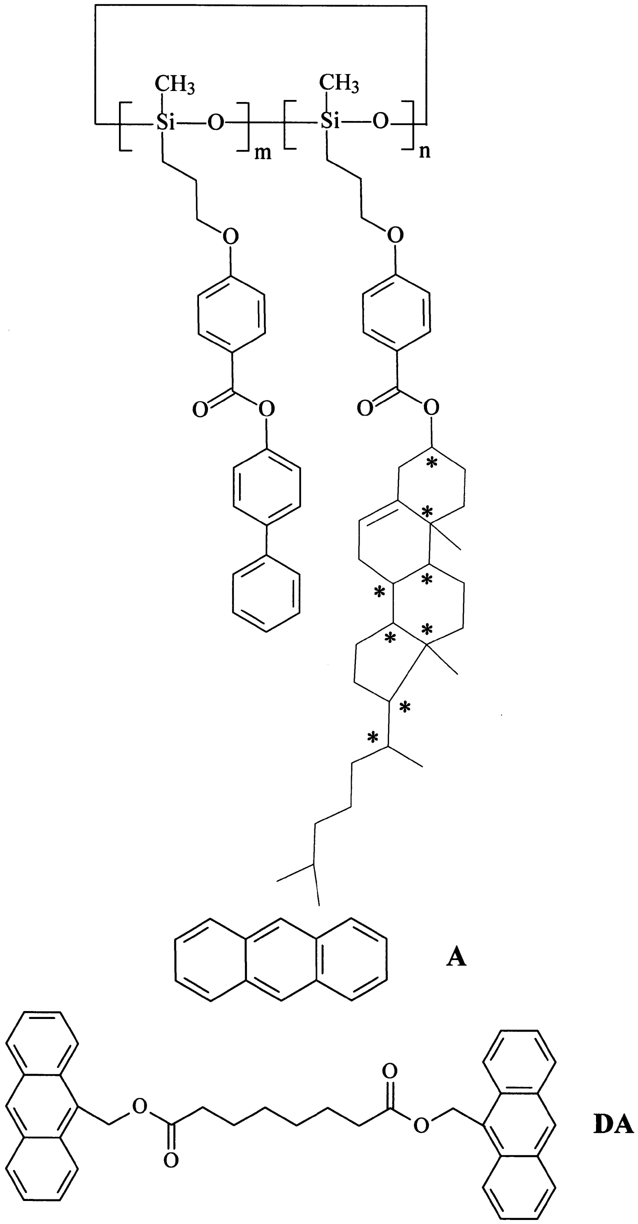
In recent work we have developed an approach for the creation of cholesteric materials with photocontrollable fluorescence intensity and polarization [22]. For this purpose we prepared mixtures containing cholesteric cyclosiloxanes as the matrix, fluorescent dopants as the emissive additive and a chiral-photochromic dopant which can change its helix twisting power under the action of UV light. This allowed us to prepare cholesteric materials with the possibility of photoregulation of helix pitch and selective light reflection band position. Changing the selective light reflection wavelength leads to a modulation of fluorescence intensity and dissymmetry factor.

In this work, for the first time glass-forming cholesteric materials containing photosensitive fluorescent dopants were prepared. Light action should result in photobleaching of the fluorescent additive and in a marked decrease in fluorescent intensity, and also in changes of dissymmetry factor. For this purpose the mixtures of cholesteric glass-forming material with two photoactive fluorescent dopants—anthracene (**A**) and a substance containing two anthracene moieties (**DA**) (scheme 1)—were prepared.

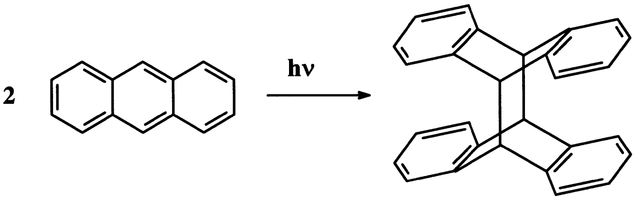
As the matrix material, we chose a glass-forming cholesteric cyclosiloxane manufactured by Wacker Company. It displays a selective light reflection of left-handed circularly polarized light in the blue region of the spectrum (λ_{max}~450 nm). Mixture **I** contains 1.5 wt% of anthracene; mixtures **II-0.5** and **II-4.0** contain 0.5 and 4.0 wt% of 'Dianthr' dopant (**DA**) respectively.

It is well known [23] that the anthracene moiety under UV irradiation undergoes a photocycloaddition reaction leading to dimer formation (scheme 2). In the case of dopant **DA** containing two anthracene fragments, more complicated behaviour, namely formation of a polymeric photoproduct, can take place.

The combination of photoreactivity with emissive properties and the presence of a helical supramolecular structure allows one to obtain a cholesteric fluorescent material with photocontrollable fluorescence behaviour, which has particular interest from the point of view of two- and three-dimensional optical data recording [1–9].



Scheme 1. Structure of cholesteric cyclosiloxane and two photoactive fluorescent dopants.



Scheme 2. Photodimerization process occurring under UV irradiation of anthracene groups.

In this connection, we have studied the optical properties, photo-optical behaviour, photoreaction kinetics and fluorescent properties of three cholesteric mixtures containing these components.

2. Experimental

2.1. *Synthesis*

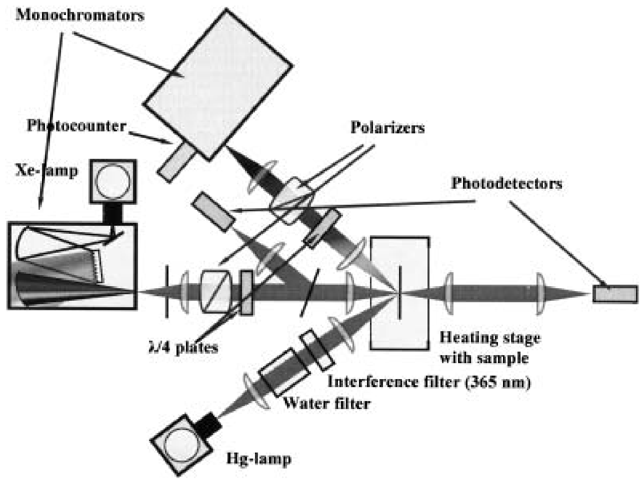
Fluorescent dopant Dianthr (**DA**) was synthesized according to standard esterification technique using DCC [24]. Cholesteric cyclosiloxane (Wacker) and anthracene (Aldrich) were used as received. Mixtures were prepared by dissolving the components in dichloromethane followed by solvent evaporation at 60°C. The mixture was dried in vacuum at 130–140°C for two hours.

2.2. *Investigation of phase behaviour*

Phase transitions of the mixtures were studied by differential scanning calorimetry (DSC) with a scanning rate of 10°C min^{-1}. All experiments were performed using a Mettler TA-400 thermal analyser and a Leitz Laborlux 12 PolS polarization microscope with a Mettler FP-80 hot stage.

2.3. *Photo-optical and fluorescence investigations*

Photochemical property investigations were made using a special set-up (scheme 3) equipped with Xe lamp (1000 W, Müller Elektronik Optik), and two monochromators (SpectraPro 300 I, Acton Research, Polytec), controlled by an NCL single-channel spectroscopy detection system (Roper Scientific GmbH, Germany). For UV light irradiation a 200 W ultra high pressure mercury lamp (Oriel Company) was used. Using a filter, light with maximum wavelength 365 nm was selected. To prevent heating of the samples due to IR irradiation of the lamp, a water filter was used. To obtain a plane-parallel light beam, a quartz lens was used. During irradiation, the constant temperature of the test samples was maintained using a Mettler FP-80 heating unit. The intensity of UV radiation was equal to 3.4 mW cm^{-2}.



Scheme 3. Experimental set-up for absorbance and fluorescence measurements.

The photochemical properties of mixtures were studied by illuminating the ~20 µm thick films 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 well above the glass transition temperature (140°C).

Fluorescence spectra were recorded with the detection normal to the film plane, whereas the excitation beam was positioned at 30° to the normal and at the same side of the film as the emission detector. Circularly polarized absorbance and fluorescence spectra were obtained by using a combination of a linear polarizer with a broadband quarter-wave plate.

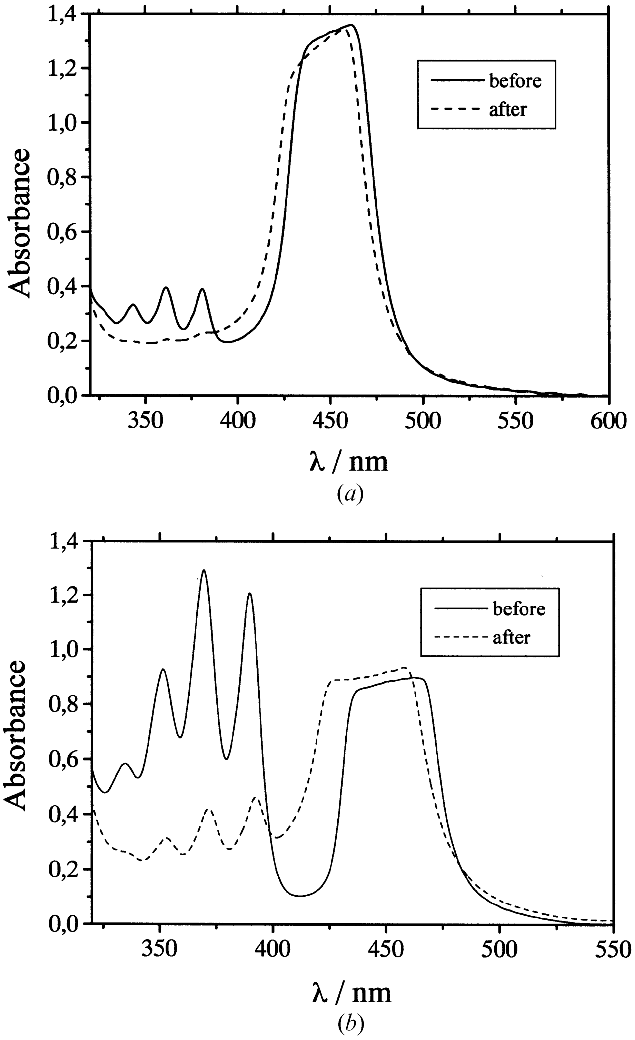
3. Results and discussion

3.1. *Optical and photo-optical properties of mixtures*

All the mixtures form a cholesteric (chiral nematic) phase with a clearing temperature around 170–174°C. The glass transition temperatures for the mixtures are about 50°C. Figure 1 demonstrates absorbance spectra of planarly oriented films of mixtures for left-handed circularly polarized light (absorbance spectra were measured along the normal to a film plane). The strong peak with maximum about 450 nm corresponds to the selective light reflection region. In this spectral range left-handed circularly polarized light strongly reflects from the planarly-oriented left-handed helical structure of the cholesteric mixtures. At wavelengths below 400 nm absorbance peaks characteristic of the anthracene moiety are clearly seen.

The action of UV light leads to a strong decrease in the absorbance of the anthracene groups and to a small shift of the selective light reflection band to a shorter wavelength spectral region (figures 1 and 2). This shift is more pronounced for mixture containing the **DA** dopant. The effect of absorbance decrease is associated with photodimerization taking place for anthracene fragments (scheme 2).

The reason for the shift of the selective light reflection band is still unclear. A more or less similar phenomenon of blue shift of selective light reflection has been observed several times for cholesterics doped by nonchiral azobenzene dopants [25–28]. The larger effect in



(*a*)

(*b*)

Figure 1. Absorbance spectra for left-handed circularly polarized light for mixture **I** (*a*) and **II-4** (*b*) before and after 60 min of UV irradiation (365 nm).

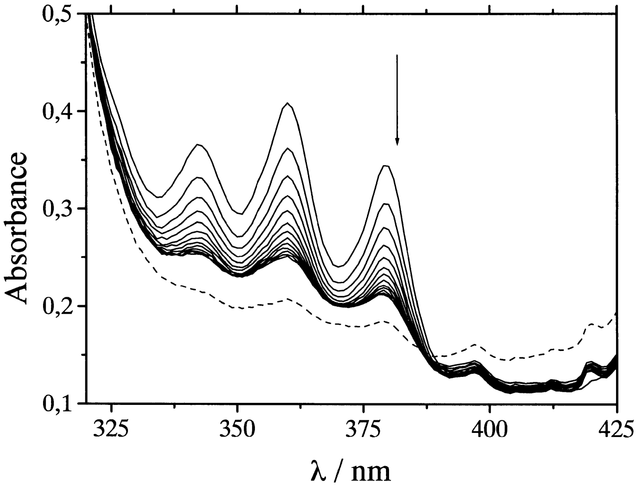


Figure 2. Time evolution of absorbance spectra for mixture **I** during UV irradiation (365 nm). Spectra were recorded each 4 min of irradiation, dashed line corresponds to steady state (100 min of irradiation).

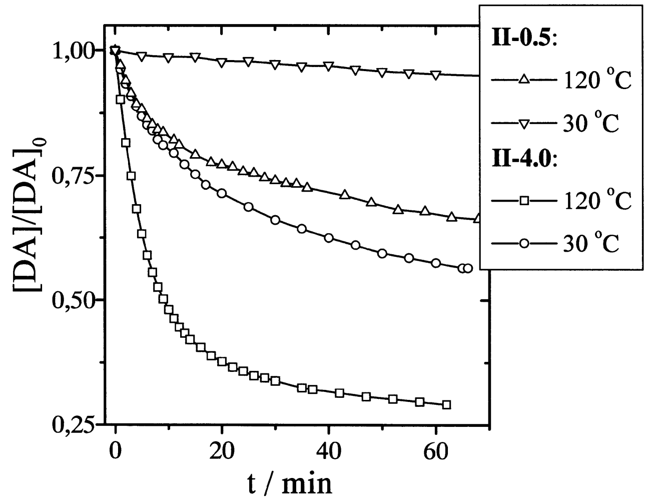


Figure 3. The decrease of the relative concentration of dopant during UV irradiation of mixtures **II-0.5** and **II-4.0** at different temperatures.

the case of the **DA** dopant is probably explained by the stronger steric influence on ordering because of the large branched structure of the dimer formed. Formation of more complicated polymeric structures can also not be excluded. It should be noted that the value of the shift of the selective light reflection band observed in this work is less than 10 nm, and many times smaller in comparison with cholesteric systems containing chiral-photochromic fragments [29–33].

For all the mixtures the rate of the photodimerization process is strongly dependent on the temperature and concentration of fluorescent dopants. At temperatures below the glass transition, the rate of the photoprocess is very low, as clearly seen from figure 3. This effect is connected with the restriction of mobility of the anthracene fragment, preventing a bimolecular photodimerization reaction. Reducing the dopant concentration also leads to a decrease in the photoreaction rate due to a lower probability of contact between two anthracene groups.

The photodimerization reaction is partially reversible: irradiation by light with shorter wavelength (313 nm) leads to a back-increase of anthracene moiety absorbance (figure 4). In this case, however, additional side photoprocesses are observed. One of them is a photo-Fries rearrangement of the nematogenic fragments of the cyclosiloxane (scheme 1), which also absorb light of 313 nm. The photo-Fries rearrangement results in the formation of products having low anisometry; after prolonged irradiation side photoprocesses lead to a

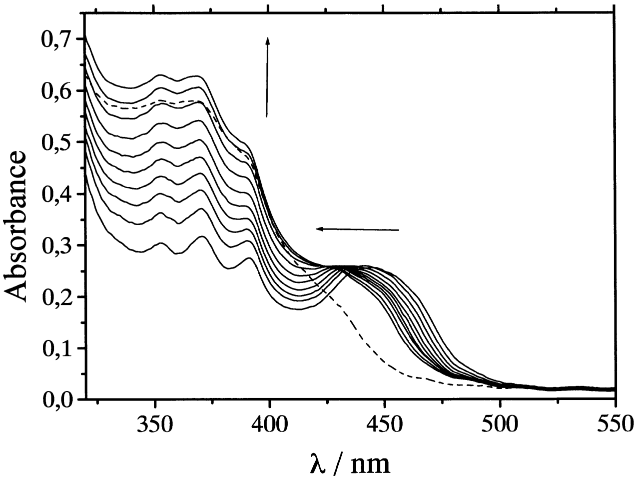


Figure 4. Changes of absorbance spectra of mixture **II-4.0** during short wavelength UV irradiation (313 nm) at 120°C. The film was pre-irradiated with light of 365 nm for 60 min at the same temperature. Spectra were recorded each 2 min of irradiation, the dashed line corresponds to 40 min of light exposure; arrows indicate the directions of the absorbance changes.

deterioration of the mesophase. Polarizing optical microscopy showed the transformation of a planar texture with oily streaks, figure 5 (*a*), to a weakly developed focal-conic texture with isotropic regions, figure 5 (*b*).

3.2. *Non-polarized and circularly polarized fluorescent properties of mixtures*

Figure 6 shows the fluorescence spectra for two mixtures, **II-0.5** and **II-4.0**, containing different concentrations of dopant **DA**. It is interesting to note that the difference between the fluorescence intensity is very low despite a very large (8 times) difference in dopant concentration. Such behaviour is related to emission self-quenching phenomena occurring in mixtures with a high concentration of a fluorescent additive, or due to intramolecular energy transfer between two anthracene moieties of dopant **DA** [23]. This is why UV irradiation does not lead to a noticeable change of fluorescence intensity in mixtures with **DA**.

In the case of mixture **I**, containing anthracene, UV irradiation results in a strong decrease in fluorescence (see figure 7). It is noteworthy that before and after irradiation. The fluorescence is strongly circularly polarized, figure 7 (*b*).

The main parameter characterizing the polarization state of the emitted light from a chiral medium is the dissymmetry factor g_e defined as

$$g_e = 2(I_L - I_R)/(I_L + I_R) \qquad (1)$$

where I_L and I_R are the intensities of the left- and right-handed circularly polarized light, respectively. We have calculated the dissymmetry factor of fluorescence for all the mixtures before and after irradiation. All the mixtures possess a relatively high value of dissymmetry which is negative inside the selective light reflection band and has a small positive value outside (figure 8). In the case of mixture **I**, the change of dissymmetry under UV irradiation is almost negligible. In the case of mixture **II-4.0** we found a relatively large decrease in absolute value of dissymmetry in the selective light reflection spectral region, and a small shift to short wavelengths, figure 8 (*b*). This shift is in accordance

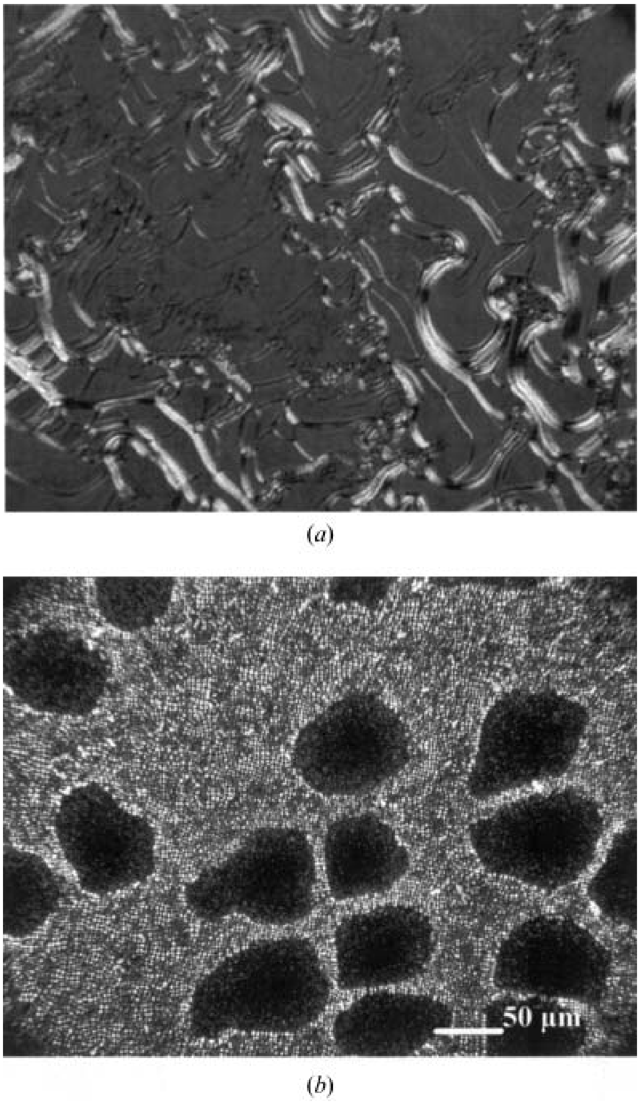


Figure 5. Photomicrographs of mixture **II-4.0** film textures (*a*) after 60 min of irradiation with light of 365 nm and (*b*) after subsequent irradiation with shorter wavelength light (313 nm, 60 min).

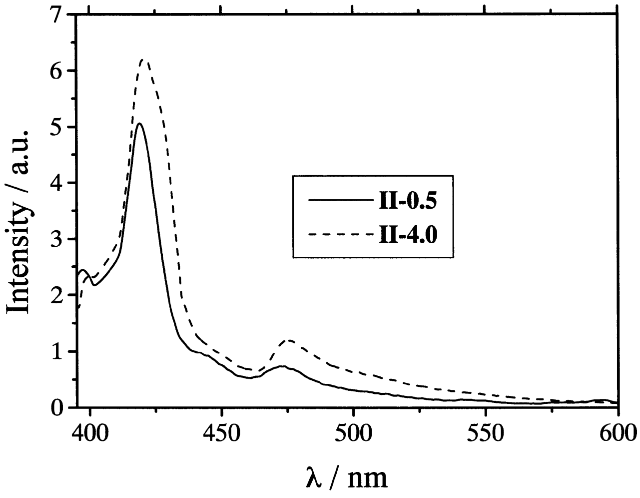


Figure 6. Fluorescence spectra for mixtures **II-0.5** and **II-4.0**.

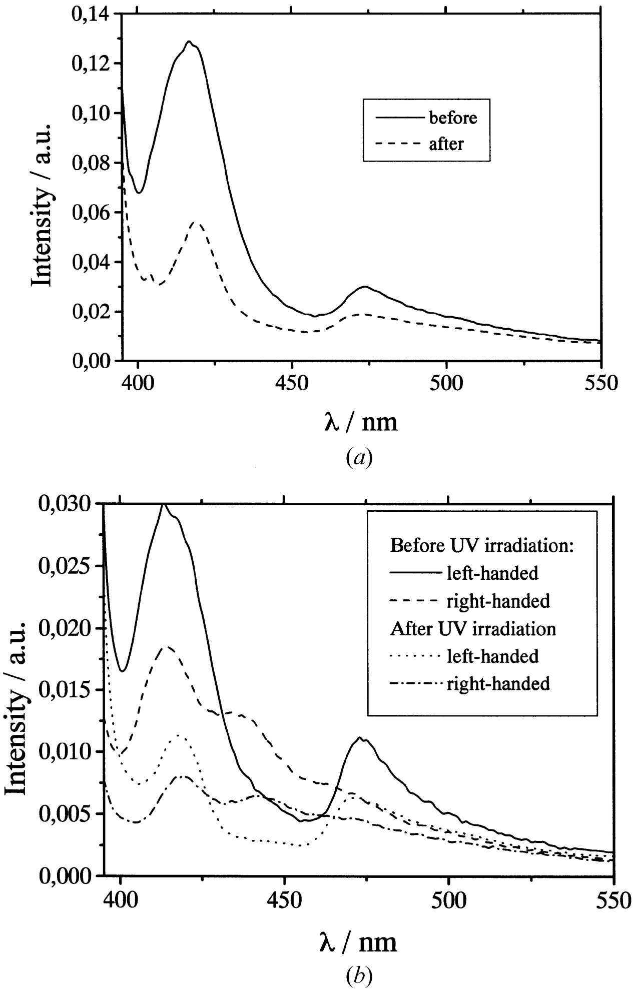


Figure 7. Non-polarized (*a*) and circularly polarized (*b*) fluorescence spectra of mixture **I** before and after UV irradiation.

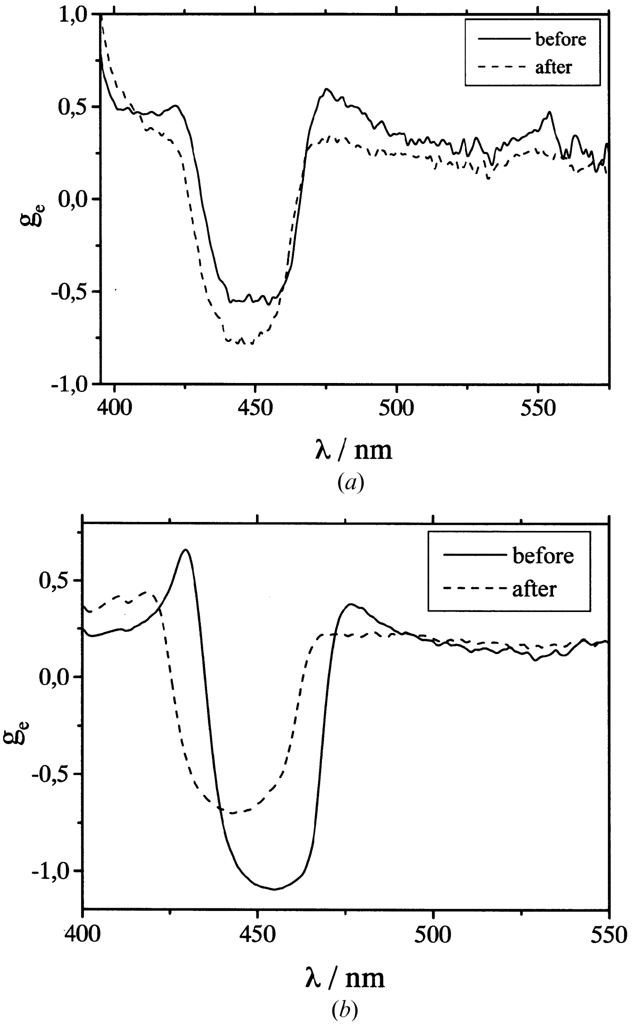


Figure 8. Dissymmetry factor of polarized emission before and after UV irradiation for mixture **I** (*a*) and **II-4.0** (*b*).

with change of selective light reflection peak position, figure 1 (*b*).

In conclusion we note that the combination of unique optical properties of cholesterics with the photoactivity of fluorescent additives opens a new possibility in the design of optically active photosensitive materials which can be used for optical data recording and information processing. The two main possibilities for photovariation of optical properties of such systems provide: photoregulation of helix pitch [22] and selective light reflection as well as photobleaching of the fluorescent dopant. Special interest in these materials is explained by the possibility to use them for two-photon three-dimensional optical data recording and reading [6–9, 34]. The cholesteric helical supramolecular structure allows us to consider an important characteristic – the degree of circular polarization—for use as an additional parameter for information processing.

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