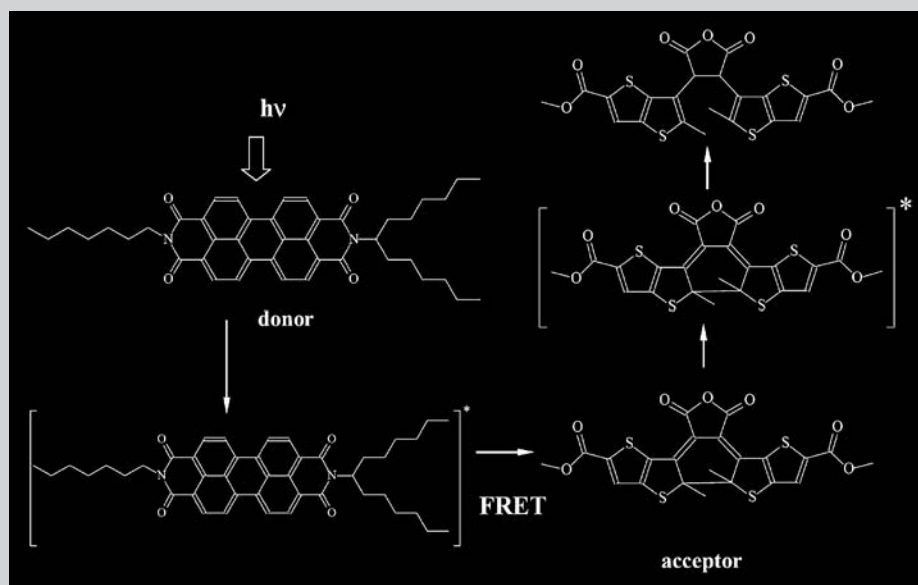


Summary: Photoorientation processes in two cholesteric mixtures were studied. Mixture I contained a nematogenic phenylbenzoate homopolymer, a photochromic diarylethene dopant and a chiral dopant. Mixture II consisted of a binary comb-shaped nematogenic copolymer with fluorescent perylene side groups and the same chiral and photochromic dopants. Irradiation of the mixtures with a polarized UV light did not induce photoorientation of the photoinduced “closed” form of the diarylethene dopant. However, the action of a polarized visible light on films of mixtures irradiated with UV light led to the appearance of dichroism.

This phenomenon is associated with the photoselection process of the photochromic diarylethene molecules in the cholesteric matrix. An investigation of the kinetics of the photosensitized back photoreaction of the photochromic molecules in the cholesteric mixture showed that the polarized energy transfer from the fluorescent groups to the photochromic diarylethene dopant caused an increase in the photoselection rate. The thermal stability of dichroism in films of the mixtures was studied and it was shown that the disappearance of the dichroism of the diarylethene molecules occurred with a noticeable rate even at room temperature.



Scheme of photophysical and photochemical processes under the indirect excitation of diarylethene molecules.

A Study of the Photoorientation Phenomena in Cholesteric Polymer Systems Containing Photochromic Diarylethene Derivatives

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Introduction

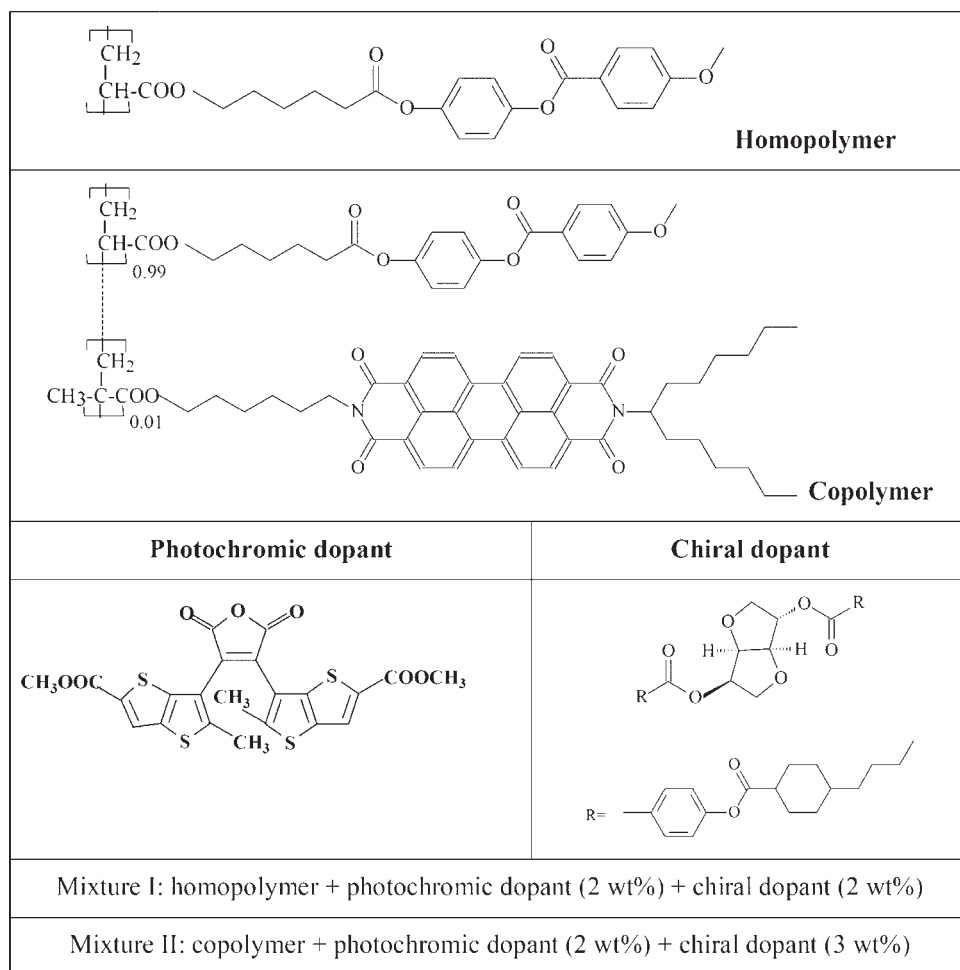
In recent years, photoresponsive polymer systems have received much consideration for the creation of materials with phototunable properties, which can be used for optical data storage, all-optical modulation and holography.^[1–3]

In previous works, we have described the principle of producing photochromic cholesteric polymer systems, which can combine photochromism with the unique optical properties of the cholesteric liquid crystals.^[4–6] Photo-optical properties of these systems can be controlled with light irradiation if the ratio between the photochromic and chiral components is selected in such a way that the absorbance peak of the photoinduced form of the photochromic groups almost coincides with the selective light reflection band (λ_{\max}) of the polymer film caused by their helical supramolecular structure. In such an event, the action of UV irradiation leads to the disappearance of the selective light reflection peak due to the strong absorbance of the photoinduced colored form (λ_{abs}) of the photochromic groups in this spectral range. Hence, the action of

irradiation with variable wavelengths could regulate the selective light reflection intensity. More recently, it has been shown that the addition of a fluorescent compound into the photochromic cholesteric polymer system allowed the emission intensity of the fluorescence of the system by the irradiation to be controlled.^[7] This phenomenon could be achieved because of the fluorescence resonance energy transfer (FRET) process from the fluorescent dopant to the photochromic molecules.

As a photochromic compound, we have used the diarylethene derivative due to some advantages of these substances, such as a marked photochromism, the thermal stability of both forms of the isomers, a high fatigue resistance and the high quantum yields of the photocyclization processes.^[1,8,9]

In this work we have made an attempt to investigate some other properties of photochromic cholesteric polymer systems, which could be controlled by light irradiation. We focused our attention on the photoinduced orientation, which would be of the interest for holographic recording^[10] and optical data storage.^[10–13]



Scheme 1. Chemical structures of compounds used for mixture preparation.

It is worth noting that a great number of publications which deal with photoorientation processes are devoted to azobenzene-containing polymer systems.^[14–29] Of special interest are nematic liquid crystalline polymers with azobenzene side groups, because they offer a few advantages over ones based on amorphous polymers. One of the advantages is the photoinduced orientation of the side groups, leading to dichroism and birefringence, which can be kept over a prolonged time below the glass transition temperature. The other one is the increase in photoorientation as a result of annealing above the glass temperature due to the ordering of mesogenic groups. However, investigations into the photoorientation of chromophores in cholesteric liquid crystalline polymers have not yet been performed. Furthermore, the influence of the helical structure of the cholesteric polymer matrix on the photoorientation of the chromophores remains unknown.

It should be pointed out that the photoorientation of other photochromic organic compounds (apart from azo-dyes) has not been studied or described in detail. We found several papers relating to the photoorientation behavior of promising diarylethene derivatives in amorphous films^[30,31] and in glassy nematic liquid crystalline films.^[32] It has been found that photochromic diarylethene molecules can be oriented under the action of UV polarized irradiation as well as visible polarized irradiation. However, after polarized irradiation, the anisotropy relaxes due to molecular rotational diffusion. It has been calculated that the transition moments in the UV and visible spectral regions of the closed form diarylethene are perpendicular to each other. The long wavelength transition moment is parallel to the long axis of the diarylethene molecule. Functionalization of the diarylethene core by nematogenic groups allows one to produce

glassy photochromic liquid crystalline materials, which can modulate refractive indices and optical birefringence to a large extent in comparison with photochromic amorphous materials. This is why such glassy photochromic liquid crystalline materials can form macroscopically ordered solid films in which the electronic transition moment of the photoresponsive core is spontaneously aligned with the nematic director.

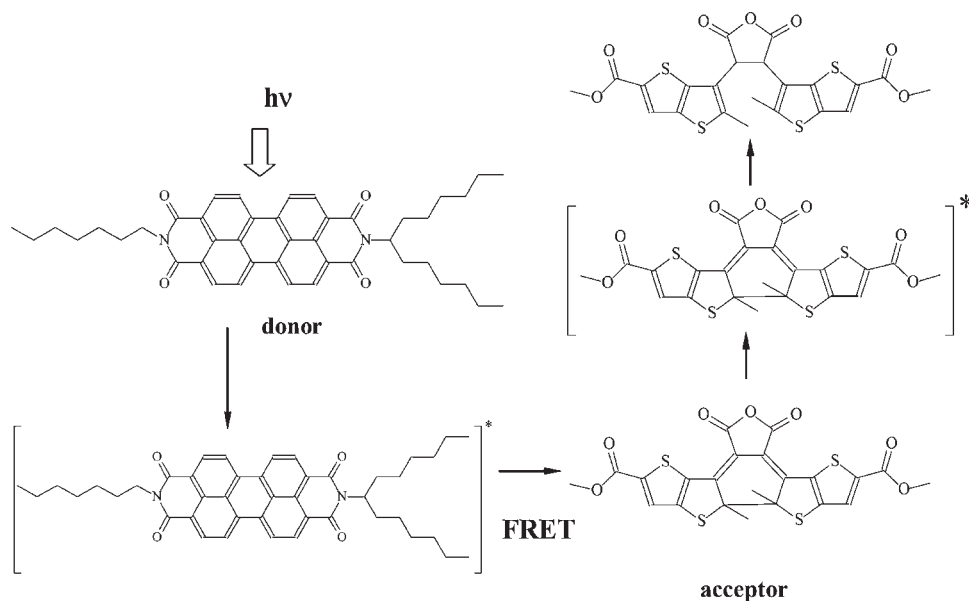
This work presents the first investigation demonstrating the features of the photoinduced orientation of a photochromic diarylethene derivative in a cholesteric polymer matrix. The other goal of the research was directed towards the study of the polarized energy transfer from the fluorescent to the photochromic molecules and the elucidation of their influence on the photoorientation of the chromophores.

Hence, the attention of this paper is focused on photochemical and photooptical studying of the two cholesteric polymer mixtures based on the diarylethene derivatives. Mixture I consisted of a comb-shaped nematogenic phenylbenzoate homopolymer, a photochromic diarylethene dopant and a chiral dopant (Scheme 1). Mixture II involved a binary comb-shaped nematogenic copolymer with fluorescent side groups based on the perylene derivative, the photochromic diarylethene dopant and the chiral dopant (Scheme 1).

Experimental Part

Synthesis and Mixture Preparation

Nematogenic homopolymer and fluorescent copolymer were synthesized by radical copolymerization of the corresponding



Scheme 2. Scheme of photophysical and photochemical processes under the indirect excitation of diarylethene molecules.

acrylic monomers according to the procedures described in ref.^[33]. The perylene-containing monomer was supplied by Professor H. Langhals (Munich University) to whom we express our sincere thanks. The synthesis of the photochromic compound is presented in ref.^[34]. The chiral dopant was obtained using the following procedure.^[35]

Synthesis of the Chiral Dopant 2,5-Bis(4-[(4-butylcyclohexyl)carbonyl]oxy}benzoil)-1,4; 3,6-dianhydro-D-sorbitol

To a solution of 0.3 g of 1,4;3,6-dianhydro-D-sorbitol (Lancaster Synthesis Ltd.) and 1.9 g of 4-[(4-butylcyclohexyl)carbonyl]oxy}benzoic acid in 3 ml of purified absolute THF, 0.1 g of *N,N'*-dimethylamoinopyridine (Fluka) was added. Then small portions of 3 g of dicyclohexylcarbodiimide (Fluka) were added. The resulting solution was stirred without heating for 3 d. The precipitate formed was filtered, washed with THF, and then diethyl ether (50 ml) was added to the filtrate. The solution was washed with water, then with a 5% solution of acetic acid, and finally with water again until pH 7 was achieved. The ether extract was dried with anhydrous MgSO_4 . After removal of the solvent, the white crude product was purified by column chromatography using chloroform as the eluent. The yield was 45% and the product had a melting point of 134–136 °C.

IR: 2920, 2860 (CH_2), 1720 (CO in COOR), 1600, 1510 (C–C in Ar), 1250 (COC) cm^{-1} .

Mixtures were prepared by dissolving the polymer and dopants in chloroform followed by solvent evaporation at 60 °C. Thereafter the mixtures were dried in a vacuum at 120 °C for 2 h.

Physical Properties

The phase transition temperatures of the synthesized polymers and mixtures were studied by differential scanning calorimetry (DSC) with a scanning rate of 10 $\text{K} \cdot \text{min}^{-1}$. All experiments were performed using a Mettler TA-400 thermal analyzer and a LOMO P-112 polarization microscope. The selective light reflection of the films of the mixtures 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 two flat glass plates, which were covered with thin polyamide films. A planar texture was obtained by shear deformation of the samples, which were heated up to a temperature 5 °C below the $\text{N}^*\text{-I}$ transition followed by ≈ 120 min of annealing at the same temperature. Prior to the tests, the samples were annealed for 20–40 min at the appropriate temperatures.

Photo-Optical Investigations

Photochemical investigations were performed using a special instrument equipped with a DRSh-250 ultra high pressure mercury lamp and a He-Ne laser (633 nm). Using a filter, light with the wavelengths 313 and 546 nm was selected. To obtain polarized light, a Glan-Taylor prism was used. To prevent the heating of the samples due to the IR irradiation of the lamp, a

water filter was used. To obtain a plane-parallel light beam, a quartz lens was used. During the irradiation, the test samples were maintained at constant temperature using a Mettler FP-80 heating unit. The intensities of the incident light were equal to 0.08 $\text{mW} \cdot \text{cm}^{-2}$ for the linearly polarized light at 313 nm, 0.29 $\text{mW} \cdot \text{cm}^{-2}$ for the non-polarized light at 313 nm, 0.36 $\text{mW} \cdot \text{cm}^{-2}$ for the linearly polarized light at 546 nm, 0.87 $\text{mW} \cdot \text{cm}^{-2}$ for the non-polarized light at 546 nm, which were measured using a LaserMate-Q intensity meter (COHERENT). The intensity of the He-Ne laser (633 nm) was equal to 1.3 $\text{mW} \cdot \text{cm}^{-2}$, measured using an IMO-2N intensity meter.

The photochemical properties of the mixtures were studied by the irradiation of 20 μm thick films. The absorption and the fluorescence spectra were recorded with a TIDAS spectrometer (J&M). The linearly polarized spectra of the film samples were studied with a TIDAS spectrometer (J&M) equipped with polarizer.

Results and Discussion

The Phase Behavior and Optical Properties of Mixture I and II

According to the DSC data, mixtures I and II formed the cholesteric mesophase over a wide temperature range (Table 1). The introduction of a small amount of photochromic dopant into the nematic polymers did not lead to a change in the mesophase type of these systems; the nematic phase was preserved. The low molar mass chiral dopant induced cholesteric mesophase formation in the mixtures. The mixtures obtained were homogeneous and stable over time and during thermal treatment. No phase separation was observed for several months.

The planar oriented films of the mixtures selectively reflected the light with a wavelength corresponding to the infrared region of the spectrum ($\lambda_{\text{max}} = 1260$ nm for mixture I and $\lambda_{\text{max}} = 850$ nm for mixture II). The maximum of selective light reflection λ_{max} weakly depended on the temperature.

The Photo-Optical Properties of Films of the Mixtures

The action of the UV irradiation with a wavelength $\lambda = 313$ nm on the planar oriented films of the mixtures led to the appearance of an absorbance peak with a maximum at $\lambda = 635$ nm (Figure 1(a)), which can be attributed to the

Table 1. The phase transitions temperatures and wavelengths of the maximum of the selective light reflection for mixture I and II.

Sample	Glass transition temperature	Phase transitions	λ_{max}
	°C	°C	nm
Mixture I	26	$\text{N}^* 117 \text{ I}$	1260
Mixture II	26	$\text{N}^* 114 \text{ I}$	850

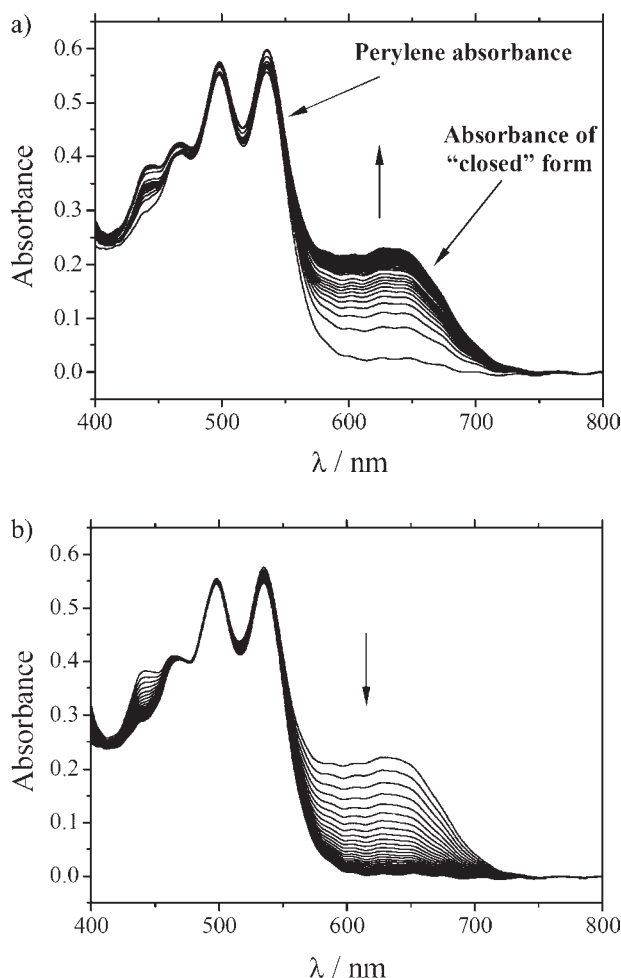


Figure 1. (a) Spectral changes in the absorbance during the process of photocyclization induced by UV irradiation (313 nm) for a film of mixture II. (b) Spectral changes in the absorbance during the back process induced by visible light (633 nm) irradiation for a film of mixture II. In both cases the spectra were recorded for 2 min and arrows indicate the direction of spectral changes.

formation of the colored closed form of the diarylethene dopant. The irradiation of the films with visible light with a wavelength $\lambda = 546$ and 633 nm induced the back opening ring process (Figure 1(b)).

It must be noted that the closed form is thermally rather stable, at least at temperatures below 80 °C. Figure 2 shows the typical time dependence of the reduced optical density for the mixtures during the annealing process.

It is important to stress that the structure of the photochromes and the fluorophores in mixture II was selected in such a way that the fluorescence peak of perylene groups almost coincided with the absorbance peak of the photoinduced form of the photochromic dopant (Figure 3). This allowed us to expect an energy transfer between these chromophores.

Figure 4(a) shows that the presence of the fluorescent groups scarcely affected the rate of the photoinduced ring-

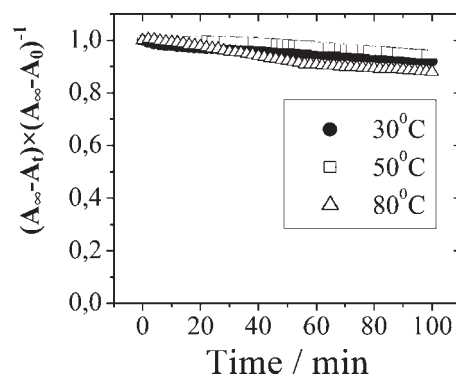


Figure 2. Kinetics of the thermal cycle opening process for mixture II at different temperatures. A_0 , A_t and A_{∞} are the absorbance of the photoinduced closed form of the diarylethene molecules at time $t = 0$, current time t and $t \rightarrow \infty$, respectively. Before annealing, the films were irradiated with UV light (313 nm) for 40 min.

opening process of the diarylethene molecules under the action of light with 633 nm, which corresponds to the direct photoexcitation of the closed form of the diarylethene molecules. Note that this wavelength is not disposed within the band of the perylene absorbance. Irradiation with the wavelength of the fluorescence excitation ($\lambda = 546$ nm) led to a higher rate of the back ring-opening photoprocess in mixture II, containing the fluorescent groups, compared with the same rate in the mixture I (Figure 4(b)). As this takes place, the open and closed forms of the photochromic diarylethene dopant slightly absorb the light at this wavelength. This phenomenon could be attributed to the fact that the irradiation with the wavelength of the fluorescence excitation ($\lambda = 546$ nm) induced the transfer of the

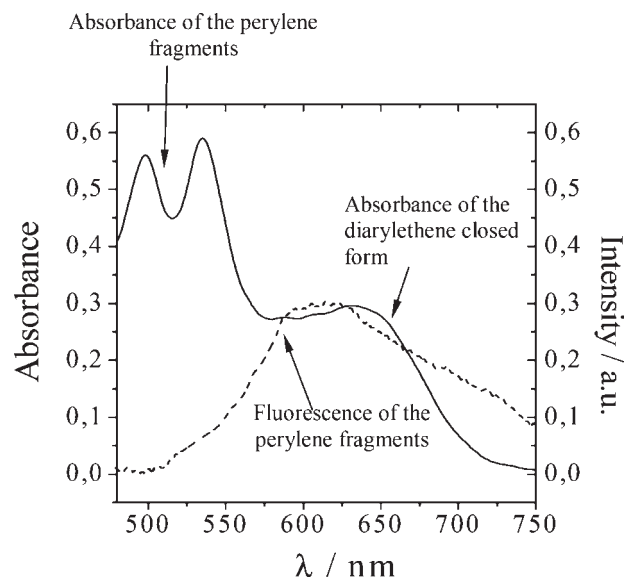


Figure 3. The fluorescence spectrum of the perylene-containing side groups and the absorption spectrum of mixture II. The excitation light wavelength was 436 nm.

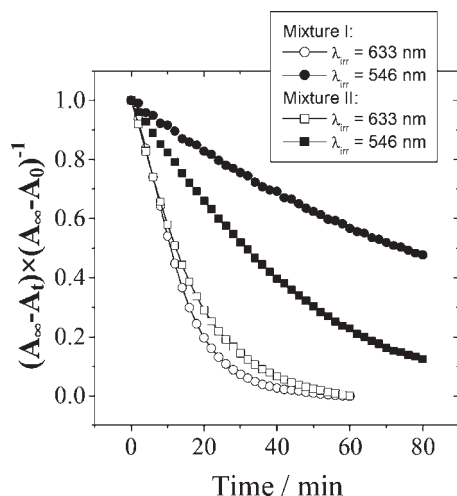


Figure 4. The kinetics of the opening cycle process during irradiation with $\lambda = 546$ and 633 nm for mixture I and II. The temperature of the samples was 25°C .

fluorescence resonance energy from the fluorescent groups (donors) to the photochromic diarylethene dopant (acceptor) in mixture II (see Scheme 2). In this way, FRET makes possible the process of photosensitization of the back ring-opening photoreaction in mixture II. The presence of FRET was additionally examined by fluorescence measurements of mixture II. The intensity of the perylene emission was quenched by more than one order of magnitude under UV irradiation and the formation of the closed form of the diarylethene dopant.

The Photo-Induced Orientation of the Diarylethene Molecules in the Mixtures

The irradiation of diarylethene derivatives in the thin amorphous and glassy liquid crystalline films with polarized UV light led to the appearance of dichroism.^[30–32] However, for mixtures containing the diarylethene molecules, dichroism was not observed under polarized UV light irradiation. The action of the polarized visible light ($\lambda = 546, 633$ nm) on the films of the mixtures, which was carried out after the non-polarized UV irradiation, resulted in a noticeable distinction between the two linearly polarized spectra of the closed form of the diarylethene molecules. These spectra were recorded for probe light that was linearly polarized parallel and perpendicular to the polarization of the irradiation light (Figure 5).

In order to determine the orientation of the long wavelength transition dipole moment of the closed form, the dependence of its absorbance on the angle between the visible irradiation and a probe beam polarization were plotted in the polar coordinates before and after irradiation at the wavelength 633 nm (Figure 6(a) and 6(b)). As is evident from the dependence, the photoorientation of the closed form of the diarylethene molecules occurred during

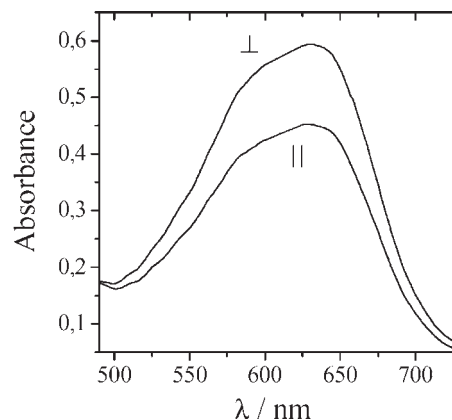


Figure 5. Absorption spectra of mixture I after linearly polarized visible irradiation with a wavelength $\lambda = 633$ nm. The spectra were recorded for probe light that was linearly polarized either in parallel (\parallel) or perpendicular (\perp) to the polarization of the irradiation light.

the linearly polarized visible irradiation ($\lambda = 546, 633$ nm). As this takes place, the diarylethene's transition dipole moment of the closed form is oriented perpendicular to the visible irradiation polarization.

However, the geometrical shape of the diarylethene molecules does not change significantly during the photoisomerization process.^[1,30] That is why the orientation of the closed form is accounted for by photoselection.^[30] In principle, the photochromic molecules are most likely to be excited and isomerized under the action of the linearly polarized irradiation on the condition that their transition dipole moments are oriented along the polarization of the exciting light. Hence, as a result of the polarized irradiation, the transition dipole moments of the closed form, which do not participate in photoisomerization, are oriented perpendicularly to the polarization of the irradiation light. In other words, polarized light action leads to the excitation and photoisomerization of the selected molecules, and the dichroism appears due to the remaining ring-closed molecules.

To study the photoorientation kinetics of the diarylethene molecules in mixture I and II during irradiation, the dichroism and the order parameter values were calculated using Equation (1):

$$D = (A_{\max} - A_{\min}) \times (A_{\max} + A_{\min})^{-1} \quad (1)$$

where A_{\max} and A_{\min} are the maximum and the minimum values of the absorbance of the closed form of diarylethene, respectively, which are measured at different angles between the irradiation and probe beam polarizations. The dichroism values, which were estimated in this work, are presented in Table 2. We compared our measurements with the results presented in other works.^[30–32] The dichroism values, which were estimated for the closed form of diarylethene derivatives in thin glass amorphous films after polarized light irradiation, were in the region of

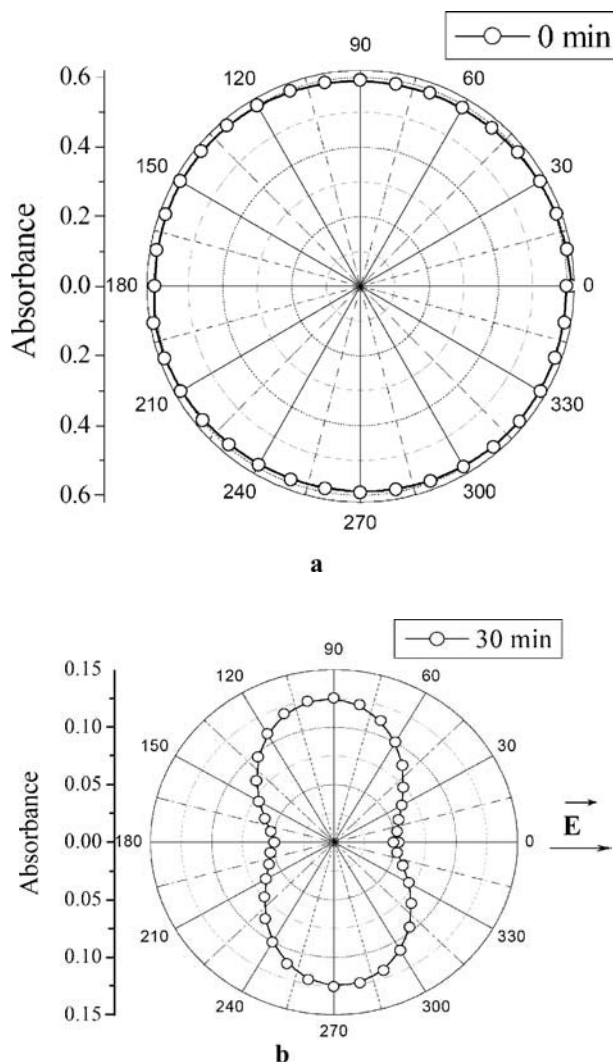


Figure 6. Polar plot of the absorbance of the closed form of the diarylethene fragments in mixture II at 635 nm. Before the spectra were recorded, the films were irradiated with UV light (313 nm) for 40 min and then for 30 min with polarized visible light ($\lambda = 633$ nm). (a) Film before visible light irradiation; (b) After polarized visible light irradiation. \vec{E} is the vector of the electric field of the polarized light.

0.02–0.06,^[30,31] which is almost one order of magnitude lower.

Figure 7 shows the time dependence of the dichroism changes of the closed form of the diarylethene molecules,

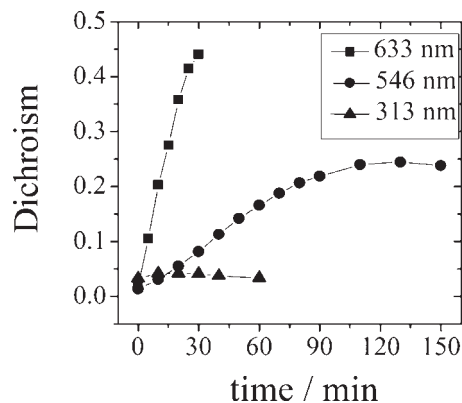


Figure 7. The time dependence of the dichroism value of the diarylethene molecules in mixture II during polarized irradiation with wavelengths $\lambda = 313$ nm, $\lambda = 546$ nm and $\lambda = 633$ nm.

which are typical for the two mixtures during irradiation with linearly polarized light.

An important point is that the rate of the dichroism growth of the diarylethene closed form in mixture I and II were the same under polarized light irradiation with the wavelength $\lambda = 633$ nm (Figure 8). However, under polarized light irradiation with the wavelength $\lambda = 546$ nm, the rate of the dichroism growth of the diarylethene closed form in mixture II is larger than that in mixture I. This could be attributable to the polarized photosensitization of the back photoreaction in mixture II. In other words, only the perylene groups, possessing the transition dipole moments, which are oriented along the polarization of the irradiation light, could be excited by the polarized light with the wavelength of the fluorescence excitation. As a consequence of this, the polarized energy transfer from the excited perylene groups to the diarylethene molecules took place in mixture II. The energy of the excited state is transferred to only the diarylethene molecules with the transition dipole moments that are parallel to the transition dipole moments of the selectively excited fluorescent perylene groups.

The annealing of the photooriented films of mixture I and II leads to a dramatic decrease in the dichroism value of the closed form of the diarylethene fragment even at temperatures near the glass transition temperature. This phenomenon suggests that the orientation disappearance of the

Table 2. The dichroism values for diarylethene molecules in the closed form for mixture I and II before and after polarized light irradiation with light of different wavelengths.

	313 nm		546 nm		633 nm	
	before irradiation	after irradiation	before irradiation	after irradiation	before irradiation	after irradiation
Mixture I	0.02	0.02	0.01	0.16	0.02	0.29
Mixture II	0.03	0.03	0.01	0.24	0.02	0.44

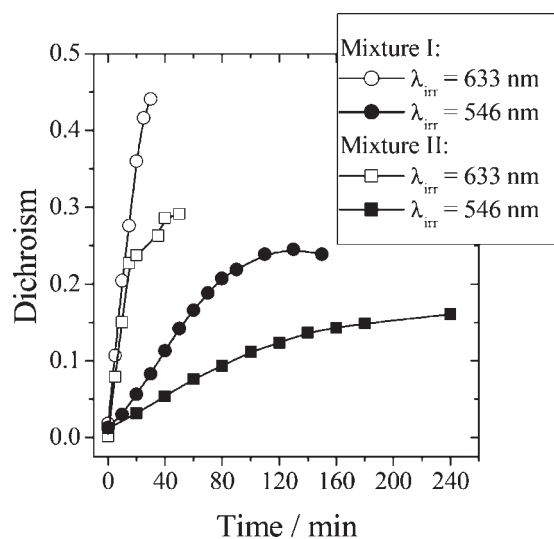


Figure 8. The time dependence of the dichroism value of the diarylethene molecules in mixture I and II during polarized irradiation with wavelengths $\lambda = 546$ and 633 nm.

photochromic molecules occurs. Similarly, the relaxation of the anisotropy of a closed form of the diarylethene molecules has been observed in a glassy amorphous film due to molecular rotational diffusion.^[31] Figure 9 demonstrates the time dependence of the dichroism value of the

diarylethene molecules, which are typical for the mixtures during annealing at different temperatures.

It is interesting to note that the dichroism disappearance of the diarylethene molecules in mixture I and II takes place to a large extent even at room temperature ($T \approx 22^\circ\text{C}$), corresponding to the glassy state of the cholesteric polymer matrix. This is due to the fact that only the photoselection process of the diarylethene molecules could occur under the action of the polarized visible light. This process cannot lead to the cooperative orientation of mesogenic fragments, contrary to what is observed for photochromic azobenzene systems.^[14–29] Apparently, there is enough free volume and thermal energy for the thermal rotation of the diarylethene molecules, even in the glassy state of the cholesteric polymer matrix.

We have calculated the activation energy of the dichroism relaxation process of the diarylethene molecules. For this purpose, we calculated the rate constants of the dichroism relaxation processes using the time dependences of the dichroism value for the mixtures during the annealing process at different temperatures (Figure 9). These dependences were approximated by a monoexponential function (curves show the results of this fit). An Arrhenius plot (see insert in Figure 9) gave a value of activation energy of about $170\text{ kJ} \cdot \text{mol}^{-1}$.

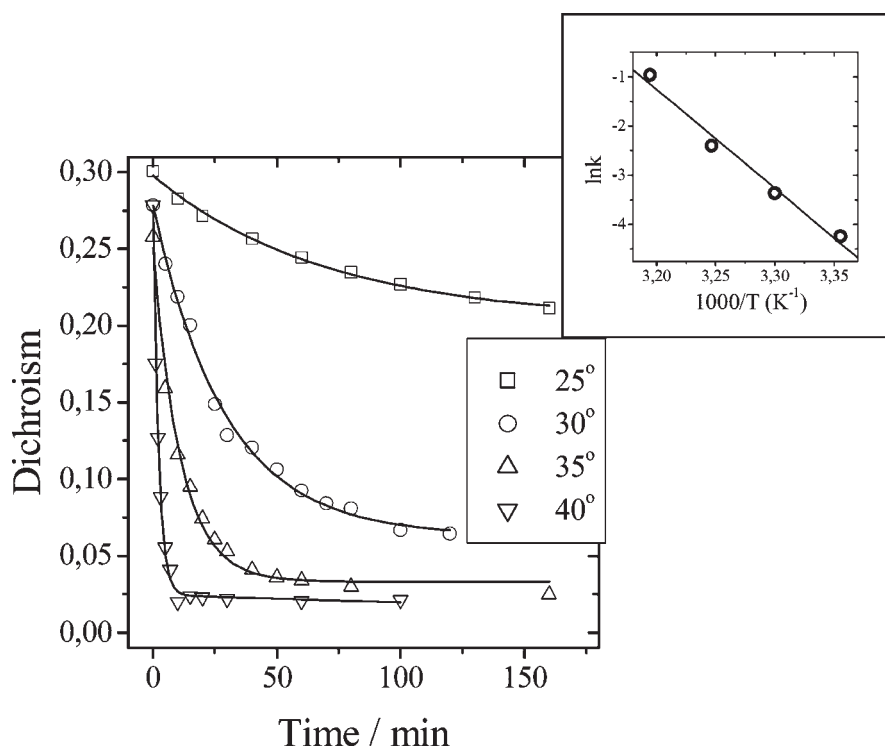


Figure 9. The time dependence of the dichroism value of the diarylethene molecules in mixture I at different temperatures during the annealing process. Solid lines are the exponential fit of dependencies. The insert shows the dependence of the rate constant logarithm on the inverse temperature.

Conclusion

The results obtained in this research permit us to draw the conclusion that the photoorientation of the diarylethene molecules in the cholesteric polymer matrix is possible due to photoselection during the polarized visible irradiation. As this takes place, the helical structure of the cholesteric polymer matrix does not prevent the photoselection process of the diarylethene molecules. However, the diarylethene derivatives (investigated in our work) are responsive only to visible polarized irradiation, different from the others, which were oriented by visible polarized irradiation as well as UV polarized irradiation.^[30–32] In addition, the possibility of polarized energy transfer from the fluorescent groups to the photochromic dopant in the cholesteric polymer systems was shown. This phenomenon allows an increase in the rate of photoselection of the photochromic molecules. The dichroism relaxation process of the diarylethene molecules occurs in the cholesteric polymer matrix with a noticeable rate even at room temperature.

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