

Comparative study of photoorientation phenomena in photosensitive azobenzene-containing homopolymers and copolymers

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Abstract

Peculiarities of photoorientational behavior under the action of polarized and nonpolarized light of different wavelengths on films of a homopolymer and a related copolymer were studied. The homopolymer consists of polyacrylate main chain and photosensitive azobenzene side groups, whereas the copolymer also contains nonphotosensitive bulky cholesterol-containing side groups. It was shown that the irradiation of thin spin-coated films of the polymers by polarized UV light leads to the appearance of small dichroism which is not stable under prolonged irradiation. This phenomenon associated with the photoselection and photoorientation processes takes place because only the azobenzenes with the molecular long axis perpendicular to the direction of the electric field vector of the incident light are inactive, but the others are activated for isomerization cycles accompanied by a motion of their molecular long axis until they are perpendicular to the direction of the electric field vector. The irradiation with linearly polarized visible light (436 nm) results in a strong increase of the in-plane orientation of the azobenzene groups. The maximal value of the photoinduced anisotropy is larger in the case of the copolymer. It was also found that the irradiation with nonpolarized visible light leads to an out-of-plane order in polymers films, i.e. in this case of the azobenzene moieties simultaneously adopt orientation along film normal.

The comparative study of above-mentioned phenomenon allowed to find the influence of different factors, such as irradiation wavelength, polymer structure and film thickness on the kinetics, the photoinduced dichroism and the order parameter values.

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1. Introduction

The phenomena of angular-dependent photoselection and photoorientation in polymer materials containing azobenzene fragments present the subject of intense study for more than 20 years [1–29]. The current interest to such systems is primarily related to their potential application as the materials for data recording and long-term optical data storage.

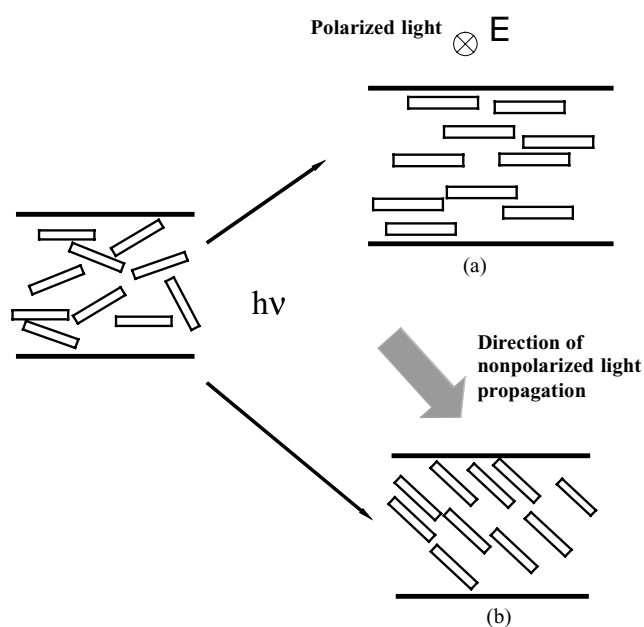
Upon the action of linearly polarized light, the films of liquid-crystalline (LC) and amorphous azobenzene-containing polymers show the selective light absorption by azobenzene groups, which are oriented along the light electric field vector E of the incident light. Repeated angular selective excitations and repeated cycles of E – Z and Z – E photoisomerization finally lead to the orientation of chromophores resulting in the appearance of linear dichroism

and photoinduced birefringence. This behavior is related to the orientation of azobenzene groups perpendicular to the electric field vector. (Scheme 1a).

The feasibility of the controlled three-dimensional structural design by varying the orientation of azobenzene chromophores under the action of nonpolarized light was demonstrated in [24–28]. In this case, azobenzene groups become oriented along the direction of incident light, i.e. an out-of-plane order is developed (Scheme 1b). The nature of this phenomenon is similar to that as observed upon irradiation with visible light. Furthermore, in some cases [24,28], the development of the biaxial order in the films of azobenzene-containing polymers was reported.

However, so far, no data concerning the correlation between the molecular structure of polymers and their tendency for the development of in-plane or out-of-plane component of the photoorientation of LC polymers are available; the kinetics of the above processes has not been studied yet.

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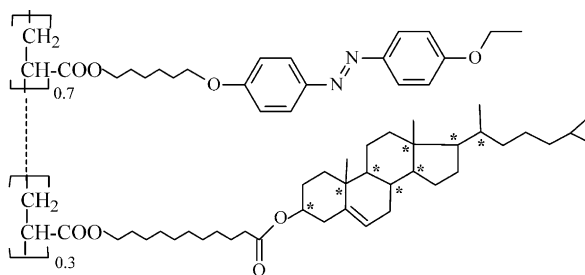
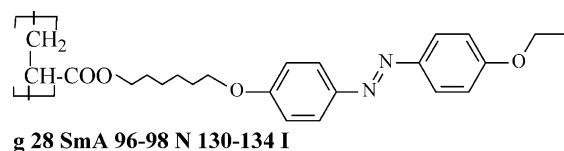
Scheme 1. Generation of in-plane (a) and out-of-plane (b) orientation of azobenzene groups by linearly polarized or nonpolarized light irradiation. In (a) electric field vector E is perpendicular to figure plane. (The main chains and spacers are omitted for simplicity.)

In our opinion, the effect of film thickness on the kinetics of photoorientation process presents also an evident interest because, in the case of very thin films (nanometric dimensions), the surface should play a key role of controlling such important parameters as the glass transition temperature, the molecular mobility, etc. [29–31].

At the same time, as was shown in [32] when studying the amorphous films with a thickness above $2\ \mu\text{m}$ and with a low content of azobenzene groups, the process of photoorientation is independent of the thickness of the test samples. On the other hand, in the case of very thin films (about $\sim 100\ \text{nm}$ and thinner), their glass transition temperature, structure, and molecular mobility markedly depend on the thickness of the polymer film [30–32].

In this connection, it seems interesting to investigate the specific features of photoorientation and photoselectivity processes in the thin films of comb-shaped LC homopolymers and copolymers containing the same photochromic azobenzene groups under the action of polarized and nonpolarized light with different wavelengths. By varying the wavelength and power density of the incident light, one may markedly control the rate and conversion of photoisomerization due to the different ratios between extinction coefficients of E and Z isomers of azobenzene groups [13]. This work dealt with the description of the pioneering results in this direction.

In this paper we describe the results of the comparative studies of thermo- and photoorientational processes of homo- and copolymers containing the same photochromic 4-ethoxy-4'-hexoxyazobenzene groups. The formulas and phase transitions of the above polyacrylates are listed below:



As follows from the above structural formulas, we deal with a homopolymer containing a photosensitive mesogenic azobenzene moiety in the side group and a random copolymer which contains in addition to the azobenzene fragments bulky cholesterol fragment in the comesogenic group. This approach offers additional advantages for studying the effect of nonphotochromic and structurally different mesogenic fragments on the optical properties and photooptical behavior of thin polymer films. The further development of this work will be focused on the detailed analysis of photoinduced processes and chiral optical properties of the polymer films. Such approach will allow one to reveal the role of chiral cholesteric fragments in the orientational behavior of copolymer.

The structure of this publication may be presented as follows. First, we will consider the optical and thermo-optical properties of the polymer films as prepared by the method of spin coating. We would like to mention that, usually, such films are isotropic [28]; here, the special emphasis is placed on the development of the smectic order upon annealing at temperatures above glass transition temperature. Then, we will discuss the specific features of the photochemical transformations in the isotropic films of the LC polymers. The next two sections of this publication present the results of studying the processes of photoorientation in the amorphous films under the action of UV and linearly polarized visible light. Finally, we will describe the specific features of out-of-plane photoorientation phenomena as induced by nonpolarized visible light.

2. Experimental

4-Ethoxyazobenzene and cholesterol-containing monomers were synthesized according to the procedures described in [33,34], respectively. The homopolymer and the copolymer were synthesized by radical polymerization of monomers in benzene solution at $65\ ^\circ\text{C}$; AIBN was used as an initiating agent. The synthesized polymers were purified

by the repeated precipitation with methanol and dried in vacuum.

The average molecular mass of the polymers were determined by gel permeation chromatography (GPC). The GPC analyses were carried out with a KNAUER instrument equipped with an KNAUER HPLC 64 column. Measurements were made by using a UV detector, THF as solvent (1 ml/min, 40 °C), and a calibration plot using polystyrene standards. The polymers obtained have the following molar mass characteristics: homopolymer: $M_n = 8000$, $M_w/M_n = 1.4$, copolymer: $M_n = 8200$, $M_w/M_n = 1.3$.

The phase transitions in the polymers 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 at room temperature with a set of a XBO 150 W lamp, water IR filter, and a metal interference filters (365 and 436 nm). The power density of the incident light was 63.8 mW/cm² for 365 nm and 36.9 mW/cm² for 436 nm. After irradiation the absorbance spectra were recorded using Lambda 2 (Perkin-Elmer) UV-Vis spectrometer.

Thin films for the photooptical experiments were obtained by spin-coating technique using solutions in chloroform. For drying the spin-coated films were kept at room temperature during 1 day. Thickness of the films was measured using DEKTAK profilometer.

The photoorientation experiments were performed with a set of a XBO 150 W lamp, water IR filter, a metal interference filter (365 and 436 nm) and polarizer (Glan-Thompson prism). The intensity of the light in this case was 27.9 mW/cm² (365 nm) and 14.1 mW/cm² (436 nm).

The orientational order was studied using polarized UV-Vis spectroscopy, because the transition moment of the *E* isomer of azobenzene moiety is directed along the long axis of this group. For this purpose the angular dependence of the absorbance was measured using a photodiode array UV-Vis spectrometer (XDAP, Polytech) with a step-width of 5°.

The values of dichroism were calculated from the spectra using Eq. (1):

$$D = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + A_{\perp}} \quad (1)$$

where A_{\parallel} is the absorbance at the preferred direction; A_{\perp} is the absorbance perpendicular to this direction.

The values of order parameter determined by spectroscopic method were calculated by Eq. (2)

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} \quad (2)$$

To study the out-of-plane photoorientation phenomena we measured the angular distribution of the polarized ab-

sorbance spectra at an angle equal of about 45° to film normal and calculated dichroism using Eq. (1).

3. Results and discussion

3.1. Optical and thermo-optical properties of spin-coated polymer films

In this work, all experiments were performed for polymer films with a thickness ranging from 100 to 300 nm; the films were prepared by the method of spin coating. According to the data of polarization optical microscopy, all as-prepared films are isotropic.

Fig. 1 presents the absorption spectra of the freshly prepared films of homopolymer and copolymer. As follows from Fig. 1, one may easily distinguish the two well-pronounced peaks, which correspond to the $\Phi-\Phi^*$ ($\lambda_{\max} = 250$ nm for both polymers) and the $\pi-\pi^*$ (at 340–360 nm) electronic transitions of the azobenzene chromophore. Taking into account the fact that the test films are characterized by the different thickness (150 nm for the homopolymer and 290 nm for the copolymer), for convenience, the spectra are normalized to the peak of the $\Phi-\Phi^*$ transition, because this transition is not sensitive to the orientational order and less sensitive to any aggregation of chromophores, if there is no overlapping with the $\pi-\pi^*$ electronic transition [15].

Let us emphasize the following specific features of the absorption spectra. First, for the homopolymer, the level of the optical density in the interval of the $\pi-\pi^*$ transition appears to be much lower, and its maximum is slightly shifted to the short-wavelength region.

The above specific features (lower values of extinction coefficient and blue shift of λ_{\max} of the $\pi-\pi^*$ transition) attest that, in the freshly prepared film based on homopolymer, the tendency of the formation of H-aggregates is stronger pronounced; that is the case forming head-to-head dimers of the azobenzene groups [15,35].

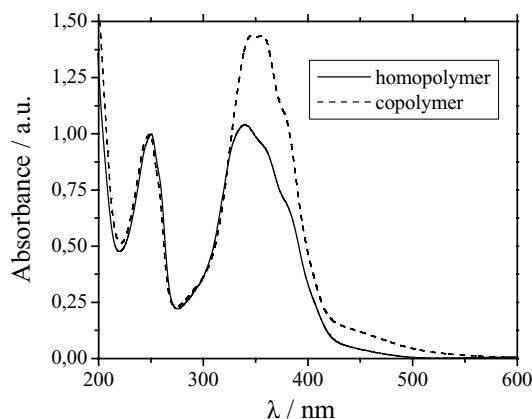


Fig. 1. Absorbance spectra of freshly prepared homopolymer and copolymer films normalized at maximum of $\pi-\pi^*$ electronic transition.

Upon annealing the test films at room temperature, no marked changes take place; however, when the films are kept at the temperature, which is above their glass transition temperature corresponding to the SmA phase, one may observe the dramatic spectral changes (Figs. 2 and 3). However, for the homopolymer and the copolymer, the character of the changes appears to be different. In the case of homopolymer, the absorption in the region of the π - π^* transition decreases by about 30%, and the maximum is further shifted to the short-wavelength spectral region (Fig. 2a). In the case of the copolymers, the optical density decreases by a factor of 5, whereas the position of the maximum remains almost unchanged (Fig. 3a). Let us mention that, in both cases, the profiles of the corresponding spectra and absorption in the region of the Φ - Φ^* transitions are preserved.

When the absorption spectra are recorded at an angle of 45° to the film normal using polarized light, one may observe a significant anisotropy indicating the development of an out-of-plane order. The corresponding plots (Figs. 2b, c and 3b, c) allow us to assess the level of dichroism. In the case of the homopolymer, the dichroism is equal 0.14; at the same time, for the copolymer, this value is equal to 0.63. (Note that, as follows from the figure, even the freshly prepared films show already a light tendency for an out-of-plane orientation.)

Therefore, the analysis of the absorption spectra and thermotropic properties of homopolymer and copolymer makes it possible to reveal a well-pronounced tendency for the development of the out-of-plane order (Scheme 2). On one hand, the introduction of cholesteric units dramatically prevents the formation of H-aggregates during the spin-coating procedure and even due to annealing. At the same time, the presence of 30% of cholesteric units in the copolymer undoubtedly leads to the change in intermolecular interactions in the LC phase; as a result, the temperatures of phase transition in copolymer are lower than those of homopolymer. This factor is likely to assist the breakdown of the H-aggregates due to a "loosened" packing of mesogenic azobenzene fragments; as the mesogenic fragments acquire a higher mobility, they are able to form the homeotropic structure, which is characterized by a higher degree of orientation as compared with that of homopolymer. In both cases, the appearance of homeotropic orientation is provided by the presence of interfacial glass/polymer and polymer/air boundaries; at these interfaces, a spontaneous orientation of mesogenic groups is observed.

In the case of the copolymer, a higher dichroism suggests that the order parameter of azobenzene groups is rather high and achieves the level of SmA mesophase.

3.2. Spectral changes in isotropic polymer films as induced by irradiation with nonpolarized UV light and subsequent action of visible light

Irradiation of more or less isotropic spin-coated films of homopolymer and copolymer with nonpolarized UV light

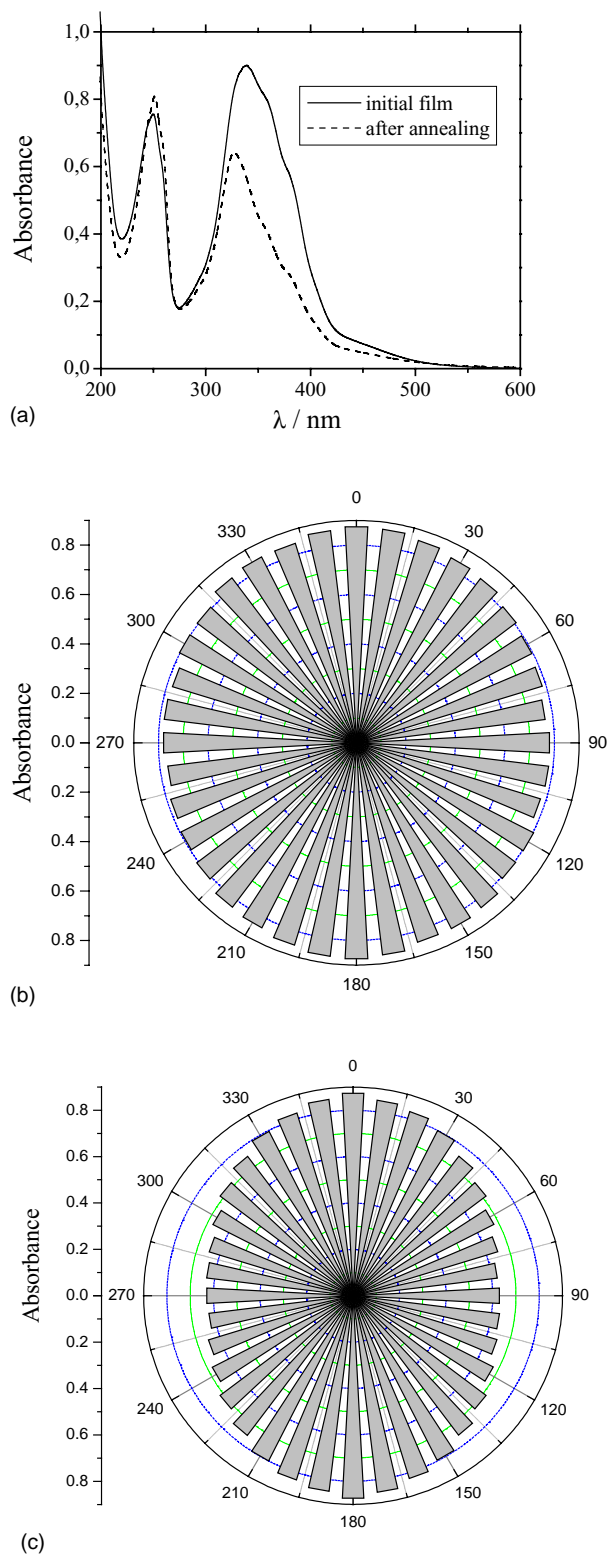


Fig. 2. Absorbance spectra of homopolymer before and after annealing at 75°C during 30 min (steady state, i.e. longer time of annealing does not lead to additional changes). (b) and (c) polar plots before and after annealing, respectively (for $\lambda = 320\text{ nm}$). For polar plots spectral measurements were made at 45° to film normal. Value of out-of-plane dichroism after annealing is about 0.14.

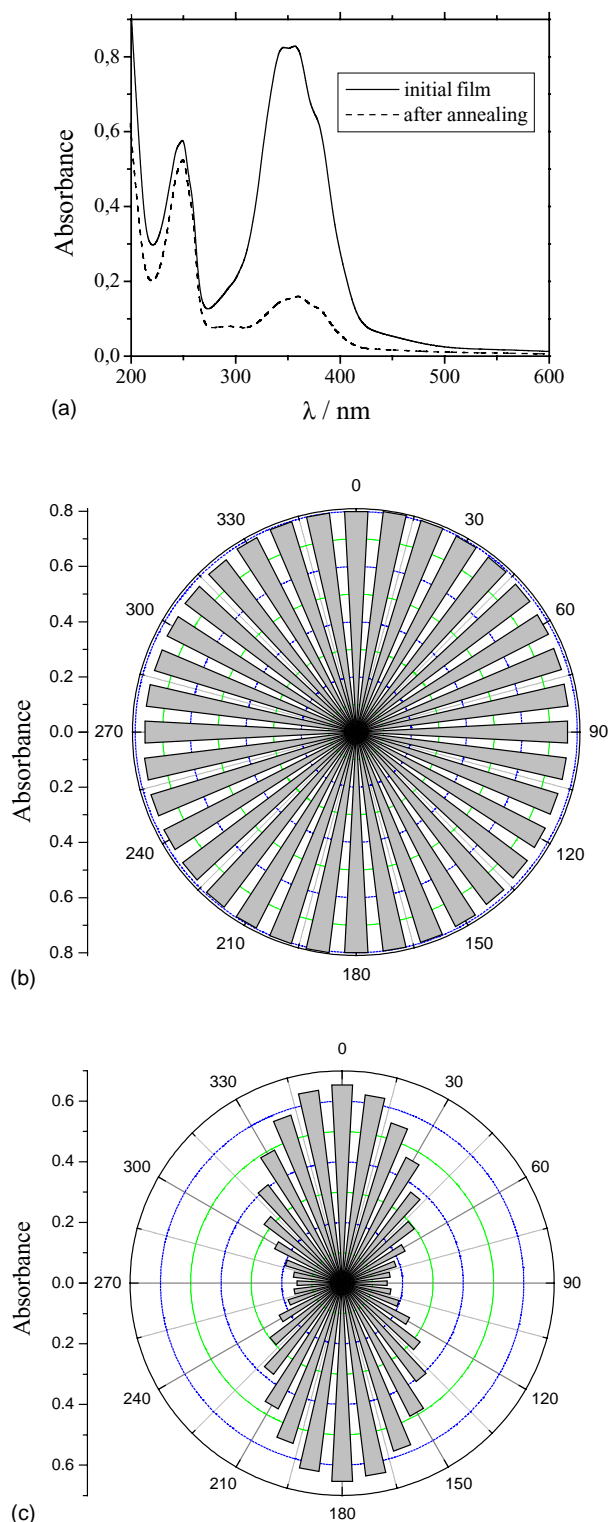
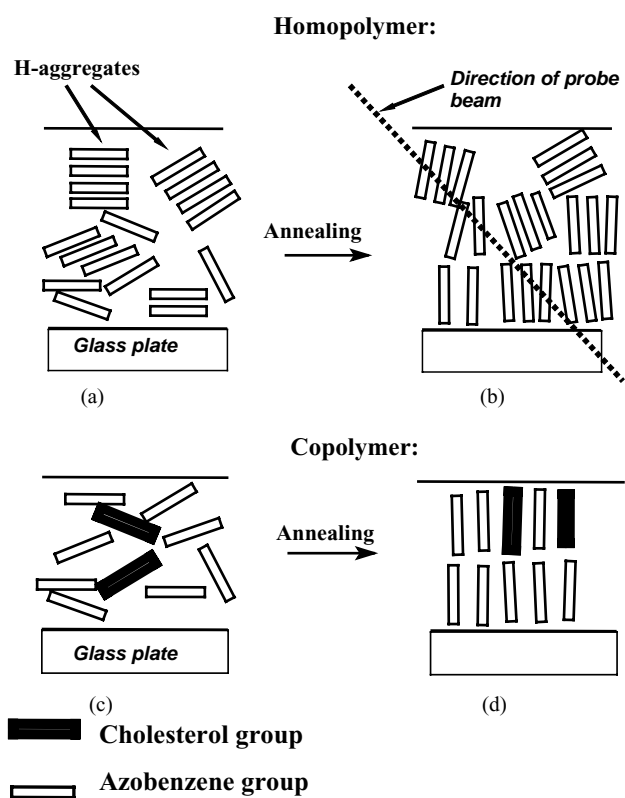


Fig. 3. Absorbance spectra of copolymer before and after annealing at 75 °C during 30 min (steady state, i.e. longer time of annealing does not lead to additional changes). (b) and (c) polar plots before and after annealing, respectively (for $\lambda = 330$ nm). For polar plots spectral measurements were made at 45° to film normal. Value of out-of-plane dichroism after annealing is 0.63.



Scheme 2. Scheme of ordering of side groups in homopolymer (a, b) and copolymer (c, d) before (a, c) and after annealing (b, d). (Backbones are not shown for simplicity.)

is accompanied by the concomitant spectral changes which are typical for the *E*–*Z* photoisomerization (Fig. 4). Upon irradiation, the absorption dramatically decreases in the region of the π – π^* transition and increases in the region of the n – π^* transition. Within less than 1 min, a photostationary state with a high content of the *Z* isomeric form is achieved. As a result of the subsequent irradiation with visible light, the reverse changes occur establishing a steady state with

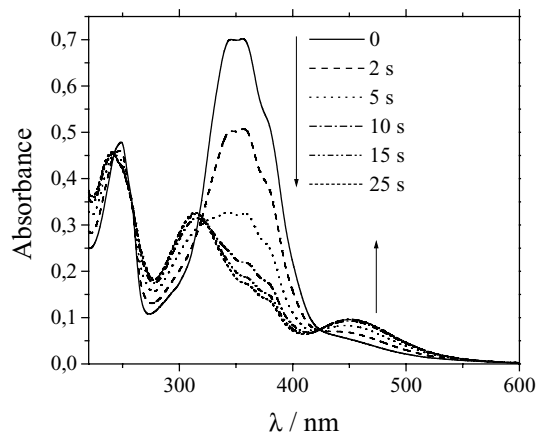
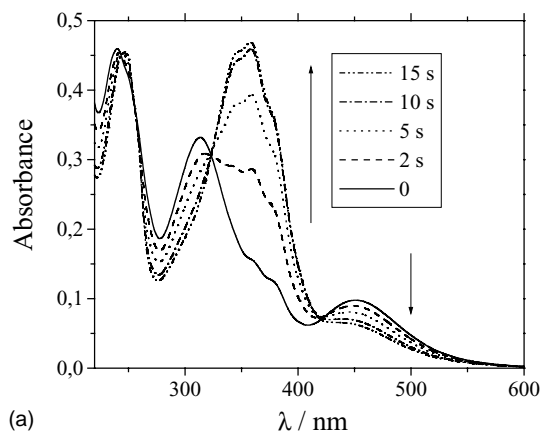
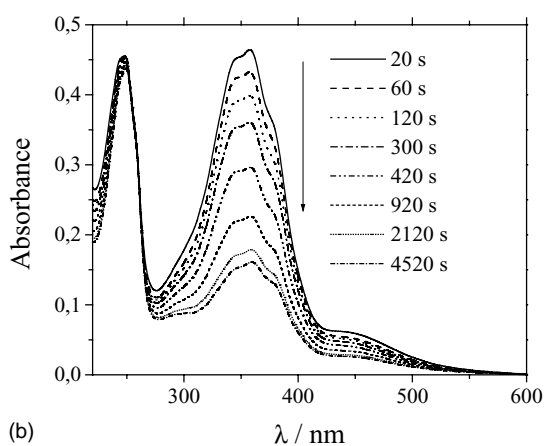


Fig. 4. Changes of absorbance spectra during UV irradiation (365 nm) of copolymer film. Photostationary state of *E*–*Z* photoisomerization is achieved less than 1 min.



(a)



(b)

Fig. 5. Changes of absorbance spectra during visible light irradiation (436 nm) of copolymer film irradiated before by UV light. (a) First 15 s of irradiation; (b) Further irradiation.

a high concentration of *E* isomers (Fig. 5a). However, the recovery of the initial spectrum is not complete: upon a prolonged irradiation (>20 s), one may observe a decrease in the absorption in both regions corresponding to the π - π^* and n - π^* transitions.

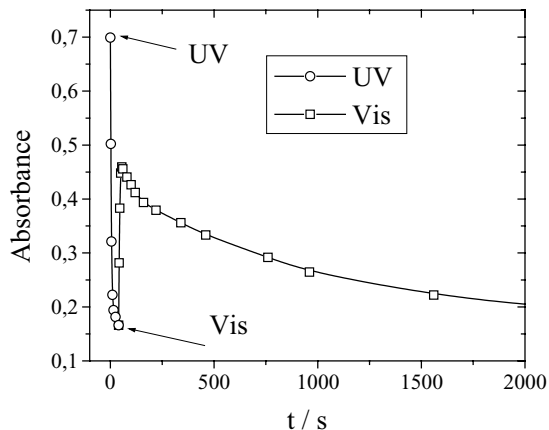
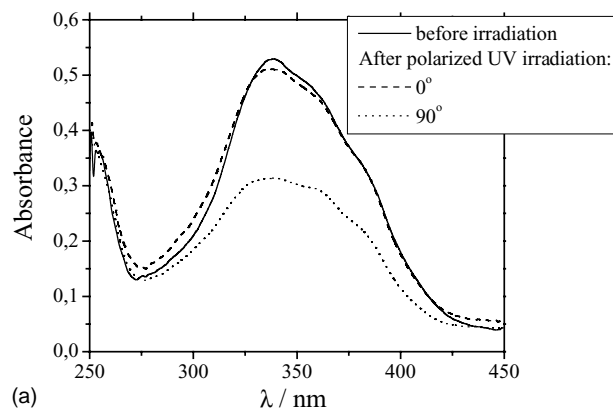
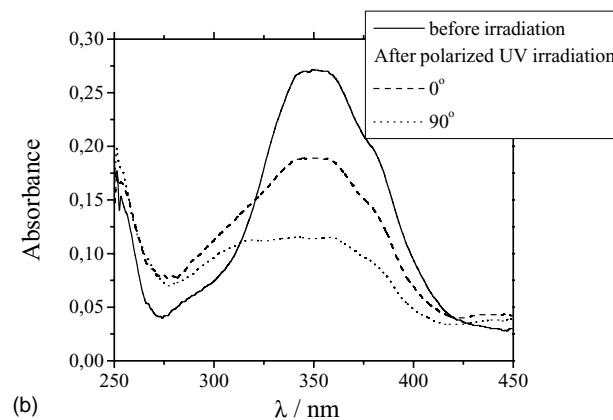


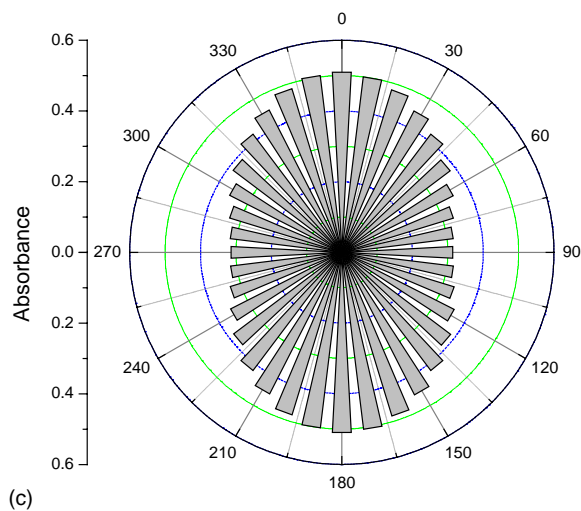
Fig. 6. Kinetics of absorbance changes (at 352 nm) for copolymer during UV and subsequent visible light irradiation.



(a)



(b)



(c)

Fig. 7. Absorbance spectra of (a) homopolymer and (b) copolymer before and after 5 s of polarized UV light irradiation; (c) corresponding polar plot for homopolymer after irradiation ($\lambda = 336$ nm). Measurements were performed at normal to film plane.

The rate of the decrease in the absorption upon the irradiation with visible light is much lower than that upon UV irradiation and the further increase in the absorption simultaneously with the irradiation with visible light (Fig. 6). This behavior is observed both for the homopolymer and the

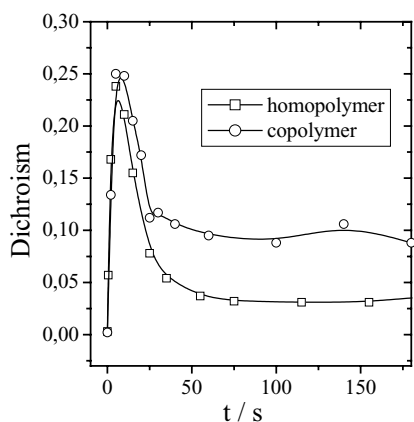


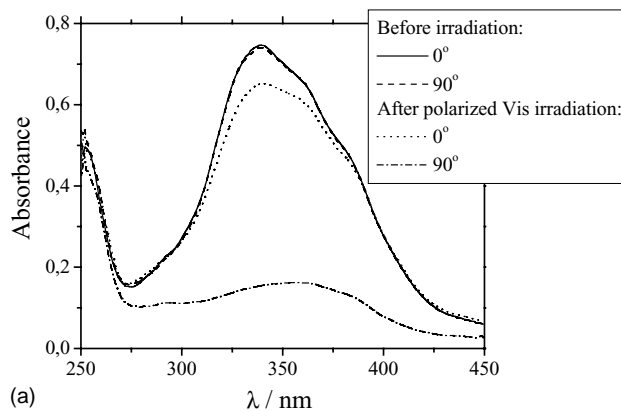
Fig. 8. Changes of dichroism (calculated at absorbance maxima) for spin-coated film of homopolymer and copolymer during polarized UV irradiation (365 nm).

copolymer; the only difference concerns the fact that, in the case of the copolymer, the rate of the decrease in absorption upon the irradiation with visible light is much lower (see below). Within the first seconds of irradiation with visible light, back *Z*–*E* photoisomerization occurs; but upon continued irradiation, the azobenzene groups are oriented along the normal of film due to photoorientation. In this case, the transition moment of these groups become oriented perpendicular to the plane of films; as a result, the probability of light absorption and, thus, optical density markedly decreases.

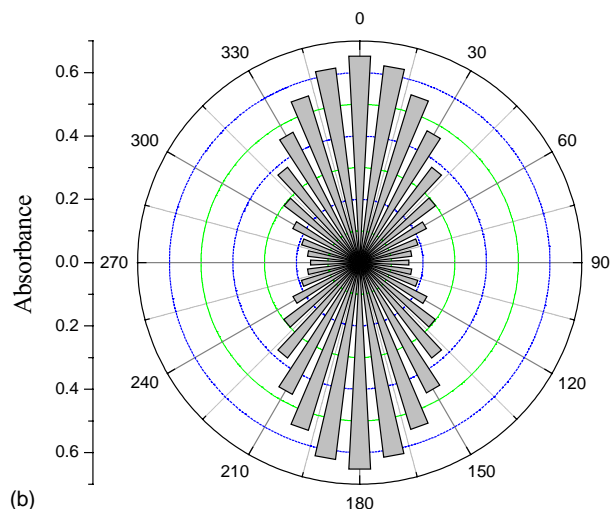
Therefore, the polymer films under study show an unorthodox phenomenon of the decrease in the optical density as induced by the irradiation with visible light. Probably the light-induced orientation process triggers the out-of-plane ordering tendency of the LC polymers. Below, this behavior will be discussed in more detail.

3.3. Study of the in-plane photoorientation in isotropic polymer films induced by polarized UV light

The action of linearly polarized UV light on the films of the homopolymer and the copolymer leads to the appearance of linear dichroism (Figs. 7 and 8). This effect is related to the fact that the polarized light is primarily absorbed by azobenzene chromophores, which direction of the transition moment coincides with the light electric field vector *E*. This angular selective absorption is accompanied by the *E*–*Z* photoisomerization of azobenzene groups, which are oriented along the vector *E*; at the same time, the fragments that are oriented perpendicular to this vector are not excited. This photosensitive conversion leads to the appearance of dichroism, and its maximum level is achieved within 5 s. Then, the dichroism dramatically decreases (Fig. 8). This is caused due to the fact that the *Z* isomer is characterized by a low anisotropy, and its high content violates the orientational order in the system. A photoorientation process takes place in the steady state of UV exposure, but the effect of



(a)



(b)

Fig. 9. (a) Polarized absorbance spectra of homopolymer film before and after polarized visible light irradiation (20 min, 436 nm); (b) corresponding polar plot ($\lambda = 340$ nm).

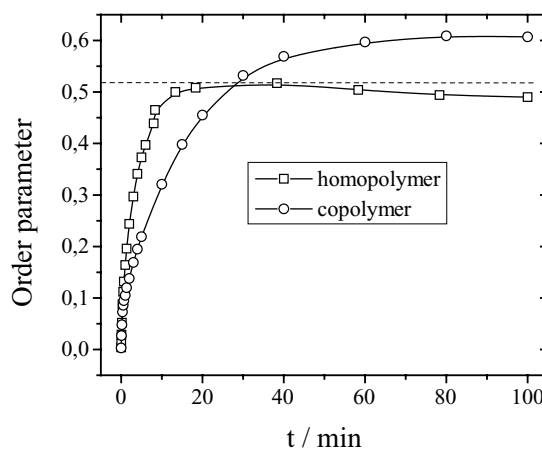
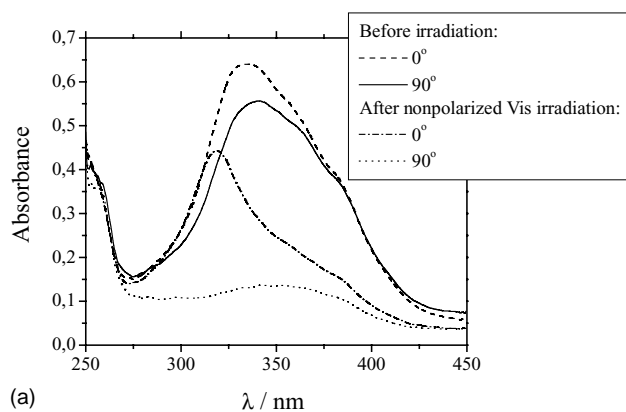
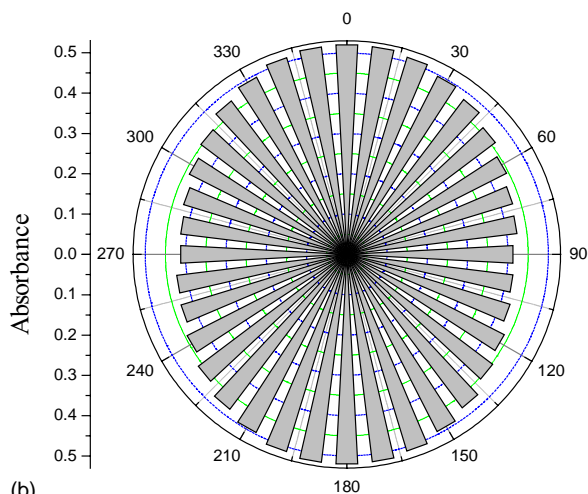


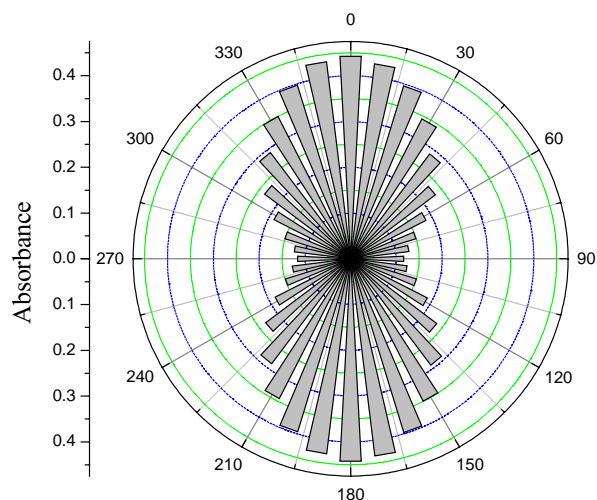
Fig. 10. Kinetics of order parameter growth during polarized visible light (436 nm) irradiation for homopolymer and copolymer. Dashed straight line shows maximal value of order parameter for homopolymer.



(a)



(b)



(c)

Fig. 11. Polarized absorbance spectra of (a) homopolymer film before and after nonpolarized visible light irradiation (20 min, 436 nm). All spectra were recorded at 45° to film normal. Corresponding polar plot ($\lambda = 316$ nm) before (b) and after irradiation (c).

photoselection and photoorientation is restricted due to the disordering effect of the generated Z isomers.

Upon continued irradiation with polarized UV light, the values of maximum dichroism are rather small so, 0.04 for the homopolymer and 0.10 for the copolymer, and the corresponding order parameter (0.17–0.18) is much lower than that of aligned LC films.

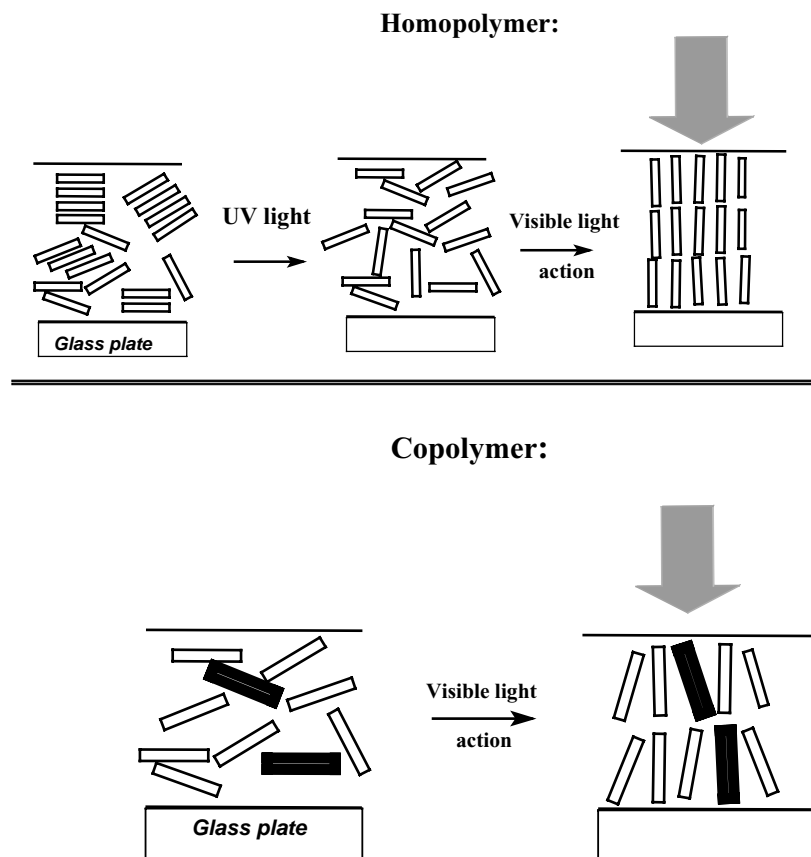
As follows from Fig. 8, the kinetic curves corresponding to the changes in dichroism appear to be similar for the homopolymer and the copolymer. Upon the prolonged UV irradiation of the films of homopolymer and copolymer, a specific dynamic equilibrium is attained: azobenzene groups experience the repeated cycles of *E*–*Z* and *Z*–*E* photoisomerization. In this case, the content of Z isomer remains virtually high. However, it seems interesting to mention that, in the case of copolymer, the “residual” dichroism upon the prolonged irradiation is much higher (Fig. 8). It was shown, that photoorientation process is cooperative even in the glassy state of the polymers orienting the nonphotochromic group as well [7,13]. In the case of the copolymer, the disordering effect of Z isomers is less pronounced as for the homopolymer. Possibly, the cholesteric fragments, which are mesogenic by themselves [34,36,37], allow the system to “remember” the photoinduced orientation of the azobenzene groups; that is, they preserve, to a certain extent, a slight orientation order.

3.4. Study of in-plane and out-off-plane photoorientation in polymer films as induced by polarized visible light

Upon the irradiation with visible light (436 nm), the behavior of the homopolymer and copolymer films appears to be quite different (Figs. 9 and 10). In this case, the rate of the photoorientation process is much lower but the corresponding order parameter approaches a level, which is typical for mesophases (Fig. 10). The principal reason behind the difference in the photooptical behavior as induced by UV and visible light is likely to be related to the different ratios between *E* and *Z* isomers at the different exposure wavelengths.

In the case of UV irradiation, at the photostationary state, a content of the Z isomer achieves about ~90%, whereas, upon the irradiation with visible light with at 436 nm, the *E* isomer prevails [38]. In the latter case, the repeated cycles of *E*–*Z* and *Z*–*E* isomerization at a high concentration of the *E* isomer assist the development of a well-pronounced uniaxial order, in which one short axis exists parallel to *E* and two long axes perpendicular to *E* vector (oblate order) in the films.

At the early stages, the rate of the photoorientation process of the homopolymer is much higher than that of copolymer (Fig. 10). However, the maximum order parameter of the homopolymer appears to be somewhat lower; furthermore, this value tends to decrease upon the prolonged irradiation. As will be shown below, this behavior is not related to any photoinduced degradation of the polymer but is provided by



Scheme 3. Schematical representation of ordering process occurring in films under nonpolarized light action.

the competing process of the development of out-of-plane photoorientation.

3.5. Specific features of out-of-plane photoorientational behavior in the films of homopolymer and copolymer as induced by nonpolarized visible light

Dramatic spectral changes are observed for polymer films exposed to the irradiation with nonpolarized light. In the region of the $\Phi\text{--}\Phi^*$ transition, the absorption remains unchanged but $\pi\text{--}\pi^*$ absorbance abruptly decreases (Fig. 11a). This behavior is accompanied by a well-pronounced development of an out-of-plane order (Scheme 3) as evidenced by the corresponding polarized light absorption spectra, which are recorded at an angle of 45° to the film normal (Fig. 11b and c). In the case of the homopolymer, the photoinduced out-of-plane orientation is much better pronounced than that as observed in the case of the thermal treatment: the level of dichroism is four times higher under this inspection conditions.

Such strong out-of-plane orientation in the films is provided only under the action of visible light; UV irradiation does not lead to the development of the out-of-plane dichroism.

For both polymers, the out-of-plane order is very stable: annealing at 150° (this temperature corresponds to the

isotropic melt of bulk polymers) for several hours followed by cooling down to room temperature is not accompanied by any marked decrease in the dichroism. Upon further annealing, the uniform character of the films is distorted due to the process of dewetting.

Photoinduced homeotropic ordering may be appreciably enhanced if the films are first UV irradiated until the photostationary state is attained (Fig. 12). As a result of the UV irradiation, H-aggregates break down; the mobility and, hence, the photosensitivity of the whole system increases. (At a wavelength of 436 nm, the extinction coefficient of Z isomer is much higher (Fig. 4).)

Even though the thermal stability of the homeotropic orientation is high, a short-term UV irradiation leads to its complete breakdown (Fig. 13). An alternative irradiation with visible and UV light allows one to play with the orientation of azobenzene groups in the films. The fatigue resistance of the homopolymer and copolymer in result of repeated irradiation cycles is rather high (Fig. 14).

The detailed analysis of the corresponding spectra and the kinetics of homeotropic orientation makes it possible to reveal the following features. First, in the case of the homopolymer, the maximum of the $\pi\text{--}\pi^*$ transition for the polarized spectra as recorded along the orientation direction of chromophores is seen to be slightly shifted to the short-wavelength spectral region (Fig. 15). For the spectra

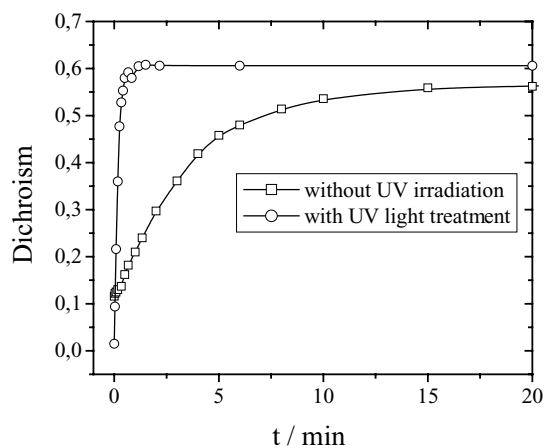


Fig. 12. Changes of dichroism for spin-coated film of homopolymer during nonpolarized visible light irradiation (436 nm). Kinetics was studied for “fresh” film and film treated by UV irradiation (1 min, 365 nm). Dichroism was calculated from spectra measured at 45° to film normal.

recorded in the perpendicular direction, this difference is small, and the maximum is located in the higher-wavelength spectral region. This behavior attests a key role of the aggregation of chromophores in the course of homeotropic photoorientation. In the case of the homopolymer, the concentration of H-aggregates is much higher.

Let us discuss another important fact: for copolymer, the rate of the whole process appears to be lower by more than one order of magnitude (Fig. 16). Taking into account the thermo-optical properties of the films, cholesteric groups are found to exert quite an opposite effect on the photoinduced behavior. In the case of the thermal treatment, the presence of cholesteric groups assists the transition to a homeotropic orientation, and its rate increases. However, upon the irradiation with visible light, this rate decreases. The kinetics of the development of the out-of-plane order is also controlled by the thickness of polymer films. As follows from Fig. 17,

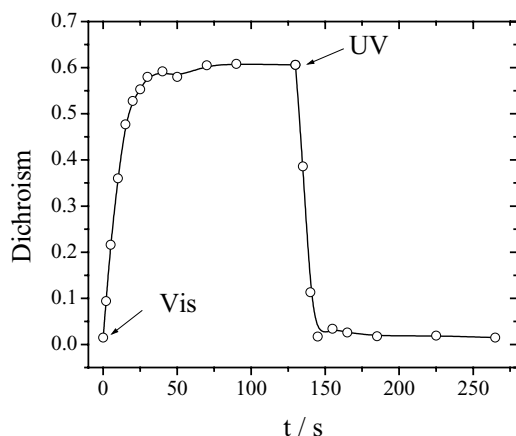


Fig. 13. Changes of dichroism for spin-coated film of homopolymer during nonpolarized visible light irradiation (436 nm) and subsequent nonpolarized UV irradiation (before irradiation by visible light film was treated by UV irradiation (1 min, 365 nm)). Dichroism was calculated from spectra measured at 45° to film normal.

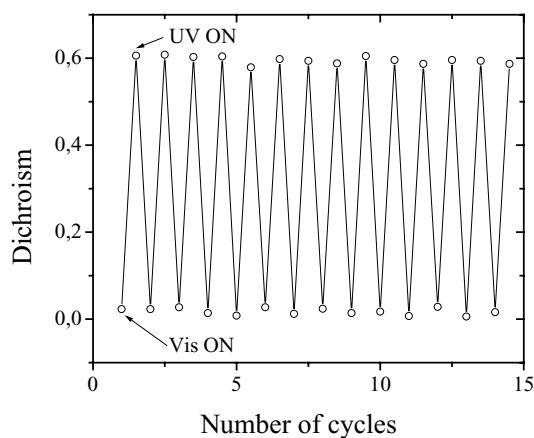


Fig. 14. Changes of dichroism value during cyclic irradiation by nonpolarized UV and visible light for homopolymer film. In each cycle homopolymer was irradiated during 2 min by visible light (436 nm) and then 1 min by UV light (365 nm).

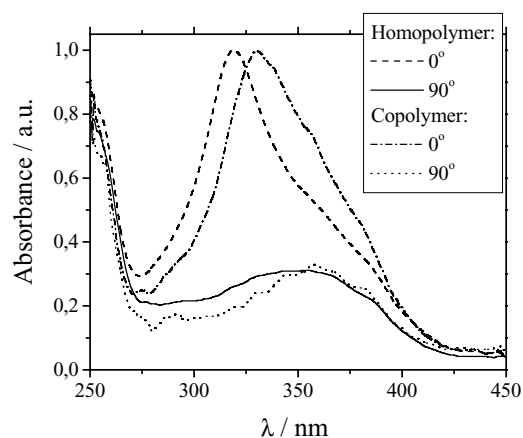


Fig. 15. Normalized polarized absorbance spectra of homopolymer and copolymer films after UV irradiation (2 min) and after subsequent nonpolarized visible light irradiation. All spectra were recorded at 45° to film normal.

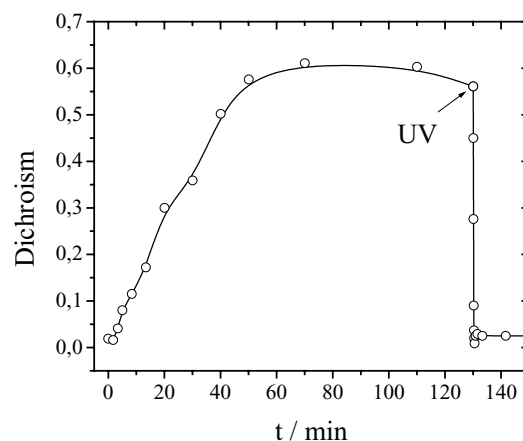


Fig. 16. Changes of out-of-plane dichroism for spin-coated film of copolymer during nonpolarized visible light irradiation (436 nm) and subsequent nonpolarized UV irradiation (before irradiation by visible light film was treated by UV light (1 min, 365 nm)).

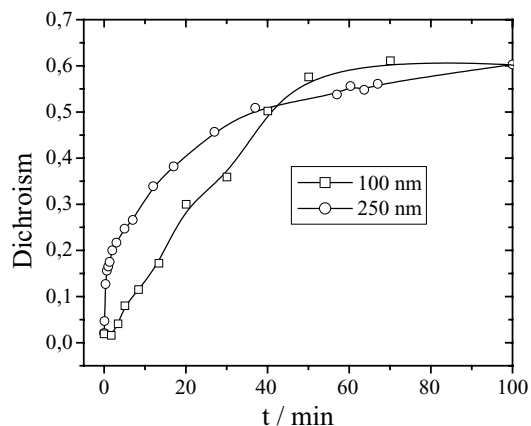


Fig. 17. Changes of out-of-plane dichroism for spin-coated film of copolymer during nonpolarized visible light irradiation (436 nm) for film of different thickness.

the initial rate of the whole process in the thicker films appears to be much higher. This evidence is likely to attest the decisive role of interfacial boundaries: evidently, their effect on the behavior of the system would be more pronounced for thin films.

4. Conclusions

Therefore, this work presents the comprehensive study of the orientational processes of azobenzene groups in the films of two polymers as induced either by thermal treatment or by the irradiation with light of different wavelengths.

A comparative analysis of the behavior of a homopolymer and a related copolymer allows us to reveal the complex mechanism of the effect of nonphotochromic bulky mesogenic groups on the mobility of the system and its tendency for aggregation and ordering.

In particular, on one hand, cholesteric groups are shown to enhance the tendency of the system for its homeotropic orientation upon thermal treatment but, on the other hand, the rate of this process decreases under the action of nonpolarized visible light. (Compared to the appropriate homopolymer.)

In our further experiments a major emphasis will be placed on studying the effect of chiral fragments on the photoinduced and thermally induced optical and orientational phenomena.

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