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Photo-orientation phenomena in photosensitive chiral nematic copolymers

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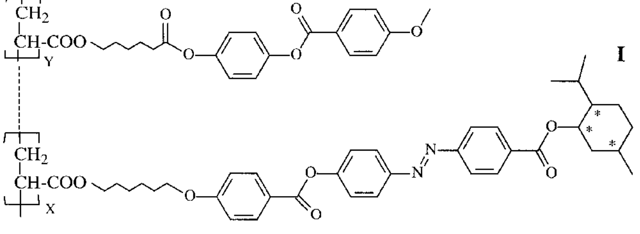
Photo-orientational phenomena have been studied for two comb-shaped cholesteric copolyacrylates containing azobenzene side groups. Copolymer **I** contains nematogenic phenyl benzoate groups and photosensitive chiral menthyl-containing azobenzene side groups. Copolymer **II** is composed of nematogenic phenyl benzoate groups, photosensitive cyanoazobenzene groups and chiral photochromic benzylidene-*p*-methan-3-one fragments. Under the action of polarized Ar^+ laser light (488 nm), orientation of the side groups of the copolymers takes place, and this orientation is perpendicular to the vector of the electric field of the incident light. This process shows a co-operative character; that is, it involves both photosensitive azobenzene and phenyl benzoate groups. The kinetics of growth of the photoinduced orientational order parameter were studied as a function of film thickness, incident light intensity, and preliminary UV irradiation. For the planar oriented films of the copolymers, irradiation with polarized light leads to the development of photoinduced birefringence Δn; maximum values of Δn reach 0.01. The photo-optical properties of copolymers **I** and **II** are compared. Such materials may be used for 'dual' data recording by varying the helix pitch, selective light reflection maximum, and photoinduced birefringence or linear dichroism.

1. Introduction

In the last 20 years, an increased interest of many scientists in various countries working in the area of polymer physics and chemistry has been focused on the synthesis and characterization of polymer materials containing azobenzene groups which are capable of photo-orientation under the action of polarized light [1–16]. The interest in such systems is related to the outstanding benefits of their practical application for optics, optoelectronics, data recording and storage [1, 2].

Another challenge in studying photosensitive and photoswitchable media involves the development of chiral nematic, optically active, low molecular mass [17–21] and polymeric materials [22–28] with a photocontrolled helix pitch and optical properties. In this case, irradiation with non-polarized light leads either to untwisting [22–26] or twisting [27, 28] of the cholesteric helix, and this process is accompanied by a concomitant shift in the selective light reflection maximum. In most cases, this behaviour is related to light-induced photoprocesses which accompany changes in geometry of chiral photochromic groups and their helical twisting power.

Recently, we synthesized and studied copolymers containing phenyl benzoate nematogenic units and chiral photochromic monomer units with menthyl and azobenzene fragments which are capable of light-induced *E–Z* isomerization [25, 26]:



I

X=0.05-0.20.

Specific features of the photoisomerization were studied in detail and it was shown that such copolymers may be used for reversible data recording and storage.

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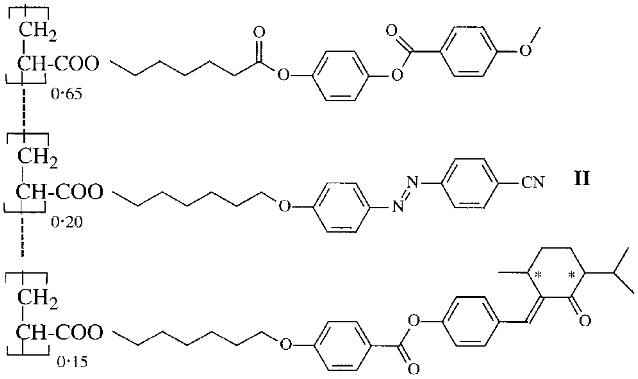
From our standpoint, investigation of the photo-orientation of azobenzene groups in such copolymers under the action of polarized light provides evident interests. It will allow us to understand whether such copolymers may be used for 'repeated' data recording by varying the helix pitch and selective light reflection wavelength, as well as by generation of photoinduced birefringence similar to common non-chiral azobenzene-containing polymers.

In work by Kreuzer *et al.*, cholesteric cyclosiloxane materials with azobenzene groups were studied, and the effect of polarized light on their planar oriented films was investigated [29, 30]. The phenomenon of generation of higher light reflection orders (second and third orders) was found. However, at present, no information concerning the kinetics of photo-orientation and photoinduced birefringence in cholesteric systems is available.

In the present work we focus on gaining this information and studying the photo-orientation processes in cholesteric copolymers. We have studied the binary copolymer **I** containing 15 mol % of combined chiral photochromic groups with menthyl and azobenzene fragments in one monomer unit, as well as a ternary copolymer **II** containing individual monomer units with nematogenic (phenyl benzoate), photochromic cyanoazobenzene, and chiral photochromic groups based on menthone:



II

As was shown in [31], upon UV irradiation of this copolymer *E–Z* isomerization of the menthone-containing groups occurs and is accompanied by untwisting of the cholesteric helix; at the same time, irradiation with polarized Ar^+ laser light allows one to perform holographic data recording on films of such a copolymer. This copolymer can be considered as a largely new material with dual photochromism, combining two different types of photosensitivity to light of different wavelengths. In this work, we have studied the kinetics of photo-orientation of the azobenzene groups under the action of polarized Ar^+ laser light.

Both copolymers form the chiral nematic phase with clearing temperatures of 111°C (**I**) and 107°C (**II**). For both copolymers, the glass transition temperature lies in the range 25–30°C.

The first stage of this work involved studying the photo-orientation in thin (below 1 μm) films of the copolymer prepared by spin-coating. We also studied the effect of film thickness and light intensity on the kinetics of the photo-orientation. Finally, we demonstrated the feasibility of using planar oriented films of the chiral nematic copolymers for optical data recording via photoinduced birefringence.

2. Experimental

Relative molecular masses of the copolymers were determined by gel permeation chromatography (GPC). GPC analyses were carried out with a Knauer instrument equipped with a 'Waters' (8 × 300 mm) column. Measurements were made by using a UV detector, THF as solvent (1 ml $\min^{-1}$, 40°C), a column of 10^3 Å; a calibration plot was constructed with polystyrene standards. The copolymers obtained had the following molar mass characteristics: $M_n = 7000–15\,000$, $M_w/M_n = 2.5–3.3$.

Phase transitions in the copolymers were studied by differential scanning calorimetry (DSC) using a Perkin Elmer DSC-7 thermal analyser (a scanning rate of 10 K $\min^{-1}$ was used, and prior to DSC measurements samples were annealed for one month at 45°C).

Investigations were also made using a Mettler TA-400 thermal analyser and an LOMO P-112 polarizing microscope was used for the optical microscopy.

The non-polarized UV irradiation was generated using a set of a XBO 150 W lamps, a water IR filter and metal interference filters (313 and 365 nm). The power density of the incident light was ~15 mW cm^{-2} for both wavelengths. After irradiation, absorbance spectra were recorded using a Lambda 2 (Perkin-Elmer) UV/visible spectrometer.

Thin films for photo-optical experiments were obtained by spin-coating using solutions in chloroform. To dry spin-coated films, they were annealed at 80°C during about 30 min. Thickness of the films was calculated from spectral data using values of the extinction coefficients of solutions of the copolymers in dichloroethane at 338 nm.

The photo-orientation experiments were performed with the linearly polarized beam of an Ar^+ laser at 488 nm (Innova 90/4 of Coherent). The excitation of the samples with linearly polarized light was carried out in the direction normal to the film. The orientational order was studied using polarized UV/visible spectroscopy, because the transition moment of the *E*-isomeric azobenzene moiety is directed along the long axis of the group. For this purpose the angular dependence of the absorbance was measured using a photodiode array UV/visible spectrometer (XDAP, Polytech) with a step-width of 5°.

The spectroscopic degrees of order (order parameter) were calculated by the formula

$$S = (A_\perp - A_\parallel)/(A_\perp + 2A_\parallel)$$

where $A_\parallel$ is the absorbance in the direction parallel to the electric vector of the incident light; $A_\perp$ is the absorbance perpendicular to this direction.

The optically induced birefringence was measured by standard methods [8–11] using a HeNe laser as the probe beam.

3. Results and discussion

3.1. *Principal features of photo-orientational behaviour in thin spin-coated films of the chiral nematic copolymers*

Let us first consider the photo-orientational processes in the thin spin-coated films of copolymers **I** and **II**. We studied two films of copolymer **I** with thickness ~0.24 and 0.6 µm; the film of copolymer **II** had a thickness of ~0.3 µm [25, 26, 31]. In these cases, the helix pitch is comparable to the film thickness (or even thinner). Hence, one may suggest that for the spin-coated films, the helical supramolecular structure is heavily deformed due to the boundary phenomena [32].

Figure 1 shows spectra for the films of copolymers **I** and **II** before and after irradiation. The long wavelength bands with maxima at 338 (copolymer **I**) and 369 nm (copolymer **II**) correspond to the π-π* transition of the azobenzene groups, whereas the short wavelength band relates to the phenyl benzoate fragment of copolymers **I** and **II**. In the case of copolymer **II**, one may observe the weak absorption of the menthone-containing chiral photochromic group in the spectral region about 300 nm. The weak π-π* transitions of both azobenzene groups at 450 nm are not shown in the spectra.

Irradiation with polarized Ar$^+$ laser light (488 nm) leads to photo-orientation of the azobenzene groups in the direction perpendicular to the electric vector of the incident light; hence, one observes a very pronounced linear dichroism (figures 1–3). The process takes place in the steady state of the *E*/*Z* photoisomerization, which is characterized by a small *Z* content at the excitation wavelength at 488 nm.

It follows from the above figures that upon irradiation with polarized light, not only the azobenzene but also the phenyl benzoate groups experience reorientation; that is, the process shows a well-defined co-operative character. However, for phenyl benzoate groups, the values of the linear dichroism and order parameter are somewhat lower, figures 3 (*a*) and 3 (*b*). Let us also note that, for copolymer **I**, the rate of growth in orientational order parameter is much lower; however, the limiting values of the order parameter in the photostationary state (about 0.4) are comparable to those of the non-chiral azobenzene-containing comb-shaped polymers which were studied in detail in [9, 10]. For copolymers **I** and **II**, the difference in the photo-orientation rates is likely to be related to the presence of the electron-acceptor CN and electron-donor alkoxy substituents in the azobenzene chromophore and, correspondingly, to the higher dipole moment of copolymer **II** [14].

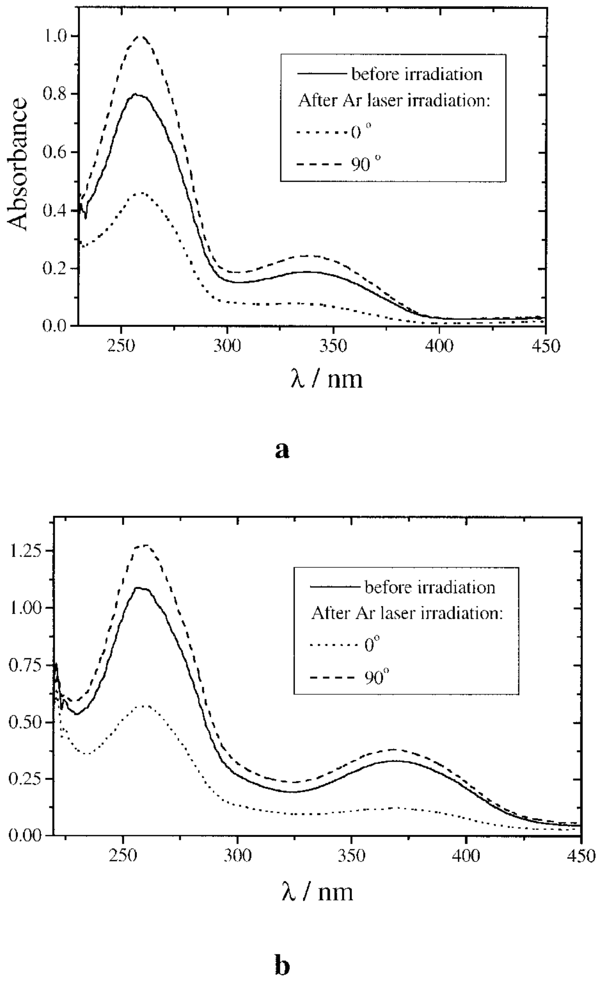
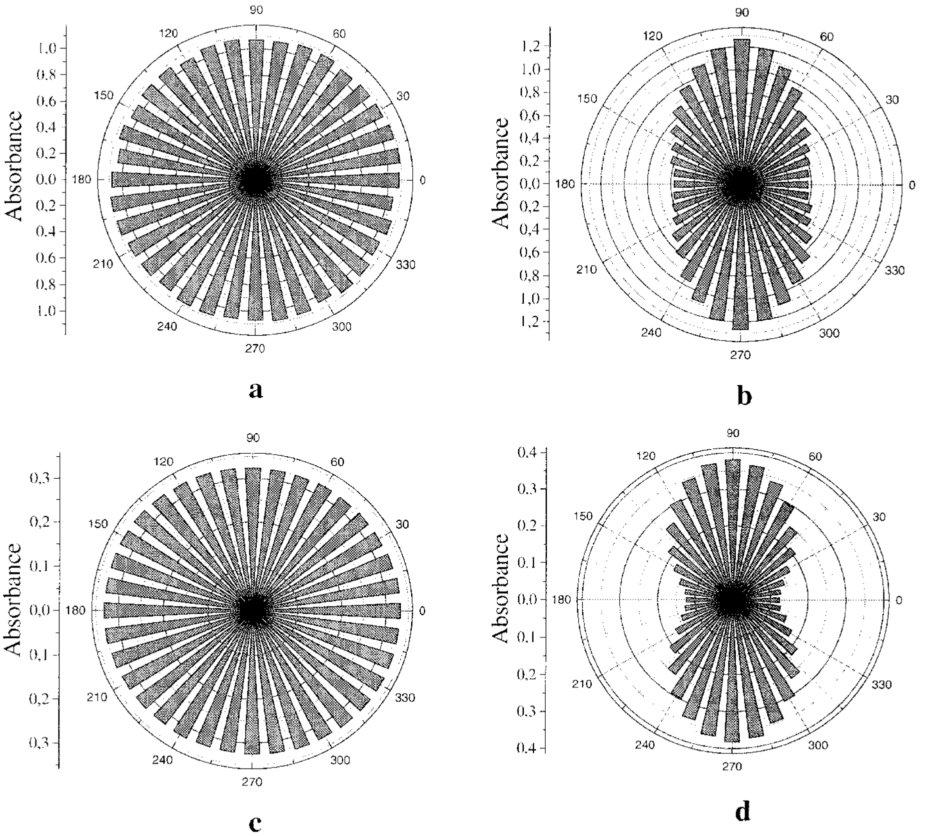


Figure 1. Linear dichroic spectra measured for spin-coated films of copolymer **I** (*a*) and **II** (*b*) before irradiation and after irradiation by Ar$^+$ laser (105 mW cm^{-2}) during 230 min (*a*) and 150 min (*b*); after-irradiation spectra were recorded along and perpendicular to the electric vector.

3.2. *The effect of various factors on the kinetics of the photo-orientational processes*

The photo-orientation rate of the side groups of copolymers is markedly controlled by the intensity of the incident light (figure 4). In this case, the dependence of the initial rate of the process on the light intensity shows a non-linear character, figure 4 (*b*).

The rate of photo-orientation is also controlled by the film thickness (figure 5). This difference may also be related to the fact that, in the case of the thicker film



a **b**

c **d**

Figure 2. Polar diagrams for copolymer **II** obtained before (*a*, *c*) and after irradiation (*b*, *d*) with the Ar$^+$ laser (105 mW cm^{-2}) during 150 min; $T = 22^\circ$C. Polar diagrams were plotted for $\lambda = 259$ nm (*a*, *b*) and 369 nm (*c*, *d*).

($\sim$0.6 µm), a more perfect helical supramolecular structure is developed and, hence, the photo-orientational process may be hindered. Generally, this effect can also be explained by the light intensity decrease which is more pronounced in the case of the thicker film. But as clearly seen from figure 1, the absorbance of the film for incident light wavelengths is very small and we can neglect this effect.

Let us consider now the effect of preliminary UV irradiation on the rate of photo-orientation. In this case, the films of copolymer **I** were irradiated with non-polarized UV light (365 nm) until the photostationary state was attained. The irradiated films of the copolymers contain a high concentration of the Z-isomer of the azobenzene groups. When such films are subjected to the action of polarized Ar$^+$ laser light, fast back Z–E isomerization and photo-orientation take place (figure 6).

It is interesting to note that, despite an evident difference in the content of E- and Z-isomers in the films of non-irradiated and UV-irradiated samples, in both cases, the initial rates of photo-orientation are almost the same. The reasons for this behaviour are still unclear, because some information concerning quite the reverse behaviour exists [33]: after preliminary UV irradiation, the rate of photo-orientation of azobenzene groups in polymers markedly increases. However, in the latter case, this behaviour is explained by the breakdown of aggregates of azobenzene groups taking place upon E–Z isomerization. In our case, the concentration of azobenzene groups is rather low (15%); hence, one can hardly anticipate the formation of aggregates.

A similar experiment was performed for copolymer **II**; however, in this case we used UV light with a wavelength of 313 nm. As has been shown earlier [31, 34], such irradiation primarily leads to the E–Z isomerization of menthone-containing chiral photochromic groups. In this case, the subsequent irradiation with polarized Ar$^+$ laser light does not lead to the Z–E isomerization of the methone-containing groups. As for copolymer **I**, the rate of growth of the spectral order parameter is almost the same (figure 7); however, the limiting value of the order parameter of the UV-irradiated film is much lower. In this case, E–Z isomerization of menthone-containing groups is likely to lead to a dramatic decrease in the ordering of the system due to the low anisometry of their Z-form.

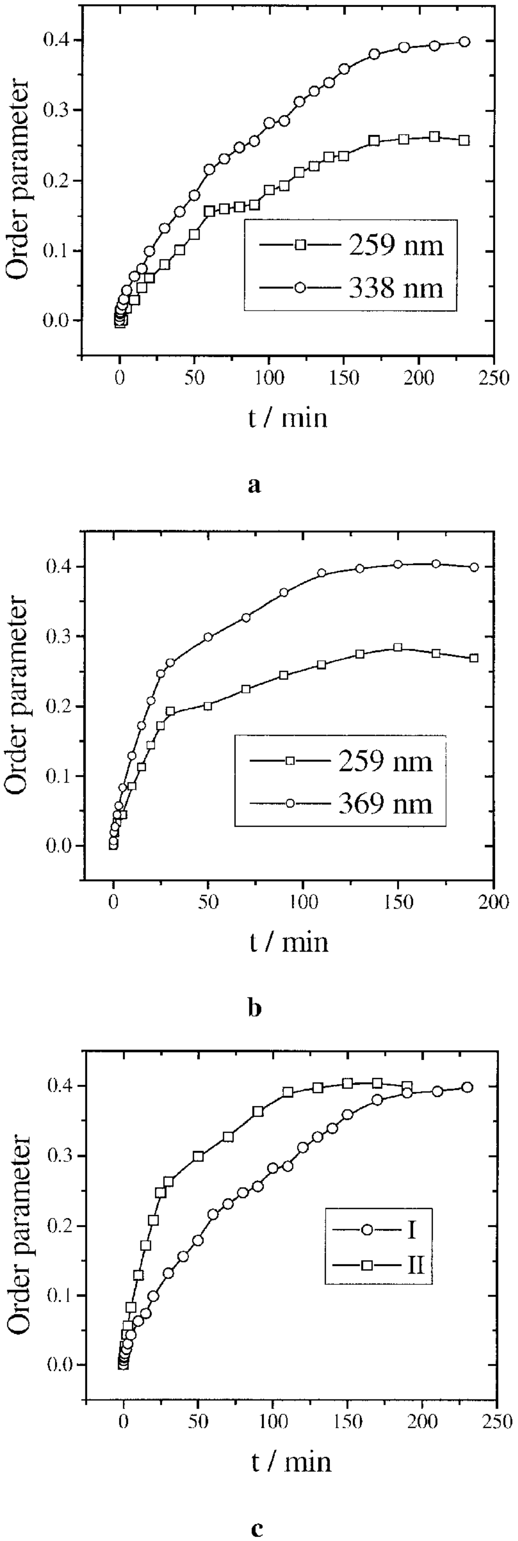


Figure 3. Change in order parameter for copolymer **I** (*a*) and **II** (*b*) during Ar$^+$ laser irradiation (105 mW cm^{-2}) calculated at different wavelengths; (*c*) shows the order parameter (calculated for wavelengths corresponding to the π-π* electronic transition of the azobenzene chromophores) for both copolymers as a function of time.

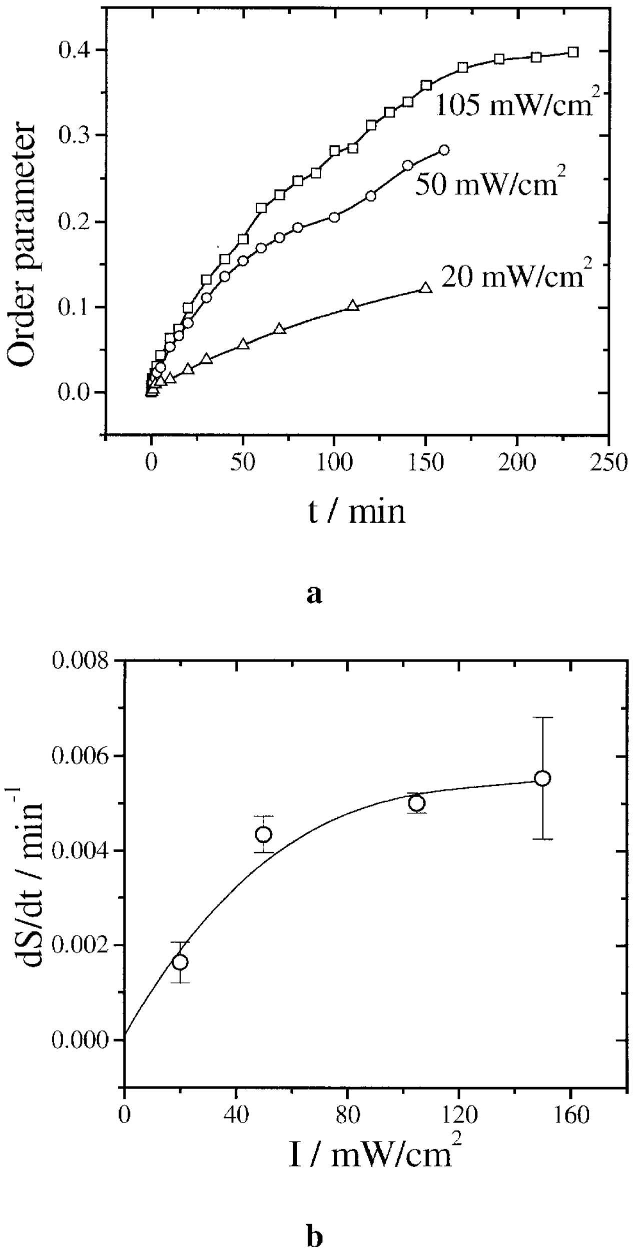


Figure 4. (*a*) Change of order parameter for copolymer **I** calculated at 338 nm during Ar$^+$ laser irradiation of varying intensity; (*b*) dependence of order parameter growth rate on the intensity of polarized light.

3.3. *Photoinduced growth of birefringence for planar oriented films of the chiral nematic copolymers*

For a planar oriented film of copolymer **I** with thickness 15 μm, we studied the growth in birefringence upon Ar$^+$ laser irradiation (figure 8). It follows from figure 8 that irradiation with polarized light leads to a development and growth in birefringence and, even within 30 min of the onset of irradiation, a photostationary state is attained. The maximum birefringence is 0.009. Once

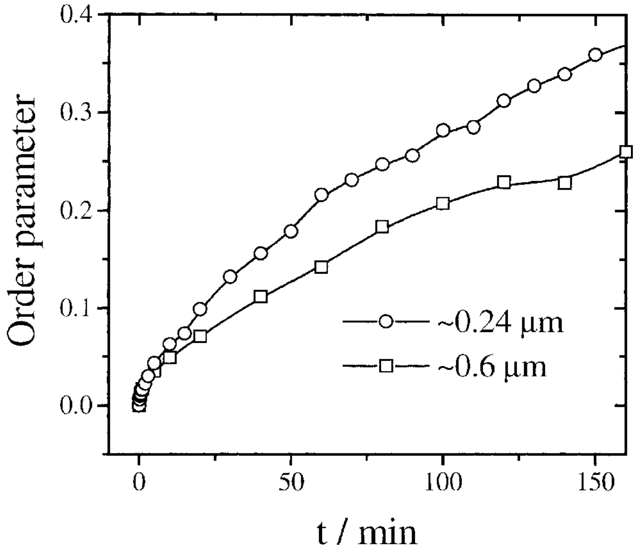


Figure 5. Change of order parameter calculated at 338 nm during Ar$^+$ laser irradiation for two copolymer **I** films of different thickness (intensity of the light 105 mW cm^{-2}).

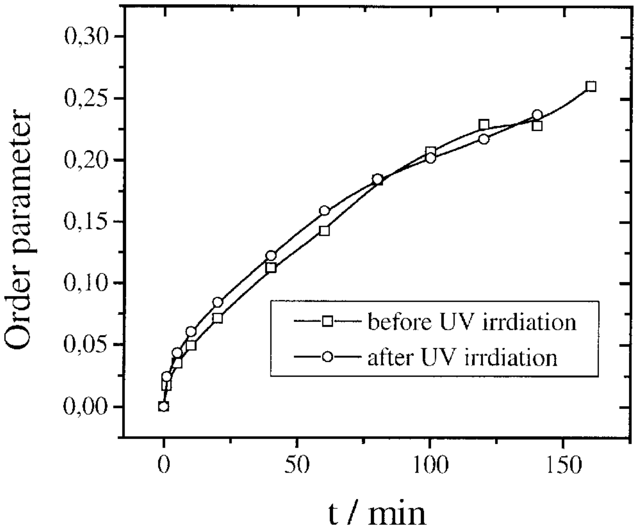


Figure 6. Kinetics of order parameter growth during photo-orientation for a copolymer **I** film with thickness ~0.6 μm irradiated and non-irradiated by unpolarized UV light; wavelength of UV light 365 nm, duration of UV irradiation 30 min, intensity of polarized Ar$^+$ laser light 105 mW cm^{-2}.

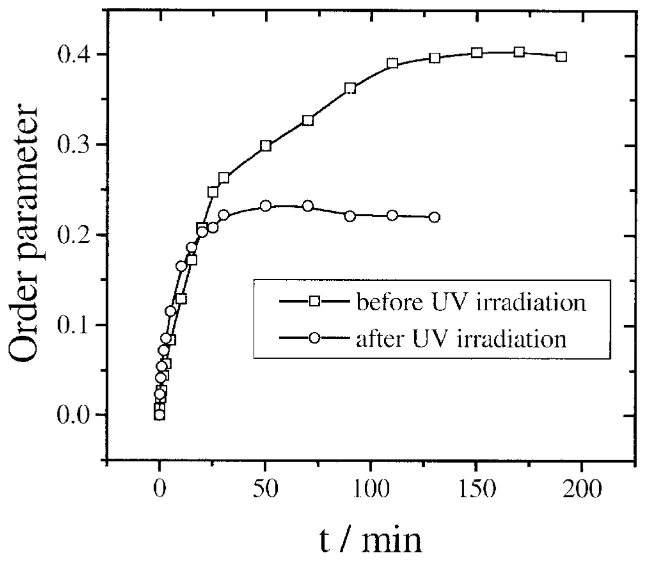


Figure 7. Kinetics of order parameter growth during photo-orientation for a film of copolymer **II** irradiated and non-irradiated before irradiation with unpolarized UV light; wavelength of UV light 313 nm, duration of UV irradiation 50 min, intensity of polarized Ar$^+$ laser light 105 mW cm^{-2}.

irradiation ceases, the value of Δn slightly decreases. To study the long term stability of the photoinduced birefringence, additional experiments are required.

After UV irradiation of the planar oriented film and a simultaneous annealing, the birefringence growth rate dramatically decreases; however, the maximum value of the birefringence is much higher, figure 8 (*b*). For the planar oriented film, UV irradiation and parallel annealing lead to a concomitant untwisting of the chiral nematic helix due to the lower value of the helical twisting power of the chiral photochromic groups of copolymer **I** in its *Z*-form. This decrease in growth rate is related to the appearance of light scattering which is associated with the development of defects in the planar texture upon helix untwisting [26, 27]. An increase in the maximum value of Δn may be explained by the fact that, in the system with a high helical pitch, the supramolecular structure 'prevents' photo-orientation to a lesser extent. (As is well known from the literature, for example, the threshold voltage corresponding to helix untwisting under the action of a magnetic or electric field is inversely proportional to the helical pitch [35].)

4. Conclusion

In this work, the specific features of the photo-orientational behaviour of chiral nematic copolymers under the action of polarized light have been studied for the first time. Such systems were chosen as promising materials for 'dual' data recording due to their changes in helix pitch or selective light reflection maximum, as well as to their photoinduced birefringence or linear dichroism. For example, it is possible to 'record' a coloured image using UV irradiation of planar oriented films of the copolymers heated well above the glass transition temperature. In this case the wavelength of the selective light reflection can be easily controlled by irradiation time and/or light intensity. Cooling the sample to room temperature is a simple way of saving the coloured image for a long period of time (at least, several months). Effective reading of recorded information

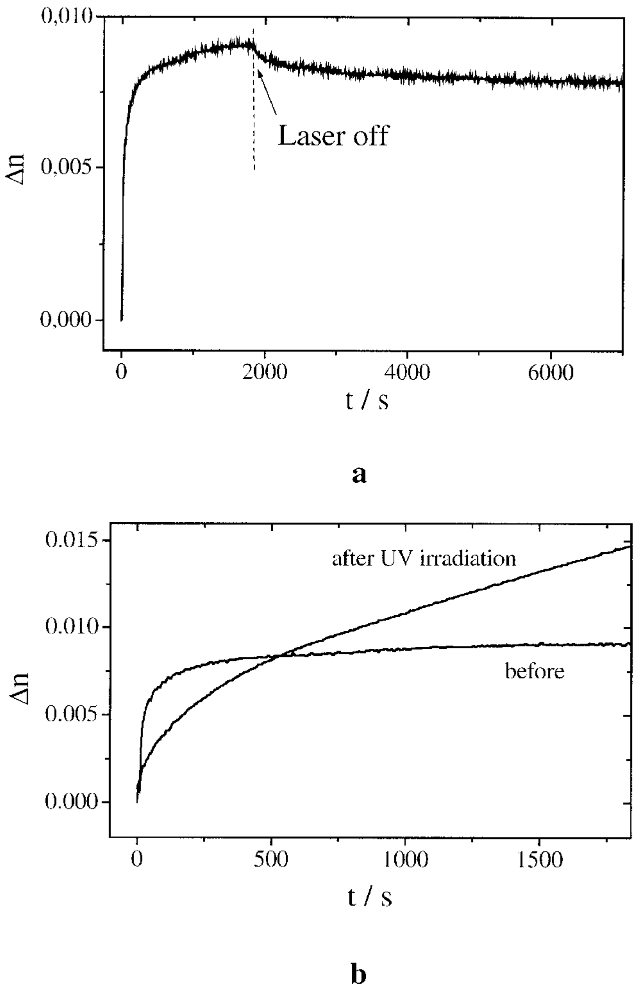


Figure 8. (*a*) Change in photoinduced birefringence for copolymer **I** during Ar$^+$ laser irradiation (107 mW cm^{-2}) and thermal relaxation after switching off the light (temperature of the sample 22°C). (*b*) Change in photoinduced birefringence for copolymer **I** during Ar$^+$ laser irradiation (107 mW cm^{-2}) before UV irradiation and after UV irradiation (365 nm, 60 min, temperature of sample 70°C).

can be achieved using circularly polarized visible light. But, in addition, the same film can be used for recording another optical informational level due to the action of visible polarized light. Information processing in this case is possible by using linearly polarized light with a wavelength far from a copolymer absorbance region, as well as from the selective light reflection peak.

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