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Photoinduced textural and optical changes in a cholesteric copolymer with azobenzene-containing side groups

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Textural changes induced by UV irradiation of planarly oriented films of a cholesteric copolymer were investigated. The copolymer is composed of photosensitive ethoxyazobenzene and chiral cholesterol-containing side groups, and displays a chiral nematic phase with a left-handed helical supramolecular structure in the temperature range 84–128°C. UV light with a wavelength of 365 nm leads to a deformation of the planar texture at temperatures higher than 100°C and to a reduction of the absorbance peak for left-handed circularly polarized light. Polarizing optical microscopy revealed the formation of a focal-conic texture in the irradiated regions. The texture induced by irradiation is very stable but the initial planarly oriented state can be recovered by mechanical stress. The observed phenomenon is attributed to the *E–Z* photoisomerization of azobenzene groups leading apparently to the formation of a thin isotropic layer in the films which in turn causes a destabilization of the planar texture. At temperatures below 100°C the textural transformations are accompanied by small shifts of the selective reflection maxima to longer wavelengths. The kinetics of the observed phenomenon were studied in detail and the influence of different parameters, such as light intensity and temperature, examined.

1. Introduction

Cholesteric liquid crystals display unique optical properties originating from the helical twisting of the nematic director [1]. Examples of these include the selective reflection of circularly polarized light with the appropriate handedness as well as the emission of light, fluorescence and electroluminescence, which is at least partially polarized. Over the last decade detailed investigations have been performed, devoted to the modification of these unique properties by photochemical means, both for low molar mass and polymer liquid crystals [2–27].

The approaches were based on photocontrol of the pitch height of the helix and thus of the location of the selective light reflection band. To this end chiral groups able to undergo *E–Z* isomerization were introduced. The isomerization process leads in these cases to a decrease of the helical twisting power of the chiral group and consequently to an increase of the pitch length [18–26]. Such effects can be used for optical storage (switching of the reflection colour) or to control

the state of polarization of fluorescence and electroluminescence, which again might be of interest not only for display application but also for storage.

A major drawback of most of these reported approaches was that the induced changes of the pitch length, and therefore of the optical properties, are irreversible. Only more recently copolymers and polymer mixtures containing azobenzene-based chiral photochromic groups have been reported, which display thermally and photochemically reversible pitch length variations [25, 26]. In addition, it was found that polymer systems containing photosensitive achiral groups can also be switched reversibly: upon annealing, the location of the selective reflection band relaxes back to its original wavelength range [28]. Such effects were found for mixtures of copolymers composed of azobenzene nematogenic groups, and menthyl-containing chiral groups as well as chiral dopants. Shifts of the selective reflection band of up to 300 nm could be achieved reversibly in such systems.

A characteristic feature of the studies reported above was that the optical properties were modified predominantly by controlling the pitch length. Here, we will

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consider materials in which the *E-Z* isomerization causes strong textural changes starting from planarly oriented films of cholesteric copolymers. These textural changes in turn modify the optical properties such as the magnitude of the selective light reflection band. In addition to this main effect, light-induced modifications of the pitch length will also contribute to changes of the optical performance.

Whereas previous studies have considered only non-polarized probing light beams, and furthermore have performed spectral investigations only after the exciting light was switched off, we have performed spectral investigations in the presence of UV and visible light excitation, thus also studying the kinetics of the light-induced changes. Our studies are concerned with a copolymer containing photosensitive ethoxyazobenzene and chiral cholesterol-containing side groups (figure 1) and we have investigated in detail the influence of parameters such as light intensity and temperature on the photochemically induced modifications of the optical properties as a function of their state of polarization. One conclusion which will emerge is that such systems can, in principle, be used for long-term optical storage.

2. Experimental

2.1. Samples

Ethoxyazobenzene and cholesterol-containing monomers were synthesized according to the procedures described in [29] and [30], respectively. The copolymer was synthesized by radical copolymerization of the monomers in benzene at 65°C; AIBN was used as an initiating agent. All the synthesized copolymer samples were purified by repeated precipitation with methanol and dried in vacuum.

The relative molecular mass of the copolymer was

determined by gel permeation chromatography (GPC). GPC analyses were carried out with a Knauer instrument equipped with a Knauer HPLC 64 column using a UV detector; THF was used as the solvent (1 ml min⁻¹, 40°C) and a calibration plot constructed with polystyrene standards. The copolymer has the following molar mass characteristics: $M_n = 8200$, $M_w/M_n = 1.3$.

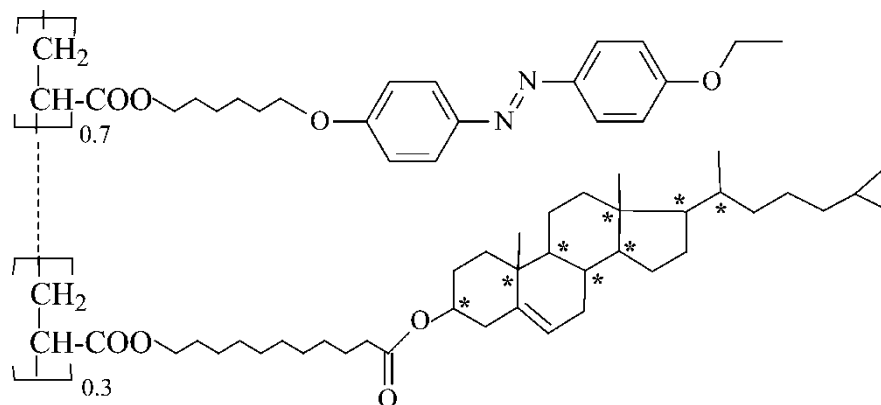
Phase transitions were studied by differential scanning calorimetry (DSC) with a Perkin Elmer DSC-7 thermal analyser (scanning rate 10 K min⁻¹). The chemical structure and the phase transitions of the copolymer are shown in figure 1. Polarizing microscopy was performed using a Mettler TA-400 thermal analyser and a LOMO P-112 polarizing microscope.

2.2. Optical experiments

Photochemical properties were studied using a special set-up (figure 2) equipped with a Xe lamp (1000 W, Müller Elektronik Optik), two monochromators (SpectraPro 300 I, Acton Research, Polytec), and controlled by an NCL single-channel spectroscopy detection system (Roper Scientific GmbH, Germany).

For light irradiation, a 200 W ultra-high pressure mercury lamp (Oriel Company) was used. Light with a maximum wavelength of 365 and 436 nm was selected using filters. The light intensity was equal to 3.4 mW cm⁻² for 365 nm and 14.8 mW cm⁻² for 436 nm. To prevent heating of the samples due to IR irradiation from the lamp, a water filter was used. During irradiation, a constant temperature of the test samples was maintained using a Mettler FP-80 heating unit.

The photochemical properties of the copolymer were studied by illuminating 20 μm thick films sandwiched



g 27 SmA 83-85 N* 127-128 I

Figure 1. Chemical structure and phase transitions of the copolymer under study.

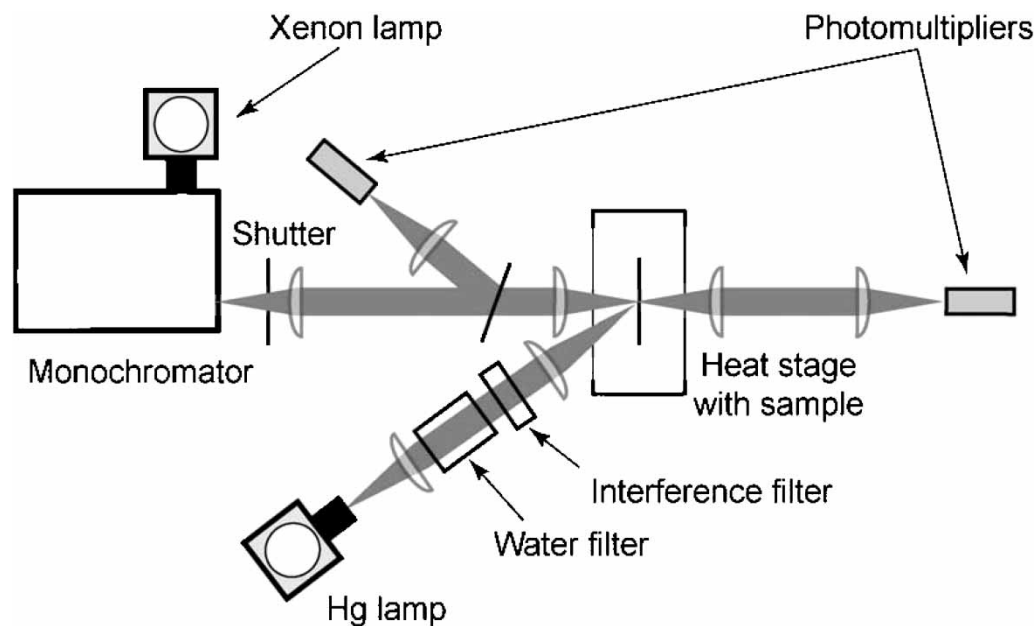


Figure 2. Principal scheme of the experimental set-up for photochemical study.

between two untreated flat glass plates. The thickness of the test samples was controlled by Teflon spacers. A planar texture was obtained by shear deformation of the samples, which were heated to temperatures well above the glass transition (120°C). During irradiation the absorbance spectra were recorded using the set-up described already.

3. Results

The copolymer forms a chiral nematic phase in the temperature range 84 – 127°C and a nonhelical smectic A phase below 84°C (figure 1). The glass transition temperature of the copolymer is about 27°C . Planarly oriented films of copolymer in the chiral nematic phase selectively reflect left-handed circularly polarized light, resulting in a strong absorbance peak for corresponding polarized light (figure 3(a)). The wavelength of the selective light reflection band is found to depend strongly on the temperature; a temperature decrease causes a strong shift to longer wavelengths (figure 3(b)). This phenomenon is associated with the formation and growth of smectic order fluctuations within the chiral nematic phase. The increasing tendency towards the formation of layer ordering leads to an increase in the twist elastic constant and thus to a helix untwisting [31, 32].

It should be emphasized that fast cooling of films from the chiral nematic state to temperatures in the neighbourhood of the glass transition allows the 'freezing-in' of the helical supramolecular structure preservation of the magnitude of the helix pitch and the

colour of the selective light reflection corresponding to the chiral nematic phase. At room temperature the wavelength of selective light reflection remains unchanged for at least several months.

Polarizing optical microscopy shows that UV irradiation causes the formation of a non-oriented focal-conics texture within the irradiated regions (figure 4). Figure 4 clearly shows that the planar texture observed before irradiation gives way to a light-scattering texture with small granular-like domains. The approximate size of these domains is in the range of 10 – $20\ \mu\text{m}$. This new photoinduced texture is very stable. Annealing of the films at temperatures corresponding to the range of the chiral nematic phase (84 – 127°C) does not induce a back relaxation to the planar texture. (It is important to note that the rate of the thermal back Z – E isomerization process is relatively high at these temperatures and the lifetime of the Z -isomer does not exceed several seconds [33].) Rapid cooling (in order to prevent the SmA phase texture formation) allows the stabilization of the scattering focal-conics state. Shearing induced by shifting the glass plates, on the other hand, restores the initial planar texture and absorbance properties. A more effective method for a back conversion to the homogeneous planar texture consists of heating the film to the isotropic state (above 128°C) followed by cooling into the chiral nematic phase, a shear process and subsequent annealing.

The interesting observation is that the UV light-induced textural changes have a strong effect on optical properties. UV light irradiation of planarly oriented

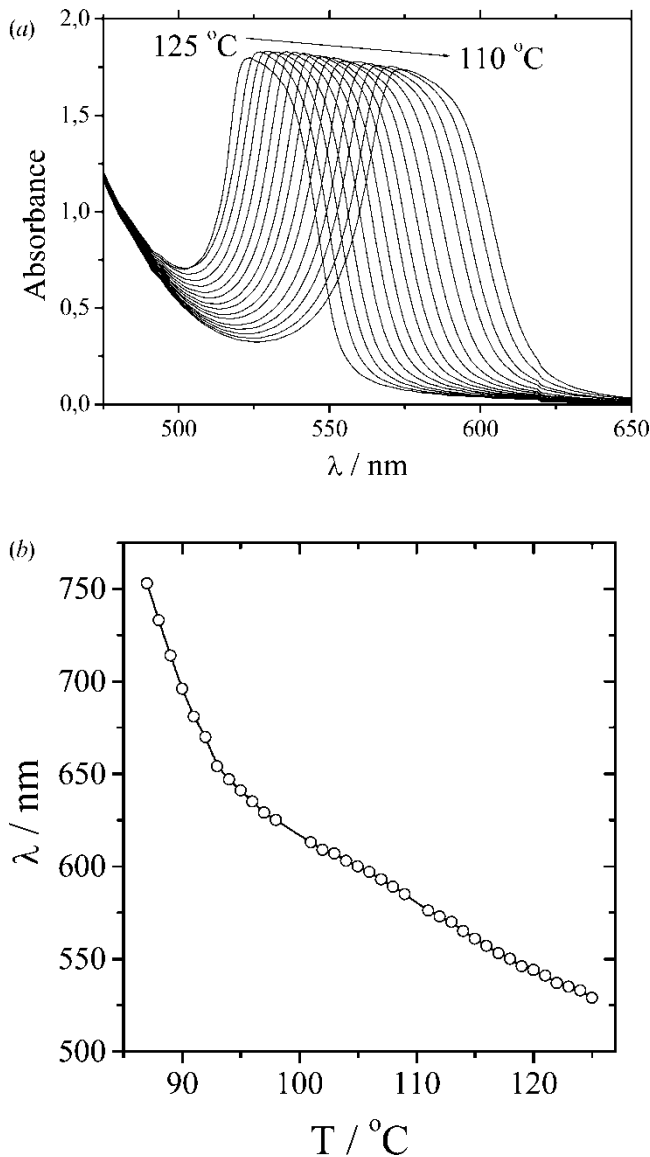


Figure 3. (a) Absorbance of left-handed circularly polarized light during cooling of the copolymer sample; (b) the temperature dependence of selective light reflection wavelength.

films at temperatures higher than 100°C causes a noticeable decrease of the absorbance for left-handed circularly polarized light (figure 5). An interesting feature is that absorbance spectra for unpolarized light remain almost unchanged (figure 6(a)), whereas a small increase of absorbance was found for right-handed circularly polarized light (figure 6(b)). A slight decrease in absorbance is found in the spectral range below the selective light reflection band (figure 5). Such behaviour obviously results from the noticeable light scattering effects induced via textural changes by UV irradiation.

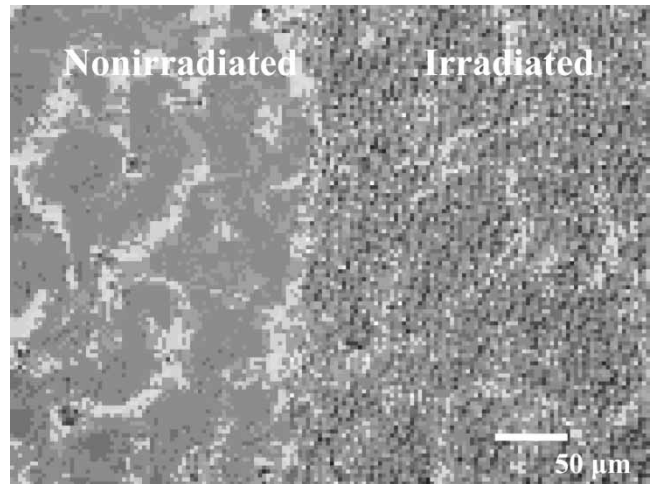


Figure 4. Microphotograph showing the textural changes occurring after UV light irradiation. Temperature of the sample was 120°C, irradiation time 60 min; after irradiation the film was cooled rapidly to room temperature.

The rate of decrease of the left-handed light absorbance is strongly influenced by temperature: the process is faster at higher temperatures. This is apparent from figure 7 showing the decay of absorbance with time at different temperatures for a constant light intensity.

Novel features occur if the irradiation is interrupted before the steady state is achieved, as shown in figure 8. The magnitude of the absorbance for left-handed circularly polarized light suddenly drops by a significant degree after switching off the UV light (figure 8). In the case of repeated cycles involving irradiation and

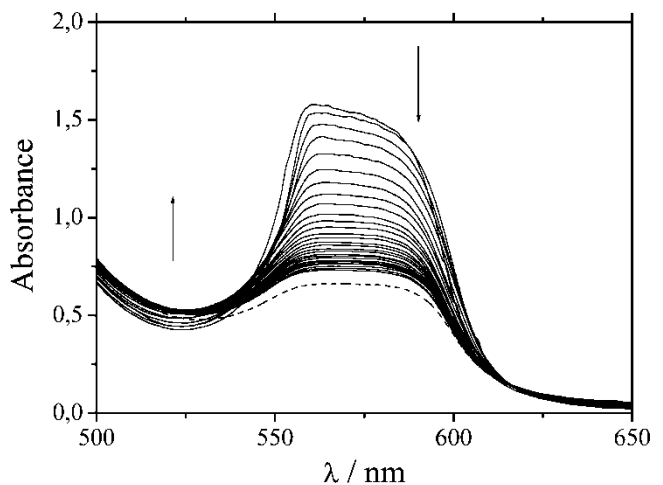


Figure 5. Changes of absorbance of left-handed circularly polarized light during UV irradiation (365 nm, 3.6 mW cm^{-2}). Spectra were recorded every 1 min of irradiation; temperature of the sample was 115°C; dashed line corresponds to 50 min of irradiation.

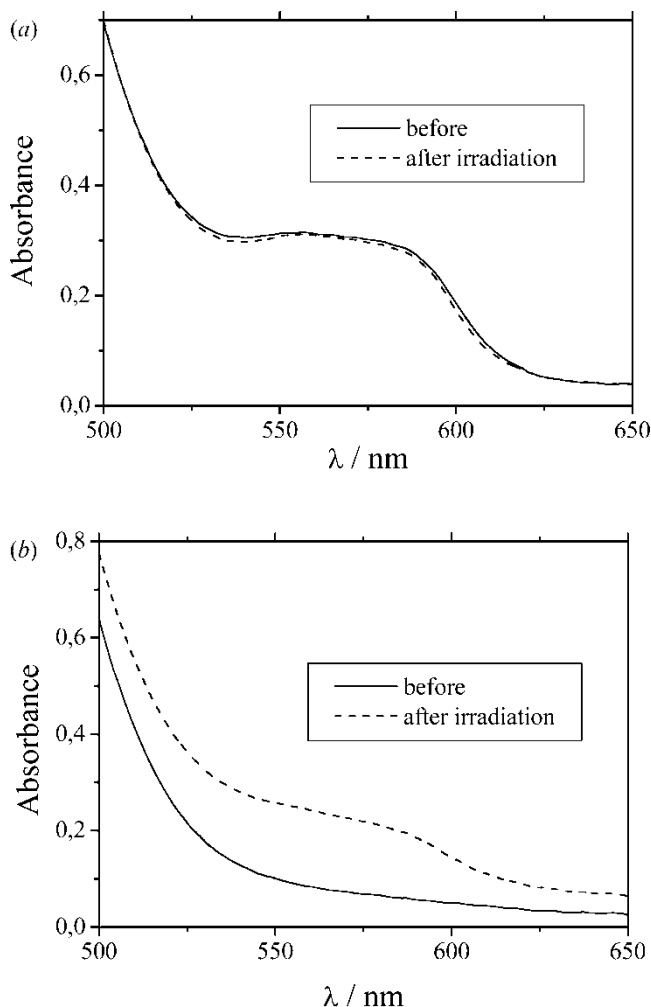


Figure 6. Absorbance spectra of (a) non-polarized and (b) right-handed circularly polarized light, before and after UV irradiation (60 min, 365 nm, 3.6 mW cm⁻²). Temperature of the sample is 115°C.

annealing the induced modulation of the absorbance assumes a rather complicated character, as seen in figure 9. Within the first 80 min of UV irradiation a systematic decrease of absorbance together with small modulations takes place. As also seen from this figure the modulations of the absorbance are in the opposite sense in the region outside the selective reflection band (this absorbance corresponds to light scattering on textural defects) at least for shorter irradiation times.

We also studied the influence of the magnitude of the light intensity on the rate of modulation of the absorbance during UV irradiation. Figure 10 shows a non-linear dependence of the maximum rate of absorbance change on the intensity. These data suggest the presence of a threshold light intensity of about 1 mW cm⁻² for the observed textural transformation phenomena.

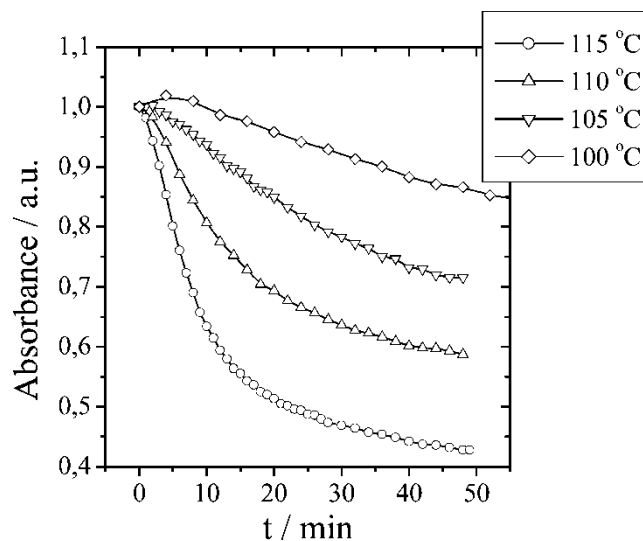


Figure 7. Rates of change of absorbance maximum for left-handed circularly polarized light during UV irradiation (365 nm, 3.6 mW cm⁻²) at different temperatures.

At temperatures below 100°C the rate of decrease of the absorbance becomes very slow and an additional process is observed in films of the copolymer: specifically, a helix untwisting and a shift of the selective light reflection band to longer wavelengths (figures 11, 12). This process is thermally reversible, and

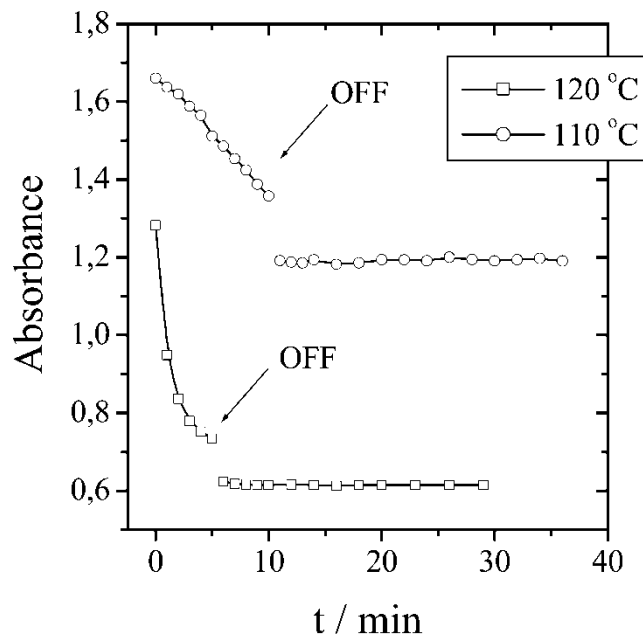


Figure 8. Rates of change of absorbance maximum for left-handed circularly polarized light during UV irradiation (365 nm, 3.6 mW cm⁻²) at different temperatures. The UV light was switched off after 5 min (120°C) and 10 min (110°C).

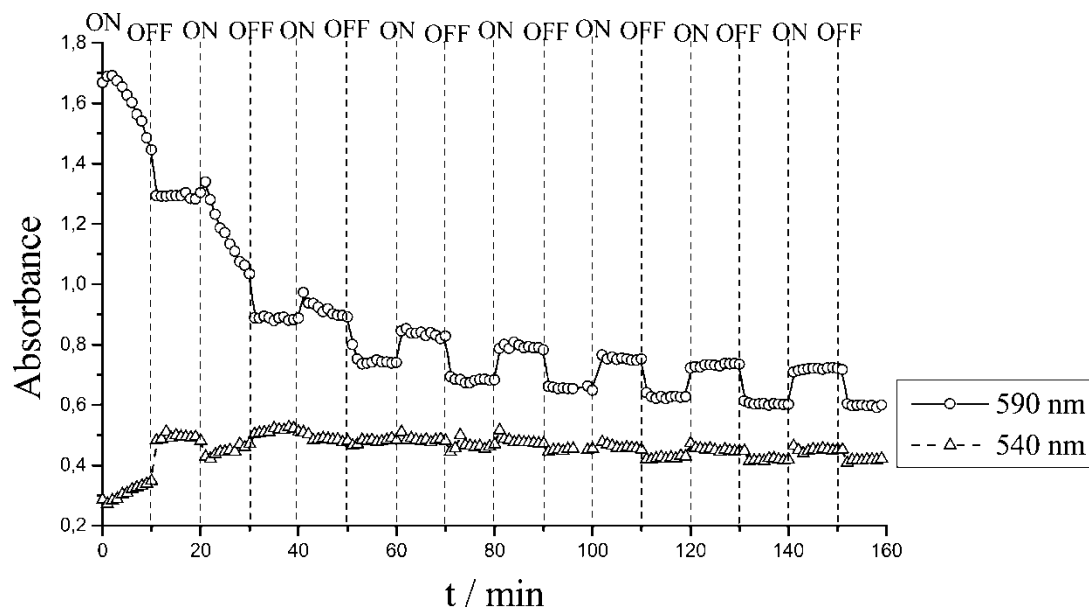


Figure 9. Changes of absorbance of left-handed circularly polarized light at different wavelengths during irradiation–annealing cycles at 110°C.

annealing at the same temperatures leads to a relaxation of the selective reflection band to its initial spectral position (figure 11). It is interesting to note that annealing the sample for about 15 min after switching off the UV light results not only in a shift of the peak

but also in an additional decrease in the absorbance of left-handed circularly polarized light. The magnitude of the shift of the reflection band is noticeably higher at lower temperatures (figure 12).

Finally we would like to point out that irradiation of planarly oriented films with visible light (436 nm) does not result in any textural changes and thus does not affect the polarized and unpolarized absorbance spectra.

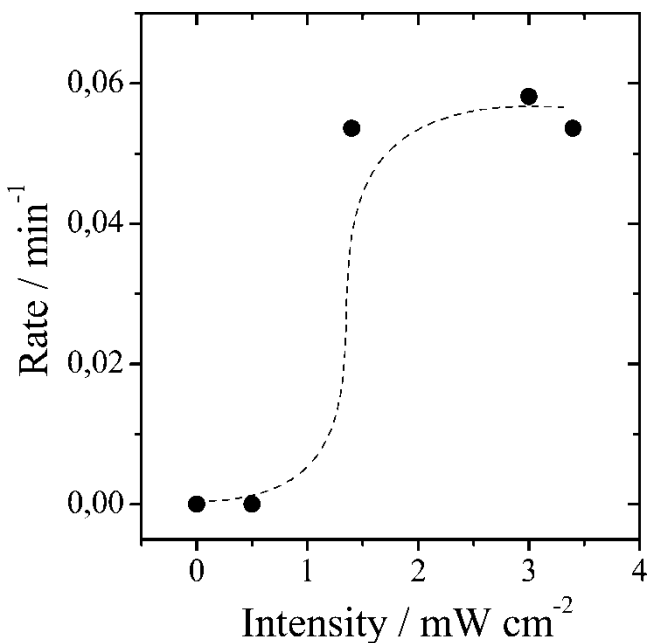


Figure 10. Maximum rates of change of absorbance maximum for left-handed circularly polarized light during UV irradiation (365 nm) with different light intensities (line is to guide the eye only). Temperature of the sample was 110°C.

4. Discussion

The experimental results reported indicate that an unusual textural phenomenon occurs. The homogeneous planar texture is destroyed by UV irradiation; the UV irradiation leads to *E*–*Z* photoisomerization of azobenzene units the *Z*-isomer tends to act as a non-mesogenic additive due to its bent shape, and thus destroys the mesophase structure (figure 13) [34–36]. We can expect that most of the *Z*-isomers produced are located in the top layer oriented towards the irradiation source, since the absorbance of the copolymer film is very high at 365 nm (more than 2). In this part of the polymer film an isothermal transition from the chiral nematic to the isotropic state takes place. Such an isothermal phase transition had been reported for nematic polymers previously by Ikeda *et al.* [34–36]. Obviously a thin isotropic layer is formed close to the upper glass plate. In the case of the cholesteric copolymer under study, this leads to a decrease of left-handed circularly polarized absorbance due to a

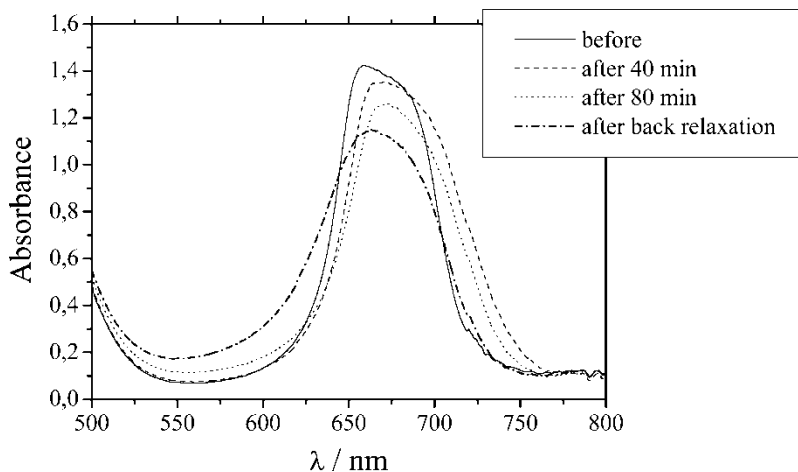


Figure 11. Changes of absorbance spectra of left-handed circularly polarized light during UV irradiation at 95°C and after 20 min annealing at the same temperature after switching off the light.

decrease of the thickness of the copolymer film in its chiral nematic state.

After switching off the UV light, an isothermal transition back to the chiral nematic phase is observed which is accompanied by the formation of a non-oriented helical structure, i.e. a focal-conic texture. The strongly light-scattering focal-conic texture is characterized by a lower intensity of left-handed circularly polarized light reflection, whereas the right-handed component of the reflected light becomes more pronounced (figure 6(b)).

The threshold behaviour of the system with respect

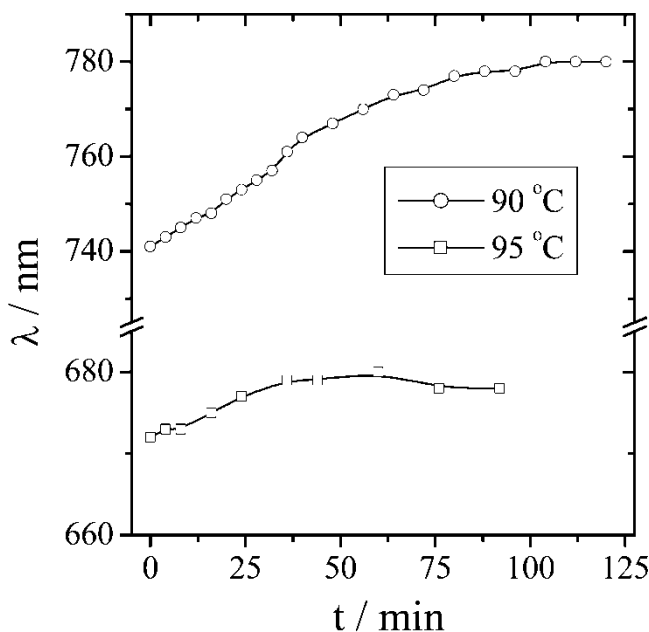


Figure 12. Kinetics of helix untwisting at different temperatures.

to the light intensity needed to induce textural changes is in agreement with this model, i.e. a certain concentration of the non-mesogenic *Z*-isomer, and thus a certain light intensity, is needed at each temperature to induce an isothermal phase transition.

The rate of the textural transformation process is strongly decreased at lower temperatures because a higher concentration of *Z*-isomer is needed for a transition to the isotropic state. On the other hand the *E*–*Z* isomerization process of azobenzene is thermally reversible and the rate of this back-isomerization increases at higher temperatures. This superposition of effects is responsible for the fact that the concentration of *Z*-isomers throughout the whole film becomes significant at temperatures below 100°C, despite the very high absorbance of the films. A small untwisting of the cholesteric helix is therefore observed. A further decrease of the temperature causes an increase of the concentration of *Z*-isomers and a shift of the selective light reflection band to the longer wavelength spectral region. This phenomenon was observed previously [28] and can be explained by a decrease in the orientational order parameter due to the development of the bent *Z*-form of the azobenzene groups. In turn, as the orientational order parameter is decreased, untwisting of the cholesteric helix takes place [31, 32].

In conclusion we have shown photochemically induced textural changes in planarly oriented films of an azobenzene-containing copolymer. UV irradiation leads to the formation of a focal-conic texture causing a strong scattering of the incident light. The photo-induced texture is thermally stable in the cholesteric mesophase, but the initial planarly oriented state can be restored by appropriate means.

At temperatures below 100°C an additional process,

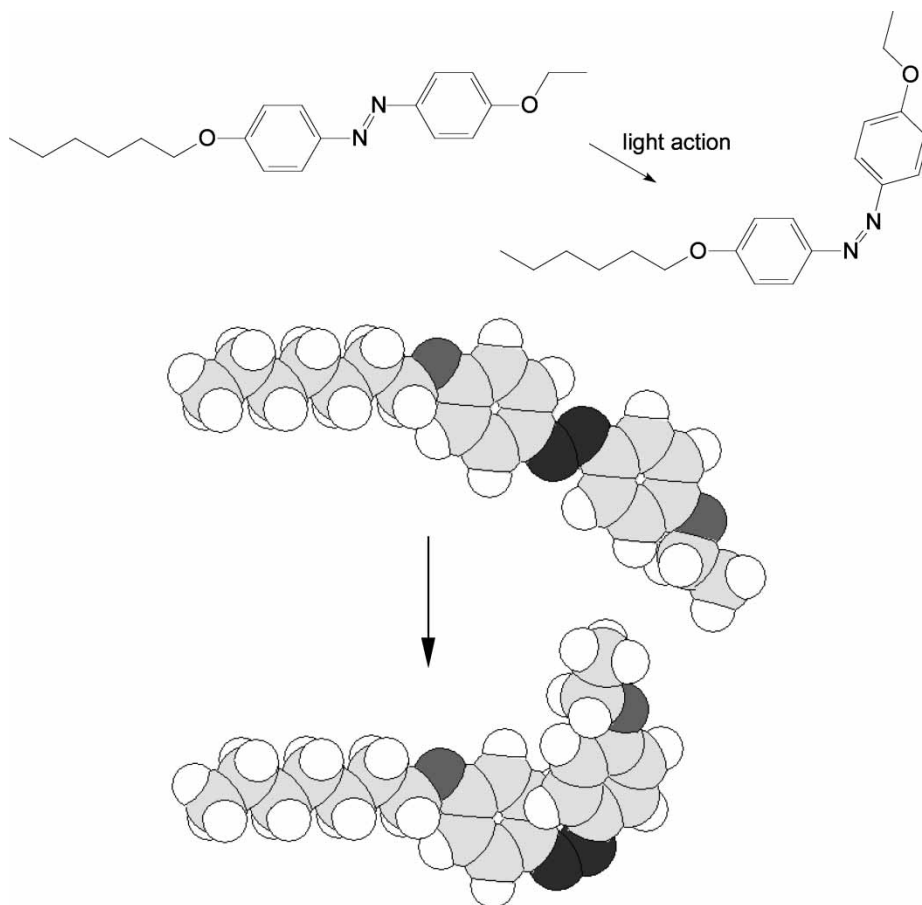


Figure 13. *E-Z* photoisomerization process of azobenzene fragments in the copolymer films.

involving the helix untwisting and a shift of the selective light reflection maximum to longer wavelengths, is observed. In all cases rapid cooling of films to room temperature causes a ‘freezing-in’ of the textures for a long time period (months). The observed effects can be used for optical data recording and long-term storage.

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References

- [1] DUNMUR, D., and TORIYAMA, K., 1998, *Handbook of Liquid Crystals*, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Vol.1 (Wiley-VCH), p.215.
- [2] KURIHARA, S., KANDA, T., NAGASE, T., and NONAKA, T., 1998, *Appl. Phys. Lett.*, **73**, 2081.
- [3] ZHANG, M., and SCHUSTER, G. B., 1992, *J. phys. Chem.*, **96**, 3063.
- [4] LEMIEUX, R. P., and SCHUSTER, G. B., 1993, *J. org. Chem.*, **58**, 100.
- [5] ZHANG, M., and SCHUSTER, G. B., 1994, *J. Am. chem. Soc.*, **116**, 4852.
- [6] JANICKI, S. Z., and SCHUSTER, G. B., 1995, *J. Am. chem. Soc.*, **117**, 8524.
- [7] FERINGA, B. L., HUCK, N. P. M., and DOREN, H. A. V., 1995, *J. Am. chem. Soc.*, **117**, 9929.
- [8] YOKOYAMA, Y., and SAGISAKA, T., 1997, *Chem. Lett.*, 687.
- [9] FERINGA, B. L., VAN DELDEN, R. A., KOUMURA, N., and GEERTSEMA, E. M., 2000, *Chem. Rev.*, **100**, 1789.
- [10] SERAK, S. V., ARIKAINEN, E. O., GLEESON, H. F., GROZHIK, V. A., GUILLOU, J.-P., and USOVA, N. A., 2002, *Liq. Cryst.*, **29**, 19.
- [11] KURIHARA, S., NOMIYAMA, S., and NONAKA, T., 2001, *Chem. Mater.*, **13**, 1992.
- [12] KOMITOV, L., RUSLIM, C., and ICHIMURA, K., 2000, *Phys. Rev. E*, **61**, 5379.
- [13] MORIYAMA, M., SONG, S., MATSUDA, H., and TAMAOKI, N., 2001, *J. mater. Chem.*, **11**, 1003.
- [14] RUSLIM, C., and ICHIMURA, K., 2000, *J. phys. Chem. B*, **104**, 6529.
- [15] TAMAOKI, N., SONG, S., MORIYAMA, M., and MATSUDO, H., 2000, *Adv. Mater.*, **12**, 94.

- [16] LEE, H.-K., DOI, K., HARADA, H., TSUTSUMI, O., KANAZAWA, A., SHIONO, T., and IKEDA, T., 2000, *J. phys. Chem. B*, **104**, 7023.
- [17] CHEN, S. H., JIN, R. J., KATSIS, D., MASTRANGELO, J. C., PAPERNOV, S., and SCHIMD, A. W., 2000, *Liq. Cryst.*, **27**, 201.
- [18] BOBROVSKY, A. YU., BOIKO, N. I., and SHIBAEV, V. P., 1998, *Polym. Sci. A*, **40**, 232.
- [19] BREHMER, M., LUB, J., and VAN DE WITTE, P., 1999, *Adv. Mater.*, **10**, 1438.
- [20] BREHMER, M., LUB, J., and VAN DE WITTE, P., 1999, *Mol. Cryst. liq. Cryst.*, **331**, 333.
- [21] VAN DE WITTE, P., GALAN, J. C., and LUB, J., 1998, *Liq. Cryst.*, **24**, 819.
- [22] BOBROVSKY, A. YU., BOIKO, N. I., and SHIBAEV, V. P., 1998, *Liq. Cryst.*, **25**, 679.
- [23] BOBROVSKY, A. YU., BOIKO, N. I., and SHIBAEV, V. P., 1999, *Liq. Cryst.*, **26**, 1749.
- [24] VAN DE WITTE, P., NEUTEBOOM, E. E., BREHMER, M., and LUB, J., 1999, *J. appl. Phys.*, **85**, 7517.
- [25] BOBROVSKY, A. YU., BOIKO, N. I., SHIBAEV, V. P., and SPRINGER, J., 2000, *Adv. Mater.*, **12**, 1180.
- [26] BOBROVSKY, A. YU., BOIKO, N. I., SHIBAEV, V. P., and SPRINGER, J., 2001, *Liq. Cryst.*, **28**, 919.
- [27] HATTORI, H., and URYU, T., 2001, *Liq. Cryst.*, **28**, 1099.
- [28] BOBROVSKY, A. YU., and SHIBAEV, V. P., 2003, *Liq. Cryst.*, **30**, 671.
- [29] KOSTROMIN, S. G., STAKHANOV, A. I., and SHIBAEV, V. P., 1996, *Polym. Sci. A*, **38**, 1030.
- [30] BOIKO, N. I., 1987, *PhD thesis*, Moscow State University (in Russian).
- [31] CHILAYA, G. S., and LISETSKI, L. N., 1986, *Mol. Cryst. liq. Cryst.*, **140**, 243.
- [32] LISETSKI, L. N., TOLMACHEV, A. V., and TISHCHENKO, V. G., 1978, *Pis'ma Zh. eksp. teor. Fiz.*, **23**, 205.
- [33] WANG, G., and WEISS, R. G., 2003, *Macromolecules*, **36**, 3833.
- [34] YAMAMOTO, T., OHASHI, A., YONEYAMA, S., HASEGAWA, M., TSUTSUMI, O., KANAZAWA, A., SHIONO, T., and IKEDA, T., 2001, *J. phys. Chem. B*, **105**, 2308.
- [35] YAMAMOTO, T., HASEGAWA, M., KANAZAWA, A., SHIONO, T., and IKEDA, T., 2000, *J. mater. Chem.*, **10**, 337.
- [36] HASEGAWA, M., YAMAMOTO, T., KANAZAWA, A., SHIONO, T., and IKEDA, T., 1999, *Adv. Mater.*, **11**, 675.