A study of photooptical processes in photosensitive cholesteric azobenzene-containing polymer mixture under an action of the polarized and nonpolarized light

Alexey Bobrovsky *, Valery Shibaev

Faculty of Chemistry, Moscow State University, Leninskie gory, Lenin Hills, 119992 Moscow, Russian Federation

Abstract

New liquid crystalline cholesteric mixture consisting of azobenzene-containing side-chain copolymer and the chiral low-molar-mass dopant (5%) was prepared and its properties were studied. It was shown that freshly prepared spin-coated thin films are optically isotropic. However, the films possess a noticeable circular dichroism with a maxima corresponding to the absorbance of the nonchiral azobenzene fragments. This phenomenon is an evidence for the existence of the helical supramolecular structure elements in the mixture films. An annealing of the films at temperatures above the glass transition leads to the strong increase in the circular dichroism due to formation of the perfect cholesteric phase. UV light irradiation results in the E–Z isomerization of azobenzene groups and the significant drop in circular dichroism values (almost to zero) both for the fresh and the annealed films that is associated with the transition from cholesteric to the fully isotropic state. An action of polarized UV and visible light leads to the photoorientation of azobenzene groups perpendicular to the electric vector of the polarized light. Kinetic features of the photoorientation processes in cholesteric phase in comparison with nematic systems were studied. It has been experimentally found that the helical order to some extent prevents the photoorientation of the side groups. Upon UV irradiation of the thick, planarly-oriented films of the mixture at temperatures higher than glass transition, the selective light reflection maximum is shifted to the long-wavelength spectral region. All photoinduced phenomena occurring in the mixture are thermally reversible and annealing of the films at temperatures above glass transition results in the back recovery to the cholesteric nonoriented state and to the initial helix pitch value.
© 2006 Elsevier Ltd. All rights reserved.

Keywords: Azobenzene-containing copolymer; Cholesteric mixture; Photoorientation

1. Introduction

After a discovery of the photoorientation phenomena in dye-containing compounds (frequently called as Weigert effect [1]) a huge number of publications dealing with the study of the similar effects in azobenzene-containing low-molar-mass and polymer systems have been appeared [2–37]. One of the mechanisms of photoorientation is based on the photoinduced E–Z isomerization of the azobenzene chromophores, accompanied by their movement and rearrangement so that their long axes are oriented perpendicular to the electric field vector of the polarized light.

Majority of such publications deals with investigation of photoselection and photoorientation processes in amorphous and liquid crystalline polymers of nematic or smectic type. Several recent papers considered an induction of chirality in amorphous or liquid crystalline polymers [11–14] and only few papers describe photoorientation phenomena in cholesteric systems [15,34,35]. However, many details of mechanism of the photoorientation as well as an influence of the helical supramolecular structure on the kinetics of photoprocesses and degree of photoinduced order remain unknown.

It is well-known that the cholesteric phase has unique optical properties; the most important of them are the very large optical rotation and the selective light reflection [38–40]. The influence of the helical supramolecular structure of the cholesteric phase on various peculiarities of the photoselection and photoorientation of the photosensitive fragments is still unclear. It would be very interesting to study a competition between a helical organization of mesogens and chromophore tendency to uniaxial orientation induced by photoselection process under polarized light irradiation. The exploitation of the optical peculiarities of these photoinduced processes in

* Corresponding author. Tel.: +7 959 395 416; fax: +7 959 390 174.
  E-mail address: bbrvsky@yahoo.com (A. Bobrovsky).

such optically active media could be also very tempting task from an application point of view.

In our previous paper [41], we studied photoorientation phenomena and chiro-optical properties of azobenzene-containing cholesteric copolymer. This polymer formed a smectic phase at room temperature in addition to the high-temperature cholesteric phase. This fact complicated the photooptical study of the polymer due to the strong tendency of the samples to homeotropic orientation or out-of-plane order formation. Both, annealing of thin films and their irradiation with nonpolarized or polarized light led to the homeotropic orientation of the side groups. Such effects strongly competed with in-plane orientation processes under polarized light action and, as a result strongly decrease value of maximal dichroism and in-plane degree of orientational order.

In this paper, we have focused our attention on investigation of purely cholesteric polymer system forming only one cholesteric mesophase over a wide temperature range.

For this purpose, we have prepared a new polymer mixture consisting azobenzene-containing copolyacrylate **PAAzo8** and chiral dopant based on isosorbitol, **HexSorb**.

PAAzo8

HexSorb (5 wt%)
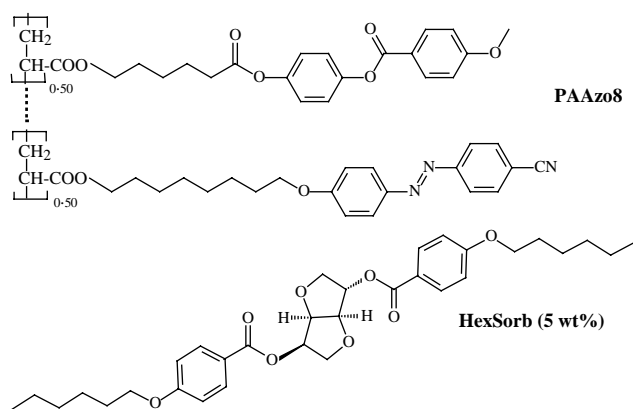
Homopolymer of the cyanoazobenzene-containing mono-mer forms only smectic phase [42], that is why the monomer was copolymerized with the nematogenic phenylmethoxy-benzoate monomer. As a result, copolymer **PAAzo8** displays only nematic phase with the high clearing temperature 122–124 °C and glass transition temperature of about 25 °C. Its mixture with **HexSorb** (5 wt%) displays cholesteric (chiral nematic) phase with the following transition temperatures: g ∼25 N* 112–113 I

The main objective of this work is the study of the peculiarities of photoorientation processes induced in choles-teric polymer films under the action of polarized light. Particular attention is given to the study of the influence of different factors, such as, the incident light wavelength, thermal treatment, prehistory of the films, on the kinetics of photoorientation and values of the photoinduced dichroism.

2. Experimental

4-Cyanoazobenzene and 4-phenyl-4′-methoxybenzoate monomers were synthesized according to the procedures described in [42,43], respectively. Chiral dopant **HexSorb**

was synthesised according standard esterification method using DCC [44]. The copolymer was synthesized by radical polymerization of monomers in benzene solution at 65 °C; AIBN was used as an initiating agent. The synthesized polymer was purified by the repeated precipitation with methanol and dried in vacuum.

The phase transitions of the polymer and mixture 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.

Thin films of the mixture and copolymer for photo-optical experiments were obtained by spin-coating technique using solutions of different concentration in chlorohorm. For drying the spin-coated films were kept at room temperature during one day. Thickness of the films was 100–200 nm as estimated from the UV–visible spectral data.

The photochemical properties were studied using a special instrument equipped with a DRSh-250 ultra-high pressure mercury lamp. Light with wavelengths 365 and 436 nm was selected using interference filters. To prevent heating of the samples due to IR irradiation of the lamp, water filter was used. To obtain plane-parallel light beam, quartz lens was used. Polarized light was obtained by using Glan–Taylor polarizer. The intensity of light was equal to $1.0 \text{ mW} \times \text{cm}^{-2}$ (365 nm) and $0.5 \text{ mW} \times \text{cm}^{-2}$ (436 nm), as measured by LaserMate-Q (Coherent) intensity meter. Spectral measurements were performed using Unicam UV-500 spectrophotometer and JASCO J-500C spectropolarimeter.

The orientational order was studied using polarized UV–visible 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 polarized light absorbance was measured using a photodiode array UV–visible spectrometer (J&M) with a step-width of 10°.

The dichroism and spectral order parameter values were calculated from the spectra using the following Eqs. (1) and (2)

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

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

where D is the dichroism, S is the order parameter, $A_{\parallel}$ is the absorbance at the preferred direction; $A_{\perp}$ is the absorbance perpendicular to this direction.

To study the out-of plane photoorientation phenomena we measured the angular distribution of the polarized absorbance spectra at an angle equal of about 45° to film normal (Scheme 1).
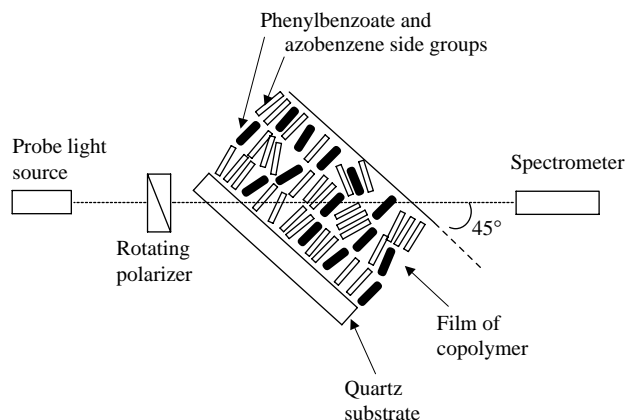
Scheme 1. Experimental optical setup for out-of-plane order formation. (The backbones of copolymer is omitted for simplicity).

3. Results and discussion

3.1. Study of photo-optical and chiro-optical properties of thin spin-coated films of cholesteric mixture

The thin spin-coated films just after preparation and drying at room temperature are optically isotropic as revealed by polarizing optical microscopy: neither any birefringence nor scattering were found.

Fig. 1 shows absorbance spectra of the thin spin-coated films of the cholesteric mixture, which are typical for the azobenzene derivatives. There are the strong absorbance peak at $\lambda \sim 360$ nm corresponding to the $\pi–\pi^*$ electronic transition and small shoulder at $\lambda > 420$ nm for $n–\pi^*$ transition. An annealing of the film samples leads to the small decrease in $\pi–\pi^*$ electronic transition absorbance and the increase in absorbance at the longer wavelengths. The decrease in the $\pi–\pi^*$ absorbance can be explained by possible aggregation of the azobenzene fragment [45,46], whereas the absorbance at longer wavelengths is mainly associated with light scattering due to the formation of the small birefringent domains of cholesteric phase after annealing. Optical anisotropy of the annealed films was clearly detected by polarizing optical
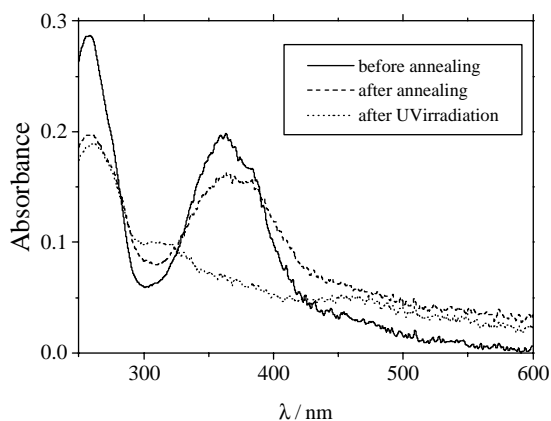

Fig. 1. Absorbance spectra of the thin spin-coated film before annealing, after annealing during 30 min at 70 °C (steady state) and after UV irradiation during 10 min at room temperature (steady state).
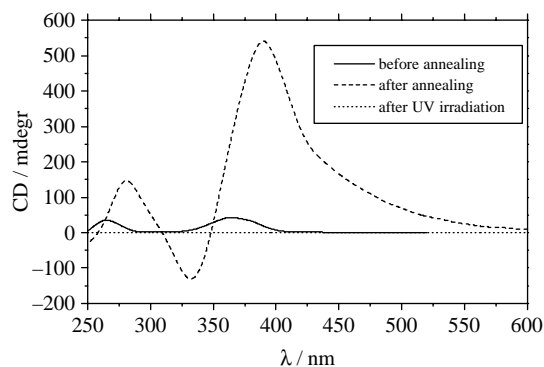

Fig. 2. CD spectra of the thin spin-coated film before annealing, after annealing during 30 min at 70 °C (steady state) and after UV irradiation during 10 min at room temperature (steady state).

microscopy showed nontypical texture with small bright grains.

An UV irradiation results in the significant drop of the absorbance for peak of the $\pi–\pi^*$ electronic transition and in an increase for the $n–\pi^*$ transition (Fig. 1). Such spectral changes clearly testify to the fact of E–Z isomerization of azobenzene groups under UV light action [7,47].

Thermal and light actions have a strong influence on chiro-optical properties films of the mixture (Fig. 2). Fresh films of the mixture are characterized by the two circular dichroism maxima at $\lambda \sim 264$ and 366 nm. An appearance of these maxima does not related to the intrinsic molecular chirality or selective light reflection of the films, because azobenzene fragments are nonchiral and spin-coated films do not have any orientation and pronounced helical structure for selective light reflection phenomena appearance. Nevertheless, an observation of two CD maxima reflects the formation of the elements of helical supramolecular structure. The similar phenomenon was observed for cholesteric azobenzene-containing copolymer in our previous work [48].

An annealing of the films results in the strong enhancement of CD signal as well as in changes of its spectral shape (Fig. 2). Thermal treatment induces the formation of a multidomain cholesteric structure with more pronounced helical organization (Scheme 2). In a response to the heating the strong increase in induced CD takes place. But due to the small thickness of the films (about 100 nm) that is less than helix pitch of the cholesteric phase and absence of any preferential orientation, we did not find any peaks corresponding to selective light reflection. An observation of selective light reflection for the mixture is possible for relatively thick films (several microns) oriented in planar texture by shearing and annealing (see below).

Let us consider the photooptical properties of spin-coated films of the mixture under nonpolarized light action in more detail. Fig. 3 shows a kinetics of changes of the absorbance corresponding to the $\pi–\pi^*$ electronic transition during action of UV light followed by visible light irradiation. UV light action leads to the E–Z isomerization of azobenzene fragments and decrease in absorbance. The subsequent visible light irradiation induces, at first, the back Z–E isomerization as is
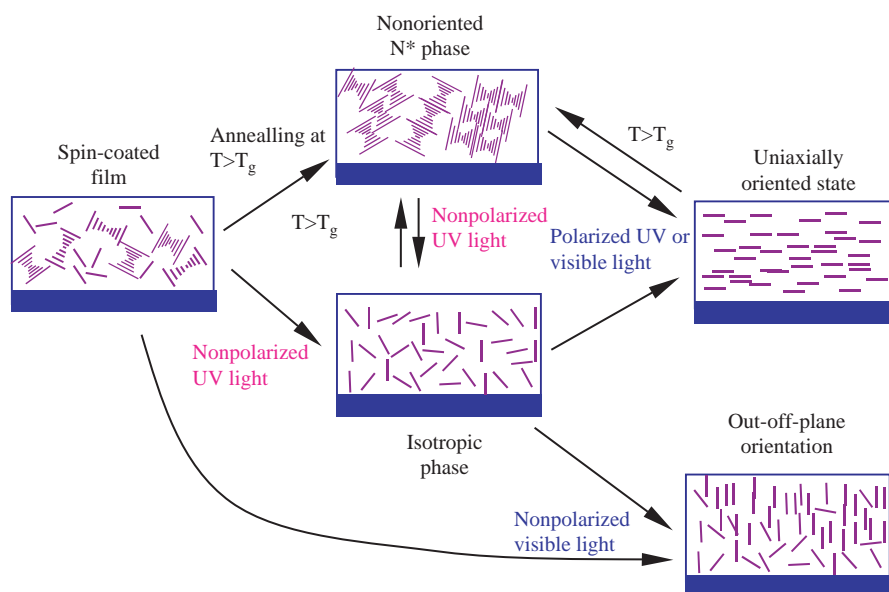
Scheme 2. Schematical representation of possible side-group organization in thin copolymer films before and after thermal and optical treatments.

clearly shown by the absorbance increase. Surprisingly, a prolonged visible light irradiation slowly decreases absorbance. This effect corresponds to slow out-off-plane photoorientation of azobenzene groups along the light incidence direction that was proved by the spectral measurements of polarized absorbance at angle 45° to film normal (Scheme 1, Fig. 4). According to these data, both azobenzene and phenylbenzoate groups are slightly oriented perpendicular by to the film plane. The similar but significantly faster and more pronounced effect was recently observed for cholesteric ethoxyazobenzene-containing copolymer described by us in [48]. As was discussed in the paper [48], this phenomenon is associated with selective excitation of azobenzene chromophores directed along electric vector of the light, in other words, in direction, perpendicular to a film normal. This activates photoorientation of chromophores along incident light propagation direction.

Thermal treatment of the films (at temperatures higher glass transition) leads to complete recovery of spectra in the initial state for the annealed films and disappearance of any out-off-plane order orientation. This is completely different from the
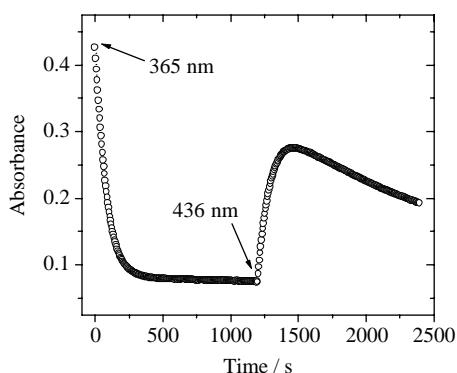
situation with cholesteric ethoxyazobenzene-containing copolymer for which smectic phase formation stabilized out-off-plane order during annealing.

3.2. Photoorientation phenomena in thin spin-coated films of cholesteric mixture

Action of the polarized UV light (365 nm) on the thin spin-coated films leads to E–Z isomerization (and π–π* absorbance decrease) accompanied by photoorientation phenomena as seen from the polar plots of absorbance of polarized light (Figs. 5 and 6). Both, azobenzene and phenylbenzoate groups are oriented perpendicularly to polarization plane of the incident light (Scheme 2). Dichroism at wavelengths
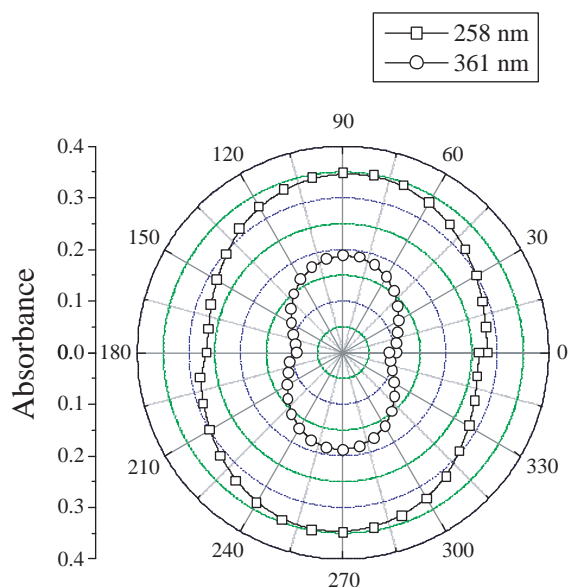

Fig. 3. Kinetics of absorbance changes during UV and subsequent visible light irradiation. Before irradiation film was of annealed at 70 °C during 1 h.

Fig. 4. Polar plots of absorbance at two wavelengths measured at 45° to film normal after irradiation by nonpolarized visible light (436 nm) during 100 min.
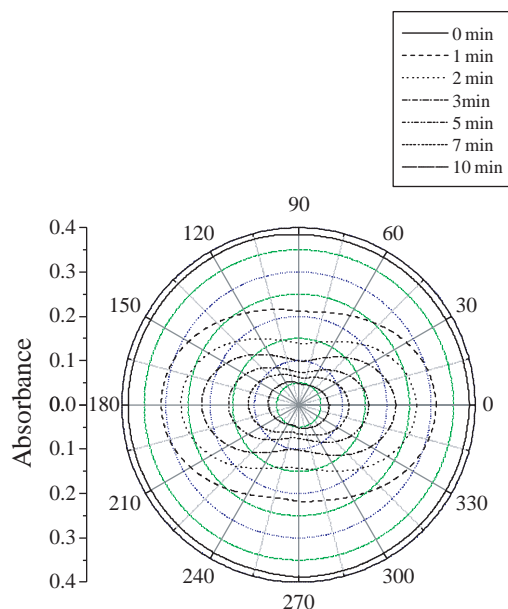
Fig. 5. Polar plots for the absorbance at 361 nm during polarized UV light irradiation (365 nm) measured at different irradiation time.
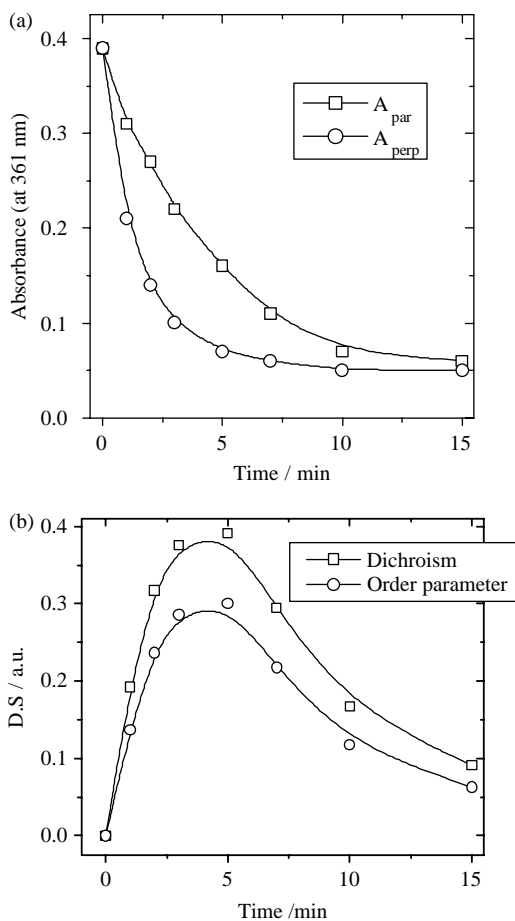
corresponding to azobenzene and phenylbenzoate fragments absorption and spectral order parameter increase during of the first 6 min of irradiation; whereas longer irradiation time decreases dichroism and order parameter values (Fig. 6(b)). This is due to the formation of the high concentration (up to 90%) of low-anisometric Z-isomers of azobenzene groups destroying the photoinduced orientation.

Photoorientation takes place both in the fresh and the annealed films (Fig. 7). As seen from Fig. 7 the formation of the helical cholesteric order only slightly reduces degree of photoinduced order. This is in quite opposite previously observed cases when smectic or more ordered phase formation makes photoorientation impossible at all [45,46].

An action of polarized visible light (436 nm) results in the high and stable dichroism in the fresh and annealed films of the mixture (Figs. 8 and 9). In this case concentration of Z-isomer is noticeably lower than in the case of UV light that makes possible a stronger photoorientation and higher dichroism, and order parameter values.

We have preformed a comparison the photoorientational behaviour of cholesteric mixture and nematic copolymer **PAAzo8**. As clearly seen from Fig. 10, the rate of the order parameter growth is slightly higher for the cholesteric mixture, probably, because of plasticizing effect of low-molar-weight dopant, **HexSorb**. But maximal value of the photoinduced order parameter is significantly lower for the cholesteric mixture (ca. 1.4 times). This fact reflects a significant influence of the helical supramolecular organization on the light-induced photoorientation of the mesogenic groups. The presence of the helical structure seems to prevent the reorientation of azobenzene moieties induced by the polarized light to a significant extent. Recently, the same effect was found during comparison of holographic recording on azobenzene-containing cholesteric copolymer and nematic homopolymer [49].

An annealing of the irradiated films of the mixture at temperature above the glass transition reduces dichroism value to zero, i.e. returns the system to the initial nonoriented state. For nematic copolymer **PAAzo8** we found that films remain

Fig. 6. Changes of absorbance measured to parallel and perpendicular azobenzene groups orientation (a) and corresponding dichroism and order parameter (b) during the polarized UV light irradiation (365 nm).
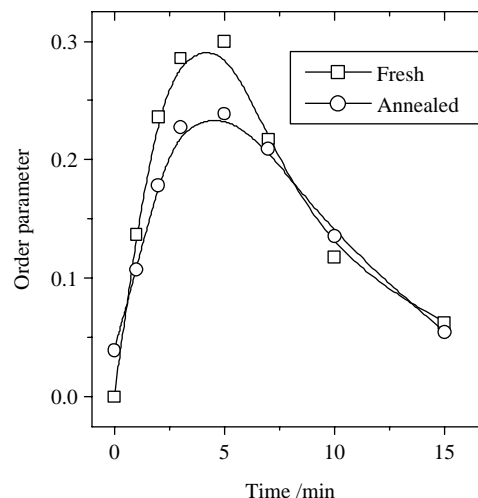

Fig. 7. Changes of order parameter measured at 361 nm during polarized UV light irradiation (365 nm) for fresh and annealed film (30 min at 80 °C).
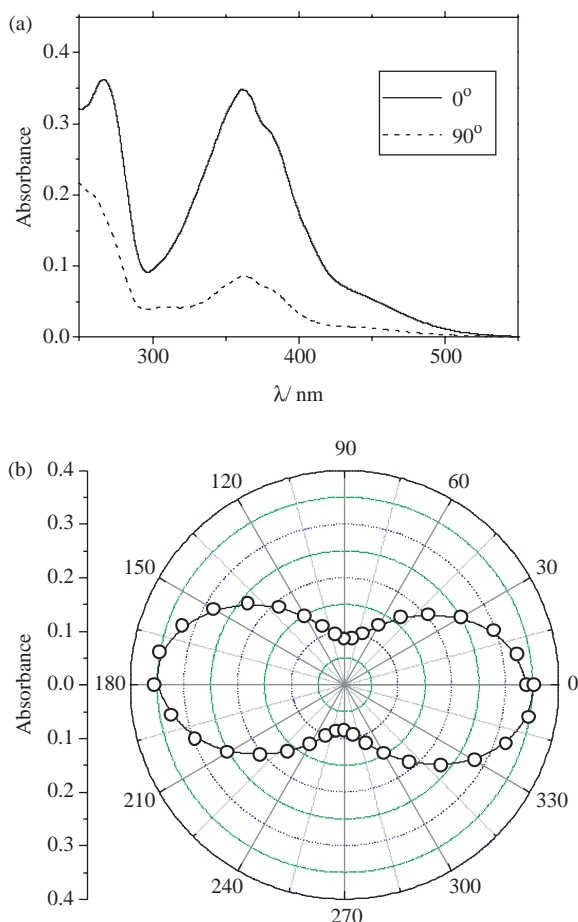
Fig. 8. Polarized absorbance spectra measured to parallel and perpendicular to azobenzene groups orientations (a) and polar plot of absorbance at 361 nm (b) after 100 min of polarized visible light irradiation (436 nm).
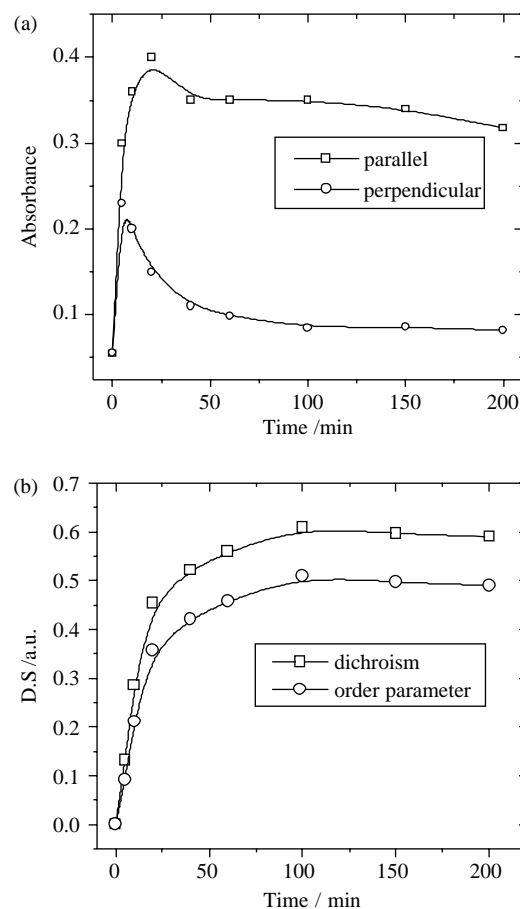

Fig. 9. (a) Kinetics of absorbance of polarized light parallel and perpendicular to azobenzene groups orientation (a) and dichroism and order parameter (b) changes during polarized visible light irradiation (436 nm).

oriented for a long time even at temperature higher than glass transition. Evidently, heating of the films in cholesteric phase allows one to reach thermodynamically stable helical state, whereas uniaxial photoinduced orientation for the nematic system is more or less stable due to same symmetry of the nematic state.

3.3. Photo-optical properties of thick planarly-oriented films of cholesteric mixture

Let us discuss the effect of light irradiation on the optical properties of the planarly oriented films of mixture. Upon UV light irradiation at temperatures higher than glass transition selective light reflection maximum is slightly shifted to the long-wavelength spectral region (Fig. 11(a)).

This phenomenon is also associated with E–Z photoisomerization of azobenzene groups. This process leads to a decrease in orientational order parameter due to the development of a bent-shaped Z-form of azobenzene groups. In turn, as the orientational order parameter is decreased, untwisting of cholesteric helix takes place [50]. The above speculations may be indirectly proved by a well-known phenomenon of the distortion of an LC order upon the E–Z photoisomerization of azobenzene groups of comb-shaped polymers [51–54].

The range of shift in selective light reflection wavelength is similar to observed for copolymers and mixtures containing chiral photochromic side groups or low-molecular-mass azobenzene dopants [55,56].

Another possible explanation of observed phenomena can involve for consideration changing in interactions between
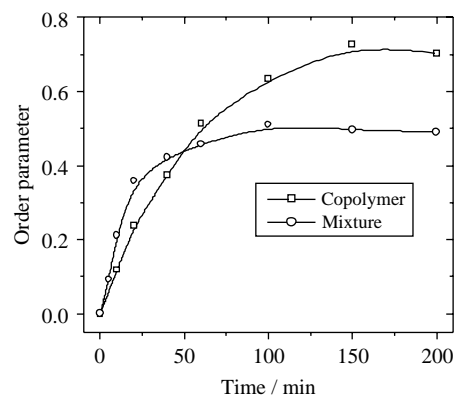

Fig. 10. Kinetics of order parameter growth during polarized visible light irradiation (436 nm) for mixture and nematic copolymer. Before visible light action film was irradiated by UV light during 10 min.
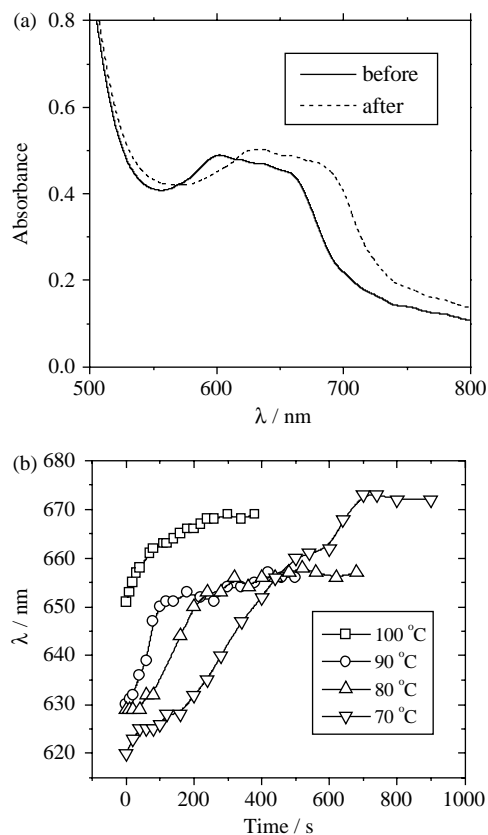
Fig. 11. (a) Absorbance corresponding to selective light reflection peak before and after 400 s of UV (365 nm) irradiation at 90 °C; (b) kinetics of helix untwisting during UV irradiation (365 nm) of cholesteric mixture at different temperatures.

chiral groups and azobenzene units during their photoisomerization.

The rate and range of changes in λ_{max} are markedly controlled by temperature (Fig. 11(b)). In all cases, the higher the temperature, the higher the rate of helix untwisting, and smaller the shift in the selective light reflection maximum to the long-wavelength spectral region. This behavior is related to the fact that the rate of the back Z–E isomerization dramatically increases with increasing the temperature; hence, at higher temperatures, the content of the Z-isomer is lower.

This photoprocess is thermally reversible, the annealing of the films at temperatures above glass transition results in back conversion to the initial helix pitch value.

In conclusion, photooptical and chiro-optical behaviour, as well as photoorientation processes occurring in thin, spin-coated films of cholesteric polymer mixture have been studied in detail. Scheme 2 represents in summary most important thermo- and photooptical processes occurring in thin spin-coated films of cholesteric mixture. It is shown that the helical organization of cholesteric phase has no noticeable influence on kinetics of photoorientation process but decreases a maximal value of the photoinduced dichroism. The photo-optical properties of the planarly oriented films with thickness of several microns were also examined at different temperatures, and a helix untwisting under UV light action was established.

References

[1] Weigert F. Werhandlungen der Deutschen Physikalischen Gesellschaft 1919;21:479.
[2] Todorov T, Tomova N, Nikolova L. Opt Commun 1983;47:123.
[3] Eich M, Wendorff JH. Makromol Chem, Rapid Commun 1987;59:467.
[4] Shibaev VP, Kostromin SG, Ivanov SA. In: Shibaev VP, editor. Polymers as electrooptical and photooptical active media. Berlin: Springer; 1996. p. 37.
[5] Eich M, Wendorff JH. J Opt Soc Am B 1990;7:1428.
[6] Anderle K, Wendorff JH. Mol Cryst Liq Cryst 1994;243:51.
[7] Sekkat Y, Knoll W. Photoreactive organic thin films. London: Academic Press; 2002.
[8] Hore DK, Natansohn AL, Rochon PL. J Phys Chem B 2003;107:2197.
[9] Sekkat Z, Morichère D, Dumont M, Loucif-Saïbi R, Delaire JA. J Appl Phys 1992;71:1543.
[10] Loucif-Saibi R, Nakatani K, Delaire JA, Dumont M, Sekkat Z. Chem Mater 1993;5:229.
[11] Nikolova L, Nedelchev L, Todorov T, Petrova Tz, Tomova N, Dragostinova V, et al. Appl Phys Lett 2000;77:657.
[12] Kim M-J, Shin B-G, Kim J-J, Kim D-Y. J Am Chem Soc 2002;124:3504.
[13] Iftime G, Natansohn A, Rochon P. Macromolecule 2002;35:365.
[14] Iftime G, Labarthet LF, Natansohn A, Rochon P. J Am Chem Soc 2000; 122:12646.
[15] Shibaev VP, Bobrovsky AY, Boiko NI. Prog Polym Sci 2003;28:729.
[16] Shibaev VP, Kostromin SG, Ivanov SA. Polym Sci, Ser A 1997;39:118.
[17] Ivanov SA, Yakovlev IA, Kostromin SG, Shibaev VP, Lasker L, Stumpe J, et al. Makromol Chem, Rapid Commun 1991;12:709.
[18] Stumpe J, Lasker L, Fischer Th, Kostromin S, Ivanov S, Shibaev V, et al. Mol Cryst Liq Cryst 1994;253:1.
[19] Brown D, Natansohn A, Rochon P. Macromolecules 1995;28:6116.
[20] Ramanujam P, Holme N, Hvilsted S. Appl Phys Lett 1996;68:1329.
[21] Natansohn A, Rochon P, Meng X, Barret C, Buffeteau T, Bonenfant S, et al. Macromolecules 1998;31:1155.
[22] Xie S, Natansohn A, Rochon P. Chem Mater 1993;5:403.
[23] Gibbons WM, Shannon PJ, Sun ShT, Swetlin BJ. Nature 1991;351:49.
[24] Geue Th, Ziegler A, Stumpe J. Macromolecules 1997;30:5729.
[25] Hvilsted S, Andruzzi F, Kulinna Ch, Siesler H, Ramanujam P. Macromolecules 1995;28:2172.
[26] Buffeteau Th, Pezolet M. Macromolecules 1998;31:2631.
[27] Blinov LM, Barberi R, Cipparrone G, Iovane M, Checco A, Lazarev VV, et al. Liq Cryst 1999;26:427.
[28] Rochon P, Gosselin J, Natansohn A, Xie S. Appl Phys Lett 1992;60:4.
[29] Meng X, Natansohn A, Rochon P. Supramol Sci 1996;3:207.
[30] Ikeda T, Tsutsumi O. Science 1995;268:1873.
[31] Zilker SJ, Bieringer Th, Haarer D, Stein RS, van Egmond JW, Kostromine SG. Adv Mater 1998;10:855.
[32] Yaroshchuk O, Agra DMG, Zakrevskyy Y, Chien L-C, Lindau J, Kumar S. Liq Cryst 2001;28:703.
[33] Wu Y, Mamiya J, Kanazawa A, Shiono T, Ikeda T, Zhang Q. Macromolecules 1999;32:8829.

[34] Kreuzer FH, Bräuchle Ch, Miller A, Petri A. In: Shibaev VP, editor. Polymers as electrooptical and photooptical active media. New York: Springer; 1996 [chapter 3].

[35] Bobrovsky A, Boiko N, Shibaev V, Stumpe J. Liq Cryst 2002;29:1469.

[36] Wu Y, Ikeda T, Zhang Q. Adv Mater 1999;11:300.

[37] Meier JG, Ruhmann R, Stumpe J. Macromolecules 2000;33843.

[38] Chandrasekhar S. Liquid crystals. New York: Cambridge University Press; 1994.

[39] Belyakov VA. Diffraction optics of complex-structured periodic media. Berlin: Springer; 1992.

[40] Chilaya GS, Lisetski LN. Mol Cryst Liq Cryst 1986;140:243.

[41] Bobrovsky A, Boiko N, Shibaev V, Stumpe J. J Photochem Photobiol, A: Chem 2004;163:347.

[42] Kostromin SG, Stakhanov AI, Shibaev VP. Polym Sci, Ser A 1996;38: 1030.

[43] Boiko NI. PhD thesis. Moscow State University (in Russian) 1987.

[44] Organikum. VEB Deutscher Verlag der Wissenschaften, Berlin 1990.

[45] Meier JG, Ruhmann R, Stumpe J. Macromolecules. 2000;33:843.

[46] Zebger I, Rutloh M, Hoffmann U, Stumpe J, Siesler HW, Hvilsted S. Macromolecules. 2003;36:9373.

[47] Dürr H, editor. Photochromism: molecules and systems. Amsterdam: Elsevier; 2003.

[48] Bobrovsky A, Shibaev V. J Photochem Photobiol, A: Chem 2005;172: 140.

[49] Bobrovsky A, Shibaev V, Wendorff J. Liq Cryst in press.

[50] Bobrovsky A, Shibaev V. Liq Cryst 2003;30:671.

[51] Ikeda T, Horiuchi S, Karanjit DB, Kurihara S, Tazuke S. Macromolecules. 1990;23:36.

[52] Hasegawa M, Yamamoto T, Kanazawa A, Shiono T, Ikeda T. Chem Mater 1999;11:2764.

[53] Lee H-K, Doi K, Kanazawa A, Shiono T, Ikeda T, Fujisama T, et al. Polymer 2000;41:1757.

[54] Yamamoto T, Hasegawa M, Kanazawa A, Shiono T, Ikeda T. J Phys Chem 1999;103:9873.

[55] Bobrovsky A, Boiko N, Shibaev V, Springer J. Liq Cryst 2001;28:919.

[56] Shibaev V, Bobrovsky A, Boiko N. Polym Sci, Ser C 2000;42:103.