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Cholesteric mixture containing a chiral azobenzene-based dopant: material with reversible photoswitching of the pitch of the helix

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A new low molar mass chiral-photochromic dopant was synthesized. It contains a menthyl fragment as the chiral group and an azobenzene group, capable of *E–Z* photoisomerization, as the photochromic component. The substance obtained was used as a chiral dopant in mixtures with a comb-shaped cholesteric acrylic copolymer with menthyl-containing chiral side groups and phenyl benzoate nematogenic side groups. Such mixtures form a cholesteric mesophase. The chiral dopant led to an additional twisting of the cholesteric helix, i.e. to a shift of the selective light reflection peak to a shorter wavelength region of the spectrum. The initial copolymer gave selective light reflection in the spectral range 1200–1400 nm; the mixture containing 3.5 mol % of chiral-photochromic dopant reflects light with $\lambda_{\max} \sim 850$ nm. The action of light with $\lambda_{\mathrm{ir}} \sim 440$ nm results in *E–Z* isomerization of the azo-group of the chiral dopant and in a shift of the selective light reflection peak to the long wavelength region of the spectrum (amplitude of shift = 30 nm). This is explained by a lower helical twisting power of the *Z*-isomer of the chiral dopant. This process is thermally reversible: annealing of irradiated films leads to a back shift of the selective light reflection peak to the short wavelength region of the spectrum due to *Z–E* isomerization. Kinetic features of the direct and backward processes of isomerization were studied: it was shown, that mixtures of the chiral-photochromic azobenzene-containing dopant with cholesteric polymers give new possibilities for the creation of polymer materials with a reversibly regulated helical supramolecular structure which determines their optical properties.

1. Introduction

The growing interest of researchers in photosensitive liquid crystalline (LC) polymers is determined by the possibility of practical uses of such systems in creating new materials for optical data recording and storage systems, holography, development of new principles for evaluating micrographical media and other electro-optical applications [1, 2].

Recently a number of papers devoted to the synthesis and investigation of cholesteric copolymers and mixtures giving variation of the pitch of the helix under the action of light have been published [3–9]. In these papers a new approach to creating chiral-photochromic systems was realized. The chiral side groups of such copolymers and the molecules of low molar mass dopants contained both a chiral and a photosensitive fragment (double C=C bond), simultaneously.

Copolymers with two types of chiral-photochromic groups—arylidene-*p*-menthane-3-one [3–8] and cinnamic acid [9] derivatives were synthesized. Under the action of UV light on such copolymer films, *E–Z* isomerization of the photosensitive units was observed, accompanied by a considerable decrease (especially in the case of arylidene-*p*-menthane-3-ones) in the helical twisting power of the photosensitive chiral groups. In the end this led to untwisting of the cholesteric helix and to shift of the selective light reflection peak to the long wavelength region of the spectrum.

However, an essential drawback of the systems described above is the irreversibility of the photoprocess, i.e. it is impossible to return the irradiated film of copolymer with a definite percentage of *E* and *Z* isomers to this initial state (with a 100% content of *E* isomer).

Quite a different situation is observed in the case of azobenzene-containing photosensitive systems [1, 2, 10–23] which have been studied in detail. It is well known, that in most cases, *E–Z* isomerization of azobenzene derivatives

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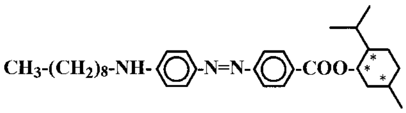
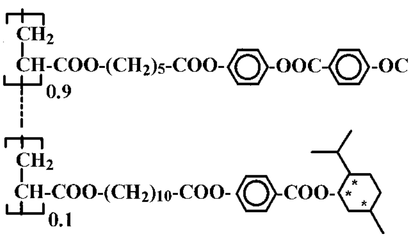
is thermally and photochemically reversible, i.e. the system can be brought back to the initial state by heating or by irradiation with light of another wavelength; in other words, the azobenzene units can be transformed back into the *E* form.

That is why is seems rather interesting to synthesize a chiral-photochromic dopant on the basis of azobenzene that will be capable of reversible *E–Z* isomerization. The dopant structure must be arranged in such a way that the helical twisting powers of the isomers differ strongly. An azobenzene group fully satisfies this demand, as the *Z*-isomer has a lower anisometry than the *E* isomer; this is why its helical twisting power is expected to be lower, as was observed for the menthone and cinnamic acid derivatives [3–9].

In the case of low molar mass mixtures [24], a number of azobenzene-containing chiral dopants, differing in helical twisting power of the *E* and *Z* isomers, have been described. Nevertheless, the values of the helical twisting power of the dopants described in [24] are low, and besides, the peculiarities of the photochemical behaviour of these substances were not investigated and the possibility of using such systems for optical data recording was not studied. Therefore in this work we have synthesized a new left-handed chiral-photochromic dopant containing an azobenzene fragment and an optically active menthyl group:



As a ‘matrix’ for the introduction of this dopant, a left-handed menthyl-containing copolymer of the following structure was used:



This copolymer forms a chiral nematic (N*) mesophase with a clearing temperature $T_{\mathrm{cl}} = 106$°C and a glass temperature $T_{\mathrm{g}} = 35$°C [25]. Also, the TDK* phase with a melting temperature of 65°C is formed on annealing for several days†. By introducing a small amount of dopant (3.5 mol %) to the polymeric matrix, it is easy to obtain a material capable of conserving the supramolecular structure in a ‘frozen’ glassy state; this is very important for creation of media for optical data recording and long-term storage.

Thus, the aim of this work was a study of the photo-optical properties of the mixture of cholesteric copolymer and chiral-photochromic dopant and an investigation of the possibility of using such a material for reversible optical data recording.

2. Experimental

2.1. *Synthesis of monomers*

The menthyl-containing and nematogenic monomers were synthesized according to procedures described in [25, 27]. For the synthesis of the chiral-photochromic dopant *l-menthyl 4′-(4-N-nonylaminophenylazo)benzoate*, to a solution of 3.81 mmols of 4′-(4-*N*-nonylaminophenylazo)benzoic acid (NIOPIK) and 4.20 mmols of *l*-menthol in 2 ml of purified THF, 0.50 mmol of *N*,*N*-dimethylaminopyridine was added. Then 5.04 mmols of dicyclohexylcarbodiimide were added and the resulting solution was stirred for 3 days. The precipitate formed was filtered off and washed with THF, and subsequently chloroform (50 ml) was added to the filtrate. The solution was washed successively with water, 5% aqueous acetic acid, and finally with water until pH 7 was achieved. The chloroform extract was dried with anhydrous $MgSO_4$. After removal of solvent, the crude product was purified by column chromatography (eluent chloroform); yield 29% of a red oil. IR (cm^{-1}): 2944, 2888, 2864 (CH_2), 1716 (CO), 1608, 1588 (C–C in Ar), 1265 (COC).

2.2. *Polymerization and preparation of the mixture*

The copolymer was synthesized by radical copolymerization of the monomers in benzene solution at 60°C; AIBN was used as initiating agent. The copolymer was purified by repeated precipitation with methanol and dried in vacuum.

The mixture was prepared by dissolving the copolymer and dopant in dichloroethane followed by solvent evaporation at 60°C. Then the mixture was dried in a vacuum at 120°C for two hours.

2.3. *Study of physical properties*

IR spectra were recorded using a Bruker IFS-88 spectrophotometer and KBr pellets of samples.

The relative molecular mass of the copolymer was determined by gel permeation chromatography (GPC) using a GPC-2 Waters instrument equipped with an LC-100 column oven and a Data Modul-370 data station. Measurements were made using a UV detector, THF as solvent (1 ml min^{-1}, 25°C), a set of PL columns of 100, 500 and 10^3 Å, and a calibration plot constructed with polystyrene standards. The copolymer obtained has the following molecular mass characteristics: $M_{\mathrm{n}} = 21\,000$, $M_{\mathrm{w}}/M_{\mathrm{n}} = 2.6$.

Phase transitions in the mixture were studied by differential scanning calorimetry (DSC) with a scanning

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†The structure of this phase was studied in detail in [26].

rate of 10 K min^{-1}. All experiments were performed using a Mettler TA-400 thermal analyser and a LOMO P-112 polarization microscope. Absorbance and selective light reflection spectra of films of copolymer and the mixture were studied using a Hitachi U-3400 UV-Vis-IR spectrometer equipped with a Mettler FP-80 hot stage. The 20 μm thick samples were sandwiched between two flat glass plates. The thickness of the test samples was preset by Teflon spacers. The planar texture was obtained by shear deformation of samples which were heated to temperatures above the glass transition temperature. Prior to tests, samples were annealed for 20–40 min at appropriate temperatures.

2.4. *Photochemical investigations*

Photochemical property investigations were made using a special instrument [4] equipped with a DRSh-250 ultra-high pressure mercury lamp. Using a filter, light with a maximum wavelength of 440 nm was selected. To prevent heating of the samples due to IR radiation from the lamp, a water filter was used. To obtain a plane-parallel light beam, a quartz lens was used. During irradiation, a constant temperature of the test samples was maintained using a Mettler FP-80 heating unit. The intensity of the incident light was 6.8 mW cm^{-2} (as measured by IMO-2N intensity meter).

Photochemical properties of the mixture were studied by illuminating 20 μm thick films or thin films obtained by casting from solution in dichloroethane by evaporation at 60°C. Immediately after irradiation, absorbance or transmittance spectra were recorded using the Hitachi U-3400 UV-Vis-IR spectrometer.

3. Results and discussion

3.1. *Phase behaviour and optical properties of the copolymer and its mixture with the chiral-photochromic dopant*

First let us consider the phase behaviour and optical properties of the mixture. According to polarizing optical microscopy, DSC and X-ray investigations, the mixture of the menthyl-containing copolymer with the chiral-photochromic dopant forms the same phases as the initial copolymer matrix—the chiral nematic phase and the highly ordered TDK* phase. The temperatures of the phase transitions are shown below:

g 33 TDK* 67 N* 96 I (°C)

The glass temperature and the TDK* phase melting temperature remain practically the same after introduction of the dopant, whereas the clearing temperature decreased by ten degrees (figure 1).

Figure 2 shows the temperature dependences of the wavelength of selective light reflection maximum (λ_{max}) for the copolymer and the mixture.

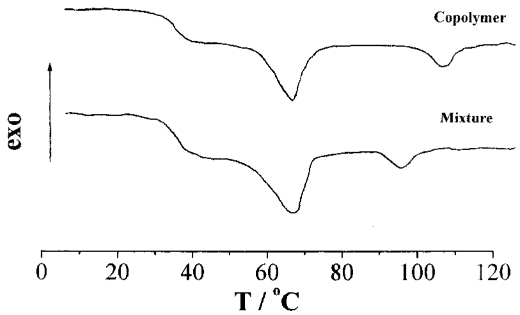


Figure 1. DSC curves for the menthyl-containing copolymer and its mixture with the chiral-photochromic dopant. Heating rate was 10°C min^{-1}; second heating scans.

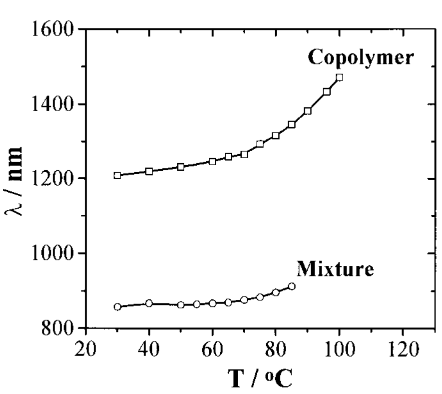


Figure 2. Temperature dependences of the selective light reflection wavelength for the menthyl-containing copolymer and its mixture with the chiral-photochromic dopant.

First it must be pointed out that the introduction of the chiral-photochromic dopant leads to a shift of the selective light reflection peak to a shorter wavelength region of the spectrum, due to the additional twisting of cholesteric helix arising from the increase in the chiral component content. Using these data and equation (1), we evaluated the helical twisting power β of the chiral-photochromic dopant in the mixture.

$$\beta/n = \Delta\lambda_{max}^{-1}/X, \quad (1)$$

where n is the average refractive index, $\Delta\lambda_{max}$ is the difference between the inverse selective reflection wavelength of the mixture and the copolymer, and X is the mol fraction of the chiral-photochromic dopant. The value of β/n is 11.6 μm^{-1}, which approximately coincides with the values of the helical twisting power for two-ring menthyl-containing side groups in cholesteric copolymers studied in detail in our previous work [25, 28].

The second important feature of the temperature dependences of the wavelength of selective light reflection is the increase of λ_{max} with temperature increase, which might be due to a decrease in the orientational order parameter [29].

3.2. *Photochemical properties of thin films of the mixture*

The photochemical behaviour of thin films, obtained by slow evaporation of the solvent from a solution of the mixture in dichloroethane on a quartz substrate, were studied. Figure 3 shows one peak with a maximum of *c.* 441 nm corresponding to the π-π* and n-π* electronic transitions of the azobenzene fragment [30] of the chiral-photochromic dopant as observed with absorption spectrum of such a film in the long wavelength region.

A decrease in the optical density of the films occurs during irradiation by blue light ($\lambda_{ir} \sim 440$ nm); the peak maximum position remains the same (figure 3) during this process. Such spectral changes provide evidence of *E–Z* isomerization of the chiral photochromic dopant [2, 30]. It should be noted that this process is easily thermally reversible as can be clearly seen from figure 4: after switching off the light, the optical density regains its initial value.

For calculation of the rate constants of the back *Z–E* isomerization, the dependences of absorbance vs. time in the first order reaction coordinate (2) were built up:

$$\ln \frac{D_\infty - D_t}{D_\infty - D_0} = -kt \qquad (2)$$

where D_0, D_t and D_∞ are the absorbance at 441 nm at times equal to zero, t and infinity, respectively. The calculated values of the constant k are presented in the table.

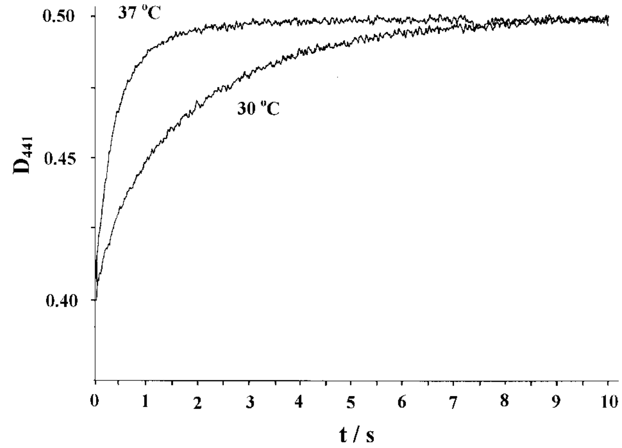


Figure 4. Absorbance increase for a film of the irradiated mixture during the back thermal *Z–E* isomerization at different temperatures.

Table. Values of the rate constant *Z–E* photoisomerization at different temperatures for a film of the mixture obtained by casting from dichloroethane solution.

T/°C	$t_{1/2}$/s	$k \times 10^3$/s^{-1}
30	78	8.9 ± 0.2
33	65	10.7 ± 0.4
35	51	13.7 ± 0.4
37	28	24.8 ± 1.1
40	29	23.5 ± 0.8

It is interesting to note, that in our case, the rate of the back process is 30–40 times greater than that for the alkoxy substituted derivatives of azobenzene; this situation is probably explained by the influence of the electron-donor substituent (–NH–Alk) in the *para*-position of the benzene ring [19, 31, 32].

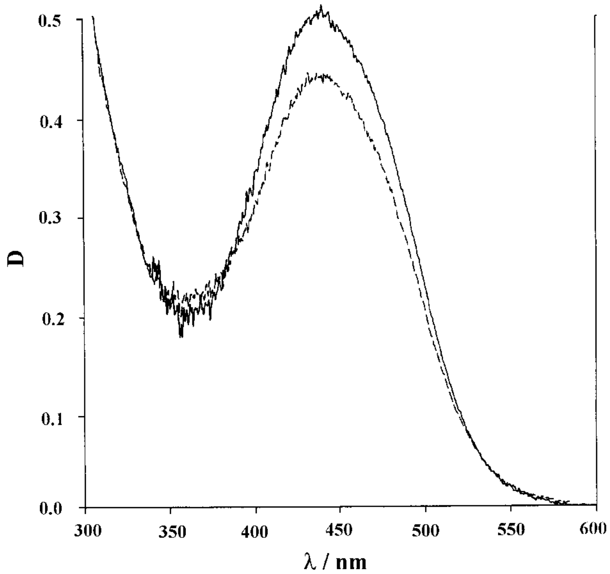


Figure 3. Absorption spectra of a film of the mixture before (solid line) and after 50 s of irradiation (steady state, dashed line).

The temperature dependences of the logarithm of the isomerization rate constant were plotted to calculate the activation energy of the thermal process (figure 5). The value of the activation energy is 21.2 ± 4.7 kcal mol^{-1}; this value is typical for the azobenzene derivatives [33].

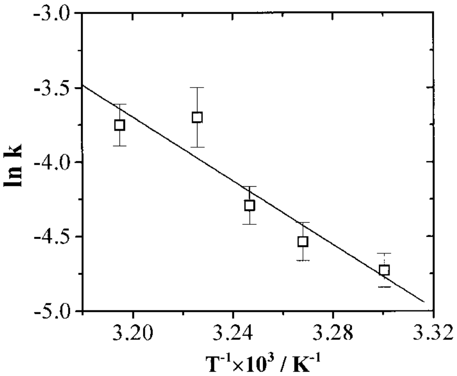


Figure 5. Arrhenius plot for the back thermal *Z–E* isomerization of the dopant in a film of the mixture.

By analysing the experimental data it can be concluded that *E–Z* isomerization of the chiral-photochromic dopant does take place through the action of light on films of the mixture. The isomerization process is easily reversible: annealing of the films even at room temperature leads to a rapid transition of *Z* isomer back to *E* isomer.

3.3. *Photo-optical properties of planar aligned films of the mixture*

Now let us consider the influence of irradiation on planar aligned films of the mixture. The polymeric films were irradiated by light with $\lambda_{ir} \sim 440$ nm during fixed intervals of time; after a certain irradiation time the transmittance spectra were immediately measured. As shown in figure 6 (*a*), light action leads to a considerable shift in the selective light reflection peak to the long wavelength region of the spectrum, i.e. cholesteric helix untwisting is observed. It is important to note, that this process is thermally reversible: annealing of the film for about 20 min (at 60°C) leads to a complete return of the peak to the initial position; the arrow in figure 6 (*b*) shows the direction of the peak shift.

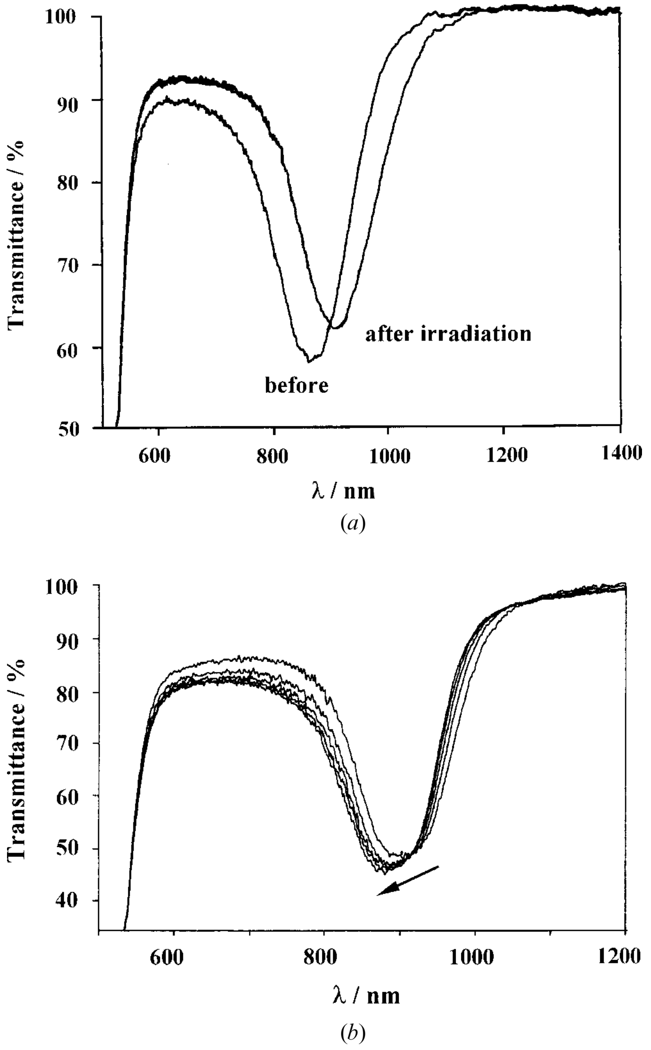
Using equation (1) we calculated the values of the helical twisting power β/n of the chiral-photochromic dopant after irradiation. The value of β/n is $9.9\,\mu\text{m}^{-1}$, which is lower by only 15% than the helical twisting power before irradiation. Probably in this case the photostationary fraction of *Z* isomer in the mixture of isomers is not so high.

Temperature has a great influence on the rate of the helix untwisting (figure 7), and as shown in figure 8, the rate of untwisting of the helix reaches a maximum at about 60°C.

This occurs because the untwisting rate is determined by several factors. Let us consider in more detail the processes taking place in the system under the action of light and temperature change. First there is a direct process of *E–Z* photoisomerization with the rate determined by equation (3):

$$-\frac{\mathrm{d}[E]}{\mathrm{d}t} = \frac{Id}{D}(\varphi_E \varepsilon_E [E] - \varphi_Z \varepsilon_Z [Z]) \tag{3}$$

where $[E]$ and $[Z]$ are the concentrations of *E* and *Z* isomers, respectively; φ_E and φ_Z are the quantum yields of the forward and back processes; *I* is the amount (in mols) of absorbed light in a unit time; ε_E and ε_Z are the extinction coefficients of the *E* and *Z* isomers, respectively; *d* is the sample thickness; *D* is the optical density of the film. According to equation (3), the rate of *E–Z* isomerization and the composition of the photostationary mixture of isomers depend on the values of the quantum yields and the extinction coefficients of the *E* and *Z* isomers.



(*a*)

(*b*)

Figure 6. (*a*) Transmittance spectra of a planar aligned film of the mixture before and after irradiation ($T = 60$°C, $\lambda_{ir} \sim 440$ nm). (*b*) Changes in the transmittance spectra of a planar aligned, irradiated film of the mixture during annealing at 60°C. Spectra were recorded every 6 min.

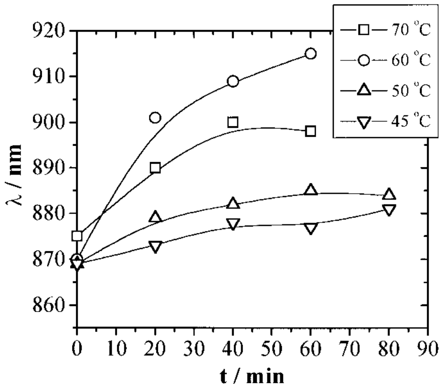


Figure 7. Changes of selective light reflection wavelength during irradiation of the mixture at different temperatures.

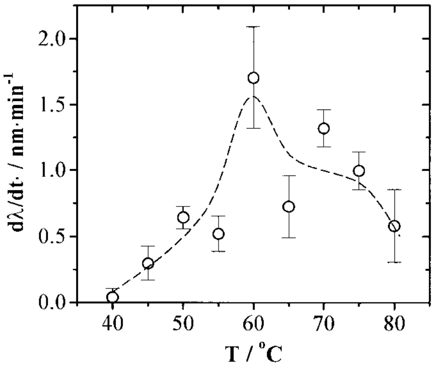


Figure 8. Temperature dependence of the helix untwisting rate for the irradiated mixture.

In addition, as shown above, the back thermal process of *Z–E* isomerization takes place in the system:

$$\frac{d[E]}{dt} = k[Z] \quad (4)$$

where k is the rate constant of the back thermal process.

By summing equations (3) and (4) one obtains the overall rate of transformation of E isomer to the Z form:

$$-\frac{d[E]}{dt} = \frac{Id}{D}(\varphi_E\varepsilon_E[E] - \varphi_Z\varepsilon_Z[Z]) - k[Z]. \quad (5)$$

The rate constant of the back thermal process strongly depends on the temperature (table 1); therefore temperature increases shifts the equilibrium to the initial E isomer formation. This explains why the rate of helix untwisting sharply decreases at temperatures higher than 60°C. At temperatures lower than 60°C, the rate of helix untwisting is limited by the high viscosity of the system, i.e. the helix does not have 'enough time' to untwist to the equilibrium value of the helical pitch.

Thus, we have demonstrated the possibility of a reversible variation of the pitch of a cholesteric helix in a mixture of cholesteric copolymer and a low molar mass chiral-photochromic azobenzene-containing dopant. However, in order to investigate the possibility of using such a material for reversible data recording, the stability of the system to 'recording–erasing' cycles had to be checked, figure 9 (*a*).

An important parameter characterizing the stability of a material to 'recording–erasing' cycles is the so called fatigue resistance:

$$\eta(n) = \frac{\lambda_{max}(n) - \lambda_0(n)}{\lambda_{max}(1) - \lambda_0(1)} \quad (6)$$

where n is the number of cycles, and λ_{max} and λ_0 are the wavelengths of selective light reflection maximum before and after irradiation, respectively.

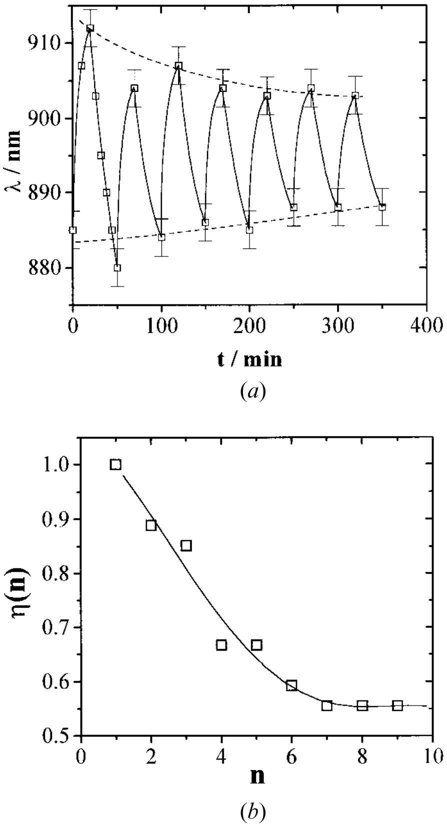


Figure 9. Fatigue resistance properties of the mixture on repeated 'recording–erasing' cycles (for more detail see text). (*a*) Effect of cycling time on the wavelength of selective light reflection; (*b*) fatigue resistance and number of cycles.

Figure 9 (*b*) represents the dependence of $\eta(n)$ on the number of cycles. It is clearly seen that the difference between the wavelengths of the selective reflection maximum before and after irradiation decreases by a factor of two, even after five cycles of 'irradiation–annealing'. The relatively low stability of the chiral-photochromic dopant is probably explained by the presence of the NH group in the azobenzene fragment‡.

In conclusion, it should be noted that in spite of the low fatigue resistance of the mixture described to 'recording–erasing' cycles, this mixture is important as a new material for reversible optical data photorecording and storage with a reversibly photoregulated pitch of the helical supramolecular structure.

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‡ Although early in a number of works [34–36] it was shown that the fatigue resistance of, for example, the alkoxy-substituted derivatives of azobenzene is relatively high.

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References

[1] McArdle, C. B. (editor), 1992, *Applied Photochromic Polymer Systems* (Blackie).

[2] Shibaev, V. P. (editor), 1996, *Polymers as Electro-optical and Photo-optical Active Media* (Berlin, Heidelberg: Springer-Verlag), p. 37.

[3] Bobrovsky, A. Yu., Boiko, N. I., and Shibaev, V. P., 1998, *Polym. Sci. Ser. A*, **40,** 232.

[4] Bobrovsky, A. Yu., Boiko, N. I., and Shibaev, V. P., 1998, *Liq. Cryst.*, **25,** 393.

[5] Bobrovsky, A. Yu., Boiko, N. I., and Shibaev, V. P., 1998, *Liq. Cryst.*, **25,** 679.

[6] Van de Witte, P., Galan, J. C., and Lub, J., 1998, *Liq. Cryst.*, **24,** 819.

[7] Brehmer, M., Lub, J., and van de Witte, P., 1998, *Adv. Mater.*, **10,** 1438.

[8] Bobrovsky, A. Yu., Boiko, N. I., and Shibaev, V. P., 1999, *Liq. Cryst.*, **26,** 1749.

[9] Bobrovsky, A. Yu., Boiko, N. I., and Shibaev, V. P., 1999, *Polym. Sci. Ser. A*, **41,** 107.

[10] Shibaev, V. P., Kostromin, S. G., and Ivanov, S. A., 1997, *Polym. Sci. Ser. A*, **39,** 118.

[11] Ivanov, S. A., Yakovlev, I. A., Kostromin, S. G., Shibaev, V. P., Lasker, L., Stumpe, J., and Kreysig, D., 1991, *Makromol. Chem. rapid Commun.*, **12,** 709.

[12] Stumpe, J., Lasker, L., Fischer, Th., Kostromin, S., Ivanov, S., Shibaev, V., and Rumann, D., 1994, *Mol. Cryst. liq. Cryst.*, **253,** 1.

[13] Brown, D., Natansohn, A., and Rochon, P., 1995, *Macromolecules*, **28,** 6116.

[14] Romanujam, P., Holme, N., and Hvilsted, S., 1996, *Appl. Phys. Lett.*, **68,** 1329.

[15] Natansohn, A., Rochon, P., Meng, X., Barret, C., Buffeteau, T., Bonenfant, S., and Pezolet, M., 1998, *Macromolecules*, **31,** 1155.

[16] Wu, Y., Demachi, Y., Tsutsumi, O., Kanazava, A., Shiono, T., and Ikeda, T., 1998, *Macromolecules*, **31,** 1104.

[17] Stumpe, J., Fisher, T., Ziegler, A., Geue, T., and Menzel, H., 1997, *Mol. Cryst. liq. Cryst.*, **299,** 245.

[18] Ichimura, K., Suzuki, Y., Seki, T., Hosoki, A., and Aoki, K., 1988, *Langmuir*, **4,** 1214.

[19] Xie, S., Natansohn, A., and Rochon, P., 1993, *Chem. Mater.*, **5,** 403.

[20] Ringsdorf, H., Urban, C., Knoll, W., and Sawodny, M., 1992, *Macromol. Chem.*, **193,** 1235.

[21] Corvazier, L., and Zhao, Y., 1999, *Macromolecules*, **32,** 3195.

[22] Kreuzer, F. H., 1996, *Polymers as Electrooptical and Photo-optical Active Media*, edited by V. P. Shibaev (Berlin, Heidelberg: Springer-Verlag).

[23] Petry, A., Brauchle, Ch., Leigeber, H., Miller, A., Weitzel, H.-P., and Kreuzer, F.-H., 1993, *Liq. Cryst.*, **15,** 113.

[24] Heppke, G., Oestreicher, F., and Scherowsky, G., 1982, *Z. Naturforsch.*, **37a,** 1176.

[25] Bobrovsky, A. Yu., Boiko, N. I., and Shibaev, V. P., 1997, *Polym. Sci. Ser. A*, **39,** 798.

[26] Ostrovskii, B. I., Sulianov, S. N., Boiko, N. I., and Shibaev, V. P., 1998, *Liq. Cryst.*, **25,** 153.

[27] Boiko, N. I., 1987, PhD thesis, Moscow State University (in Russian).

[28] Bobrovsky, A. Yu., Boiko, N. I., and Shibaev, V. P., 1998, *Liq. Cryst.*, **24,** 489.

[29] Finkelmann, H., and Stegemeyer, G., 1978, *Ber. Bun., phys. Chem.*, **82,** 1302.

[30] Bekker, H. O. (editor), 1976, *Einfuhrung in die Photochemie* (Berlin: VEV Deutscher Verlag der Wissenschatten).

[31] Gabor, G., and Fisher, E., 1971, *J. phys. Chem.*, **75,** 581.

[32] Rau, H., 1990, *Photochemistry and Photophysics*, Vol. II, edited by J. F. Rabek (Boca Raton: CRC Press), Chap. 4.

[33] Otruba III, J. P., and Weiss, R. G., 1983, *J. org. Chem.*, **48,** 3448.

[34] Li, H., Zhang, L., Zhang, X., Shen, J., Yang, Y., and Fei, H., 1998, *Polym. Bull.*, **40,** 735.

[35] Ortler, R., Braeuchle, C., Miller, A., and Riepl, G., 1989, *Makromol. Chem., rapid Commun.*, **10,** 189.

[36] Kanazawa, A., Harano, S., Shishido, A., Hasegawa, M., Tsutsumi, O., Shiono, T., Ikeda, T., Nagase, Y., Akiyama, E., and Takamura, Y., 1997, *Liq. Cryst.*, **23,** 293.