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Dual photochromism of copolymers containing two different types of photoisomerizable side groups

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Abstract

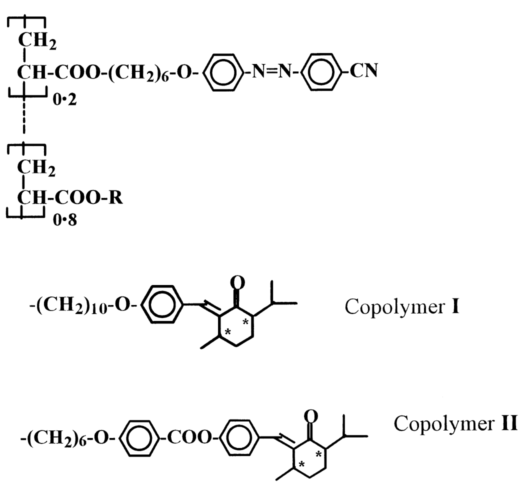
Copolyacrylates containing the side groups presented by the two types of photosensitive fragments such as cyanoazobenzene and benzylidene-*p*-menthane-3-one groups were synthesized. As was shown, upon irradiation of the films of copolymers with a wavelength of 313 nm, primarily E–Z photoisomerization of benzylidene-*p*-menthane-3-one chromophores is observed whereas, under irradiation with a wavelength of 365 nm, a preferential isomerization of azobenzene groups takes place. Hence, selecting the light wavelength, one may easily control the type of the groups participating in photoprocess. Isomerization of benzylidene-*p*-menthane-3-one groups was found to be thermally irreversible whereas, in the case of cyanoazobenzene groups, annealing leads to the back process of Z–E isomerization. The kinetics of forward and back processes was studied. The effect of the configuration of benzylidene-*p*-menthane-3-one groups (content ratio between E and Z form) of polymer matrix on the kinetics of forward and back processes of isomerization of cyanoazobenzene groups was demonstrated. © 2001 Published by Elsevier Science B.V.

Keywords: Dual photochromism; Photoisomerizable side groups; Copolymers

1. Introduction

Introduction of photochromic dopants to polymer matrix via mixing or chemical modification of polymers with photochromic groups allows one to obtain new unique materials for optics, data recording and storage, etc. [1,2]. An ever growing interest to such materials is also related to the recently discovered possibilities of holographic image recording via the two-photon addressing on polymers containing minor amounts of dissolved photochromic dopant [3–5]. Possibly, in near future, such polymer materials will be able to compete with traditional magnetic data carriers, and this tendency has attracted the attention of many scientists to study the specific features of their photochemical and photo optical properties.

Relatively big number of publications devoted to photochemistry of azobenzene [6–10] and spiropyran photochromic compounds [11–14], fulgides [15,16], and diarylethylenes [17–19] has clearly demonstrated a complex character of the kinetic features of photoprocesses taking place in polymer matrix. This behavior is associated with the effect of local surrounding of photosensitive group, wide free volume distribution, high local viscosity of polymer medium, etc.[1] In this work, a detailed investigation of photochemical processes taking place in the synthesized copolymers containing the two different types of photosensitive units such as derivatives of benzylidene-*p*-menthane-3-one and azobenzene was carried out.



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[1] For example, for azobenzene and spiropyran photochromic compounds [6–14], a marked effect of viscosity and free volume on the occurrence and features of photoprocesses was clearly demonstrated.

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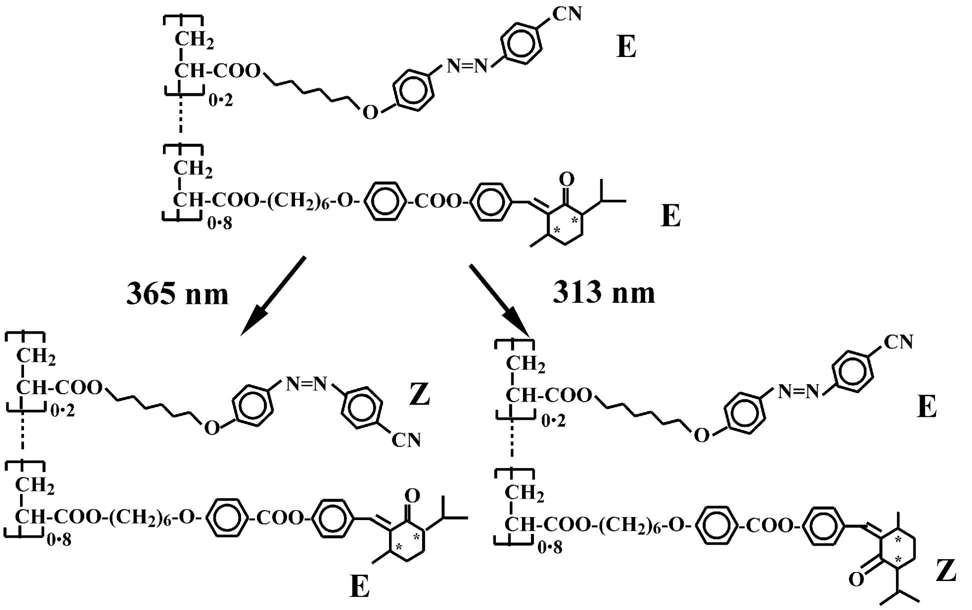


Fig. 1. Schematic representation of possible photochemical processes in copolymers induced by the light of different wavelength.

These copolymers belong to acrylic polymers and contain 20 mol% of cyanoazobenzene groups and 80 mol% of benzylidene-*p*-menthane-3-one groups. In this case, the structure of the latter groups is distinguished by the length of rigid aromatic fragment and flexible methylene spacer.

Both types of photosensitive units are well known to experience the E–Z isomerization relative to double N=N and C=C bonds. However, first, the location of absorption bands of benzylidene-*p*-menthane-3-one and azobenzene chromophores is different; second, if photoisomerization of azobenzene groups is thermally reversible (i.e., occurrence of the back Z–E process is possible) [1], in the case of benzylidene-*p*-menthane-3-one groups, this process is irreversible [20,21]. Hence, selecting the wavelength of incident light, one may induce a preferential isomerization either of benzylidene-*p*-menthane-3-one or cyanoazobenzene photochromic groups [22] (Fig. 1). Such copolymers offer a unique possibility (by selecting UV irradiation time) to control smoothly the properties of polymer matrix due to irreversible photoisomerization of benzylidene-*p*-menthane-3-one relative to C=C bond and, hence, to govern the viscosity, free volume of medium, and optical properties.

The principal task of this work involves studying the specific features of photoisomerization of the two types of photosensitive groups depending on the wavelength of incident light and finding the specific features of the effect of configurational state of benzylidene-*p*-menthane-3-one polymer matrix on the kinetics of forward and back processes of the E–Z isomerization of cyanoazobenzene groups.

2. Experimental

2.1. Synthesis of copolymers

Menthone-containing and azobenzene-containing monomers were synthesized according to the procedures described in [23] and [24], respectively.

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

2.2. Physicochemicals methods of investigations

Relative molecular weight of copolymers was determined by gel permeation chromatography (GPC). GPC analyses were carried out with a GPC-2 Waters instrument equipped with an LC-100 column oven and a Data Modul-370 data station. Measurements were made by using a UV detector, THF as solvent (1 ml/min, 40°C), a set of PL columns of 100, 500 and 10^3 Å, and a calibration plot constructed with polystyrene standards. The copolymers obtained have the following molecular mass characteristics: $M_n = 10\,000$–$12\,000$, $M_w/M_n = 2.1$–3.0.

Phase transitions in copolymers 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. X-ray diffraction analysis was carried out using a URS-55 instrument (Ni-filtered Cu Kα radiation, $\lambda = 1.54$ Å).

2.3. Photochemistry investigations

Photochemical investigations were performed using a special instrument [21] equipped with a DRSh-250 ultra-high pressure mercury lamp. Using filter, light with maximum wavelength of 365 nm or 313 nm was selected. 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. During irradiation, the constant temperature of the test samples was maintained using a Mettler FP-80 heating unit. The intensities of UV irradiation at appropriate wavelength λ_{ir} were determined actinometrically [25] and were equal to 1.0×10^{-9} einstein s^{-1} cm^{-2} ($\lambda_{ir} = 313$ nm) and 1.1×10^{-8} einstein s^{-1} cm^{-2} ($\lambda_{ir} = 365$ nm).

Photochemical properties of copolymers were studied by illuminating thin films obtained by casting of solution in dichloroethane followed by evaporation and drying at 60°C. Immediately after irradiation, absorbance spectra were recorded using Hitachi U-3400 UV–vis–IR spectrometer.

3. Results and discussion

According to the data of polarizing optical microscopy and X-ray analysis, both synthesized copolymers are amorphous. For copolymers I and II, glass transition temperature (T_g according to the DSC data) is equal to 20 and 60°C, respectively. Higher glass transition temperature T_g of copolymer II is related, on one hand, to the presence of longer aromatic fragment and, on the other hand, to shorter methylene spacer [23,26,27].

Let us discuss the specific features of spectral changes in the films of copolymers upon UV irradiation with different wavelengths λ_{ir}: 313 and 365 nm. As follows from Fig. 2, light irradiation with $\lambda_{ir} = 313$ nm primarily leads to changes in the short wavelength peak responsible for the π–π^* and n–π^* electron transitions of benzylidene-*p*-menthane-3-one chromophore [20].

Such spectral changes suggest the occurrence of the E–Z photoisomerization relative to the double C=C bond. Let us also note that, in the case of copolymer II, spectral changes are less pronounced, and this trend is related to the presence of additional phenylbenzoate chromophore which

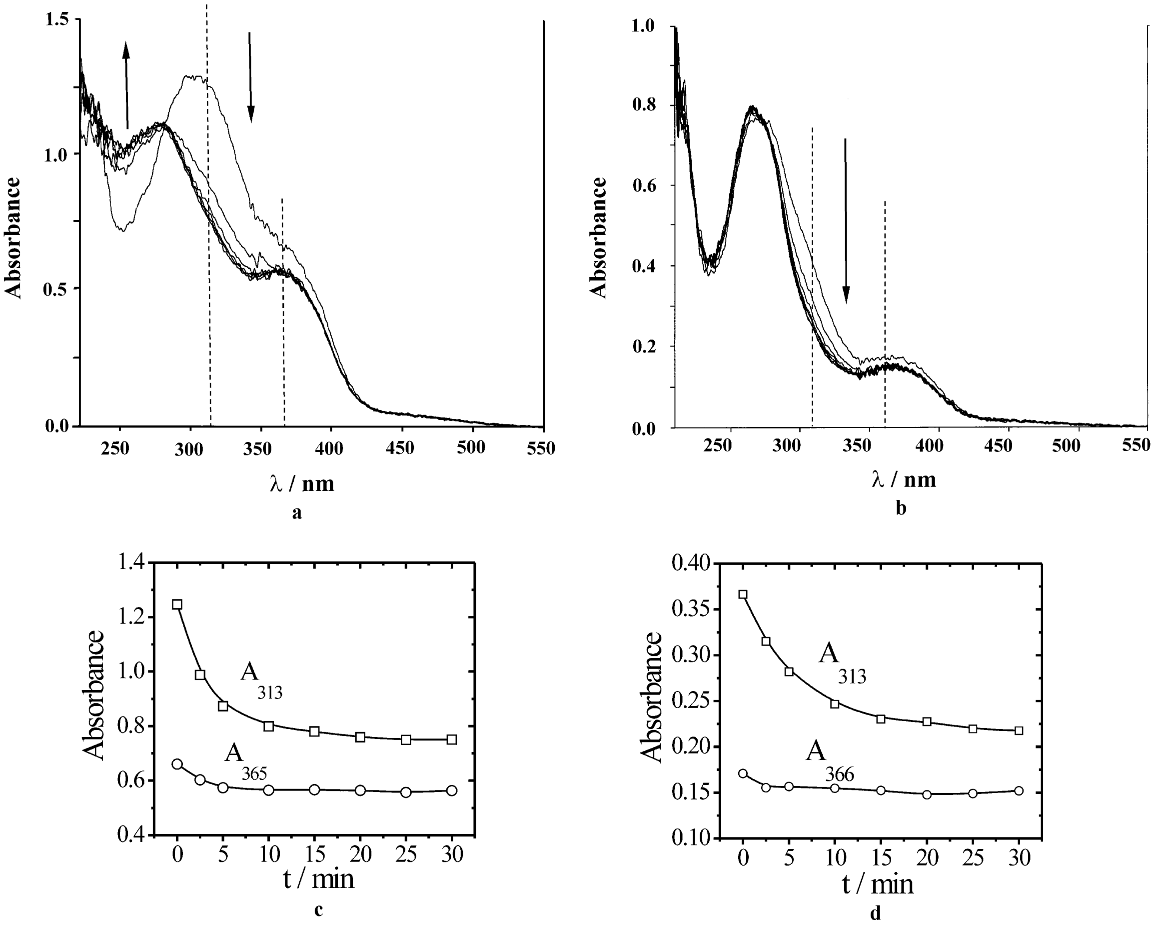
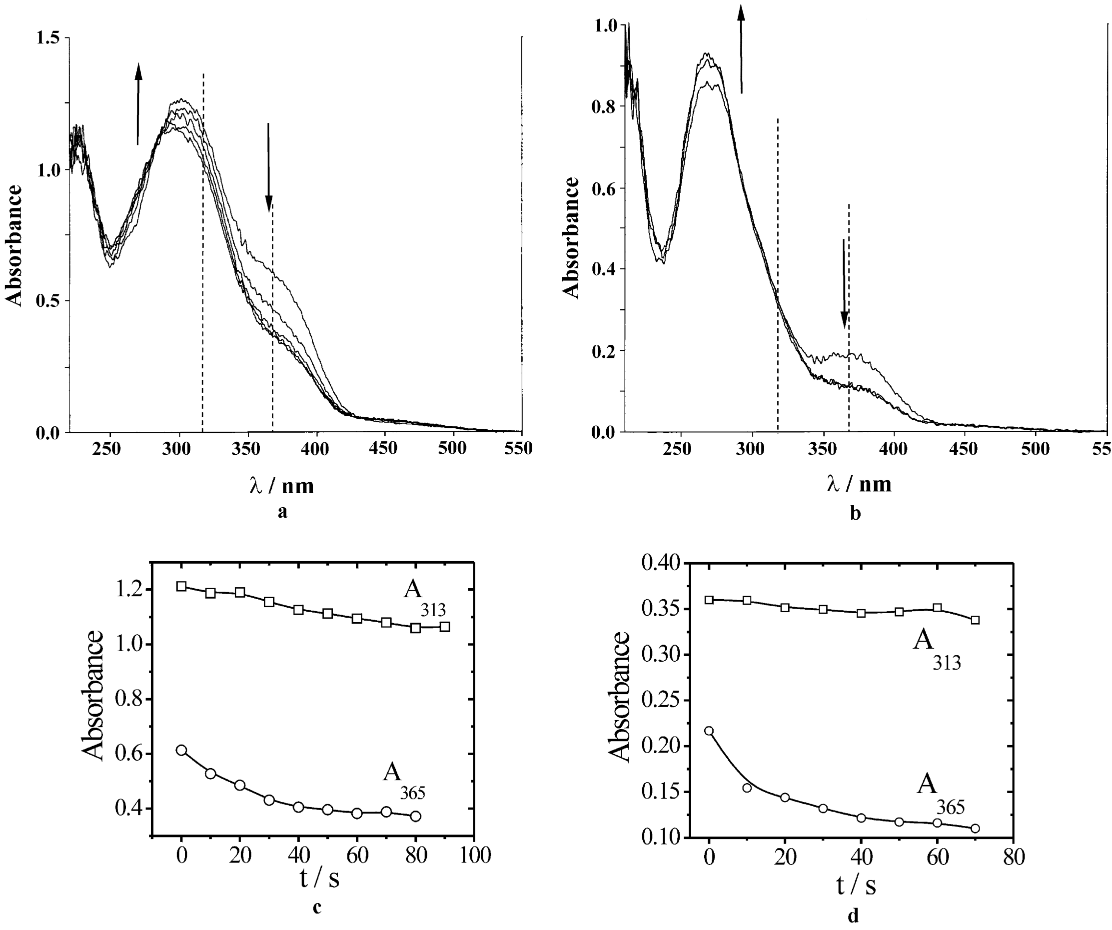


Fig. 2. Spectral changes (a and b) and absorbance decrease (c and d) for copolymer I (a and c) and II (b and d) during UV irradiation with light of 313 nm. Spectra were recorded each 5 min of UV irradiation.



a

b

c

d

Fig. 3. Spectral changes (a and b) and absorbance decrease (c and d) for copolymer I (a and c) and II (b and d) during UV irradiation with light of 365 nm. Spectra were recorded each 1 min of UV irradiation.

experiences no photochemical light-induced transformations and provides a marked contribution to the total absorption of the system [23].

Upon irradiation with $\lambda_{ir} = 365\,nm$ (Fig. 3), quite different spectra are obtained. Upon irradiation, mostly long wavelength "shoulder" related to the π–π^* transition of azobenzene groups is changed ($\lambda_{max} = 365\,nm$ [22]). In other words, in this case, cyanoazobenzene side groups are primarily involved in photoisomerization. Unfortunately, all earlier attempts to estimate the contribution of particular groups to photoprocess showed only qualitative character. However, the experimental data presented in Figs. 2 and 3 convincingly prove a marked selectivity of photosensitive groups relative to light irradiation with different wavelengths.

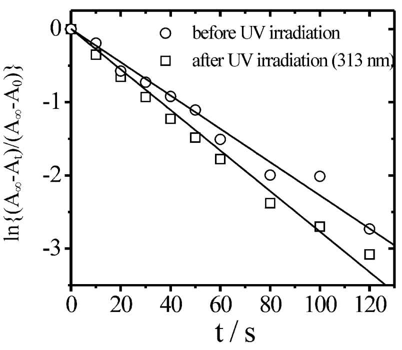


Fig. 4. First-order plots of E–Z photoisomerization process for film of copolymer II induced by the light with $\lambda_{ir} = 365\,nm$. Measurements were made before and after short wavelength UV irradiation (313 nm, irradiation time: 30 min).

Let us emphasize that the changes in the short wavelength peak are irreversible; at the same time, upon annealing, the

Table 1
Rate constant of E–Z photoisomerization of azobenzene groups for copolymers I and II (at 25°C) induced by the light with $\lambda_{ir} = 365\,nm$[a]

Copolymer	k (s^{-1}) before UV irradiation	k (s^{-1}) after UV irradiation
I	0.028 ± 0.001	0.043 ± 0.001
II	0.023 ± 0.001	0.028 ± 0.001

[a] Kinetics measurements were performed before and after short wavelength UV light irradiation ($\lambda_{ir} = 313\,nm$, 30 min).

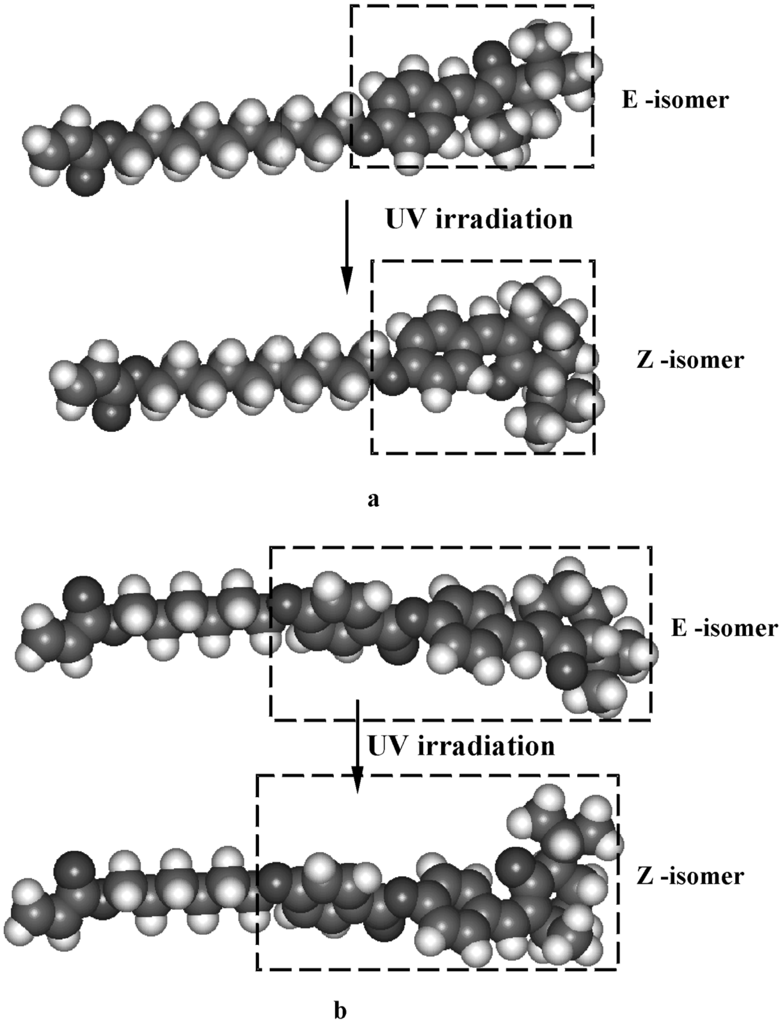


Fig. 5. Changes of benzilidenementane-3-one groups anisometry during their E–Z photoisomerization in the case of: (a) copolymer I and (b) copolymer II. Molecular models have been derived from a computer molecular modeling program HyperChem^{TM}.

absorption of long wavelength “shoulder” responsible for the π–π^* transition of azobenzene groups is restored (the kinetics of the back thermal process of the Z–E isomerization of cyanoazobenzene groups will be discussed below). As compared with isomerization relative to N=N bond, photoisomerization of benzylidene-*p*-menthane-3-one groups is irreversible.

Let us consider in more detail the kinetics of the E–Z isomerization of cyanoazobenzene groups as a function of preliminary short wavelength UV irradiation ($\lambda_{ir} = 313\,nm$). In other words, the effect of the configuration of benzylidene-*p*-menthane-3-one groups (which dominate in the system) on the rate of E–Z photoisomerization will be studied.

As follows from Fig. 4 and Table 1, for both copolymers, the E–Z isomerization of azobenzene groups proceeds with a higher rate upon light irradiation with $\lambda_{ir} = 313\,nm$. Note that this effect is mostly pronounced for copolymer I with single-ring menthanone-containing groups. This behavior may be explained by the fact that the polymer matrix enriched with the Z-form of benzylidene-*p*-menthane-3-one groups is characterized by a higher free volume due to a lower anisometry of Z-isomer of these fragments [20,21,23] (Fig. 5). Taking into account that the rate and quantum yield of the E–Z isomerization of azobenzene groups are controlled by the level of free volume[2] [6,8–10,29], this explanation seems to be plausible. Seemingly, the difference in the content of free volume also manifests itself in a higher rate of photoprocess for copolymer I as compared with that of copolymer II. In this case, one should take into account that, under given irradiation conditions (25°C), copolymer I exists in rubbery state ($T_g = 20°C$) and copolymer II in glassy state ($T_g = 60°C$).

Let us now proceed to the examination of the kinetics of the back thermal Z–E process of cyanoazobenzene groups. Thin films of copolymers were irradiated with $\lambda_{ir} = 365\,nm$

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[2] In [28], a decisive role of free volume on the kinetics of forward and back processes of E–Z isomerization was demonstrated. As was shown, free volume necessary for isomerization is equal to about 127 Å^3.

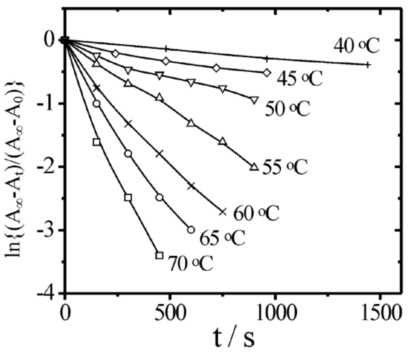

Fig. 6. First-order plots of Z–E thermal back process for copolymer II. Thin film of copolymer was irradiated with light ($\lambda_{ir} = 365$ nm) for 2 min, then the corresponding absorption spectra were recorded as a function of the time of annealing at different temperatures.

for 2 min; then, the corresponding absorption spectra were recorded as a function of the time of annealing at different temperatures. Finally, the plots of absorption versus annealing time were constructed using the first-order kinetic coordinates (Fig. 6):

$$\ln\{(A_\infty - A_t)(A_\infty - A_0)^{-1}\} = -kt \quad (1)$$

where A_0, A_t, and A_∞ stand for the absorption at 365 nm at $t = 0$, current time t, and infinite time, respectively. Rate constants were estimated from the slope of the initial portion of the above dependences.

To calculate the values of activation energy of this process, semi-log temperature dependences of isomerization rate are constructed (Fig. 7). The calculated values of activation energy are summarized in Table 2. As follows from Table 2, for copolymer I, one may observe an increase in activation energy of the thermal Z–E process upon preliminary irradiation of the film with short wavelength light (313 nm). In the case of cyanoazobenzene groups, the Z-form is more stable in polymer matrix enriched with the Z-form of benzylidene-*p*-menthane-3-one groups.

A far more complex case is observed for copolymer II (Fig. 7b, Table 2): at temperatures above and below T_g, the values of activation energy appear to be different; preliminary UV irradiation (313 nm) has almost no effect on E_A at temperatures above T_g and leads a marked growth in E_A at temperatures below T_g. Before and after light irradiation with $\lambda_{ir} = 313$ nm, the activation energy of Z–E isomerization in glassy state is much higher. This behavior is likely to be related to a higher local viscosity (and, possibly, lower free volume of polymer matrix). One may anticipate that the Z–E isomerization of benzylidene-*p*-menthane-3-one groups should provide no marked changes in viscosity but leads to an increase in free volume which, in turn, stabilizes the Z-form of cyanoazobenzene groups.

Table 2
Activation energy of back thermal Z–E isomerization process for copolymers I and II[a]

Copolymer	E_A (kJ/mol) before UV irradiation		E_A (kJ/mol) after UV irradiation	
	$T < T_g$	$T > T_g$	$T < T_g$	$T > T_g$
I	–	92.0	–	102.5
II	116.0	75.2	145.7	62.2

[a] Kinetics measurements were performed before and after short wavelength UV light irradiation ($\lambda_{ir} = 313$ nm, 30 min).

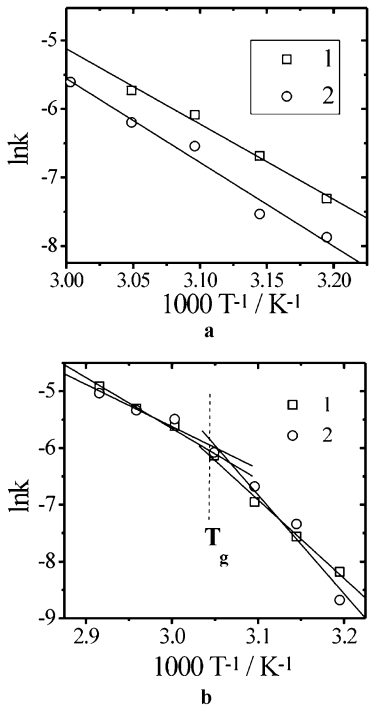

Fig. 7. Arrhenius plots of thermal back Z–E process for film of copolymer I (a) and copolymer II (b). Data were obtained for films before (1) and after (2) UV irradiation (313 nm) during 30 min.

At temperatures above T_g in rubbery state, the configuration of benzylidene-*p*-menthane-3-one groups of copolymer II exerts no marked effect on the activation energy barrier of the process. Probably, in the case of copolymer II, the E–Z isomerization of benzylidene-*p*-menthane-3-one groups leads to a marked increase in free volume only for polymers in glassy state. This behavior may be related to the fact that, as was mentioned above, a decrease in anisometry of these groups is less pronounced for copolymer II (Fig. 5).

Evidently, our assumptions are hypothetical and require additional experimental verification. In any case, analysis of the above specific features vividly demonstrates the complex character of the specific features of isomerization observed in polymer medium.

Hence, finally, one may conclude that the synthesized copolymers containing the two types of photochromic groups sensitive to the different light wavelengths present a marked interest from the viewpoint of studying the photochromic processes in polymer materials with dual photochromism. On the other hand, such copolymers may present a certain interest from the viewpoint of their application (data recording and storage) as the materials with photocontrolled optical properties. In our forthcoming studies, we are planning to study the induction of birefringence under the action of polarized light and to investigate the effect of the ratio between the E- and Z-isomers of benzylidene-*p*-menthane-3-one of polymer matrix on the kinetics of photo-orientation processes.

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