ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 120 (1999) 55–62

Journal of Photochemistry and Photobiology A:Chemistry

Photochromic network polymers

A.V. Lyubimov, N.L. Zaichenko, V.S. Marevtsev*

N.N. Semenov Institute of Chemical Physics of Russian Academy of Sciences 4, Kosygin St., Moscow 117977, Russia

Received 22 July 1998; accepted 28 July 1998

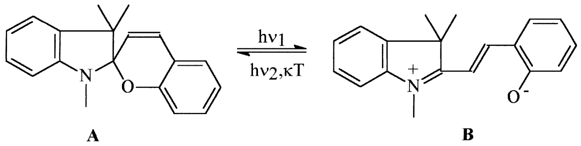
Abstract

New photochromic polymers having network structure have been studied. These polymers have been obtained on the base of spiropyrans (SP) with one or two polymerizable groups. It has been shown that the photochromic properties of SP molecules linked with macromolecules by one polymerizable group depend on supermolecular structure of network polymer. So, these SP molecules can be used as indicators of microheterogeneity of network polymer. It has been established that the photochromic behavior of SP molecules having two polymerizable groups is determined by the number of chemical bonds (one or two) of such a SP molecule with macromolecule. The copolymers of these SP molecules with alkyl methacrylates are of special interest because using these copolymers make it possible to create photochromic polymer material having large and adjustable time of storage of optical information. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Network polymer; Photochromism; Polarized fluorescence; Spiropyran

1. Introduction

Properties of photochromic compounds introduced in polymer films are of great interest because of the possibilities of their practical use. Among photochromic systems spirocompounds are of particular concern. Their photochromism involves photodissociation of spirobond and *cis–trans* isomerization from an initial form **A** to a highly coloured plane merocyanine form **B**, which undergoes bond closure to reproduce the initial spiroform **A** under action of heat or visible light irradiation. It is well known [1,2] that the introduction of the photochromic compounds of spiropyran (SP) class into polymer films both as a copolymer and a matrix mixture leads to significant decreasing rates of their photocolouration and dark bleaching processes in comparison with those in liquid solutions. The reason is a steric barrier in polymer films preventing from the isomerization reactions taking place during photochromic transformation **A**→**B** as well as decolouration process **B**→**A**.



But polymer films obtained from matrix mixtures, in which photochromic molecules are mechanically distributed in polymer, suffer from the SP molecule diffusion on the film surface leading to the step-by-step lost of the film's photochromic properties. It is evident that the chemical linkage of photochromic molecule and polymer macromolecule, that is, copolymerization, prevents from this undesirable process. It appears that besides this main distinction the rest photochromic properties of matrix mixture films and copolymer films are practically identical. So in both systems the kinetics of dark decolouration does not obey the monoexponential law. The deviations from this law are attributed to the dispersion of distribution of microcavities on sizes, those microcavities, in which the photochromic molecules are located and a sum of which represents a free volume of polymer. However, this conclusion is true only for linear polymers and it is not clear which photochromic properties of SP molecules will be in films of network polymers having three-dimensional net supermolecular structure and increased rigidity. At present such data are absent.

So, in this paper we present our results on creation of photochromic network polymers based on SP molecules and study of their photochromic properties.

2. Experimental details

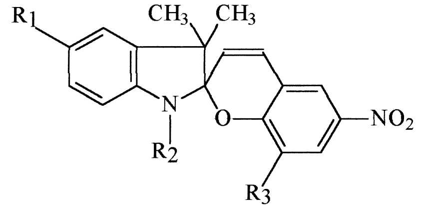
2.1. Materials

The photochromic compounds under study were indolinospiropyrans having the following structure

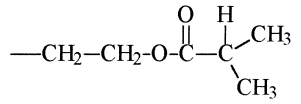
---

*Corresponding author.

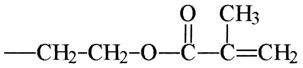
PII: S1010-6030(98)00360-8



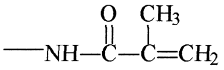
N	R_1	R_2	R_3	T mp, °C
1	H	X	H	112-113
2	H	Y	H	113-115
3	H	Y	Y	oil
4	Z	CH_3	Y	53-55

where X=


$$-CH_2-CH_2-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{C}(CH_3)_2$$

Y=


$$-CH_2-CH_2-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{C}=CH_2$$

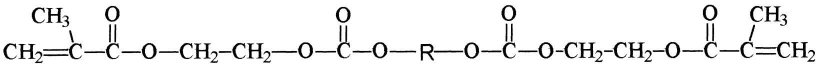
Z=


$$-NH-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{C}=CH_2$$

Compounds **1–4** were prepared and purified as described in [3,4]. Nuclear magnetic resonance and thin layer chromatography techniques showed no trace of impurities in these samples. It is important to note that **1** has no polymerizable groups, **2** has one such group and **3** and **4** have two groups able to polymerize.

Decyl methacrylate (DMA), methyl methacrylate (MMA), *n*-butyl methacrylate (*n*-BMA) and iso-butyl methacrylate (*i*-BMA) were used as comonomers at polymerization with SP having two polymerizable groups. All alkyl methacrylates were commercial products containing hydroquinone inhibitor. They were purified by flash vacuum distillation. UV analysis showed less than 10^{-4} M inhibitor to be present.

Oligocarbonate methacrylates (OCMs) were used as the base for network polymer films at polymerization with SP having one polymerizable group. OCMs were commercial products and were used without any additional purification. The molecular structure of OCM is



$$CH_2=\overset{\overset{CH_3}{|}}{C}-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_2-O-\overset{\overset{O}{\|}}{C}-O-R-O-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_2-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{C}=CH_2$$

R = $-(CH_2)_2-$ OCM-1

$-(CH_2)_2O(CH_2)_2-$ OCM-2

Dicyclohexylperoxidicarbonate was used as an initiator of polymerization. It was a commercial product and was recrystallized and dried before use.

Because the OCMs form insoluble three-dimensional network polymers the films on their base were obtained by polymerization between two glass plates. The common procedure was used to obtain the films of the matrix mixtures or copolymers of OCMs and SP. Two gram of double mixture consisting of OCM and SP in necessary concentration (0.2–2 wt.%) and 0.01 g of polymerization initiator were dissolved in a small amount (5–10 ml) of dry benzene, then the solvent was evaporated using pump without heating. Obtained solution of SP and initiator in OCM was placed between two glass plates separated by a spacer with thickness 40–60 µm. The polymerization took place at 55°C during 3 h. In the case of a matrix mixture the photochromic compound was SP **1**, in the case of a copolymer it was compound **2**.

The polymer films of copolymers of SP **3** or **4** and corresponding alkyl methacrylate were also obtained between two glass plates using two-step polymerization. The first step was the preliminary polymerization. The solution of SP and initiator in corresponding alkyl methacrylate was placed into sample tube and degassed using vacuum installation (residual pressure was 10^{-3} mm Hg). The tube was sealed and heated at 55°C during 10–15 min. At the second step the obtained viscous solution was placed between two glass plates and polymerized for 3–4 h at 55°C.

The polymerization degree was determined in terms of the conversion of double bonds by measuring IR spectra according to [5]. In our cases it was equal to 90–95%.

2.2. Spectroscopic study

The absorption spectra were measured using a spectrophotometer 'Specord UV–VIS'. The luminescence polarization spectra were recorded on a JY-3 spectrofluorimeter. Polaroid films were used as polarizer of the excitation light and as analyzer of the emission. Polarization degree of luminescence was obtained by static method, i.e. by direct measuring I_v and I_h, where I_v and I_h are the luminescence intensities at the vertical or horizontal position of polarization plane of the analyzer at the vertical orientation of the excitation light polarization plane. I_v and I_h were measured at the definite wavelengths of the luminescence excitation (λ_{ex}) and luminescence recording (λ_{reg}). The P value was calculated by the Eq. (1)

$$P = \frac{I_v - kI_h}{I_v + kI_h} \qquad (1)$$

where k is the correction factor taking into account the polarization effect of the recording monochromator. This factor was determined using a method described in [6].

The angles between the directions of oscillators of electronic transitions corresponding to the separate bands of absorption spectrum from experimental data on P were calculated using the dependence of P on the angle α between absorption and emission oscillators [6] which is given by Eq. (2)

$$P(\alpha) = \frac{3\cos^2\alpha - 1}{\cos^2\alpha + 3} \tag{2}$$

All spectral measurements were carried out at room temperature. Photocolouration of the samples was made using a 1000 W high pressure mercury lamp and a set of interference filters.

3. Results and discussion

3.1. *Influence of network polymer supermolecular structure on photochromic properties*

Firstly, let us consider the polymer films obtained by polymerization of OCMs in the presence of SP molecules. The polymer films based on both copolymers and matrix mixtures show photochromic properties, i.e., they become coloured under UV irradiation and return to the initial state in dark conditions. Because the molecular structures of SP **1** and **2** are very similar it can be expected that the coloured forms of these compounds will have the same absorption spectra. However, the positions of long-wave bonds of coloured form absorption spectra are slightly different for copolymer and mixture films (587 and 578 nm, respectively independent on OCMs). Besides, the significant differences are observed at dark decolouration process of these films (Fig. 1). The kinetics of thermal fading of copolymer films does not proceed as first-order kinetics. As stated above, this fact is usually observed for linear polymers containing photochromic molecules and is explained by a distribution of the steric barriers (connected with a distribution of free volumes) for the *trans–cis* isomerization of the form **B** to the form **A**. We have obtained that the decolouration kinetics of the OCM network copolymer films is very well described by biexponential Eq. (3)

$$D(t) = a\exp(-k_1 t) + b\exp(-k_2 t) \tag{3}$$

where $D(t)$ is the optical density at absorption maximum of the form **B**, a and b are contributions to the $D(0)$ of SP molecules decolourizing with the rate constants k_1 and k_2.

At the same time the thermal decolouration kinetics of matrix mixture films for both OCM-1 and OCM-2 is the kinetics of first order and is excellently described by monoexponential dependence that is very surprising for the glassy polymer systems. The obtained data on the decolouration process are given in Table 1, in which E_1 and E_2 are the corresponding activation energies.

The analysis of results shows that the values of rate constants for polymers based on OCM-2 are somewhat higher than the same for polymers based on OCM-1. This difference is likely to be connected with the larger length and flexibility of OCM-2 oligomer unit in comparison with OCM-1 one.

The difference in the photochromic behavior of matrix mixtures and copolymers can have two explanations. It is well known that the coloured form molecule of spirocompound can exist as four stereoisomers (**B1–B4**) differing in molecular structure. The formation of one stereoisomer or the other depends on temperature and medium properties [7,8]. So, the first explanation is that there are two stereoisomers of coloured form **B** in the copolymer films and these stereoisomers have the different molecular structures as well as the rate constants of thermal decolouration but the same absorption spectra. Moreover, these stereoisomers are different from the stereoisomer forming in the matrix mixtures. The second explanation is connected with the existence of one stereoisomer located in nonequivalent regions presence of which is due to microheterogeneity of network polymer structure [5,9]. In order to clarify this situation we have studied the polarized fluorescence of the coloured form in polymer films of matrix mixtures and copolymers.

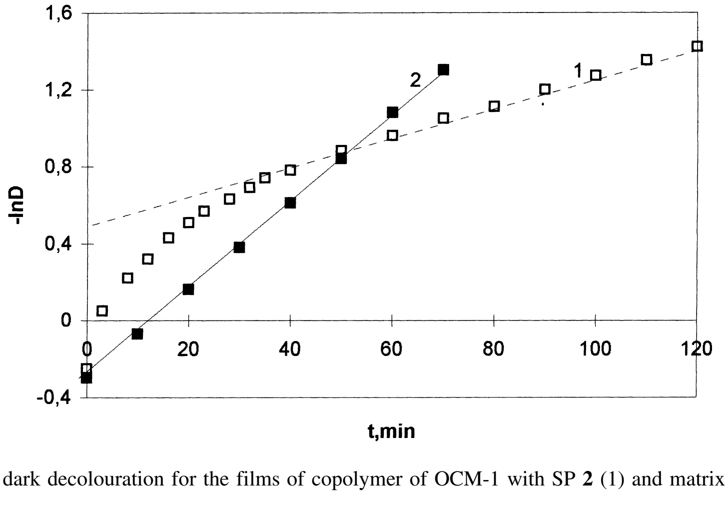


Fig. 1. Kinetics curves of the dark decolouration for the films of copolymer of OCM-1 with SP **2** (1) and matrix mixture of OCM-1 and SP **1**

Table 1
Photochromic parameters of films of network copolymers of SP **2** with OCM

Comonomer	Concentration (%)	T (°C)	a (%)	$k_1 \times 10^3$ (s^{-1})	$k_2 \times 10^4$ (s^{-1})	E_1 (kcal mol^{-1})	E_2 (kcal mol^{-1})
OCM-1	0.17	22	11	1.65	1.51	4.0	5.0
		29	38				
		36	59				
	0.26	21	22	1.58	1.43	3.8	3.8
	2.04	30	47	1.29	1.27	8.4	4.0
OCM-2	0.15	22	27	1.73	2.01	5.1	9.5
		29	33				
		36	47				
	2.05	23	45	1.47	1.26	4.2	7.1
OCM-1[a]	1.98	22	–	–	4.06	–	22.5
OCM-2[a]	2.07	22	–	–	4.44	–	21.0

[a] Matrix mixtures with SP **1**.

Fig. 2 represents the spectral and polarization characteristics of the fluorescence of the SP **1** form **B** in the matrix mixture film of OCM-1. The similar dependencies were obtained for photocoloured copolymer films of OCM-1 and OCM-2 with SP **2**. It is seen that in the region of long-wave absorption band (λ_1) the polarization degree of fluorescence P is equal to 44%, that is quite near to the maximum theoretical value of 50% for the case of coinciding in direction oscillators of absorption and emission [6]. The relative constancy of P in this region let us conclude that this band corresponds to the one $S_0 \rightarrow S_1$ electron transition.

In the region of the short-wave band (λ_2) the P has a mean value between those for parallel and perpendicular oscillators of absorption and emission, i.e., is between +50% and −33%. It means that the band at λ_2 corresponds to the second electron transition $S_0 \rightarrow S_2$ and oscillator of this transition is directed at the angle α comparatively to the direction of $S_0 \rightarrow S_1$ transition. The P at both absorption bands has positive values. This fact indicates that the moments of the transitions responsible for light absorption and emission in the visible region for the form **B** are located in the molecular plane, that is they are π–π^* transitions. This, our conclusion, is in agreement with the data on an absorption dichroism of the SP's coloured form in polyvinylbutirale films [10].

We have found that the fluorescence polarization degrees at λ_2 for both matrix mixtures and copolymers have the same value +7% which does not depend on time of dark decolouration in the case of copolymer films. It means that the angle between the directions of oscillators of $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions is equal to 47°. Because each of four stereoisomers of the form **B** is characterized by its own value of α depending on molecular structure [7], the coincidence of these angles for matrix mixtures and copolymers allows us to conclude that the same stereoisomer is formed under action of UV light in both systems. Consequently, the difference in the position of the long-wave maxima of the absorption spectra of coloured forms in copolymer and matrix mixture films is caused by the different intermolecular interaction of the forms **B** with surrounding medium. Besides, the complex kinetics of thermal decolouration of copolymer films is explained by the existence of non-equivalent positions in the network polymer and reflexes the network's inhomogeneity.

In order to explain the influence of inhomogeneity of network polymer structure on photochromic behavior of the matrix mixture and copolymer films let us consider the mechanism of network formation. Nowadays, this mechanism is described as follows [11–15]. On the first stage of polymerization the increase of the number of initial poly-

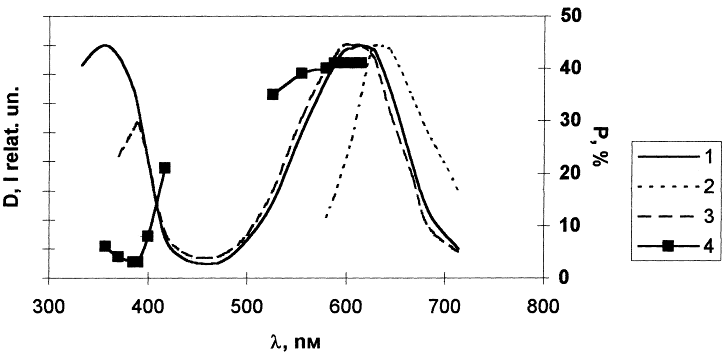


Fig. 2. The spectra of absorption (1), fluorescence (2), excitation of fluorescence (3) and polarization of fluorescence (4) of SP **1** coloured form **B** in matrix mixture film of OCM-1.

meric chains occurs. Each polymeric chain is a center of a discrete particle of microgel. The number of these particles comes quickly up to a limit value and then the polymerization takes place at the constant number of particles. On this stage there is only a growth of particles due to a build-up of peripheral layers with a formation of so-called kernels. At definite degree of transformation the separate kernels begin to touch each other. This stage is named monolithization. Because the kernels may have different sizes, beginning from this stage there are two topologycally different types of polymerization. One process occurs in narrow zones of kernel coupling, the other takes place in wide gaps between kernels. So, at the end of the polymerization the supermolecular structure of network polymer consists of kernels and interkernel space, namely, gaps. The size and rigidity of kernels depend on many factors, in particular, on nature of oligomers. So in the case of oligomers having rigid blocks such as OCM-1 the formed kernels have higher rigidity in comparison with those in the case of oligomers with flexible blocks such as OCM-2. The monolithization is the stage of intensive formation of defects in structure of network polymer. One of the reasons of this formation is a presence of different admixtures in polymerizable system not taking part in polymerization, for example, residual solvent, inhibitor and etc. It appears [12] that during the kernel formation the admixtures stay in the interkernel space and furthermore, their concentration in gaps increases in course of this process.

From data presented in Table 1, it is clear seen that the influence of inhomogeneity of the network supermolecular structure takes place only in the case of SP molecules chemically bonded with macromolecules. For copolymers the value of activation energy of thermal decolouration (E) is significantly lower than that for matrix mixtures. It is known [16] that the activation energy of segmental mobility of oligomer blocks equals to 6–8 kcal mol^{-1}. The values E_1 and E_2 obtained in our experiments for the copolymers are very closed to these values. It gives us a possibility of concluding that the relaxation of network macromolecules but not the SP's isomerization or the closure of pyran ring is the limited stage of the thermal decolouration of SP molecule form **B** chemically bonded with polymeric network. The photochromic molecules may be located in places differing in density of packing, namely in polymeric kernels and in interkernel space. SP molecules located in the gaps have the higher mobility and, therefore, decolourate with the higher rate constants (k_1). The SP molecules located in kernels are characterized by lower values of the rate constants (k_2). Temperature rising and increasing SP's concentration result in the increasing microinhomogeneity of network polymer, namely, the additional regions with decreased density of packing appear [9].

In the case of the polymerization of matrix mixtures the SP molecules having no polymerizable groups migrate into the interkernel space. As a result nearly all SP molecules are located in the equivalent microcavities and decolourate with the same rate. The E values for the thermal decolouration of the matrix mixtures are very close to that for liquid solutions of SP [17]. It means that kinetics of dark bleaching of such SP in network polymers is governed by the rates of the processes occurring in SP molecule, namely by the rate of pyran ring closure.

So, the data obtained in this section show that the photochromic spirocompound linked chemically with macromolecule can serve as an indicator of microinhomogeneity of the network polymer. Really, the relative value of contribution a Eq. (3) can be a quantitative characteristic of inhomogeneity because it is evident that the smaller a is, the more homogeneous is a structure of network polymer.

3.2. Network polymers on the base of SP molecules having two polymerizable groups

In the previous section we have studied copolymers of SP molecules having only one polymerizable group. So, these molecules are side pendants in the macromolecules. Naturally, it was of interest to create and study photochromic polymers in which SP molecules are bonded with macromolecules through two groups. SP molecules having two polymerizable groups are compounds **3** and **4**.

To describe quantitatively a capacity of copolymer film for photocolouration and to compare the photochromic properties of these films it was defined a new parameter f named an efficiency of photocolouration and equaled to the ratio of the highest value of optical density at maximum of coloured form absorption spectrum to the optical density at isosbestic wavelength at the same conditions of photocolouration for all films.

$$\begin{aligned}&f=\frac{D_{\mathrm{B}}}{D_{\mathrm{is}}};\\&D_{\mathrm{B}}=\varepsilon_{\mathrm{B}}[B]l;\\&D_{\mathrm{is}}=\varepsilon_{\mathrm{is}}([B]+[A])l;\\&[B]+[A]=C_0;\\&f=\frac{\varepsilon_{\mathrm{B}}}{\varepsilon_{\mathrm{is}}}\cdot\frac{[B]}{C_0}\end{aligned}\qquad(4)$$

where ε is the extinction coefficient, l the optical length and C_0 the total SP concentration.

It was found that the photochromic properties of copolymers on the base of SP **3** and MMA do not nearly differ from those of copolymers based on SP **2** having one polymerizable group and described earlier [16]. Firstly, independently on relative concentrations of **3** and MMA the obtained copolymers have a good solubility in the most organic solvents. Secondly, the kinetics of thermal decolouration of the solutions of these copolymers is monoexponential. Thirdly, the values of rate constants and activation energy of dark bleaching for these copolymers are in agreement to those for photochromic copolymers of SP **2** and MMA [16]. Besides, the photocolouration efficiencies f for films and solutions of copolymers of SP **3** and MMA are practically identical (1.7 and 2.0, respectively). All these facts allow us to conclude that there are no SP **3** molecules linked by two

Table 2
Photochromic parameters of films of copolymers of SP **4** with alkyl methacrylates

No	Comonomer		T_g (°C)	λ_B (nm)	$k_1\times10^4$ (s^{-1}) 20°C	$k_2\times10^5$ (s^{-1}) 20°C	E_1 (kcal mol^{-1})		E_2 (kcal mol^{-1})	
							$<T_g$	$>T_g$	$<T_g$	$>T_g$
1	DMA		<−50	604	3.4	1.5	–	23.4	–	23.2
2	DMA (85%)	MMA (15%)	<−50	600	3.0	1.7	–	19.8	–	22.5
3	MMA		136	600	17.1	4.8	0.5	–	15.3	–
4	*n*-BMA		48	600	22.2	2.7	0.5	–	9.1	35.2
5	*i*-BMA		72	598	11.6	3.3	2.4	–	10.0	–

polymerizable groups in these copolymers. In other words the copolymers of SP **3** and MMA have no network structure. It is likely that the relative positions of two polymerizable groups in the SP **3** molecule prevent from their simultaneous polymerization and network polymer formation.

In the case of SP **4** the copolymers with alkyl methacrylates have different solubility depending on the nature of comonomer. So, if the copolymers **I** and **II** (Table 2) are soluble in the most of organic solvents, the copolymers **III**–**V** only swell a little. It should be noted that kinetics of film thermal decolouration of all copolymers is described by Eq. (3) at any temperature. Spectral and kinetic parameters measured for films of these copolymers are shown in Table 2.

The copolymers **I** and **II** have very low glass-transition temperatures (T_g) which are shown in Table 2. The values of photocolouration efficiency f for these copolymer films in the temperature region 15–60°C coincide with those for their solutions in toluene and are equal to 1.5. It is well known [1] that the kinetics of thermal decolouration of copolymer films as well as matrix mixture films obey the first-order equation at the temperatures higher than T_g because on these conditions all photochromic molecules become kinetically equivalent due to the averaging of free volume. The deviation of dark bleaching kinetics from monoexponential law for the copolymers **I** and **II** at temperatures rather higher T_g is possibly caused by the presence of SP molecules linked by two polymerizable groups with macromolecule. This deviation of thermal decolouration kinetics from first-order equation is also observed for the solutions of copolymers **I** and **II** in toluene.

The explanation of the existence of two rate constants has been received at a study of the polarized luminescence of SP **4** coloured form **B** in copolymer **II** film. It has been established that the fluorescence polarization degree at excitation into the band of electron transition $\mathbf{S_0}\rightarrow\mathbf{S_2}$ depends on the time of decolouration. So, it is equal to 0% at the initial stage of decolouration and to +8% at the final stage of this process. These data show that the structure of the coloured form at the initial period of bleaching process differs from that at the finish in spite of the fact that the position of maximum absorption of the coloured form does not change during the decolouration process. It was shown earlier [18] that only one, the most stable, stereoisomer of coloured form **B1** is normally formed in polymer films at room temperature. But when SP molecule is linked by both of its parts with macromolecule, there is a significant sterical hindrance to *cis–trans* isomerization of SP molecule to form the stereoisomer **B1**. It is likely that in this case either some intermediate and less stable stereoisomer of form **B** is realized or isomer **B1** exists as some stressed state having deformed structure in comparison with the equilibrium structure causing the change of fluorescence polarization degree at the transition $\mathbf{S_0}\rightarrow\mathbf{S_2}$. We believe that the second explanation is more probable because, firstly, it was shown earlier [7,8] that different stereoisomers of form **B** have different absorption maxima, and secondly, the angle between directions of $\mathbf{S_0}\rightarrow\mathbf{S_1}$ and $\mathbf{S_0}\rightarrow\mathbf{S_2}$ oscillators calculated from the value of polarization degree at the second transition (0%) using Eq. (2) is equal to 54° but this value is intermediate one between those for **B1** and **B2** stereoisomers (42° and 65°, respectively, [18]). In any case a rate of decolouration of the stereoisomer linked by two groups will be higher than that of isomer **B1** linked by only one group. So, we can attribute a 'fast' rate constant k_1 (Table 2) to SP molecules which are bonded with macromolecule by two groups and just these molecules form a network polymer. Then a 'slow' rate constant k_2 must belong to SP molecules which are linked by one group, i.e., these molecules are the side pendants.

Glass-transition temperature of copolymer **IV** is equal to 48°C. It allows us to examine a behavior of this polymer at temperatures both below T_g and above T_g. At room temperature the efficiency of photocolouration of this copolymer film is rather small (0.2) but it increases with temperature rising (Fig. 3) and has a maximum at T_g (0.45). The kinetics of its dark bleaching is described by two rate constants (Table 2). A value of activation energy for 'slow' rate constant E_2 is close to that for copolymer having photochromic groups as side pendants [1,2,16].

At $T > T_g$ the photocolouration efficiency for **IV** film decreases with temperature rise (Fig. 3) and the Arrhenius dependence of k_2 has the point of inflection at T_g. Beyond this point the value of E_2 increases significantly and becomes equal to 35 kcal mol^{-1} (Fig. 4).

We have observed the following essential distinctions in the photochromic behavior of copolymer **IV** film after its

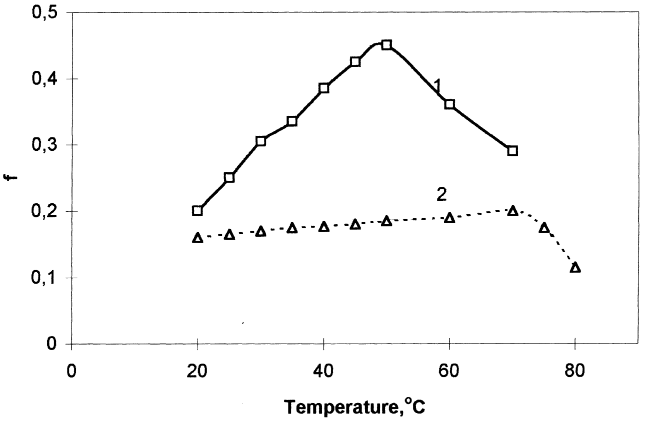


Fig. 3. Dependencies of the photocolouration efficiency f on temperature for films of copolymers **IV** (1) and **V** (2).

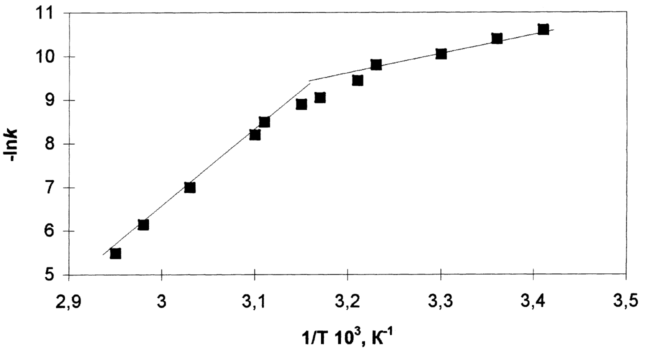


Fig. 4. Plot of Arrhenius dependence for slow rate constant of dark decolouration of copolymer **IV** film.

treatment by any organic solvent leading to the partial swelling of this film.

1. Photocolouration efficiency increases after treatment by a lot of solvents ($f = 1.2$ after treatment by toluene for 30 s at 20°C in comparison with f=0.2 for untreated film).
2. After photocolouration of the treated film the optical density at the maximum absorbance of the coloured form decreases on 30% of the initial value on dark conditions, then it reaches some constant values which does not change for a long time.
3. Being treated by organic solvent once more after colouration, this film bleaches fully under visible light action.

We can explain these results by the fact that the copolymer **IV** has a cross-linked structure. The SP **4** molecules act as crosslinks between polymer chains and the number of such crosslinks in copolymer **IV** is sufficiently bigger than in the case of soluble copolymers **1** and **2**. The small f value shows that the contribution of SP molecules linked by two groups into absorbance of coloured form is small for copolymer **IV**. Increase of the f value with temperature rise in the region $T < T_g$ is caused by the increase of segment mobility of macromolecules, and as a result of this an additional part of SP molecules linked by two groups takes part in the photocolouration. Like the case of copolymers **I** and **II**, a ‘fast’ rate constant of thermal decolouration of copolymer **IV** film characterizes the SP molecules taking part in forming network polymer and a ‘slow’ one describes the dark bleaching of SP molecules linked by one group. Naturally, a temperature rising results in decreasing rigidity of polymer film but not sufficiently that all SP molecules linked by two groups to be coloured under UV light action. It is an evident that these molecules are not equivalent. A part of them is located between the large network polymer blocks and these molecules do not take part in processing of photocolouration even at T_g. Only after the treatment of film by organic solvents and following its partial swelling the rigidity of polymer film decreases in such a degree that practically all SP molecules undergo the photochromic transformations. Subsequent conversion of this film into a glass state freezes the relaxation processes in network polymer and the reverse process of bleaching becomes impossible. Partial decrease of optical density (30%) is connected with decolouration of both SP molecules linked by only one group and a part of two-linked SP molecules which are located in the places with less degree of cross-linkage and consequently can be transformed into the coloured form by light action at increased temperature. The following fact supports this conclusion. When the copolymer **IV** film coloured at 50°C is sharply cooled down to 20°C, its thermal decolouration occurs significantly slower than in the case when the film photocolouration is achieved at 20°C.

The photochromic behaviors of the films of copolymers **III** and **V** are identical to that of copolymer **IV** film (Table 2). Since they have high values of T_g, the absolute increase of f with temperature rise is not strongly marked (Fig. 3). At T>T_g the photocolouration efficiency f cannot be used as a quantitative parameter for these films because the lifetime of coloured form at high temperature is shorter than the irradiation time which was equal to 30 min in all experiments (the time of reaching the stationary state at 20°C).

4. Conclusions

So, in the present paper the new class of photochromic polymers, namely, network photochromic polymers is described. The properties of these polymers depend on both the number and interposition of polymerizable groups and a nature of comonomers. The SP molecules with one polymerizable group linked with macromolecules of network polymer are shown to be an indicator of microinhomogeneity of this polymer.

The copolymers of photochromic molecules having two polymerizable groups and alkyl methacrylates are of special interest because using these copolymers makes it possible to create photochromic polymer material having large and adjustable time of storage of optical information.

References

[1] G. Smets, Adv. Polym. Sci. 50 (1983) 17.

[2] T. Tsutsui, A. Hatakeyama, S. Saito, Chem. Phys. Lett. 132 (1986) 563.

[3] A.V. Lyubimov, V.D. Ermakova, T.Ya. Kefeli, V.T. Shashkova, M.I. Cherkashin, A.A. Berlin, Vysokomolek. Soedineniya 21 (1979) 620 (in Russian).

[4] A.V. Lyubimov, N.L. Zaichenko, V.S. Marevtsev, M.I. Cherkashin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 31 (1982) 585.

[5] A.A. Berlin, L.A. Suhareva, T.Ya. Kefeli, N.L. Marshavina, L.M. Krylova, N.G. Taraskina, Vysokomolek. Soedineniya 18 (1976) 432 (in Russian).

[6] P.P. Feofilov, Polarized Luminescence of Atoms, Molecules and Crystals, Gosfitmatgiz, Moscow (1959), (in Russian).

[7] V.S. Marevtsev, A.T. Gradyushko, V.D. Ermakova, V.A. Linski, M.I. Cherkashin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 30 (1981) 984.

[8] V.G. Luchina, Yu.D. Khamchukov, V.S. Marevtsev, A.T. Gradyushko, A.V. Lyubimov, M.I. Cherkashin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 37 (1988) 2029.

[9] A.A. Berlin, L.A. Suhareva, T.Ya. Kefeli, N.L. Marshavina, L.M. Krylova, N.G. Taraskina, Vysokomolek. Soedineniya 18 (1976) 2542 (in Russian).

[10] V.S. Marevtsev, A.T. Gradyushko, Yu.D. Khamchukov, V.D. Ermakova, V.A. Linski, M.I. Cherkashin, Zh. Prikl. Spektrosk 35 (1981) 925 (in Russian).

[11] V.A. Usol'tsev, N.G. Chistyakov, Russ. Chem. Rev. 32 (1963) 495.

[12] G.V. Korolyev, M.M. Mogilevich, I.V. Golikov, Network Polyacrylates, Moscow, Chemistry (1995) (in Russian).

[13] A.A. Berlin, S.M. Kireeva, Yu.M. Sivergin, L.A. Suhareva, Doklady Akademii nayk of USSR 213 (1973) 109 (in Russian).

[14] H.G. Matveeva, M.P. Kisilev, A.A. Berlin, P.I. Zubov, Vysokomolek. Soedineniya 16 (1974) 157 (in Russian).

[15] A.A. Berlin, S.M. Mezhikovski, Mendeleev Chem. J. 21 (1976) 63.

[16] V.V. Arsenov, E.I. Merkulov, G.M. Chernov, V.D. Ermakova, A.V. Lyubimov, A.V. Vannikov, M.I. Cherkashin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 28 (1980) 1394.

[17] R.C. Bertelson, in: G.H. Brown (Ed.), Photochromism, Techniques of Chemistry, vol. III, Wiley-Interscience, New York, 1971.

[18] V.S. Marevtsev, S.I. Beshenko, V.D. Ermakova, V.A. Linski, A.T. Gradyushko, M.I. Cherkashin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 29 (1980) 81.