Full Articles

Photochromic transformations of 6-nitrospiropyran in matrices of linear and branched polymers

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Photochromic transformations of 6-nitrospiropyran in matrices of linear polystyrene and poly(methyl methacrylate) and branched polymethacrylates of various composition and structure were studied by absorption spectroscopy. In the case of linear polymers the kinetics of bleaching of the colored merocyanine form of 6-nitrospiropyran is determined by polarity and molecular mobility of the polymer matrix. The kinetic regularities of merocyanine transformations into the initial spiropyran in the branched polymer matrices are apparently caused by specific features of their architecture, differences in the degree of branching, and the properties associated with molecular mobility.

Key words: 6-nitrospiropyran, merocyanine, half-life time, poly(methyl methacrylate), polystyrene, branched polymethacrylates, molecular mobility, glass transition temperature.

Transformations of photochromic compounds in polymer films attract attention due to a possibility of their wide practical use, for example, in holography, optical information systems, and others. The introduction of spiropyrans as functional additives into polymer matrices decreases considerably the rate of their coloring and dark bleaching compared to analogous processes in liquids.[1,2] This is due to steric factors preventing *cis—trans*-transformation of spiropyran.

Polystyrene, poly(methyl methacrylate), and poly(hydroxyethyl methacrylate) possessing good physicomechanical properties, high optical transparency, and compatibility with photochromic compounds, are most frequently used as polymer matrices. Poly(methyl methacrylate) is mostly needed due to high optical transparency and resistance to photoaging. It has earlier[3] been shown that the rate of photochromic transformations of spiropyran increases considerably in polymer matrices based on methyl methacrylate copolymers with methacrylates containing bulky alkyl substituents. The introduction of comonomer units with bulky substituents into the polymer chain and elongation of the side chain of methacrylates increase the free volume and decrease the molecular packing density and, as a consequence, steric hindrance for the manifestation of segmental mobility of macromolecules.[4] However, possibilities of free volume

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† Deceased.

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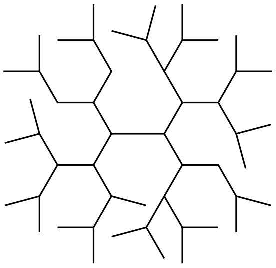
growth due to side substituent elongation are impeded because of the enhancement of hydrophobic interaction between hydrocarbon units of the substituents, which results in the formation of ordered structures and decreases the segmental mobility of the macromolecules.[4]

The polymer properties can drastically be changed, in particular, its free volume can be increased by the introduction of macromolecules of branched or hyperbranched polymers of the below presented architecture into the polymer matrix.



These polymers are highly soluble in various organic media and characterized by high thermodynamic compatibility with polymers of different chemical nature. Macromolecules of branched polymers introduced into the matrix of linear polymer can loosen the molecular packing of the initial polymer and favor an increase in the mobility of the macromolecules. The excessive free volume in polymers of branched architecture allows them to be used as sources of microcavities in which molecules of photochromic compounds can be localized. Thus, new prospects appear for the solution of problems on retarding photochromic transformations of a functional substance in glassy polymeric media. The use of polymers of branched architecture makes it possible to isolate a functional additive from the influence of the polymer matrix due to its high capability of sorbing low-molecular-weight substances (including spiropyran) in the inner part ("core") of a progressively branching macromolecule like an isolating nanocontainer.[5]

The purpose of the present work is the comparative study of photochromic transformations of spiropyran in matrices of linear and branched polymers based on methyl methacrylate and its derivatives. Polymer matrices used were linear polystyrene and poly(methyl methacrylates) with different molecular weights and branched polymethacrylates synthesized by crosslinking radical copolymerization of methyl methacrylate (MMA) and/or butyl methacrylate (BMA) and of lauryl methacrylate (LMA) with dimethacrylates of different structure, *viz.*, ethylene glycol dimethacrylate (EGDM) and triethylene glycol dimethacrylate (TEGDM), acting as branching centers in a growing macromolecule in the presence of chain-transfer agents.

Experimental

1′,3′,3′-Trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] (**1**) (6-nitrospiropyran, Aldrich) was used. Compound **1** was not specially purified. Linear polystyrene (**2**) and poly(methyl methacrylate) with $M_n = 19 \cdot 10^4$ (**3a**) were synthesized by radical bulk polymerization in the presence of AIBN (0.2 wt.%) as the initiator at $T = 60$ °C. Low-molecular-weight poly(methyl methacrylates) **3b,c** were synthesized by radical polymerization in a toluene solution (80 wt.%) at $T = 80$ °C in the absence or presence of 5 mol.% 1-decanethiol (DT) as a chain-transfer agent, respectively. Branched copolymers **4** of different composition and structure were obtained by crosslinking radical copolymerization of MMA and/or its derivatives, *viz.*, BMA, LMA, with EGDM and TEGDM in toluene according to an earlier proposed method.[6] Usual (DT) or catalytic

Table 1. Physicochemical characteristics of the linear and branched (co)polymers[a]

Polymer matrix	$M_n \cdot 10^{-3}$	M_w/M_n	$T_g{}^b$/°C	Content of C=C bonds per mole	[η]/dL g^{-1}
2	83.0	2.3	98	—	—
3a	190.0	1.7	110	—	—
3b	7.0	2.6	108	—	—
3c	1.8	1.7	70	—	—
4a (100 : 2 : 2)[c]	3.7	4.7	98	6.5	0.07
4a (100 : 12 : 12)	3.8	6.9	73	3.2	0.10
4a (100 : 21 : 21)	7.1	5.7	66	3.6	0.12
4b (100 : 12)	3.0	5.2	90	3.6	0.026
4c (100 : 12 : 12)	18.9	1.9	—	—	—
4d (75 : 25 : 12 : 12)	19.6	1.8	60	—	—
4e (100 : 12 : 12)	1.3	5.7	59	2.1	0.04

[a] M_n and M_w are the numerical-mean and weight-average molecular weights, respectively; T_g is the glass transition temperature; [η] is the intrinsic viscosity.

[b] The T_g values for polymers **3b,c** and branched copolymers **4** have been measured earlier.[7]

[c] Here and in Tables 2 and 5, the data in parentheses are the compositions of the branched copolymers: MMA—EGDM—DT (**4a**), MMA—EGDM (**4b**), BMA—EGDM—DT (**4c**), MMA—LMA—EGDM—DT (**4d**), and MMA—TEGDM—DT (**4e**).

(cobalt(II)porphyrin, Co$^{\text{II}}$Pn) chain-transfer agents were used to prevent cross-linking reactions. The polymers were characterized by gel permeation chromatography, IR spectroscopy, and differential scanning calorimetry; their average molecular-weight characteristics, glass transition temperatures (T_g), and content of unreacted C=C bonds were determined (Table 1). The glass transition temperatures of low-molecular-weight poly(methyl methacrylates) **3b,c** and branched copolymers **4** were measured on a DSM-3 microcalorimeter with a scanning rate of 8 deg min^{-1}.[7]

Polymer films containing compound **1** were prepared by sprinkling from solutions in benzene (nonpolar solvent) and acetone (low-polarity solvent). The use of benzene makes it possible to exclude probable association of macromolecules of polymer **3** and the effect of its associated structure (formed due to dipole-dipole interactions of the C=O ester groups[8]) on photochromism of spiropyran **1**. The content of compound **1** was 0.1—0.2 wt.% based on polymer. To remove the solvent, the polymer films were kept at 20 and 60 °C to a constant weight and stored in the dark. The film thickness was ~10—15 μm.

A DRT-400 lamp equipped with the UFS-5 filter was used for irradiation of the polymer films containing spiropyran **1**. The irradiation time was 10 s. The kinetics of transformation of colored merocyanine form **1′** into the initial structure of compound **1** in different polymer matrices was studied by absorption spectroscopy (Specord M-40 spectrophotometer) under dark conditions. The change in the absorbance (A) of the absorption band of colored form **1′** was recorded as a time function at $T = 20$ °C.

The half-life time ($t_{1/2}$) corresponding to the transformation of 50% molecules of compound **1′** (Fig. 1) was chosen as the quantitative characteristic of the bleaching kinetics. For correct comparison of the $t_{1/2}$ values, different polymer matrices were colored to close A values.

Results and Discussion

Photochromic transformations of compound 1 in matrices of linear polymers 2 and 3. After UV irradiation spiropyran **1** transforms into colored form **1′** due to the cleavage of the C—O covalent bond. Merocyanine **1′** is a zwitterion capable of being reversibly reduced to the initial structure as a result of the thermal or photochemical reaction (Scheme 1).

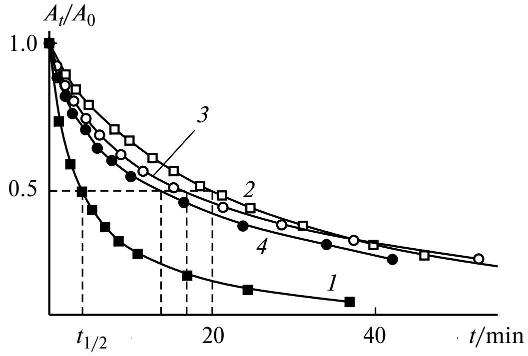
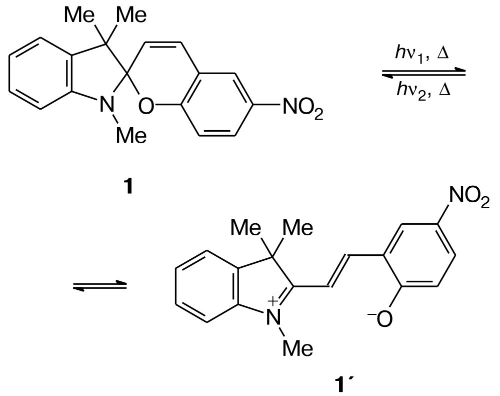
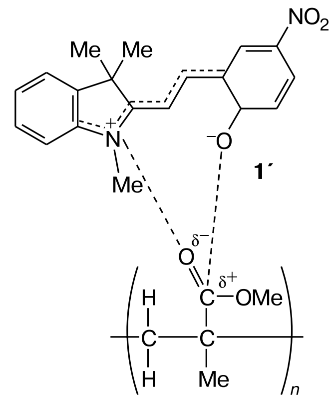


Fig. 1. Kinetics of transformation **1′** → **1** in linear polymers **2** (*1*), **3a** (*2*), **3b** (*3*), and **3c** (*4*) ($T = 20$ °C).

Scheme 1



The bleaching kinetics of merocyanine **1′** in the matrices of linear polymers **2** and **3** is presented in Fig. 1. It is seen that the rate of transformation **1′** → **1** is higher in the matrix of polymer **2**. The $t_{1/2}$ value for the latter is much lower than those for polymers **3a—c** (Table 2). Thus, merocyanine **1′** is more stable in polymers **3** than in polymers **2**. These differences are caused by the interaction of form **1′** due to its ionic nature with the polar matrix of polymers **3**.[9]



3

The above phenomena are indicated by the spectra of compound **1** in the matrices of polymers **2** and **3** after UV irradiation. The maximum of the absorption band of form **1′** in the nonpolar matrix of compound **2** corresponds to 603.9 nm. In the spectrum of the polar matrix of compound **3a** the absorption band maximum is shifted to 577.4 nm. This "blue" (hypsochromic) shift is caused, evidently, by the strong interaction of the polar matrix of **3a** with the zwitterionic form of compound **1**. This result is confirmed by published data,[9] according to which the activation energy (E_a) of the transformation **1′** → **1** at $T < T_g$ in the matrix of polymer **3** is 71.1±4.18 kJ mol^{-1}, whereas in the nonpolar matrix (for instance, of the styrene—butadiene—styrene copolymer) this value is 59.4±2.1 kJ mol^{-1}.

The interaction between **3** and **1′** is proved by the data on comparative studies of the dielectric properties of pure polymer **3** and polymer **3** containing compound **1**.[9] Compound **1** induces a decrease in dielectric losses (ε″) at $T < T_g$ due to a decrease in the polarity of **3**. In this case, T_g of polymer **3** containing **1** rises from 107 to 115 °C, *i.e.*, increases by 8 °C. In authors′ opinion,[9] this shift of T_g is

Table 2. Main parameters of transformation **1**´ → **1** in different polymer matrices

Polymer matrix*	λ_{max}(**1**´)** /nm	$t_{1/2}$ /min
2	603.9	4.0
3a	577.4	20.0
3b	578.7	16.3
3c	581.4	13.5
4a (100 : 2 : 2)	578.7	21.4
4a (100 : 12 : 12)	580.1	14.0
4a (100 : 21 : 21)	581.4	27.4
4b (100 : 12)	578.7	22.9
4c (100 : 12 : 12)	581.4	14.3
4d (75 : 25 : 12 : 12)	582.8	21.6
4e (100 : 12 : 12)	574.7	12.8

* The polymer films were prepared by sprinkling from benzene and dried at 20 °C to a constant weight.

** After UV irradiation of spiropyran **1**.

caused by the interaction of the polymethacrylate chains with the form **1**´. Dipole-dipole interactions between compound **1** and polymer **3** restrict mobility of the polymer molecules.[10] By contrast to polymer **3**, the introduction of spiropyran **1** into the matrix of the styrene—butadiene—styrene copolymer only insignificantly increases T_{g}, which is caused by a lower level of interaction between **1**´ and the nonpolar matrix.

To study the effect of mobility of the polymer matrix of **3** on the photochromic transformations of compound **1**, we used polymers differed by molecular-weight characteristics and, hence, by T_{g} (see Table 1). The kinetic curves of bleaching of merocyanine **1**´ in polymers **3** with different numerical-mean molecular weights (M_{n}) are presented in Fig. 1. It can be seen that the decrease in M_{n} of polymer **3** from $19 \cdot 10^4$ to $(1.8—7) \cdot 10^3$ increases the rate of transformation **1**´ → **1** and decreases $t_{1/2}$ (see Table 2). Since polarity of the polymer matrix in the series of polymers **3** with different M_{n} remains unchanged, the bleaching kinetics of **1**´ changes, most likely, due to an increase in the level of molecular mobility of the polymer matrix, which is indicated by the T_{g} values. The stability of form **1**´ in the matrix of **3** decreases with a decrease in T_{g}. This result is confirmed by published data,[9] according to which the bleaching rate of **1**´ increases in the series poly(methyl methacrylate)—poly(ethyl methacrylate)—poly(butyl methacrylate) with a decrease in T_{g} from 107 to 66 and 27 °C, respectively.

The experimental data indicate that the lifetime of merocyanine **1**´ in linear polymers **2** and **3** is determined by two factors: polarity and molecular mobility of the polymer matrix.

Photochromic transformations of compound 1 in matrices of branched copolymers 4. The bleaching kinetics of merocyanine **1**´ to form the initial compound **1** in the matrices of branched copolymers **4** of different composition, architecture, and degree of branching was studied. The branched structure of copolymers **4** was confirmed by the results of rheological measurements. The viscosimetric studies of the rheological properties of polymers **4** and **3** with close molecular weights in toluene showed polymers **4** to be characterized by the dependence of the reduced viscosity (η_{r}/c) on the polymer concentration (c) in solution, which is weaker than that for linear polymer **3**. The low values of intrinsic viscosity ([η]) (see Table 1) are a consequence of the compact globular structure of the macromolecules in solution.[11] The architecture and physicochemical properties of copolymers **4** change with an increase in the degree of branching. Therefore, it could be expected that the kinetics of photochromic transformations of compound **1** would depend substantially on the structure and properties of branched copolymers **4**.

The kinetic curves of bleaching of merocyanine **1**´ in the matrices of the MMA—EGDM—DT branched copolymers (**4a**) with the compositions 100 : 2 : 2, 100 : 12 : 12, and 100 : 21 : 21 (mol.%) are shown in Fig. 2. The main parameters of transformation **1**´ → **1** in these systems are given in Table 2. The data obtained show that form **1**´ is most stable in polymers **4a** of compositions 100 : 2 : 2 and 100 : 21 : 21.

Copolymer **4a** of composition 100 : 2 : 2 is, most likely, least branched and the behavior of compound **1** in this copolymer is close to that in linear polymers **3a,b**. The degree of branching increases with an increase in the EGDM content, and the molecular mobility of the polymer matrix increases in copolymer **4a** with the composition 100 : 12 : 12, as can be concluded by the decrease in $t_{1/2}$ (see Table 2). Copolymer **4a** of composition 100 : 21 : 21 has the most branched structure in the series of matrices studied, and the further decrease in $t_{1/2}$ could be expected. A prerequisite is the decrease in T_{g} of the copolymer (see Table 1). However, in this matrix colored form **1**´ is most stable. This is related, most likely, to

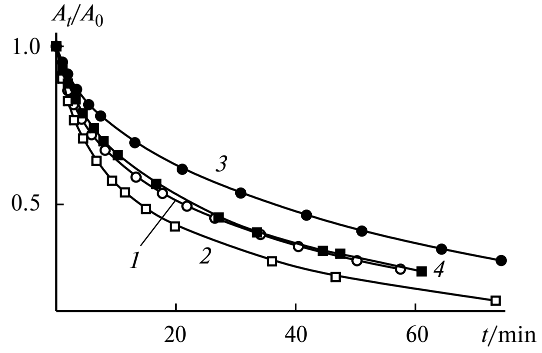


Fig. 2. Kinetics of transformation **1**´ → **1** in the matrices of branched copolymers **4a** of composition 100 : 2 : 2 (*1*), 100 : 12 : 12 (*2*), and 100 : 21 : 21 (*3*) and **4b** of composition 100 : 12 (*4*) (T = 20 °C).

a special architecture of macromolecules of the copolymer preventing fast bleaching of **1´**. Perhaps, either the high sulfur content or an increase in the degree of cyclization of the branched structure, or both these factors simultaneously are significant in this case. Macromolecules of copolymer **4a** of composition 100 : 21 : 21 have the shortest primary polymer chains (10 units), contain many terminal chains, and are characterized by the high content of the $—SC_{10}H_{21}$ groups (DT residues inserted into the polymer chain due to chain transfer).

Therefore, the composition of copolymer **4a** equal to 100 : 12 : 12 is most optimal for the $t_{1/2}$ value, and polymer chains of this copolymer are characterized by the maximum molecular mobility compared to other poly(methyl methacrylates) obtained using EGDM as a branching agent.

The MMA—EGDM copolymer (**4b**) of composition 100 : 12 prepared in the presence of $Co^{II}Pn$ ($1 \cdot 10^{-3}$ mol L^{-1}) was also studied as a polymer matrix. Copolymer **4b** differs from those studied above by the absence in the polymer chains of the $—SC_{10}H_{21}$ groups affecting the mobility of the reaction medium and by the presence of an additional amount of the C=C terminal bonds formed due to catalysis of chain transfer.[12] As found for this case, the bleaching rate of form **1´** decreases (see Fig. 2, curve *4*) and the $t_{1/2}$ value increases, correspondingly, over that for polymer **4a** of the same composition obtained in the presence of DT. Copolymer **4b** has T_g (see Table 1) by almost 20 °C higher than that of copolymer **4a** of composition 100 : 12 : 12. Thus, the decrease in the bleaching rate of merocyanine **1´** correlates with the decrease in the molecular mobility of the polymer matrix of **4b**.

It was of considerable interest to study photochromic transformations in the matrices of branched copolymers **4** containing the bulky BMA and LMA units. The replacement of MMA by methacrylic monomers with bulky alkyl substituents can substantially change the architecture and properties of copolymers **4**, first of all, the free volume of the polymer matrix and mobility of the polymer chains and, hence, can effect the rate of photochromic transformations of compound **1**. For this purpose, we studied the kinetics of bleaching **1´** → **1** in the matrices of the branched copolymers BMA—EGDM—DT (**4c**) and MMA—LMA—EGDM—DT (**4d**) of compositions 100 : 12 : 12 and 75 : 25 : 12 : 12, respectively (Fig. 3), whose physicochemical properties are described in Table 1.

Transformation **1´** → **1** in the matrix of branched copolymer **4c** occurs with a high rate and is characterized by the $t_{1/2}$ value close to that observed for copolymer **4a** with the same composition. Thus, the increase in the alkyl substituent size from one to four carbon atoms exerts no effect on the rate of photochromic transformations of compound **1** in the matrix of polymer **4c**.

Different results were obtained for copolymer **4d** with the composition 75 : 25 : 12 : 12. The LMA units randomly distributed in the main polymer chain were assumed to favor worsening of the molecular packing and, hence, an increase in the free volume of the polymer. It is noteworthy that in this polymer matrix the frequency of the absorption band maximum of form **1´** upon UV irradiation is shifted to higher wavelengths (bathochromic shift). This indicates a decrease in the level of dipole-dipole interaction of form **1´** with the polymer matrix. As a result, the rate of transformation **1´** → **1** should increase and the $t_{1/2}$ value should decrease compared to the corresponding values for copolymer **4a** of composition 100 : 12 : 12. However, an opposite effect is observed: the introduction of the LMA units into the polymer chain decreases the rate of **1´** bleaching and increases the $t_{1/2}$ values in spite of a decrease in T_g (see Table 1). The most probable reason for the retarded photochromic transformations of compound **1** in the matrix of branched copolymer **4d** is the formation of ordered structures due to the enhancement of hydrophobic interactions between the hydrocarbon units of the $—C_{12}H_{25}$ substituents and the free ends ($—SC_{10}H_{21}$) inserted in the polymer due to the chain-transfer reaction. The formation of ordered structures is characteristic of the polymers containing more than 10 carbon atoms in the side chain.[4]

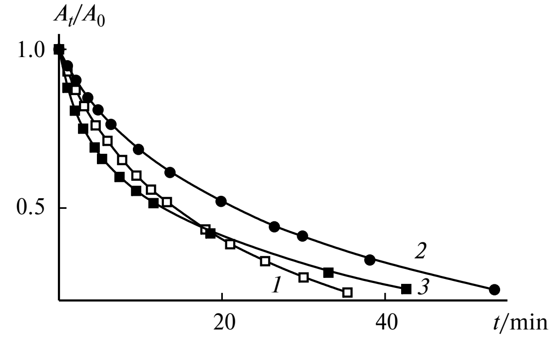


Fig. 3. Kinetics of transformation **1´** → **1** in the matrices of branched copolymers **4c** of composition 100 : 12 : 12 (*1*), **4d** of composition 75 : 25 : 12 : 12 (*2*), and **4e** of composition 100 : 12 : 12 (*3*) (T = 20 °C).

It is known[13] that the architecture and properties of the branched copolymers are determined by the monomer : branching agent : chain-transfer agent ratio and also by the structure of the branching agent. We studied the MMA—TEGDM—DT copolymer (**4e**) of composition 100 : 12 : 12 as a polymer matrix. The TEGDM branching agent has the same reactivity as EGDM but differs substantially in length of the oligomeric unit between the methacrylic fragments. Elongation of the latter (when TEGDM is used instead of EGDM) can create additional steric hindrance for the interaction of these fragments. Thus, the elongation of the branching agents should increase the molecular mobility of the polymer matrix. The bleaching kinetics of merocyanine **1´** due to transformation into the initial compound **1** in branched copolymer **4e** is shown in Fig. 3 (curve *3*). It turned out that the bleaching rate of form **1´** increases insignificantly in fact and, hence, the $t_{1/2}$ value decreases compared to analogous parameters for the matrix of copolymer **4a** with the same composition. The increase in the bleaching rate of merocyanine **1´** in copolymer **4e** correlates with the T_g decrease (see Table 1).

Based on the above data, we can conclude that, unlike the linear polymers, for the branched copolymers T_g is not a factor controlling the rate of photochromic transformations of compound **1**. The major effect is exerted, most likely, by the architecture of a branched macromolecule and molecular mobility determined by the level of interaction of its fragments, *viz.*, polymethacrylate chains or long alkyl substituents with the number of carbon atoms ≥10.

Reaction order of bleaching of merocyanine 1´ in matrices of linear and branched polymers. In liquids the coloring and bleaching of compound **1** obey regularities of the first-order reaction.[3,9] In solid matrices the reaction mechanism becomes more complicated. It is assumed[14] that in the linear polymers the deviation from the exponential law is caused by dispersion of the size distribution of microcavities, where photochromic molecules are localized and whose sum composes the free volume of the polymer. The bleaching of merocyanine **1´** is believed[15] to consist of two parallel first-order processes differed by numerical values of the rate component.

In the polymer matrices based on the MMA—octyl methacrylate copolymers, the kinetics of film bleaching is not described by the exponential law of the first-order reaction and the kinetic curves are approximated by the superposition of two exponents corresponding to two monomolecular processes with considerably different rate constants.[3] The complicated dependence of the transformation from metastable state **1´** into ground state **1** under dark conditions in the polymer matrices can be caused by heterogeneity of the supermolecular structure of the polymer,[16,17] which results in differences in the bleaching rates of **1´**. It should be accepted that the heterogeneity of the polymer matrix depends substantially on the copolymer composition and is manifested as a difference in numerical values of the transformation rate constants.

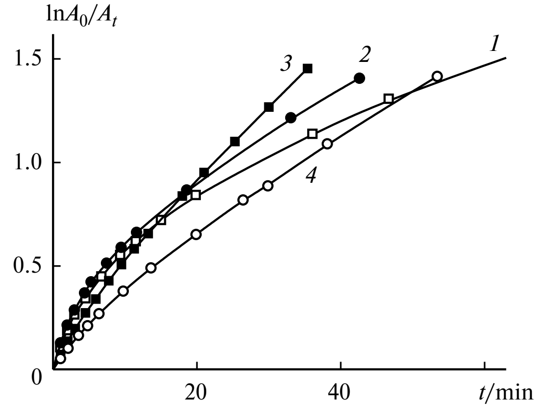


Fig. 4. Kinetics of transformation **1´** → **1** in the matrices of branched copolymers **4a** of composition 100 : 12 : 12 (*1*), **4e** of composition 100 : 12 : 12 (*2*), **4c** of composition 100 : 12 : 12 (*3*), and **4d** of composition 75 : 25 : 12 : 12 (*4*) in the coordinates of the first-order equation (T = 20 °C).

The kinetics curves of transformation **1´** → **1** in the matrices of branched copolymers **4a,c—e** in the coordinates of the first-order equation are presented in Fig. 4. It can be seen that the mechanism of transformation **1´** → **1** in the matrices of the branched copolymers prepared using benzene is complicated and is not described by an exponential law. Two linear regions are distinguished in the kinetic curves of bleaching merocyanine **1´** in the matrices of the branched copolymers. The slopes of these plots were used to calculate the apparent rate constants (k) of transformation **1´** → **1** (Table 3). It should be mentioned that the kinetic curves of bleaching of **1´** in the film of branched copolymer **4c** prepared from acetone can be linearized in the coordinates of the first-order equation in the whole interval of transformations and $k_{app} = 5.2 \cdot 10^{-2}$ min^{-1}, *i.e.*, it is by two orders of magnitude lower than that in a liquid, for instance, in ethanol.[18] This assumes that the solvent nature also affects, most likely, the formation of the supermolecular structure of the polymer, its free volume, distribution of compound **1** in the polymer, and, as a consequence, the mechanism of transformation of merocyanine **1´**.

Effect of the number of transformation cycles on the kinetics of photochromic transformations of compound 1 in matrices of branched copolymers. The dependence of the kinetic parameters on the number of transformation cycles can be observed during the process of photochromic transformations **1** $\rightleftharpoons$ **1´**. Therefore, we studied the influence of the number of irradiation cycles of spiropyran **1** on the main parameters of bleaching of **1´** in the matrices of the branched copolymers. The kinetic curves of bleaching of form **1´** in branched copolymer **4e** of composition 100 : 12 : 12, which were obtained in six irradiation cycles of compound **1**, are shown in Fig. 5. The main parameters

Table 3. Apparent rate constants (k) of transformation **1´** → **1** in the matrices of branched copolymers **4**

Copolymer	Composition	$k_1 \cdot 10^2$	$k_2 \cdot 10^2$
		min^{-1}	
4a	100 : 12 : 12	9.3	1.3
4c	100 : 12 : 12	5.8	3.6
4c*	100 : 12 : 12	5.2	—
4d	75 : 25 : 12 : 12	4.4	2.4
4e	100 : 12 : 12	10.3	2.4

* The film was prepared by sprinkling from acetone.

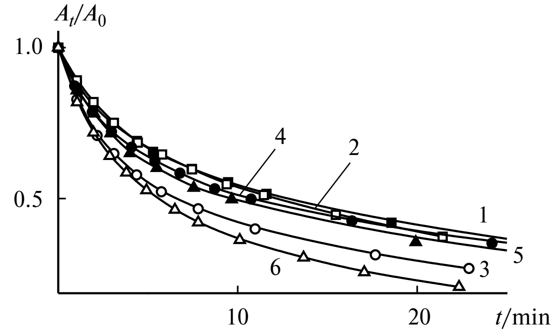


Fig. 5. Effect of the number of irradiation cycles (1—6) on the kinetics of transformation **1′** → **1** in the matrices of branched copolymer **4e** of composition 100 : 12 : 12 (T = 20 °C).

Table 4. Effect of the number of irradiation cycles on selected parameters of transformation **1′** → **1** in the matrix of branched copolymer **4e**

Irradiation cycle	λ_{max}(**1′**) /nm	A_0(**1′**) at t = 0	$t_{1/2}$ /min
1	574.7	0.24	12.8
2	574.7	0.19	12.2
3	572.1	0.18	6.6
4	576.0	0.19	10.8
5	574.7	0.13	9.6
6	574.7	0.12	5.7

of the transformation of **1′** into the initial compound **1** at different numbers of cycles are given in Table 4. It turned out that the rate of bleaching of **1′** in copolymer **4e** increases with an increase in the number of irradiation cycles, whereas the $t_{1/2}$ value decreases by ~2 times after the sixth cycle. This indicates a possible change in the properties of the polymer matrix during multiple photochromic transformations **1** $\rightleftharpoons$ **1′**. The photochromic transformations of merocyanine **1′** are known[19] to induce an increase in the volume of small (submicronic) cavities in the polymer matrix. Due to this, the transformation of compound **1′** in the polymer matrix, is most likely accelerated.

During cyclic transformations **1** $\rightleftharpoons$ **1′** the absorbance of the absorption band of colored form **1′** was found to decrease with an increase in the number of irradiation cycles. This is probably caused by the phenomenon of "fatigue" of spiropyran **1** caused by processes of photodestruction and oxidation.[20] It is considered that this process is less pronounced *in vacuo*, and this is an evidence for the effect of oxygen.

Effect of annealing on photochromic transformations of compound 1 in matrices of linear and branched polymers. The effect of thermal treatment of the films of the linear and branched polymers on the kinetics of bleaching of merocyanine **1′** was studied. The films of linear and branched polymers **2—4** containing compound **1** were annealed for ~2.5 days at 60 °C. Then the kinetics of transformation **1′** → **1** was studied in the thermally treated films of the considered polymers. The main parameters of transformation **1′** → **1** are presented in Table 5.

Table 5. Effect of thermal treatment of the polymer matrices on the main parameters of transformation **1′** → **1**

Polymer matrix*	λ_{max}(**1′**)** /nm	$t_{1/2}$ /min
2	606.8	4
3a	584.1	20
3b	581.4	29
3c	581.4	22.6
4a (100 : 2 : 2)	578.7	21
4a (100 : 12 : 12)	580.1	14.4
4a (100 : 21 : 21)	584.1	28
4c (100 : 12 : 12)	581.4	15
4d (75 : 25 : 12 : 12)	582.8	30
4e (100 : 12 : 12)	574.7	30

* The polymer films were prepared by sprinkling from benzene, dried at 20 °C to a constant weight, and annealed at 60 °C.

** After UV irradiation of spiropyran **1**.

It turned out that substantial changes in the kinetics of transformation **1′** → **1** are observed after annealing in the films of branched copolymers **4d,e**: the bleaching rates of form **1′** decrease and, hence, the $t_{1/2}$ values increase. For example, the $t_{1/2}$ parameter in branched copolymer **4d** after the thermal treatment increases from 22 to ~30 min. This effect is most pronounced for copolymer **4e**: the $t_{1/2}$ value increases from 12.8 to ~30 min. Similar changes in the bleaching kinetics of merocyanine **1′** occur in linear poly(methyl methacrylates) **3b,c**. After the thermal treatment, the $t_{1/2}$ value for the transformation of **1′** in polymers **3b,c** increases to ~23 and 29 min, respectively. This indicates, most likely, relaxation during the process of thermal treatment of an excessive (superequilibrium) free volume in the polymer matrices studied.

According to available data,[21] at $T < T_g$ the polymer contains two components of the free volume related to the thermal mobility of fragments of the polymer chains and to the nonequilibrium structure of the glassy polymer matrix. The free volume of the first type is formed predominantly from mobile holes and that of the second type is formed of immobile holes. The size of the immobile hole changes (pulses), because during motion the mobile holes are united and separated with the immobile holes.[22] The formation of the mobile holes is associated with internal rotation of different chain fragments. Depending on the rotation angle of the chain fragments, the holes appear and migrate over the whole polymer volume. The hole sizes are determined by sizes of rotating fragments of the polymer chain. Evidently, the thermal treatment of the polymer matrices of both linear polymers **3b,c** and branched copolymers **4d,e** decreases the free volume formed due to the immobile holes in which, most likely, the major part of molecules of compound **1** is localized.

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