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Synthesis and study of photochromic properties of copolymers based on functionalized chromenes

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Chromenes functionalized with methacryl groups were synthesized and involved into the radical polymerization to obtain copolymers with ethyl acrylate. Comparison of spectral kinetic characteristics of poly(methyl methacrylate) glasses containing chromenes and photochromic copolymers as additives led to a conclusion that incorporation of a photochromic compound as a part of a copolymer into the polymeric glass increases efficiency of photocoloration of photochromic compounds in the polymeric layer.

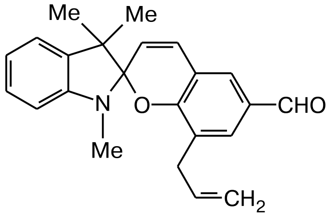
Key words: chromenes, photochromic copolymers, photochromic glasses, radical polymerization, spectral kinetic characteristics.

Development of photochromic materials for different designations in most cases is based on the use of polymeric binders, which makes it necessary to optimize their component composition to provide high light sensitivity and acceptable rate of thermal relaxation.[1] This can be reached, for example, by the use of comb-like polymers as the polymeric binders, since they are characterized by the large free molecular volume.[2] The efficiency of photochromic transformations of spiro compounds in polymeric matrices based on methyl methacrylate (MMA) can be increased by its copolymerization with alkyl methacrylates having bulky substituents.[3] The free molecular volume in a polymer increases if branched or hyperbranched polymers are incorporated into the polymeric matrix of macromolecules.[4] In fact, it was found that the rate of photochromic transformations in the matrices of branched, as well as linear polyacrylates, existing at room temperature in the highly elastic state, is by 5—10 times higher than in polymers based on methacrylates.[5,6]

Later it was shown[7] that the efficiency of photochemical reactions of molecules of photochromic 8-allyl-6-formyl-1´,3´,3´-trimethylspiro[2*H*-1-benzopyran-2,2´-indoline] increases in the glasses of poly(methyl methacrylate) (PMMA) modified with linear and branched poly(ethyl acrylates) (PEA). The maximum effect occurs in the presence of the linear PEA additives, which form sites with increased molecular lability. A suggestion was made that it is reasonable to localize all the molecules of a photochromic compound in such sites; the efficiency of photochemical reactions in the polymers under consideration can significantly increase. This can result from the covalent binding of a spiro compound with the molecule of elastomer, which is separated in the PMMA matrix as a microphase.

The purpose of the present work is to study possibilities for the synthesis of photochromic PMMA glasses containing sites with increased molecular lability in the form of the elastomer microphase, in which all the molecules of photochromic compound are localized.

To solve this problem, we synthesized a low-molecular-weight PEA by radical polymerization in the presence of photochromic 8-allyl-6-formyl-1´,3´,3´-trimethylspiro[2*H*-1-benzopyran-2,2´-indoline] (**Phot-1**) containing an allyl group, which can be involved into copolymerization with ethyl acrylate (EA) in order for the photochromic fragments to be fixed on the polymeric chain.



Phot-1

The process was performed in ethanol (70 wt.%). However, attempted synthesis of the photochromic elastomer failed. Kinetic studies showed that when the ratio of re-

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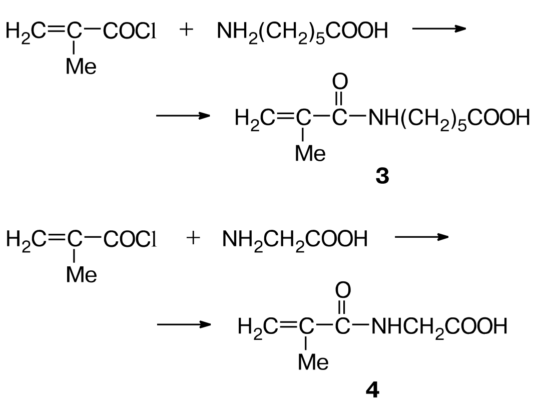
agents EA : **Phot-1** = 5 : 1, **Phot-1** strongly inhibits the process of polymerization of EA and decreases its highest conversion to 23%. Moreover, the copolymer synthesized did not exhibit photochromic properties. The negative result that obtained can be explained, from the one hand, by low stability of spiropyrans to radical reactions, and form the other hand, by high activity of the acrylate radical. In this connection, in this work we synthesized spiro compounds from the chromene class functionalized with the reactive methacryl group. Such compounds differ from spiropyrans by higher stability to irreversible phototransformations. We also obtained copolymers on their basis and studied their photochromic properties in solutions, films, and PMMA glasses.

Results and Discussion

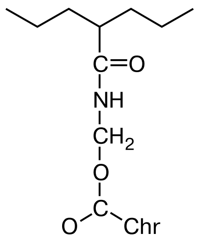
Synthesis of functionalized chromenes. Photochromic naphthopyrans **Phot-2**, **Phot-3**, and **Phot-4** were synthesized by the reaction of hydroxynaphthopyrans **1** and **2** with methacryloylamino acids **3** and **4**. Amino acids **3** and **4** were obtained by the reaction of methacryloyl chloride with aminohexanoic and aminoacetic acids, respectively (Scheme 1).

Synthesis of copolymers of ethyl acrylate with photochromic compounds. Copolymers of EA with photochromic compounds **Phot-2** (linear **Pol-1** and branched **Pol$_B$-1**), **Phot-3** (linear **Pol-2**), and **Phot-4** (linear **Pol-3**) were synthesized by radical copolymerization according to the procedures developed earlier.^{7}

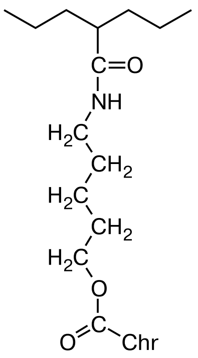
Scheme 1



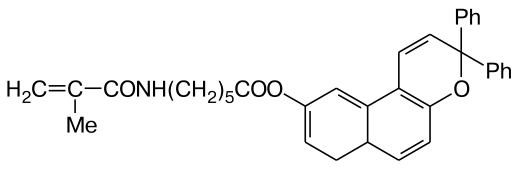
Since chromenes **Phot-3** and **Phot-4** differ only in the size of their alkyl fragments between the methacryl group and the photochromic part of the molecules, the absolutely identical photochroms are attached to the polymeric chain at different distances.



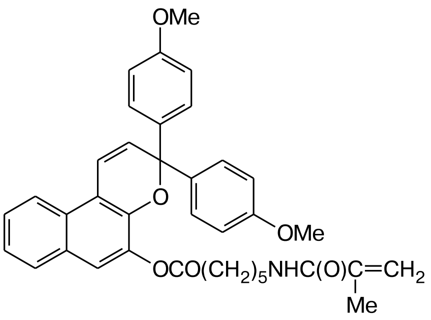
Pol-3



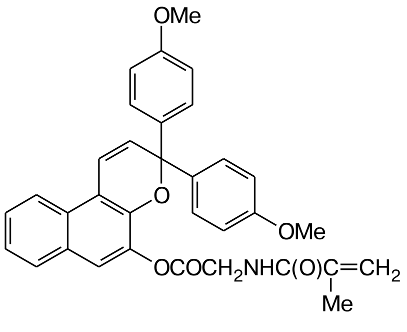
Pol-2



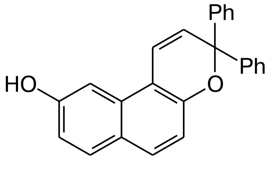
Phot-2



Phot-3



Phot-4



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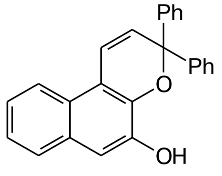

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Table 1. Molecular mass characteristics of photochromic copolymers*

Polymer	$M_n \cdot 10^{-3}$	$M_w \cdot 10^{-4}$	M_w/M_n
Pol-1	24.0	4.9	2.1
Pol$_B$-1	2.9	2.6	9.0
Pol-2	20.0	5.5	2.8
Pol-3	22.0	5.3	2.4

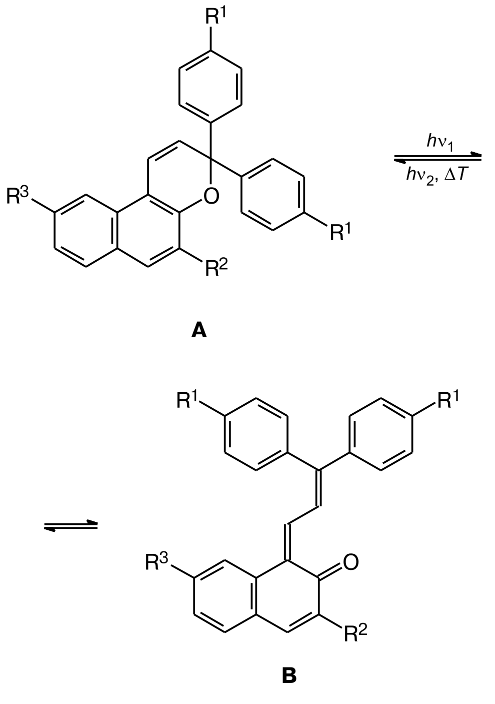
* M_n and M_w are the number average and weight average molecular masses, respectively.

The molecular mass characteristics of the synthesized copolymers are given in Table 1.

The procedure[7] was used for the synthesis of PMMA glasses containing additives of the synthesized copolymers, as well as chromenes and linear low-molecular-weight PEA.

Spectral kinetic studies. It is known[1] that chromenes undergo reversible phototransformations of the starting colorless cyclic form **A** to the photoinduced colored form **B** upon irradiation with the UV light absorbed by the starting form (Scheme 2).

Scheme 2



Spontaneous bleaching of the photoinduced form **B** can be accelerated upon the action of visible irradiation absorbed by this form or upon heating.

The research results on spectral kinetic characteristics of photochromic compound **Phot-2**, its copolymers **Pol-1**, **Pol$_B$-1** in solutions and in films, as well as the samples of the PMMA glasses obtained with the additives of chromene **Phot-2** and derived from it copolymers are given in Table 2 and in Figs 1—3.

Figure 1 shows the photoinduced changes in the absorption spectra of compound **Phot-2** in solution and polymeric films.

In the PMMA film, unlike in solutions, a somewhat growth in the $\tau_{1/2}$, is observed in addition to some changes in the absorption spectra, and, as it was expected, the efficiency of photocoloration falls by 2.5 times (see Table 2). Introduction of the PEA additives to the composition under consideration does not lead to the expected improvement in kinetic characteristics. Conversely, degree of the photocoloration becomes somewhat smaller. If the rate constants k_1 and k_2 remain unchanged values of the content of the polymer described by the slow constant k_2 increases (proportion of the preexponents A_1/A_2 decreases).

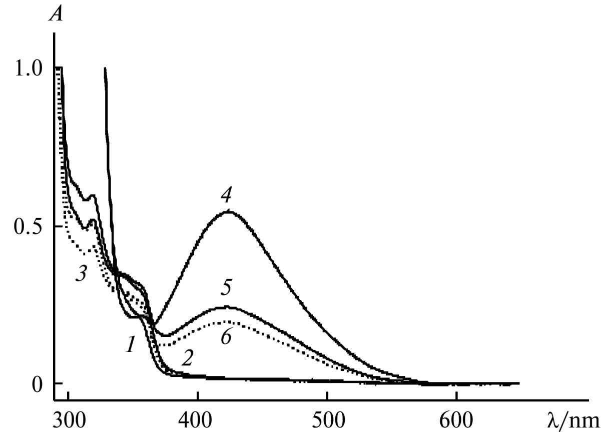


Fig. 1. Absorption spectra of the starting (*1—3*) and photoinduced (*4—6*) forms of compound **Phot-2** in acetone (*1*, *4*), in PMMA (*2*, *5*), and in PMMA with 2% PEA additive (*3*, *6*).

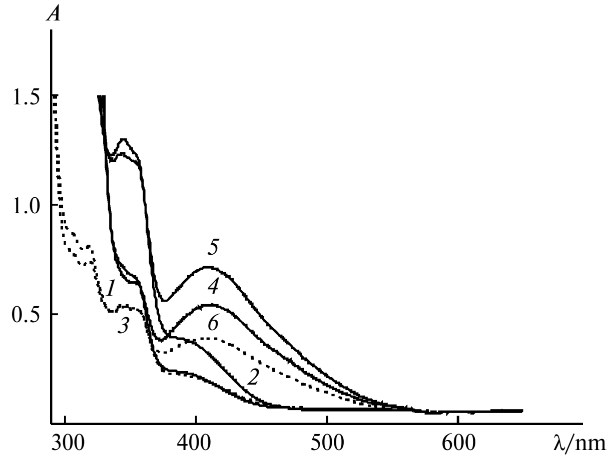


Fig. 2. Absorption spectra of starting (*1—3*) and photoinduced (*4—6*) forms of copolymer **Pol-1** in acetone (*1*, *4*), in film (*2*, *5*), and in PMMA (*3*, *6*).

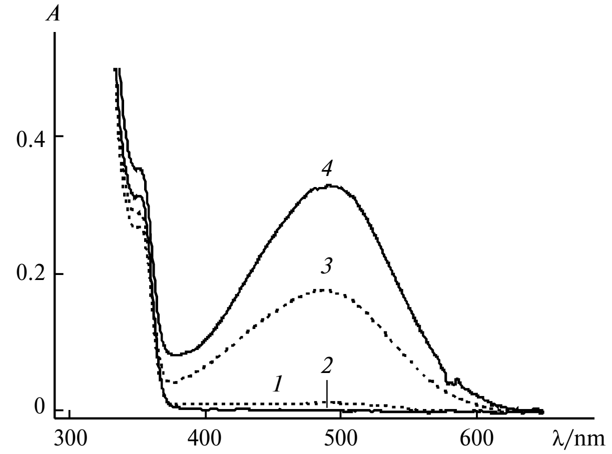


Fig. 3. Absorption spectra of the starting (*1*, *2*) and photoinduced (*3*, *4*) forms of chromenes **Phot-3** (*1*, *3*) and **Phot-4** (*2*, *4*) in acetone.

Copolymerization of compound **Phot-2** with EA virtually does not change the rate of bleaching in acetone (the $\tau_{1/2}$ values are close). Copolymers **Pol-1** (see Fig. 2) and **Pol$_B$-1** have similar spectral characteristics. However, the efficiency of photocoloration for the linear copolymer **Pol-1** in all the compositions under study is lower than for the branched copolymer **Pol$_B$-1**. The content of photochromic fragments in the sites with reduced molecular lability characterized by the slow constant is by 3—4 times lower for **Pol-1** than for **Pol$_B$-1** in all the compositions. Apparently, in the branched polymer **Pol$_B$-1**, the branching nodes considerably restrict the segmental lability of the chain units around the photochromic fragment, that affects characteristics of its photochromic transformations. Going from solutions to the copolymer films and PMMA glasses, the efficiency of photocoloration of both copolymers falls, but, like in solutions, it is ~2 times higher for the branched copolymer **Pol$_B$-1** than for **Pol-1**. Kinetics of the dark bleaching in films remains the same as in solution, whereas in glasses the rate decreases and the $\tau_{1/2}$ values in both samples increase twofold.

Analysis of the results of spectral kinetic studies of photochromic transformations of compound **Phot-2** and copolymers **Pol-1** and **Pol$_B$-1** allows us to draw the following conclusions. Kinetic curves of the dark bleaching of compound **Phot-2** and its photochromic copolymers are not described by one exponential dependence neither in solutions, nor in polymeric films and glasses. The curves are approximated corresponding to the biexponential equation $D(t) = A_1\exp(-k_1t) + A_2\exp(-k_2t)$, whose constants reflect molecular lability in the sites where the photochrom is localized. The difference in the constants indicates the presence of structural heterogeneity in the polymeric glasses, that is not unexpected, and a relatively even distribution of photochromic fragments in the glass-like matrix. In photochromic copolymers, which are in the highly elastic state at the temperature of experiment (ambient), and in their solutions, the difference in lability of the photochromic part of the molecule can be due to the uneven distribution of the photochromic fragments in the macromolecular chain. Where the density of the chain units with photochromic fragments is larger, their lability can be restricted due to the interaction with each other. This can also be the reason for the smaller contribution of the slow constant k_2 in the linear copolymer **Pol-1** as compared to the branched **Pol$_B$-1**. Judging from the proportion of the preexponential factors (see Table 2), the fast component prevails in all the cases. The unexpected presence of two constants in the description of kinetics of the bleaching of the starting **Phot-2** in the solvent is apparently due to the position and the nature of the substituent in the pyran fragment.

The synthesized chromene **Phot-2** is characterized by the high rate of relaxation of the photoinduced form. In this case, its covalent binding to the elastomer polymeric chain does not decrease the indicated value. The time of half-conversion during the dark bleaching in the PMMA glass is just by 1.5—2 times longer than in the solvent, *i.e.* even a glass-like matrix affects weakly the dark bleaching of the photoinduced form of chromene **Phot-2**. Therefore, the $\tau_{1/2}$ value in the case of PMMA film apparently is virtually the same for the starting chromene in the absence and in the presence of the elastomer additives and for the chromene covalently bound to the elastomer. This result differs from that obtained in the experiments with the formyl-substituted spiropyran, where both the rate of the reaction and efficiency of photocoloration of the photochrom in the glass-like matrices changed significantly in the presence of the elastomer additives.[7] Apparently, such a behavior of the chromene is due to the fact that the rate constants of its dark relaxation is by the order of magnitude higher as compared to the formyl-substituted spiropyran and the open merocyanine form is characterized by low thermodynamic stability. The weak effect of the PMMA matrix on the rate of photochemical transformations can be also due to the low level of intermolecular interaction of the phenyl fragments of the spiropyran ring with the PMMA macromolecules.

To sum up, it should be noted that copolymers **Pol-1** and **Pol$_B$-1** are inferior in the efficiency of the photocoloration process in both films and PMMA glasses to the PMMA glasses based on chromene **Phot-2** (see Table 1).

In this connection, we studied behavior of the synthesized chromenes **Phot-3** and **Phot-4** with methoxy substituents in the phenyl fragments, which were incorporated in order to intensify intermolecular interactions with the matrix and increase the activation volume, as well as with the methacryl substituents as R^2.

The results of the studies of the obtained photochrom samples, as well as copolymers **Phot-2** and **Phot-3** on their basis are given in Table 2 and in Fig. 3.

Table 2. Spectroscopic kinetic characteristics of chromenes and their copolymers*

Object under study	$\lambda^{\max}$/nm ($D_{\mathbf{A}}$)	$\varepsilon \cdot 10^{-3}$ /L mol^{-1} cm^{-1}	$\lambda_{\mathbf{B}}^{\max}$/nm ($\Delta D_{\mathbf{B}}^{\mathrm{Phot}}$)	$\Delta D_{\mathbf{B}}^{\mathrm{Phot}}/D_{\mathbf{A}}$	$k_{\mathbf{BA}}$/s^{-1} (k_1/k_2)	A_1/A_2	$\tau_{1/2}$/s
Phot-2 in acetone ($c = 7.0 \cdot 10^{-5}$ mol L^{-1})	353 (0.22)	3.1	424 (0.5)	2.5	(0.160/ 0.050)	1.43	6.0
Pol$_{\mathbf{B}}$-1 in acetone	353 (0.43)	2.9	422 (0.5)	1.2	(0.192/ 0.005)	1.92	5.0
Pol-1 in acetone	353 (0.62)	3.5	424 (0.4)	0.7	(0.225/ 0.003)	8.33	5.0
Film **Pol$_{\mathbf{B}}$-1**	344 (0.3)	—	431 (0.2)	0.7	(0.297/ 0.007)	2.04	5.0
Film **Pol-1**	345 (1.2)	—	428 (0.5)	0.4	(0.208/ 0.013)	7.14	4.0
Phot-2 (0.05 wt.%) in PMMA	342 (0.3)	—	424 (0.3)	1.0	(0.125/ 0.009)	3.03	8.0
Phot-2 (0.05 wt.%) in PMMA + 2% PEA	342 (0.3)	—	423 (0.2)	0.7	(0.123/ 0.011)	2.22	9.0
Pol$_{\mathbf{B}}$-1 (2%) in PMMA	345 (0.3)	—	425 (0.2)	0.7	(0.213/ 0.027)	0.92	9.0
Pol-1 (2%) in PMMA	345 (0.5)	—	425 (0.2)	0.4	(0.130/ 0.013)	2.70	8.0
Phot-3 in acetone ($c = 7.0 \cdot 10^{-5}$ mol L^{-1})	352 (0.26)	3.7	487 (0.2)	0.8	0.211	—	4.0
Pol-2 in acetone	351 (0.28)	3.9	488 (0.3)	1.0	0.210	8.20	4.0
Film **Pol-2**	355 (2.1)		498 (>2.5)	>1.2	0.110	—	8.0
Phot-3 (0.1%) in PMMA	342 (1.0)	—	490 (0.2)	0.2	(0.021/ 0.0023)	0.91	81.0
Pol-2 (2%) in PMMA	340 (1.7)	—	491 (0.6)	0.4	(0.160/ 0.0094)	4.60	7.0
Phot-4 in acetone ($c = 7.0 \cdot 10^{-5}$ mol L^{-1})	352 (0.29)	4.2	490 (0.3)	1.0	0.172	—	4.5
Pol-3 in acetone	351 (0.22)	4.0	491 (0.3)	1.5	0.133	12.7	6.0
Film **Pol-3**	341 (1.4)	—	501 (0.9)	0.6	0.070	—	12.0
Phot-4 (0.1%) in PMMA	342 (1.0)	—	493 (0.2)	0.2	(0.018/ 0.0023)	0.81	93.0
Pol-3 (2%) in PMMA	340 (1.9)	—	493 (0.7)	0.2	(0.090/ 0.0062)	2.7	11.0

* $\lambda_{\mathbf{A}}^{\max}$ and $\lambda_{\mathbf{B}}^{\max}$ are the wavelengths of the absorption band maxima of the starting (**A**) and photoinduced (**B**) forms; $D_{\mathbf{A}}$ is the optical density in the absorption band maximum of the starting form; $\Delta D_{\mathrm{B}}^{\mathrm{Phot}}$ is the photoinduced change in the optical density in the absorption band maximum of the photoinduced form **B** in the photoequilibrium state; k_1 and k_2 are the rate constants of the dark bleaching; A_1/A_2 is the ratio of preexponential factors of the dark bleaching reaction; $\tau_{1/2}$ is the time of spontaneous twofold decrease in the photoinduced optical density in the photostationary state.

Comparison of the data (see Table 2, Figs 1 and 3) shows that chromenes **Phot-3** and **Phot-4** (methoxy derivatives of chromene **Phot-2**) are characterized by the same absorption spectra of the cyclic form **A** as those of chromene **Phot-2**, whereas the absorption bands of the photoinduced form **B** in acetone are shifted by ~65 nm to the long-wave region of the spectrum.

An increase in the spacer length in the case of chromene **Phot-3** as compared to compound **Phot-4** leads to the insignificant hypsochromic shift of the absorption bands of the photoinduced form **B**, that, probably, is due to the steric effects of the spacers on the conformation of the merocyanine form of the molecule.

Unlike for chromene **Phot-2**, the process of dark relaxation of the photoinduced form in acetone is described by the first order kinetics, whereas the rate constants of the dark relaxation insignificantly depend on the spacer length.

Similar properties are also observed in the case of solutions of copolymers in acetone, however, the efficiency of the photocoloration process either increases, as in the case of copolymer **Pol-3**, or is not changed, as in the case of copolymer **Pol-2**. The degree of photocoloration of the solution of photochromic copolymer with a short spacer **Pol-3** is even higher than for compound **Pol-3** in acetone, that is apparently due to the reduced rate of the dark

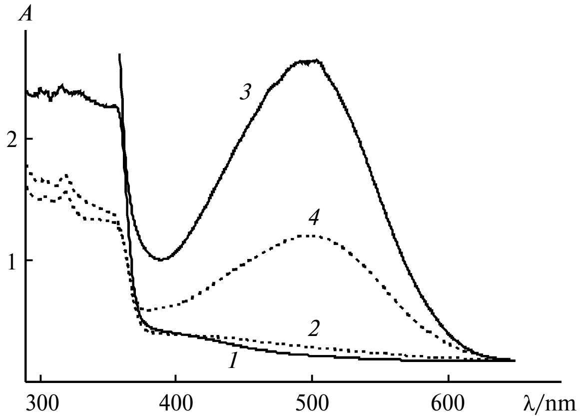


Fig. 4. Absorption spectra of the starting (*1*, *2*) and photoinduced (*3*, *4*) forms of copolymers **Pol-2** (*1*, *3*) and **Pol-3** (*2*, *4*) in film.

bleaching. Conversely, for the thin films and PMMA glasses the efficiency of photocoloration becomes higher for the copolymers derived from chromene **Pol-3** with the long spacer. In the case of films of copolymers, it considerably exceeds this parameter for compounds **Phot-3** and **Phot-4** in PMMA.

The rate constants of the dark bleaching for copolymer **Pol-2** with the chromene having a long alkyl fragment is higher than that for copolymer **Pol-3** with a short spacer, whereas the $\tau_{1/2}$ time is shorter by 1.5 times.

The photoinduced changes in the absorption spectra of the **Pol-2** and **Pol-3** copolymer films are shown in Fig. 4.

Copolymers behave similarly in the PMMA glasses. The glass-like matrix does not significantly affect the rate of the dark relaxation in the photochrom ($\tau_{1/2}$ remains virtually the same), however, the kinetic curves are described by the biexponential equation. The efficiency of the photocoloration processes also sharply drops.

Unlike copolymers, the individual chromenes **Phot-3** and **Phot-4** in the PMMA glasses are characterized by a sharp decrease in the rate constant of the dark bleaching and a fall in the photocoloration efficiency. In this case, the highest efficiency of photocoloration was obtained in the PMMA glasses containing copolymer **Pol-2**.

In conclusion, the results of the present studies suggest a possibility to control efficiency of photocoloration of chromenes upon the action of a UV irradiation and the rate of their dark relaxation through the use of copolymers with spacers of different lengths.

Experimental

^{1}H NMR spectra were recorded on a Bruker AM300 SF spectrometer (300.13 MHz) in DMSO-d_6 using Me_4Si as an internal standard; TLC was performed on DC-Alufolien Kieselgel 60 F_{254} plates (Merck).

9-Hydroxy-3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (1). A catalytic amount of *p*-toluenesulfonic acid (0.01 g) was added to a solution of 2,7-dihydroxynaphthalene (5.0 g, 0.03 mol) and 1,1-diphenyl-2-propyn-1-ol (6.5 g, 0.03 mol) in diethyl ether (50 mL). The reaction mixture was stirred for 4 h at ~20 °C and filtered, diethyl ether was evaporated off from the filtrate, and the residue was extracted with toluene. The solvent was evaporated *in vacuo*, the product that obtained was subjected to chromatography on silica gel using the benzene—ethyl acetate (10 : 1) mixture as an eluent. Evaporation of the solvents gave chromene **1** (2.5 g). Crystallization from toluene yielded a light yellow powder (2.1 g), m.p. 152 °C.

5-Hydroxy-3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (2). A catalytic amount of *p*-toluenesulfonic acid was added to a solution of 2,3-dihydroxynaphthalene (1.14 g, 7.5 mmol) and 1,1-di-(4-methoxyphenyl)-2-propyn-1-ol (2.0 g, 7.5 mmol) in anhydrous benzene (60 mL). The reaction mixture was stirred for 2 h at 50 °C and filtered, the solvent was evaporated *in vacuo*. The oil that obtained was subjected to chromatography on silica gel (eluent: benzene—ethyl acetate (10 : 1)) and recrystallized from the benzene—hexane (1 : 2) mixture to yield a light pink powder (2 g, 65%), m.p. 116—118 °C.

***N*-Methacryloyl-ε-aminohexanoic acid (3).** A solution of 6-aminohexanoic acid (7.51 g, 0.10 mol) and hydroquinone (60 mg) in 2 *M* aq. NaOH (50 mL) was cooled with stirring in an ice bath, followed by addition in portions of 2 *M* aq. NaOH (50 mL) and methacryloyl chloride (10.45 g, 0.10 mol L^{-1}) so that the pH of the reaction mixture corresponded to 9—10. A colored solution was stirred for 3 h at ~20 °C, followed by addition of concentrated HCl to pH 1—3, saturation with sodium chloride, and extraction with ethyl acetate (2×100 mL). The extract was washed with water to neutrality, the organic layer was separated, dried with magnesium sulfate, and concentrated *in vacuo*. The compound thus obtained was subjected to chromatography on a column with silica gel using ethyl acetate as an eluent. The yield was 8.0 g (40%), light yellow oil. ^{1}H NMR, δ: 1.10—1.60 (m, 6 H, $CH_2(C\underline{H}_2)_3CH_2$); 1.82 (s, 3 H, Me); 2.21 (t, 2 H, CH_2CO); 3.12 (m, 2 H, CH_2N); 5.30 (s, 1 H, $C=CH_2$); 5.63 (s, 1 H, $C=CH_2$); 7.80 (t, 1 H, NH); 11.90 (s, 1 H, COOH).

***N*-Methacryloylaminoacetic acid (4).** A solution of glycine (7.51 g, 0.10 mol) and hydroquinone (60 mg) in 2 *M* aq. NaOH (50 mL) was cooled to −10 °C with mechanical stirring. The thus obtained solution was diluted with 2 *M* aq. NaOH (50 mL) and methacryloyl chloride (10.5 g, 0.10 mol). The reaction mixture was stirred for 2 h, keeping the pH within 9—10. A solution that obtained was treated with conc. hydrochloric acid to pH 1—3, saturated with NaCl, and extracted with THF. The extract was washed with water, dried with magnesium sulfate, the solvent was evaporated *in vacuo*. The solid product thus obtained was recrystallized from the acetone—diethyl ether (10 : 1) mixture, m.p. 104—105 °C. The yield was 6.1 g (43%). ^{1}H NMR, δ: 1.86 (s, 3 H, Me); 3.76 (d, 2 H, CH_2N); 5.38 (s, 1 H, $C=CH_2$); 5.71 (s, 1 H, $C=CH_2$); 8.21 (t, 1 H, NH); 12.44 (t, 1 H, COOH).

9-(*N*-Methacryloyl-ε-aminohexanoyloxy)-3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (Phot-2). A solution of 9-hydroxy-3,3-phenyl-3*H*-naphtho[2,1-*b*]pyran (**1**) (0.53 g, 1.5 mmol), *N*-methacryloyl-ε-aminohexanoic acid (0.30 g, 1.5 mmol), *N*,*N*-dicyclohexylcarbodiimide (0.30 g, 1.5 mmol), and 4-pyrrolidinopyridine (0.023 g, 0.15 mmol) in anhydrous dichloromethane (40 mL) was stirred at ~20 °C for 16 h. The *N*,*N*-dicyclohexylurea that formed was filtered off, the filtrate was washed with water (3×50 mL), 5% aq. acetic acid, and again with water (3×50 mL). The organic layer was separated and dried with magnesium sulfate, the solvent was evaporated *in vacuo*. A benzene—ethyl acetate (2 : 1) (10 mL) mixture was added to the product obtained, which was stirred and filtered. The filtrate was subjected to chromatography on silica gel eluting with the benzene—ethyl acetate (2 : 1) mixture. The yield was 0.21 g (29%), light red oil. ^{1}H NMR, δ: 1.91 (s, 3 H, Me); 4.28 (d, 2 H, CH_2); 5.47 (s, 1 H, 7´-CH_2); 5.81 (s, 1 H, 7´-CH_2); 6.59 (d, 1 H, 2-H); 6.86 (m, 4 H, Ar); 7.40 (m, 5 H, Ar); 7.50 (m, 2 H, Ar); 7.59 (s, 1 H, Ar); 7.81 (d, 1 H, 6-H); 8.09 (d, 1 H, 1-H); 8.63 (t, 1 H, NH).

5-(*N*-Methacryloylaminoacetoxy)-3,3-di(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (Phot-4). A solution of compound **2** (0.60 g, 1.5 mmol), *N*-methacryloylaminoacetic acid (0.21 g, 1.5 mmol), *N*,*N*-dicyclohexylcarbodiimide (0.30 g, 1.5 mmol), and 4-pyrrolidinopyridine (0.023 g, 0.15 mmol) in anhydrous dichloromethane (40 mL) was stirred at ~20 °C for 16 h. *N*,*N*-Dicyclohexylurea was filtered off, the filtrate was washed with water (3×50 mL), 5% aq. acetic acid (3×50 mL), water (3×50 mL), and dried with $MgSO_4$. The organic solvent was evaporated *in vacuo*. The final product (5 mL) was stirred in the benzene—ethyl acetate (2 : 1) mixture, filtered, and the filtrate was subjected to chromatography on silica gel using benzene—ethyl acetate (2 : 1) as an eluent. The yield was 0.46 g (59%), a light pink powder; m.p. 138—140 °C. ^{1}H NMR, δ: 1.91 (s, 3 H, Me); 3.69 (s, 6 H, $(OMe)_2$); 4.28 (d, 2 H, CH_2); 5.47 (s, 1 H, CO—CH_2); 5.81 (s, 1 H, CO—CH_2); 6.59 (d, 1 H, 2-H); 6.86 (m, 4 H, Ar); 7.40 (m, 5 H, Ar); 7.50 (m, 2 H, Ar); 7.59 (s, 1 H, Ar); 7.81 (d, 1 H, 6-H); 8.09 (d, 1 H, 1-H); 8.63 (t, 1 H, NH).

5-(*N*-Methacryloyl-ε-aminohexanoyloxy)-3,3-di(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (Phot-3). Photochrom **Phot-3** was obtained according to the procedure for compound **Phot-4** using *N*-methacryloyl-ε-aminohexanoic acid as an acylating agent. The yield was 0.26 g (62%), a white powder; m.p. 127—129 °C. ^{1}H NMR, δ: 1.38 (m, 2 H, CH_2); 1.45 (m, 2 H, CH_2); 1.71 (m, 2 H, CH_2); 1.84 (s, 3 H, Me); 2.67 (t, 2 H, CH_2); 3.07 (m, 2 H, CH_2); 3.70 (s, 6 H, OMe); 5.29 (s, 1 H, =CH_2); 5.63 (s, 1 H, =CH_2); 6.51 (d, 1 H, Ar); 6.88 (d, 4 H, 3-Ar); 7.30 (d, 4 H, 3-Ar); 7.38—7.52 (m, 3 H, Ar); 7.60 (s, 1 H, 6-H); 7.79 (d, 1 H, Ar); 7.86 (t, 1 H, NH); 8.11 (d, 1 H, Ar).

Synthesis of photochromic copolymers. Linear copolymers of EA (**Pol-1**, **Pol-2**, and **Pol-3**) were obtained by radical copolymerization in ethanol (70 wt.%) in the presence of azobis(isobutyronitrile) (AIBN) as initiator ($1 \cdot 10^{-2}$ mol L^{-1}). The polymerization was performed in the evacuated tubes at 60 °C until the reaction reached completion (120 h). The branched copolymer of EA (**Pol$_B$-1**) was synthesized by the three-dimensional radical copolymerization with butanediol diacrylate (BDDA), which was controlled by the agent of the chain transfer, *i.e.*, 1-decanethiol, according to the method described earlier.[8] The content of the branching agent, BDDA and 1-decanethiol, was 12 mol.% with respect to EA. Conditions for the synthesis of **Pol$_B$-1**: $T = 80$ °C, the reaction time was 5.5 h, AIBN was the initiator (0.02 mol L^{-1}). The content of the reaction mixture in toluene was 80 wt.%. The polymers that obtained were dried *in vacuo* at ~20 °C until the weight was constant.

Photochemical studies. Absorption spectra of the samples were recorded on an Ocean Optics HR 2000 spectrometer in the automatic scanning mode through the given periods of time and then processed as massifs of data using the software based on the Igor Pro 4.0. Irradiation was produced by a DRSh-1000 UV lamp with an UFS-2 light filter, which transmitted the UV irradiation in the region 280—380 nm. The intensity of photolyzing irradiation was $2.4 \cdot 10^{-4}$ Einstein s^{-1}, the measurements were performed by chemical actinometer based on potassium ferrioxalate.

Efficiency of photocoloration (degree of photocoloration) of photochromic systems was evaluated based on the value of the photoinduced optical density in the absorption band maximum of the photoinduced merocyanine form **B** in the state of photoequilibrium, normalized on the value of optical density in the absorption band maximum of the starting spiropyran form **A** ($\Delta D_{\mathbf{B}}{}^{\mathrm{Phot}}/D_{\mathbf{A}}$). This parameter totalizes effects of all the photo and thermal transformations of photochromic molecules in the state of photoequilibrium ($\Delta D_{\mathbf{B}}{}^{\mathrm{Phot}}$) with allowance for the absorption of light by the photochromic systems with different concentration of photochromic molecules in the layer ($D_{\mathbf{A}}$) and allows us to evaluate the real efficiency of photocoloration of photochromic systems as a whole. To exclude significant errors in the evaluation of the photocoloration efficiency, the comparative spectroscopic kinetic studies were performed under the same experimental conditions.

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