

Photochromism of indoline spiropyrans of the coumarin series in polymeric matrices

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The photochromic properties and aggregation processes of merocyanine forms of indoline spiropyrans of the coumarin series in the block and film poly(methyl methacrylate) (PMMA) were studied and compared by spectral and kinetic methods. Photochromism of the synthesized compounds depends on their structure. The efficient formation of J-aggregates was observed for indoline spiropyrans of the coumarin series based on 8-formyl-7-hydroxy-4-methylcoumarin and 3-formyl-4-hydroxycoumarin.

Key words: spiropyrans, indole derivatives, coumarin derivatives, photochromic transformations, spiro form, merocyanine form, block poly(methyl methacrylate), poly(methyl methacrylate) film.

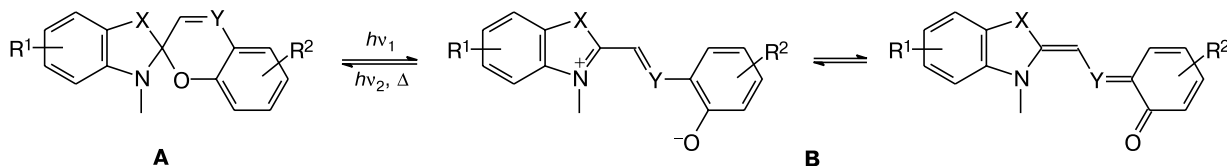
Insignificant attention was given to indoline spiropyrans of the coumarin series compared to other photochromic spiropyran derivatives.^{1–5} Photochromic transformations of these compounds, as those of other spiropyrans, consist in reversible photoinduced pyran ring opening of the initial colorless spiro form **A** followed by thermal *cis*–*trans*-isomerization and subsequent formation of colored merocyanine form **B**. The recyclization of the merocyanine form can proceed both *via* thermal relaxation and under irradiation with the visible light absorbed by the colored merocyanine form (Scheme 1).

Intending to systematic investigation of photochromism of indoline spiropyrans of the coumarin series, we have previously synthesized a series of spiropyrans containing 8-formyl-7-hydroxy-4-methylcoumarin, 5-formyl-6-hydroxy-4-methylcoumarin, or 3-formyl-4-hydroxy-3-coumarin fragments.⁶

The study of photochromism of these compounds showed that compounds based on 8-formyl-7-hydroxy-4-methylcoumarin have the most interesting photochromic properties. Spiropyrans based on 5-formyl-6-hydroxy-4-methylcoumarin in solutions are characterized by too short lifetime of the photoinduced merocyanine form at room temperature.⁷ The compounds based on 3-formyl-4-hydroxycoumarin turned out to be non-photochromic and exist at room temperature only in the merocyanine form. In the framework of quantum chemical calculations, the experimental data obtained are explained by differences in the negative charge delocalization on different coumarin fragments of the spiropyrans.⁷

The aggregation of merocyanine molecules of the synthesized spiropyrans in solutions and polymolecular layers was found.⁸ The dependence of the efficiency of aggre-

Scheme 1

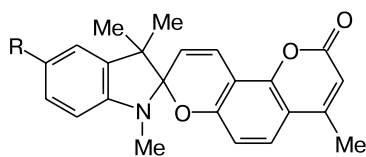


gation on the solvent polarity and structure of the compounds was revealed.

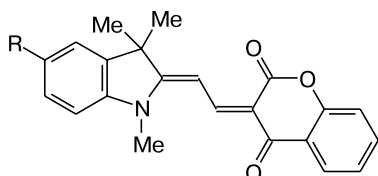
This work is devoted to investigation of the photochromic properties of indoline spiropyrans of the coumarin series in polymeric matrices.

Results and Discussion

Objects of the study were indoline spiropyrans of the coumarin series of two types: compounds involved in the most efficient photochromic transformations (**1a**, **1c,d**) and compounds **2a,b** that exist only in the merocyanine form.



1a–d



2a,b

R = H (**1a**), Me (**1b**), OMe (**1c**), NO₂ (**1d**, **2a**), Br (**2b**)

The photoinduced changes in the spectral characteristics typical of samples of polymeric blocks containing spiropyran **1a** unsubstituted at the benzene ring of the indoline fragment or spiropyrans with electron-releasing substituents (**1b,c**) are shown in Fig. 1 for compound **1c** as an example. The data in Fig. 1 show one broad absorption band of the photoinduced form at 594 nm, whose

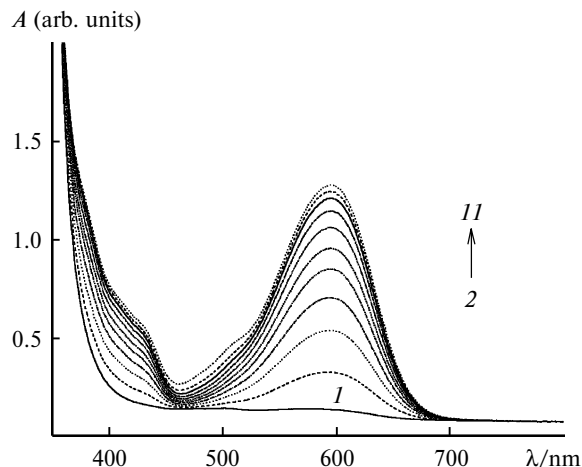


Fig. 1. Absorption spectra of the initial (*I*) and photoinduced forms of **1c** with the growing duration of UV irradiation (*2–II*) in block PMMA.

intensity increases with an increase in the duration of UV irradiation.

It follows from the comparison of the obtained spectral data that the position of the absorption band maximum of the photoinduced merocyanine form for compounds **1a–c**, as well as in the case of solutions,⁷ depends insignificantly on the nature of the substituent in position 5' of the indoline fragment and on the method of preparation of the polymer sample (Table 1).

Unlike compounds **1a–c**, the absorption spectrum of the photoinduced form of nitro-substituted spiropyran **1d** in the polymer block exhibits an absorption band of the photoinduced form with two maxima: at 574 and 599 nm (Fig. 2). Remarkably, the initial absorption spectrum of compound **1d** in PMMA (see Fig. 2. curve *I*) contains only one maximum at 562 nm. An increase in the concentration of the photoinduced merocyanine form during UV irradiation results in the transformation of the absorp-

Table 1. Spectral kinetic characteristics of the polymeric materials based on spiro[coumarinopyran-2,2'-indolines] and polymethyl methacrylate

Compound	Concentration/mol L ⁻¹		Thickness/mm		λ _{max} ^B /nm		ΔA _{max} ^{ph}		t ^{sp} _{0.5} /s	
	I	II	I	II	I	II	I	II	I	II
1a	2.8 · 10 ⁻⁴	4.1 · 10 ⁻³	4.61	0.18	590	595	0.32	0.26	1030	70
1b	2.7 · 10 ⁻⁴	4.7 · 10 ⁻³	4.67	0.23	589	581	0.42	0.25	1370	630
1c	2.6 · 10 ⁻⁴	5.6 · 10 ⁻³	4.41	0.25	594	588	1.14	1.29	3200	1060
1d	2.5 · 10 ⁻⁴	4.9 · 10 ⁻³	4.09	0.28	600	584	0.10	0.08	1170	250
2a	1.0 · 10 ⁻⁴	2.7 · 10 ⁻⁴	1.6	0.23	501	494	—	—	—	—
2b	1.3 · 10 ⁻⁵	8.5 · 10 ⁻⁵	1.3	0.15	492	502	—	—	—	—

Note. I, in PMMA blocks; II, in PMMA films; λ_{max}^B is the wavelength of the absorption band maximum of the photoinduced merocyanine form; ΔA_{max}^{ph} is the photoinduced change in the absorbance in the absorption band maximum of the photoinduced merocyanine form; t^{sp}_{0.5} is the time within which the absorbance in the absorption band maximum of the photoinduced merocyanine form halved spontaneously.

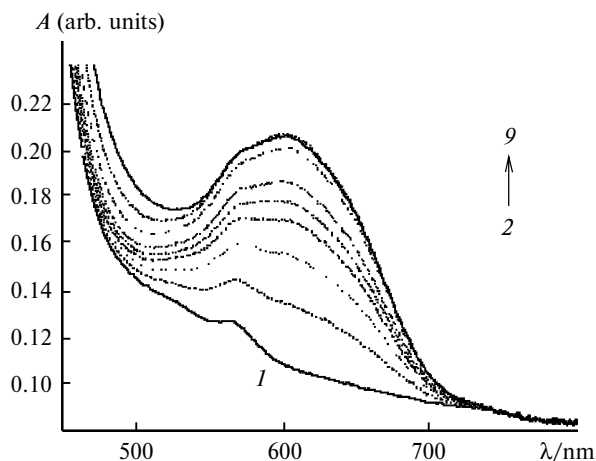


Fig. 2. Absorption spectra of the initial (*1*) and photoinduced forms **1d** with the growing duration of UV irradiation (*2–9*) in block PMMA.

tion spectrum of the sample with the appearance of a new long-wavelength maximum at 599 nm, whose intensity at maximum concentrations of the photoinduced merocyanine form becomes the highest (see Fig. 2, curves *2–9*). Similar photoinduced spectral changes were also observed for the polymeric film with a thickness of 0.28 μm containing the same spiropyran (Fig. 3).

The comparison of the spectra of the photoinduced forms of compounds **1c** and **1d** (see Figs 1 and 2) shows that the photoinduced absorption band for the nitro-substituted compound is much broader than the corresponding absorption bands of the unsubstituted compound and spiropyrans containing electron-releasing substituents.

The overlapped absorption bands of compound **1d** for the block polymeric samples were separated using the

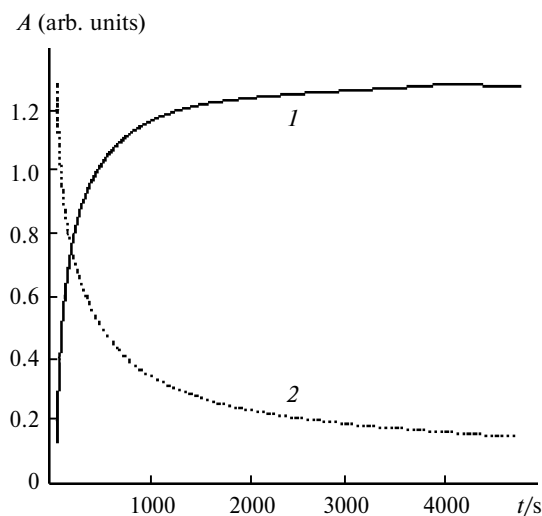


Fig. 3. Curves of photocolorization (*1*) under UV irradiation and photobleaching of form **1d** (*2*) under visible light irradiation in block PMMA.

Microcal Origin program and allowed us to elucidate the real position of maxima of this compound in PMMA: at 563 and 625 nm. The corresponding absorption band maxima for compound **1d** in the polymeric film lie at 588 and 652 nm.

The increase in the absorption intensity in the long-wavelength region of the photoinduced absorption band of spiropyran **1d** in PMMA is due, most likely, to J-aggregation of molecules of the merocyanine form of nitro-substituted spiropyran similarly to that observed earlier for nitro-substituted indoline spiropyrans in the polymeric matrix.⁹

Figure 3 shows the photocolorization curve of compound **1d** in the polymeric PMMA-based block sample under UV irradiation (curve *1*) and the curve of photobleaching under visible light irradiation (curve *2*). It can be seen that the times of photocolorization and photobleaching necessary for the twofold change in the photoinduced absorbance are about 3 min.

Unlike the absorption spectra of the polymeric samples of the block or film type containing initial compound **1a**, which show an insignificant long-wavelength absorption of the merocyanine form in the visible spectral region (Fig. 4, curve *1*), the absorption spectra recorded after the photobleaching of the photoinduced merocyanine form (see Fig. 4, curves *2* and *3*) exhibit a distinct short-wavelength absorption band (see Fig. 4, curve *4*) with a maximum at 495 nm, whose position changes insignificantly in a spectral range of 487–498 nm depending on the structure of the compound.

Further irradiation of the samples with the visible light or their heating to 80 $^{\circ}\text{C}$ does not decrease the intensity of this absorption band. Its intensity in the spectra of the photobleached polymeric samples was found to be higher

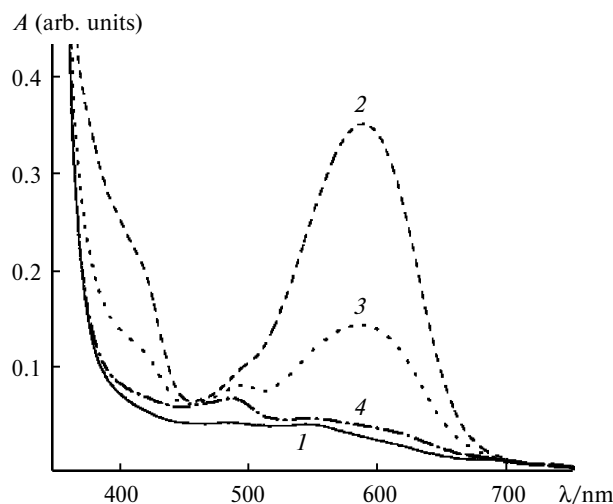


Fig. 4. Absorption spectra of **1a** in block PMMA before (*1*) and after UV irradiation (810 s) (*2*) and after visible light irradiation for 20.5 (*3*) and 35.5 min (*4*).

than that in the initial samples. The highest intensity was observed for both the block and film polymeric samples containing compound **1c**. This band is completely absent from the absorption spectra of the polymeric samples based on nitro-substituted spiropyran **1d**.

Nevertheless, the nitro-substituted spiropyran also demonstrated the absence of complete photobleaching of the polymeric samples that exhibited photochromism (Fig. 5). In this case, however, the absorption band that undergoes no photo- and thermal bleaching (see Fig. 5, curve 3) lies in a longer-wavelength spectral region (562 nm). Remind that this band is observed immediately after preparation of the polymeric samples (see Fig. 2, curve 1).

By analogy to the earlier studied indoline spiropyran,⁹ the absorption bands at 495 and 562 nm can be attributed to the dimeric and monomeric forms of coumarin spiropyran, respectively. However, their retention after irradiation with the visible light and heating assumes that the photoinduced form of the compounds can interact with the polymeric matrix. The nature of this phenomenon will be studied elsewhere.

At ambient temperatures compounds **1a–c** undergo spontaneous transformations of the photoinduced merocyanine form into the initial form. However, unlike the processes in solutions,⁷ spontaneous bleaching lasts for tens of minutes rather than tens of seconds and is not exponential (Fig. 6), which is characteristic of polymer-bound spiro compounds.¹⁰ The comparison of the times of thermal bleaching corresponding to the spontaneous twofold decrease in the photoinduced absorbance (Table 1) suggests that the rate of thermal bleaching decreases with an increase in the electron-releasing ability of substituents in the indoline cycle, as for solutions of these compounds,⁷ and is rather high in the presence of an electron-withdrawing group. Similar regularities were

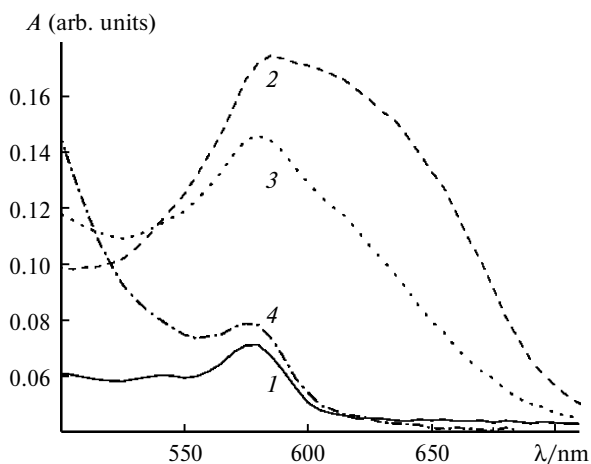


Fig. 5. Absorption spectra of **1d** in PMMA before irradiation (1), after UV irradiation (2), subsequent irradiation with the visible light (3), and heating for 27 min at 39–90 °C (4).

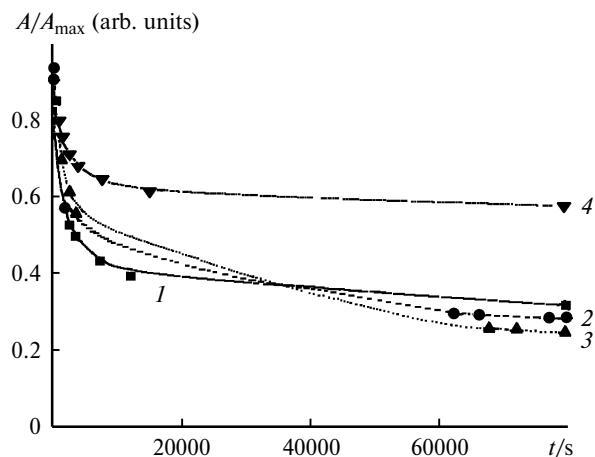


Fig. 6. Kinetic curves of spontaneous bleaching of samples **1a**-PMMA (1), **1b**-PMMA (2), **1c**-PMMA (3), and **1d**-PMMA (4).

observed for polymeric films containing the same compounds. The rate of thermal bleaching of the photochromic compounds in the polymeric films turned out to be by 1–2 orders of magnitude lower than those in solutions. Due to this, we succeeded to obtain appropriate values of the photoinduced absorbance in the absorption band maximum of the merocyanine form (see Table 1). The most changes in both the polymer blocks and films were observed for compound **1c** containing the OMe group. These values and the decrease in the rate of thermal bleaching of the merocyanine forms in PMMA make it possible to consider possibilities of practical use of indoline spiropyran of the coumarin series as photochromic materials.

The lowest photoinduced absorbances observed for the films and blocks containing spiropyran with the NO₂ substituent, which is possibly related to the aggregation of the photoinduced merocyanine molecules appeared in the above considered absorption spectra of the photoinduced form.

The comparative study of the kinetics of photodegradation of compound **1c** (Fig. 7) in different polymeric matrices shows that the film samples are most likely more photoresistant (see Fig. 7, curve 1). The photodegradation of the block samples proceeds more rapidly (see Fig. 7, curve 2).

Photochromic compounds **1a–c** in the polymeric matrices exhibit photoinduced fluorescence (Fig. 8), which is due to the formation of the photoinduced merocyanine form.^{11–13} It was found for compound **1c** that the Stokes shift (difference in the wavelengths of the maxima in the absorption (585 nm) and fluorescence (640 nm) bands) is 55 nm.

Unlike compounds **1a–c**, the Stokes shift for spiro compound **1d** in the PMMA film is only 5 nm (Fig. 9), which additionally evidences for a possibility of J-aggre-

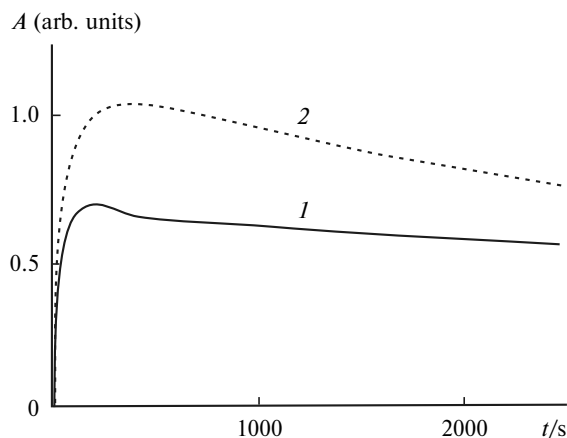


Fig. 7. Kinetic curves of photodecomposition under irradiation with the filtered (365 nm) UV light from a DRS-250 mercury lamp for **1c** in film PMMA (*1*) and block PMMA (*2*) obtained by measuring the absorbance in the absorption band maximum of the photoinduced form at $\lambda = 620$ nm.

gation of merocyanine molecules of nitro-substituted spirocoumarinopyran.

Compounds **2a,b** in the polymeric matrix, as in solutions,⁷ exhibit no photochromic transformations. Already in the initial state they exist in the merocyanine form, which is indicated by their absorption spectra (see Fig. 9, curve *1*). As can be seen from the comparison of the absorption spectra of the merocyanine form of photochromic compound **1c** (see Fig. 8, curve *1*) and non-photochromic compound **2b** (Fig. 10, curve *1*), the absorption bands of the latter are considerably narrower. The half-width of the absorption bands is about 100 and 30 nm, respectively. Compound **2b** also fluoresces (see Fig. 10, curve *2*). The Stokes shift for this compound is much smaller, being 38 nm, than those for the photo-

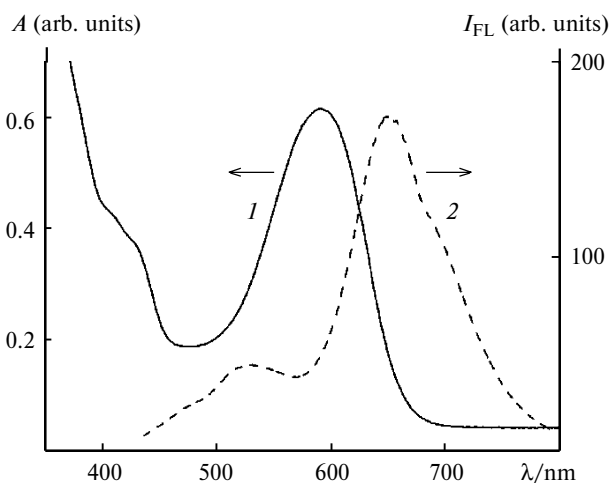


Fig. 8. Absorption (*1*) and fluorescence (*2*) spectra upon irradiation (420 nm) of the photoinduced merocyanine form of compound **1c** in the PMMA film.

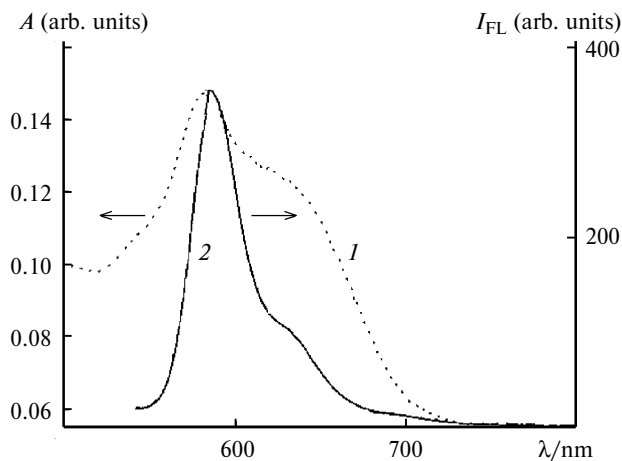


Fig. 9. Absorption (*1*) and fluorescence (*2*) spectra upon photoexcitation (530 nm) of the merocyanine form of compound **1d** in the PMMA film.

chromic compounds. This also indicates, most likely, a possibility of aggregation of non-photochromic merocyanine molecules in polymeric matrices. However, unlike polymolecular layers of this compound, which are characterized by resonance fluorescence,⁸ the efficiency of aggregation in the polymeric PMMA matrix is less considerable.

As found by the study of photochromism of the indoline spiroyrans of the coumarin series in the polymeric blocks and films, these photochromic compounds, which undergo rapid relaxation in solutions from the photoinduced merocyanine form to the initial spiro form, in polymethyl methacrylate sharply decrease the relaxation rate to the value appropriate for practical use of the corresponding polymeric photochromic materials. In this case, however, as in solutions, the rate constant of dark bleaching depends on the structure of the photochromic compound.

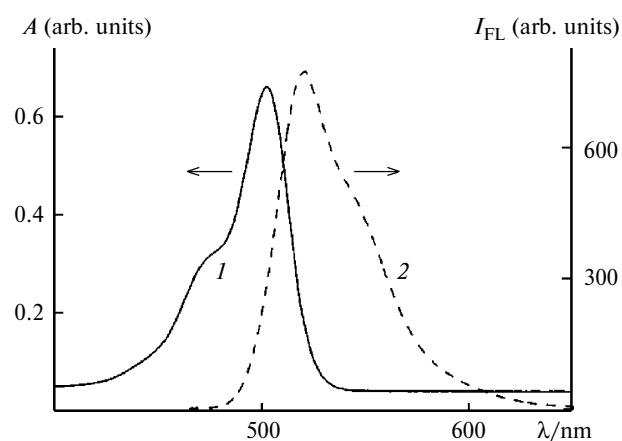


Fig. 10. Absorption (*1*) and fluorescence (*2*) spectra of the merocyanine form of non-photochromic compound **2b** in the PMMA film.

The high concentrations of the photoinduced merocyanine form observed in polymeric materials can result (unlike rapidly bleached solutions) in the aggregation of these molecules, which is indicated by the obtained spectral data. It is most likely that the highest degree of aggregation of merocyanine molecule is observed for the photochromic nitro-substituted spiropyrans and non-photochromic compounds, viz., 4-hydroxycoumarin derivatives.

Merocyanine forms of both photochromic and non-photochromic compounds of the coumarin series have fluorescence properties.

Experimental

Photochromic transformations of compounds **1a–d** and non-photochromic compounds **2a,b** were studied in solid polymeric blocks and films of poly(methyl methacrylate).

Samples of the polymeric materials were prepared by both block polymerization and dissolution of the photochromic compounds in PMMA.

Thermal polymerization was carried out in sealed glass ampules at 40–70 °C in a water-cooled thermostat. Azobisisobutyronitrile in a concentration of 0.1 wt.% was used as the initiator of polymerization. To completely decompose the initiator, the final stage of the process was carried out in a desiccator at 110–115 °C for 2 h. The resulting polymeric blocks were cut into discs of a certain thickness, whose front surfaces were polished for spectral kinetic investigation.

Samples of the photochromic PMMA films were obtained by combined dissolution of the polymer and a photochromic compound in a toluene–ethyl acetate (9 : 1) mixture followed by the removal of the solvent by drying. The thickness of the obtained films was 150–280 μm.

The concentration of the photochromic compounds in samples of the polymeric blocks and films was varied within $1.3 \cdot 10^{-3}$ – $2.8 \cdot 10^{-4}$ and $8.5 \cdot 10^{-5}$ – $9.8 \cdot 10^{-3}$ mol L⁻¹, respectively.

Absorption spectra were recorded on a Cary 50 spectrophotometer (Varian, USA). Fluorescence spectra were detected on a Cary Eclipse spectrofluorimeter (Varian, USA). The kinetics of the photocolorization and photo- and thermal bleaching reactions of the photoinduced form was detected on a special kinetic installation consisting of the photoactivation and probing sources, monochromator, radiation receiver, and signal amplifier. Experimental data were processed on a personal computer.

High-pressure SVD-120A and DRSh-250 mercury lamps were used for the photoactivation of the studied polymeric samples and investigation of the photodecomposition kinetics, respectively. The radiation of the lamps was filtered by glass light filters from the standard set of colored glasses for isolation

of the UV and visible radiation coinciding with the absorption bands of the initial and photoinduced forms of the spiropyrans of the coumarin series, respectively.

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