

MACROMOLECULAR COMPOUNDS  
AND POLYMERIC MATERIALS

# Fluorescent Properties of Polymer Systems with Negative Photochromism Based on Complexes of Spiropyran with Metal Ions

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**Abstract**—A spectral-kinetic investigation was carried out to study the fluorescent properties of complexes of molecules of photochromic nitro-substituted spiropyran with metal cations differing in electron affinity in polymer matrices of various nature. It is shown that the photoinduced dynamic color change is determined by the change not only in the absorption, but also in the luminescence of complexes exhibiting negative photochromism. The role of proton complexes in the photochromic transformations of the merocyanine form of spiropyran was revealed.

**Keywords:** photochromism, spectroscopy, spiropyran, metal cations, complexes

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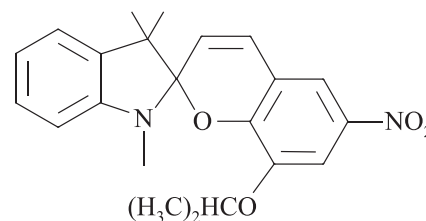
The increasing use of photochromic materials [1] contributed to the growth of interest in the study of the phenomenon of negative photochromism, which consists in the reversible fading of photochromic substances [2, 3].

We have previously shown that photochromic systems with negative photochromism can be created on the basis of complexes of photochromic nitro-substituted spiropyrans with metal ions formed both in solutions and in polymer matrices [4]. This work is a logical continuation of an earlier study.

This work is aimed at researching the fluorescent properties of polymer systems based on complexes of spiropyran with metal ions, which exhibit negative photochromism in polymer matrices of various nature.

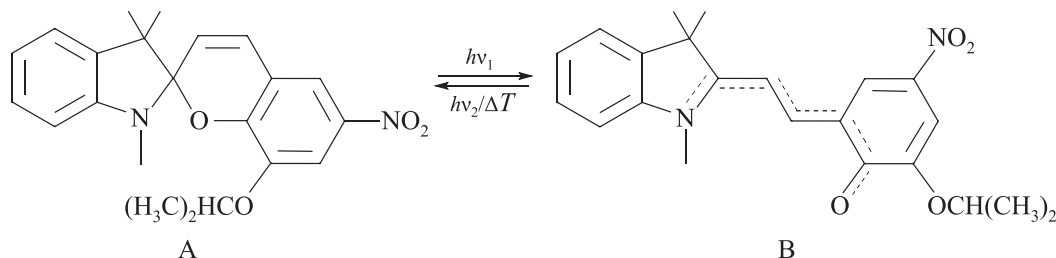
## EXPERIMENTAL

The objects of study were complexes of spiropyran [4] with metal ions  $Mg^{2+}$  and  $Tb^{3+}$ , formed upon dissolution of anhydrous salts  $Mg(ClO_4)_2$  (no. 222283, Aldrich) and  $Tb(NO_3)_3$  (no. 217212, Aldrich).



Commercial polymethyl methacrylate (no. 445746, Aldrich), cellulose acetobutyrate (no. 419036, Aldrich), and amide-containing copolymer AC-A (Technical Specification TU 2216-009-95611404-2006, LLC NPK Shuravi) were taken as polymer binders. A mixture of acetonitrile (no. 271004, Aldrich) and toluene (no. 244511, Aldrich) was used as solvents for the preparation of films based on copolymer AC-A. Polymethylmethacrylate films were prepared using a mixture of acetonitrile and acetone (no. 154598, Aldrich). In the case of producing films with the cellulose acetate butyrate polymer, acetonitrile was used. Polymer photochromic compositions were prepared by mixing solutions of a polymer and a photochromic compound or a complex thereof. For the studies, polymer compositions were prepared with a spiropyran content  $c = 0.75$  wt %

Scheme 1.



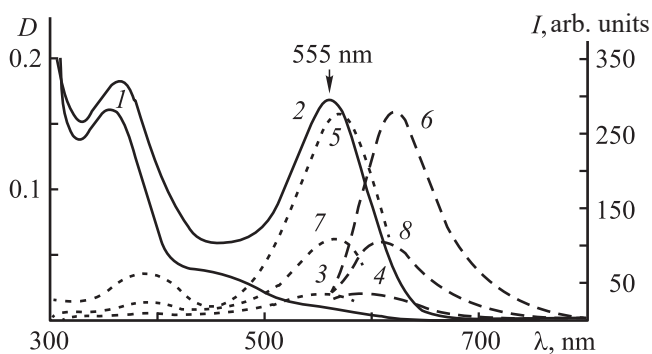
with respect to the weight of the dry polymer. The ratio of the content of spiropyran and metal ions was 1 : 100. The prepared polymer compositions were applied to quartz glasses by casting, dried at room temperature in a dark place until the solvent completely evaporated, and then dried in an oven at 60°C for 60 min.

Spectral measurements of polymer films were recorded by a Cary 50 bio spectrophotometer (Varian). Fluorescence spectra were registered on a Cary Eclipse spectrofluorimeter (Varian).

Photocoloration of the polymer layers was carried out by UV radiation from an L8253 xenon lamp of an LC-4 UV spot light sourcer (Hamamatsu) through an UFS 1 light filter; photobleaching was achieved by exposure to visible radiation through a ZhS-10 light filter.

## RESULTS AND DISCUSSION

Reversible changes in the photoinduced absorption spectra, fluorescence excitation and fluorescence (Fig. 1)

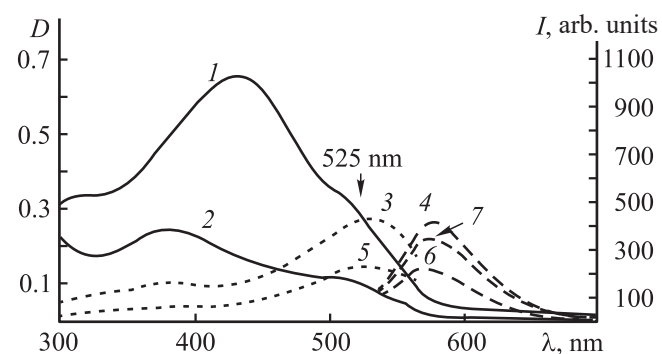


**Fig. 1.** (1, 2) Absorption spectra, (3, 5, 7) excitation of fluorescence when measured at a length of 600 nm, and (4, 6, 8) fluorescence spectra when excited with light of a wavelength 555 nm of spiropyran in a polymethyl methacrylate film (1, 3, 4) before and (2, 5, 6) after UV irradiation through an UFS-1 light filter and (7, 8) subsequent dark relaxation.

of spiropyran in the polymethyl methacrylate film indicate the manifestation of positive photochromism by this compound, which consists in its reversible photocoloration and dark discoloration (Scheme 1).

During irradiation of a photochromic film with UV light, the cyclic form A of spiropyran as a result of photodissociation of the –C–O– bond in the pyran fragment and subsequent dark *cis-trans* isomerization is converted into open merocyanine form B, which spontaneously or under the action of visible radiation returns to the original form A (Scheme 1) [4]. This process is accelerated at heating the film.

The fluorescence excitation spectra (Fig. 1, curves 3, 5, 7) evidence that the appearance of fluorescence (Fig. 1, curves 4, 6, 8) is due to the photoinduced formation of the merocyanine form of spiropyran. The absorption and fluorescence spectra are characterized by maxima at 555 and 600 nm, respectively (Table 1). The fluorescence intensity varies in the process of



**Fig. 2.** (1, 2) Absorption spectra, (3, 5) excitation of fluorescence when measured at a length of 575 nm and (4, 6, 7) fluorescence spectra when excited with light of a wavelength 525 nm of spiropyran in the presence of Mg<sup>2+</sup> in a polymethyl methacrylate film (1, 3, 4) before and (2, 5, 6) after UV irradiation through an UFS-1 light filter and (7) subsequent dark relaxation.

**Table 1.** Spectral and luminescent characteristics of spiropyran in polymer films without and in the presence of metal ions (at a concentration ratio of spiropyran to metal ions of 1 : 100)

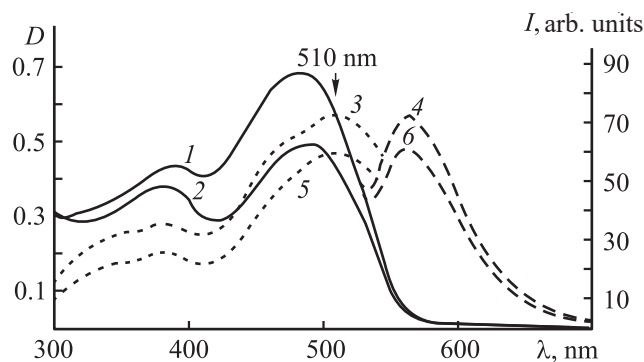
Polymer	Ion	Maximum of the absorption band $\lambda$ , nm (optical density $D$ at the maximum of the absorption band)		Maximum of the fluorescence band $\lambda_{fl}$ , nm (fluorescence intensity at the maximum of the fluorescence band $I_{fl}$ , arb. units)	
		before irradiation	after irradiation	before irradiation	after irradiation
Polymethyl methacrylate	–	355 (0.16) 445 (0.04) 555 (0.01)	555 (0.17)	600 (35)	625 (275)
	Mg <sup>2+</sup>	430 (0.66) 500 sh (0.36)	380 (0.24) 500 (0.12)	575 (420)	575 (220)
	Tb <sup>3+</sup>	388 (0.43) 485 (0.68)	380 (0.38) 485 (0.48)	565 (75)	565 (60)
	–	350 (0.08) 550 (0.03)	– 550 (0.08)	600 (70)	620 (140)
	Mg <sup>2+</sup>	430 (0.46) 505 sh (0.25)	380 (0.27) 505 (0.07)	572 (240)	565 (65)
	Tb <sup>3+</sup>	377 (0.30) 490 (0.45)	370 (0.29) 490 (0.34)	555 (55)	555 (50)
Amide-containing copolymer AC-A (sample prepared in 2017)	–	350 (0.13)	375 (0.28) 560 (0.71)	600 (45)	630 (675)
	Mg <sup>2+</sup>	430 (0.57) 515 sh (0.25)	365 (0.28) 515 (0.10)	575 (760)	575 (185)
	Tb <sup>3+</sup>	375 (0.32) 490 (0.56)	500 (0.36)	560 (65)	560 (52)
Amide-containing copolymer AC-A (sample prepared in 2015)	–	350 (0.26) 465 (0.03) 560 (0.01)	370 (0.34) – 560 (0.71)	595 (65)	623 (775)
	Mg <sup>2+</sup>	430 (0.77) 515 sh (0.35)	415 (0.28) 515 (0.09)	555 (1275)	580 (500)
	Tb <sup>3+</sup>	430 (0.62) 510 sh (0.26)	420 (0.38) 510 (0.11)	577 (740)	517 (577)

“sh” is the shoulder of the absorption band.

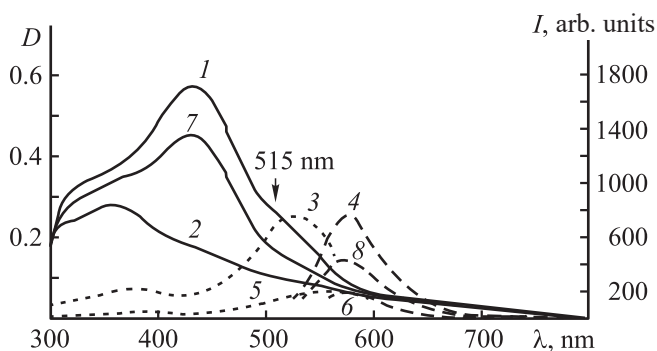
photochromic transformations symbatically with a change in optical density in the absorption band of the merocyanine form.

After the introduction of magnesium ions into the polymer solution, the absorption spectrum of spiropyran changes. Absorption bands appear in the spectrum in the visible region with two maxima at 430 and 500 nm

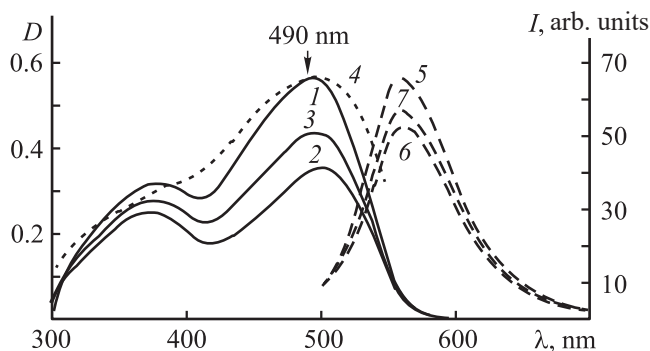
(Table 1, Fig. 2, curve 1). Irradiation of the film with visible light leads to its reversible discoloration (Table 1; Fig. 2, curve 2), i.e., to the manifestation of negative photochromism [4], due to the formation under dark conditions of a photochromic complex of a metal ion with phenolate oxygen of the merocyanine form of spiropyran (Scheme 1).



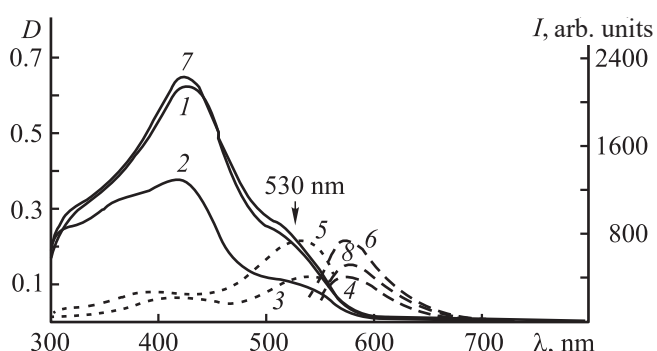
**Fig. 3.** (1, 2) Absorption spectra, (3, 5) excitation of fluorescence when measured at a length of 563 nm and (4, 6) fluorescence spectra when excited with light of a wavelength 510 nm of spiropyran in the presence of  $Tb^{3+}$  in a polymethyl methacrylate film (1, 3, 4) before and (2, 5, 6) after UV irradiation



**Fig. 4.** (1, 2, 7) Absorption spectra, (3, 5) excitation of fluorescence when measured at a length of 575 nm and (4, 6, 8) fluorescence spectra when excited with light of a wavelength 515 nm of spiropyran in the presence of  $Mg^{2+}$  in a AC-A copolymer (1, 3, 4) before and (2, 5, 6) after UV irradiation and (7, 8) subsequent dark relaxation.



**Fig. 5.** (1–3) Absorption spectra, (4) excitation of fluorescence when measured at a length of 570 nm and (5–7) fluorescence spectra when excited with light of a wavelength 490 nm of spiropyran in the presence of  $Tb^{3+}$  in a AC-A copolymer (1, 4, 5) before and (2, 6) after UV irradiation and (3, 7) subsequent dark relaxation. The sample was prepared in 2017.



**Fig. 6.** (1, 2, 7) Absorption spectra, (3, 5) excitation of fluorescence when measured at a length of 577 nm and (4, 6, 8) fluorescence spectra when excited with light of a wavelength 530 nm of spiropyran in the presence of  $Tb^{3+}$  in a AC-A copolymer (1, 5, 6) before and (2–4) after UV irradiation and (7, 8) subsequent 5 day dark relaxation.

The fluorescence band with a maximum at 575 nm (Fig. 2, curve 4) is due to the presence in the film of spiropyran molecules in the merocyanine form, which derive complexes with magnesium ions. This band is hypsochromically shifted by 25 nm relative to the absorption band of the merocyanine form recorded in the absence of ions in the polymer (Table 1). The second short-wavelength absorption band, apparently, belongs to the protonated merocyanine form of spiropyran [3], which does not exhibit luminescent properties.

Similar spectral and fluorescent changes are observed for spiropyran with terbium cations (Table 1; Fig. 3).

In contrast to complexes with magnesium ions, the absorption spectrum contains only a long-wavelength absorption band of the complex of the merocyanine form with the terbium ion, the maximum of which shifts by 35 nm to the short-wavelength region of the spectrum relative to the maximum of the absorption band of the merocyanine form, recorded in the absence of the terbium cation (Table 1). In this case, in the spectrum there is no the absorption band of the proton complex with a maximum at 430 nm (Table 1).

The use of cellulose acetobutyrate as a polymer binder practically does not results in significant differences in

the change in the spectral and fluorescent properties of polymer films containing complexes of spiropyran with magnesium and terbium ions (Table 1).

Similar results were obtained for photochromic films with direct and reverse photochromism when using the AC-A copolymer, which is characterized by a large free molecular volume (Figs. 4, 5). A distinctive feature is the more intense fluorescence of complexes of the merocyanine form of spiropyran with metal ions (Table 1).

Interesting features of the spectral manifestation of the complexation of the merocyanine form of spiropyran with metal ions are observed for samples that have been stored for a long time (Table 1). The absorption spectra of complexes of the merocyanine form of spiropyran with magnesium ions remain unchanged after 2 years (Table 1), while in the absorption spectra of complexes with terbium ions there occur significant changes (Table 1; Fig. 6). As in the case of polymer layers containing complexes with magnesium ions, an absorption band of the protonated merocyanine form of spiropyran appears with a maximum at 430 nm. It should be noted that the fluorescence intensity increases with the storage time of photochromic films, which can be explained by the evaporation of solvent residues and, as a consequence, an increase in the rigidity of the polymer matrix.

The results of a study of the fluorescent properties of polymer films based on photochromic spiropyran in the absence of metal ions show that the films, possessing positive photochromism, exhibit, as in solutions, photoinduced fluorescence due to the formation of the merocyanine form under the action of UV light. The same properties are demonstrated by polymer films based on complexes of spiropyran and metal ions, which exhibit negative photochromism. However, the fluorescent properties of these films are caused by the complexes of the merocyanine form with metal ions formed in the dark.

The absorption band in the spectral region at 430 nm is associated with the appearance in the polymer matrix of non-luminescent proton complexes of spiropyran molecules, which are formed as a result of the destruction of complexes with metal ions. The absence of absorption bands of proton complexes of spiropyran with terbium ions in freshly prepared polymer layers in comparison with complexes of spiropyran with magnesium ions and their appearance after 2 years is apparently due to the higher efficiency of the interaction of phenolate oxygen of the merocyanine form of spiropyran with terbium ion

due to its higher affinity to an electron in comparison with magnesium ions [3].

## CONCLUSIONS

Photochromic polymer materials based on complexes of nitro-substituted spiropyran with metal ions exhibit a reversible photoinduced change not only in absorption, but also in fluorescent properties due to complexes of the merocyanine form with metal ions. This feature is promising for improving coatings of various types with dynamic color changes due to photoinduced changes not only in absorption, but also in luminescence. When developing such coatings, attention should be paid to the formation of non-luminescent proton complexes, the formation of which depends on both the nature of the photochromic compound and the electron affinity of metal cations.

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## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest requiring disclosure in this article.

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