

Spectral study of the protonation of photochromic chromenes in polymeric matrices

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For the first time, proton complexes of the photoinduced colored form of chromene have been obtained in polymer binders. It is shown that UV irradiation of photochromic chromene leads to spectral changes due to the structure of the compounds and the nature of the polymer binder.

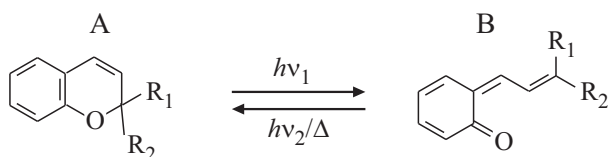
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Introduction

Among the known photochromic organic compounds, photochromic chromenes are highly resistant to irreversible phototransformations, so they were used to create photochromic ophthalmic lenses [1–3]. Functionalized photochromic chromenes proved to be suitable for the development of optical chemosensors [4–6], photo switches, photocontrolled molecular electronic devices, etc. [7].

Photochromic transformations of these compounds are based on the reversible photodissociation of C–O bond in the pyran cycle of a colorless cyclic compound A and the subsequent *cis-trans*-isomerization with the formation of a colored form B (Scheme 1). The reverse reaction occurs spontaneously and accelerates by heating or exposure to visible light.



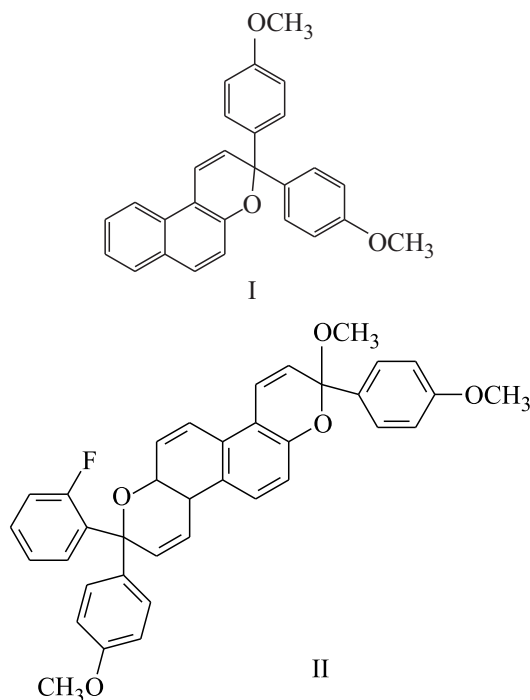
Scheme 1

In contrast to photochromic spiro compounds (spiropyrans and spirooxazines), for which it is known, that under UV light in the presence of acids they form protic complexes [8], such information is practically absent for chromenes. The main studies were related to the study of the effect of intramolecular hydrogen bonds on the thermal stability of the merocyanine form of functionalized chromenes [9–15].

This study is a continuation of the studies on photoinduced protonation of merocyanine form of chromenes in solutions [16].

Experimental part

Compounds I and II were used as photochromic chromenes. Compound I was synthesized according to the known method [17]. Chromene II was obtained from 3,3'-di(4-methoxyphenyl)-8-hydroxy[3H]naphto[2,1-b]pyran and 1-(2-fluorophenyl)-1'-(4-methoxyphenyl)-2-propyn-1-ol in anhydrous toluene solution by heating to 60°C in the presence of toluenesulfonic acid as a catalyst.



The studies were carried out in polymethylmethacrylate (PMMA) and polyvinylbutyral (PVB) films. To obtain polymer films, a photochromic compound in an amount of

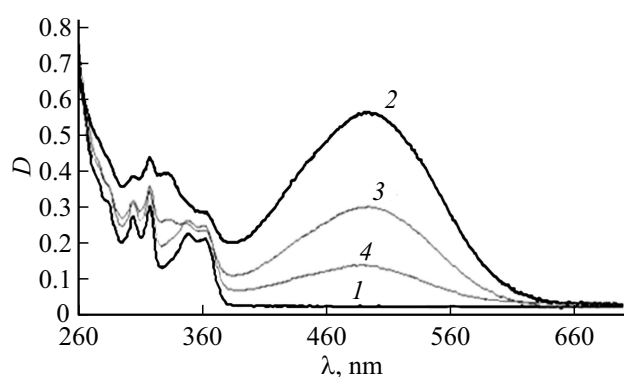


Figure 1. Absorption spectra of compound I in a PVB film before (1), after UV irradiation (2) and during dark relaxation to the initial state (3, 4).

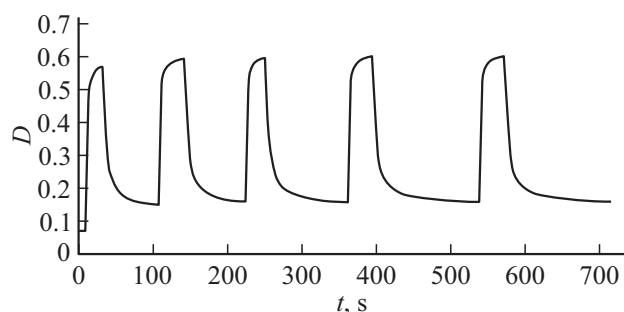


Figure 2. Kinetics of photocoloring under UV radiation and dark spontaneous bleaching of compound I in a PVB film recorded at a wavelength of 495 nm.

0.5 mg was dissolved in 1 ml of methoxypropanol. 50 mg of polymer (5 mas.%) was added to the obtained solution. The prepared composition was applied to quartz glass by pouring (large drop). To prepare a sample with a protonated complex, 0.02 μl of HClO_4 acid solution in methoxypropanol ($C = 10^{-3} \text{ M}$ and $C = 10^{-2} \text{ M}$) was added into polymer composition, and then the polymer solution with protonated complex was applied onto quartz glass.

Spectrophotometric measurements (photostationary spectra) of the studied compound in polymer layers were carried out using „CARY 50 bio“ spectrophotometer.

Irradiation was performed with filtered light from LC-4 Hamamatsu lamp. For photocoloring a glass light filter UFS-1 was used, which transmits UV radiation.

Results and discussion

Figure 1 shows photoinduced changes in the spectrum of absorption of chromene I in a PVB film in the absence of acid. An initially colorless film, when irradiated with UV light, is colored with the appearance of an absorption band with a maximum at 490 nm (see Table). It has photochromic properties (Fig. 2).

When adding compound I of perchloric acid ($C = 10^{-3} \text{ M}$) into polymer solution, as in the absence of acid, the film remains colorless up to irradiation and becomes colored after UV irradiation (Fig. 3). The difference lies in the appearance of a second long-wavelength absorption band with a maximum at 635 nm, which is bathochromically shifted by 153 nm relative to the first absorption band at 482 nm (table). This absorption band observed in the presence of acid and in solution [16], is associated with the protonation of the phenolate oxygen of the photoinduced colored form B [16]. The appearance of the short-wavelength absorption band is due to molecules of the photoinduced colored form B of chromene, which do not participate in protonation.

Similar to an acid-free film, protonated complexes exhibit photochromism, since reversible photoinduced changes in its optical density are observed (Fig. 4). In this case, the rate of thermal relaxation of the photoinduced form to the initial state reduces significantly. In the absence of the acid the rate of dark discoloration of this form is characterized by complex kinetics, described by the constants $k_1 = 0.190 \text{ c}^{-1}$ and $k_2 = 0.038 \text{ c}^{-1}$, and in the presence of the acid ($C = 10^{-3} \text{ M}$) — $k_1 = 0.03 \text{ c}^{-1}$ and $k_2 = 0.005 \text{ c}^{-1}$. The rates of photoinduced formation of the colored open and protonated forms turned out to be comparable.

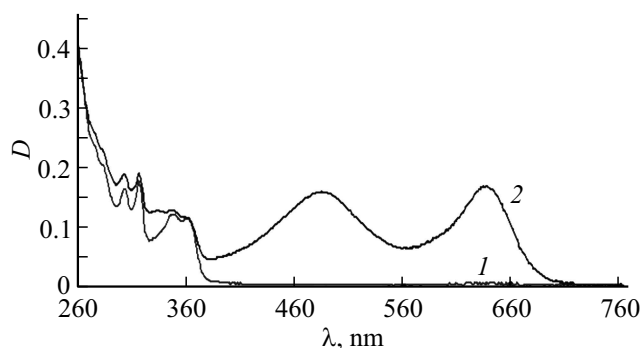


Figure 3. Absorption spectra of compound I in a PVB film in the presence of perchloric acid ($C = 10^{-3} \text{ M}$) before (1) and after UV irradiation (2).

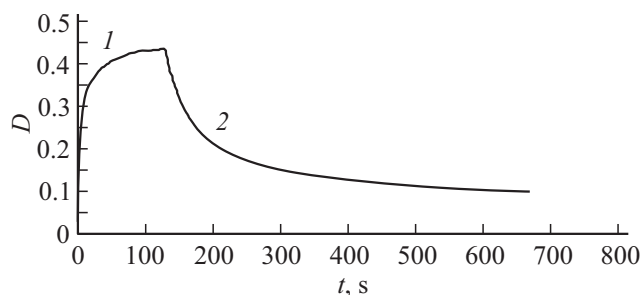


Figure 4. Kinetics of photocoloring (1) and dark discoloration (2) of the protonated complex of compound I in a PVB film in the presence of perchloric acid ($C = 10^{-3} \text{ M}$) when registering at a wavelength of 635 nm.

Spectral-Kinetic Characteristics of Photochromic Chromenes and Proton Complexes in Polymer Films

Compound	CHClO ₄ , M	λ_A^{\max} , nm	λ_B^{\max} , nm	ΔD^{phot}
I	—	355, 345, 313, 300	490	0.56
	10 ⁻³	355, 345, 313, 300	482 635	0.16 0.16
	10 ⁻²	355, 350, 313, 300, 494, 635	484 635	0.10 0.10
II	—	395, 375, 326, 311	505	0.15
	10 ⁻³	395, 375, 326, 311	500 700	0.08 0.06
	10 ⁻²	395, 375, 326, 311, 500, 700	500 700	0.06 0.17

Note. CHClO₄ — perchloric acid concentration in the polymer layer; λ_A^{\max} and λ_B^{\max} — wavelengths of the maxima of the absorption bands of the original and long-wavelength absorption bands of photoinduced forms of photochromic chromenes respectively; ΔD^{phot} — photoinduced value of the optical density in the maxima of the absorption bands of B chromenes photoinduced form.

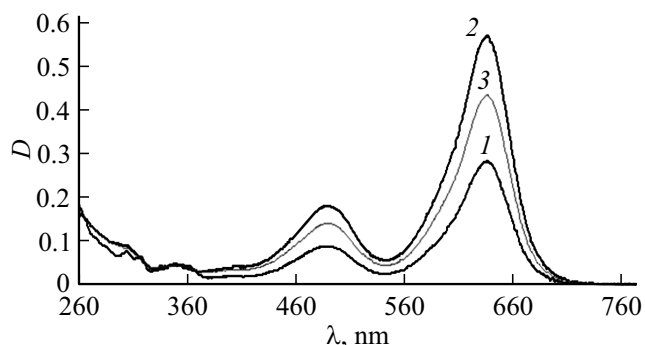


Figure 5. Absorption spectra of compound I in a PVB film in the presence of perchloric acid ($C = 10^{-2}$ M) before (1), after UV irradiation (2) and during subsequent spontaneous relaxation (3).

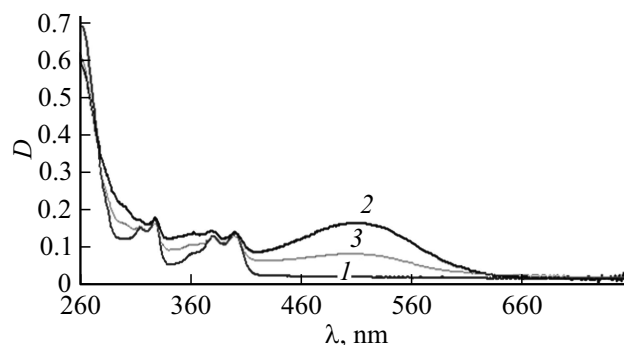


Figure 6. Absorption spectra of compound II in a PVB film in the presence of perchloric acid ($C = 10^{-3}$ M) before (1), after UV irradiation (2) and during subsequent spontaneous relaxation (3).

An increase in the acid concentration by an order of magnitude leads to the appearance of a film color before UV irradiation, which is accompanied by the appearance in the initial absorption spectrum of two absorption bands with maxima at 484 and 635 nm, coinciding with the maxima of the photoinduced absorption bands at a lower acid concentration (compare the spectra in Fig. 5 and 3). As in solutions [16], substances formed before UV irradiation, like photoinduced protonated complexes, do not decolorize under the visible light, but relax extremely slowly into the initial colorless form A. This may be due to the formation of associates of protonated colored forms.

Similar results were also obtained for bis-chromene II (See Fig. 6 and 7, Table). In this case, the emerging second absorption band is bathochromically shifted by 200 nm relative to the photoinduced short-wavelength absorption band. This shift is by 47 nm larger, than for monochromene I, that may be due to the different planarity of the protonated forms of mono- and bis-chromene.

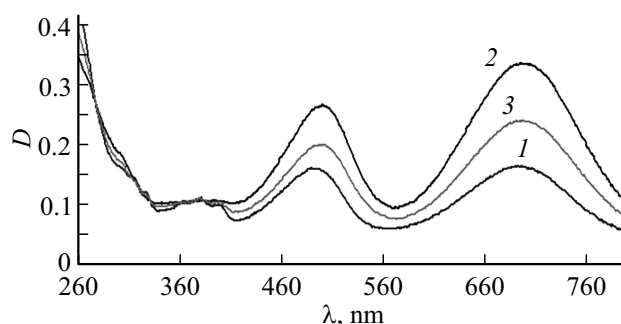


Figure 7. Absorption spectra of compound II in PVB film in the presence of perchloric acid ($C = 10^{-2}$ M) before (1), after UV irradiation (2) and in the process of spontaneous relaxation (3).

PMMA films of chromene II exhibit photochromic transformations similar to those observed in solution (Fig. 8, curves 1, 2).

In contrast to the films based on PVB binder, in solid PMMA layers the acid in the form of long-wavelength

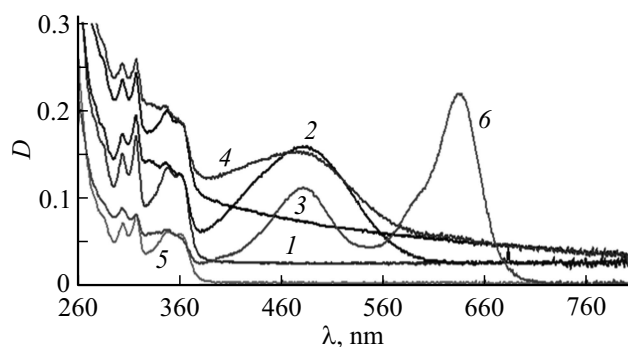


Figure 8. Absorption spectra of compound II in PMMA film in the absence of perchloric acid (1, 2), in the presence of acid in solid (3, 4) and gel-like (5, 6) layers before (1, 3, 5) and after UV irradiation (2, 4, 6).

absorption bands does not appear (Fig. 8, curves 3, 4). Protonated complexes are found only in gel-like layers (Fig. 8, curves 5, 6).

The observed difference in the formation of protonated complexes in PVB and PMMA films is explained by the difference in rigidity and, as a result, in free molecular volume of these polymer films. This is confirmed by the formation of protonated complexes in the gel-like PMMA layers.

Conclusions

The formation of proton complexes of the photoinduced colored form of chromenes in polymeric binders has been demonstrated for the first time. It was shown, that UV irradiation of photochromic chromenes leads to spectral changes due to the structure of the compounds and the nature of the polymer binder.

In the case of PVB binder the protonation occurs similarly to the process observed in solutions, that is proved by the appearance of the second absorption band in the long-wavelength region of the spectrum (with maxima at 630 and 700 nm for chromenes I and II respectively). It should be noted, that with an excess of acid in the layer, a protonated complex is already initially formed without exposure to UV light.

The polymethylmethacrylate layer, in contrast to the PVB film, prevents from chromene protonation. The effect is observed only in the gel-like composition.

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Conflict of interest

The authors declare that they have no conflict of interest.

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