Solid state photochromism of spiropyrans

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ABSTRACT. A series of spiropyrans possessing photochromic properties in solid state were investigated. UV irradiation ($\lambda_{\max} = 365 \text{ nm}$) of the thin vacuum deposited spiropyran films results in conversion of the colorless form to the photocolored one. The reaction is photochemically and thermally reversible. The photochromic activity of the solid material and polystyrene matrix has been compared. Raman spectroscopy has been used for studying the influence of metallic surface on the adsorbed spiropyran layers.

1. INTRODUCTION

An active research work is carried out all over the world in the field of nonsilvered light sensitive materials, such as organic photochromic compounds capable of coloration under irradiation in various spectral regions [1].

Spiropyrans is one of the major classes of organic photochromes [2, 3]. The photochromic behavior of spiropyrans is usually enhanced if a molecule possesses strong electron acceptor substitutes such as a nitro group in the 6' and/or 8' positions of its 2H-chromene fragment.

However, the replacement of the nitro group by other π -acceptor results in effective coloration and good adhesion. This could lead to deposition of the photosensitive layer on the end-window of glass fiber optic. It has been proposed that spiropyrans could be used for recording digital information [3]. Because of the technological importance of this class of compounds we will report here about the investigation of some new spiropyrans.

2. METHODS AND MATERIALS

All spiropyrans I-IV [2, 4, 5] have been purified with column chromatography.

The structures of all synthesized compounds have been determined with elemental analysis, IR and ^1H NMR spectroscopy.

^1H NMR spectra have been detected using a NMR spectrometer "Varian Unity 300" (300 MHz, USA) in CDCl_3 . Chemical shifts are reported in δ (ppm) relative to tetramethylsilane.

Electronic absorption spectra of the spiropyran solid films before and after irradiation have been detected by using "Specord UV VIS" spectrophotometer equipped with special rotating mirror. The vacuum thermal deposition process was carried out for obtaining the transparent spiropyran thin films on quartz or glass plates. The VUP-4 apparatus was used for vacuum deposition (at $\sim 1.5 \times 10^{-5}$ Torr, temperature of evaporation $\sim 250\text{--}400^\circ\text{C}$) for both spiropyrans and silver films. The control of the film homogeneity had been realized with a polarity interference microscope MPI-5 (PZO Warszawa, Poland produced) by scanning two coordinate axis and observing interference signals. The Raman spectra were recorded with a DFS-52M (LOMO) spectrometer and ILA-120 argon laser (Carl Zeiss) was used as an excitation source. The power density of laser radiation was about 10 mW/mm^2 . A 250 W high-pressure mercury discharge lamp (DRSh-250) was used in irradiation. The absorption spectra were detected with the spectrophotometer "Specord M 40" (Germany).

3. RESULTS AND DISCUSSION

3.1. Photochromism of the thin films of spiropyran I-IV. It has been found that compound I exhibits photochromic properties not only in solutions but also in the solid state.

Figure 1 shows the effect of the UV irradiation time ($365 \text{ nm} \sim 27307 \text{ cm}^{-1}$) on the vacuum deposited thin films. Irradiation results in conversion of

Figure 1. The effect of the time of UV-irradiation on the absorption spectra of the thin film of spiropyran **I** (1) 0, (2) 30, (3) 120, (4) 240, (5) 360 sec.

colorless (360 nm) form of **I** into photocolored one with $\lambda_{\max}$ 615 nm ($\sim 16260 \text{ cm}^{-1}$), (Figure 1). Photocoloration reaction was found thermally ($+70^\circ\text{C}$) and photochemically reversible. The half-life of a colored form is about 5 minutes (Figure 2).

Thin solid spiropyran **II** and **III** films were studied.

Similar behavior has been noticed in compounds **II** and **III** (Figures 3 and 4). UV irradiation (365 nm) of vacuum deposited spiropyrans **II** and **III** films results in conversion of colourless forms to photocolored ones. The reaction is photochemically reversible. Heating of photocolored forms results in stabilising photocolored form of **III**, whereas **II** shows reversible behavior.

It would be of interest to compare the photochromic behavior of the thin solid films of the studied spiropyrans **I**, **II**, and **III** with the 1,3,3-trimethyl-6'-

Figure 2. The absorption spectra of the back dark reaction of compound **I** after different time interval (1) photoinduced form; (2)–(5) spectra recorded after 5, 15, 30, and 60 mins after irradiation, respectively.

nitro-indolinospiro-pyran **V**, which is considered as one of the best photochromic material.

The photocoloration rate of thin solid films of spiropyrans **I–IV** is faster than those of the thin spiropyran **V** films (Figure 5). But in polymeric polystyrene matrixes the photocoloration rate of spiropyran **V** is higher than one of spiropyrans **I–IV** (Figure 6).

Spiropyran **I** contains the nitro group and has the maximum rate in polymeric matrix, but at transition to thin solid films spiropyran **IV** greatly exceed the compound **I** in rate.

Initial rate constants (asymptotic slope with $t \rightarrow 0$ [6]) are given in the table. The table shows, that spiropyrans **IV** in a solid phase exceeds 21 times compound **V**, and besides, enables reversible record of the optical information in solid state.

Figure 3. The effect of the time of UV-irradiation on the absorption spectra of the thin film of spiropyran **II** (1) 0, (2) 30, (3) 120, (4) 240, (5) 270, (6) 360 sec, (7) after heating at 70 °C-“erasing”.

Figure 4. The effect of the time of UV-irradiation on the absorption spectra of the thin film of spiropyran **III** (1) 0, (2) 30, (3) 120, (4) 240, (5) 270 sec, (6) after heating at 70 °C-“fixing”, (7) UV irradiation of fixed film during 60 sec.

3.2. Raman studies of thermo- and phototransformation. We have studied the structure and also the thermo- and phototransformation of spiropyran **VI** that is adsorbed on the surface of silver film with Raman spectroscopy (RS). The photocoloration reaction of **VI** could be presented as a sequence of structural transformations [7].

UV irradiation of the solution of **VI** results in conversion from colorless to the colored form; that has the absorption bands in the visible region with maxima around 382, 404, 562, and 582 nm.

On the first step of our investigation we have compared RS spectra of the adsorbed layers of compound **VI** and the perchlorate **VII**.

Perchlorate **VII** is the model compound of the colored (merocyanine) form of spiropyran **VI** as a **non substituted model of the parent spiropyran IV**. Thin lay-

ers of **VI** and **VII** adsorbed on silver films were obtained by evaporation of solvent from acetonitrile solutions.

Figure 8 presents the Raman spectra of spiropyran **VI** and perchlorate **VII** adsorbed on silver films. In our experiments with application of the RS only the colored (with an open pyran cycle) forms of the spiropyran molecules have been detected.

There are no typical peaks for closed spiropyran molecule bond at the 1640 cm⁻¹. Dissociation of the C_{spiro}-O bond in the adsorbed spiropyran molecules could be associated with the fact that the interaction of the heteroatom O and the sorbent surface results in a decrease of the energy of the C_{spiro}-O bond. The important role of the surface is well seen from the comparison of the Raman spectra of spiropyran **VI** adsorbed on an unannealed (curve 1) and annealed (curve 3)

Table 1. Asymptotic slope if $t \rightarrow 0$ and the ratio of rate constants for spiropyrans I–V in polystyrene matrix and thin solid film.

Compound	Structure	Brutto constants of photocoloration rates in Abs. s ⁻¹		Rate ratio vs. V	
		Polystyrene matrix	Thin solid film	Polystyrene matrix	Thin solid film
I		0,056	0,042	0,22	21
II		0,04	0,006	0,16	3
III		0,047	0,01	0,19	5
IV		0,03	0,004	0,12	2
V		0,25	0,002	1	1

silver films. On the annealed silver film the intensity of the RS signal is several times smaller (Figure 7). This could be linked with the fact that the efficiency of the interaction of the heteroatom O with the surface is in this case smaller and therefore a smaller number of the spiropyran open molecules have been formed.

Since the investigated spiropyran is showing both the photochromic and the thermochromic behavior, the structure study of the adsorbed spiropyran VI molecules and of their photochromism with the temperature is of interest. Cooling of the compound VI film to 77 K results in a noticeable change in the reflectance

Figure 5. Evolution of the maximum visible absorption band during the Photocoloration of 1,3,3-trimethyl-6'-nitro-indolinospiropyran V and spiropyrans I-IV (thin solid films) under 365 nm irradiation.

Figure 6. Evolution of the maximum visible absorption band during the Photocoloration of 1,3,3-trimethyl-6'-nitro-indolinospiropyran V and spiropyrans I-IV (in polystyrene matrix) under 365 nm irradiation.

Figure 7. The reflectance Raman spectra ($\text{exc} = 514.5 \text{ nm}$) of spiropyran VI (1, 3) and colored form VII (2), adsorbed from acetonitrile solutions on the unannealed (1, 2) and annealed (3) silver films.

Figure 8. The reflectance Raman spectra ($\text{exc} = 514.5 \text{ nm}$) of spiropyran VI adsorbed on silver film:

1 - before irradiation at $T = 293$;
 2 - before irradiation at $T = 77 \text{ K}$;
 3 - after UV irradiation for 20 min at $T = 77 \text{ K}$;
 4 - after irradiation by visible light through a UV light filter for 20 min at $T = 77 \text{ K}$ (4);
 5 - the effect of raising the temperature to 263 K of sample 4.

Raman spectra (Figure 8). The comparison of curves 1 and 2 shows that freezing of spiropyran VI results in the formation of spiro form (curve 2). It could be concluded that freezing leads to the reorganization of the structure of the adsorbed merocyanine layers, which results in attenuation of its interactions with the surface. This could be explained by the intermolecular interactions which, with decrease in the thermal energy, induce the formation of the aggregates of spiro form molecules on the surface. These aggregates at low concentration could exist also at room temperature, as indicated by the large width of the band of the reflectance Raman spectra, whose intensity increases considerably with decrease in temperature (see Figure 8, curves 1 and 2). However, the concentration of the aggregates is relatively small at room temperature.

UV irradiation of the adsorbed spiropyran VI layer at 77 K does not lead to fundamental changes in the giant Raman spectrum (Figure 8, curve 3). It should be noted that only a certain decrease in the Raman signal as a whole was observed, which could be due to the photodestruction of the adsorbed molecules and their desorption. As is evident from the comparison of curves 1 and 4 (Figure 8), the irradiation with visible light favors further structural changes in the adsorbed layer of the spiropyran VI molecules. This could be attributed to the formation of associated forms of the merocyanine molecules which were already manifested by the decrease in the temperature. Just as for spiropyran solutions the effect of visible light favors the cyclization of the merocyanine molecules. For the molecules adsorbed on the silver surface this effect favors their association. In heating of the irradiated specimen, the shape of the Raman spectrum is completely recovered (Figure 8, curve 5).

4. CONCLUSION

A new series of spiropyran molecules that exhibit photochromic behavior in solid state were studied.

Photochromic behavior in thin solid spiropyran films was compared with the well known 1,3,3-trimethyl-6'-nitro-indolinospiropyran ones in solid films and polystyrene matrix.

Using Raman spectroscopy the influence of the metallic surface properties on photochromic behavior of the adsorbed spiropyran layers was studied. It has been shown that interactions with the surface could be resulted in dissociation of the C_{spiro}-O bond.

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