

Photochromic transformations in doped polymers upon two-photon excitation

S N Letuta, G A Ketsle, Yu D Lantukh, S N Pashkevich

Abstract. Physical photochromic transformations are studied in doped polymer films upon two-photon excitation. It is shown by the example of fluorescein halogen derivatives that the triplet-level population of molecules can be controlled by exciting the system by light into the $T_1 \rightarrow T_n$ triplet–triplet absorption band of molecules. It is proposed to use this effect for fabrication of materials with controllable photochromic properties.

Keywords: photochromism, highly excited electronic states of molecules.

1. Introduction

Light modulators and switchers are important elements of optoelectronic devices, the requirements imposed on their parameters being constantly made more stringent. In this connection, a search for new methods for controlling light fluxes and a study of molecular mechanisms underlying these methods are quite urgent.

The operation of some light modulators is based on photochromism – the reversible change in the material colour caused by the redistribution of its absorption upon photoexcitation [1]. Photochromism is called chemical if photochemical products are produced upon optical excitation of a substance. If a change in the sample absorption is caused by the transition of molecules to excited electronic states with finite lifetimes, photochromism is called physical. In this case, high switching rates can be achieved (the switching time $\tau \sim 10^{-9} - 10^{-8}$ s) and the number of switchings is infinite [1].

In this paper, we study physical photochromic transformations in polymer films doped with xanthene dyes caused by two-photon excitation.

2. Photoprocesses in polyatomic molecules upon two-photon excitation

To describe the mechanism of photochromic transformations, we consider intra- and intermolecular processes pro-

ceeding upon two-photon step excitation of polyatomic molecules via an intermediate triplet state. The energy level diagram and intra- and intermolecular transitions in polyatomic organic molecules are shown in Fig. 1.

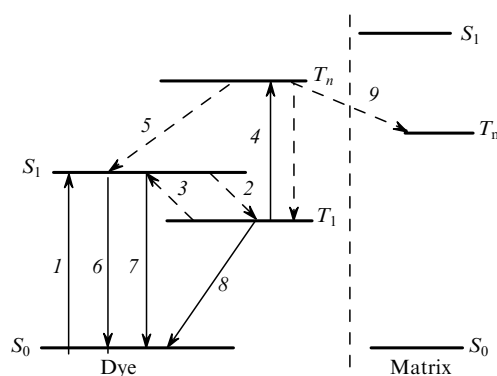


Figure 1. Energy level diagram and intra- and intermolecular transitions. (1) $S_0 \rightarrow S_1$ excitation; (2) intersystem crossing to the triplet state; (3) thermally induced transition to the S_1 state; (4) $T_1 \rightarrow T_n$ excitation by an additional light source; (5) reverse $T_n \rightarrow S_1$ intersystem crossing; (6) fluorescence induced by excitation of molecules to the triplet state; (7) thermally induced delayed fluorescence; (8) phosphorescence; (9) triplet–triplet energy transfer to matrix molecules.

After excitation of molecules into the $S_0 \rightarrow S_1$ absorption band and its subsequent $S_1 \rightarrow T_1$ intersystem crossing to the T_1 triplet state, the molecules are accumulated in the lower triplet state. Because the triplet-state lifetime is, as a rule, much longer than that of a singlet state, the greater part of the molecules can be transferred to the triplet state. The sample becomes bleached within the $S_0 \rightarrow S_1$ absorption band, whereas it becomes nontransparent within the $T_1 \rightarrow T_n$ triplet–triplet absorption band. The molecules return back to the initial state during the triplet-state lifetime. If the $S_1 - T_1$ energy gap is small ($\sim 2000 - 3000 \text{ cm}^{-1}$), the T_1 state relaxes due to thermally stimulated delayed fluorescence [2], phosphorescence, and (or) due to nonradiative transitions to the ground state.

In this paper, we develop the method for external controlling the triplet-state populations of dye molecules intended for the creation of a material with controllable photochromic properties. This aim was achieved by exciting molecules by an external controlling light flux into the $T_1 \rightarrow T_n$ triplet–triplet absorption band. The controlling flux was a nanosecond light pulse incident on a sample, which caused the depletion of the T_1 state, resulting in the

S N Letuta, G A Ketsle, Yu D Lantukh, S N Pashkevich Orenburg State University, prosp. Pobedy 13, 460352 Orenburg, Russia; e-mail: lantukh@com.osu.ru

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sample bleaching in the triplet-triplet absorption band and in the restoration of the absorption.

The T_n triplet states of polyatomic molecules can relax via the following channels: (i) the $T_n \rightarrow T_1$ internal conversion or $T_n \rightarrow T_1$ fluorescence; (ii) photochemical reaction; (iii) triplet-triplet energy transfer to the environment; (iv) the $T_n \rightarrow S_1$ intersystem crossing.

The T_n states populated upon absorption of photons in the visible range mainly relax in most compounds due to the nonradiative internal $T_n \rightarrow T_1$ conversion. Fluorescence at transitions between the triplet levels was observed for anthracene and some of its derivatives [3–4]. The quantum yield of this fluorescence is low ($\sim 10^{-7} - 10^{-5}$), so that this relaxation channel does not virtually change the triplet-state population. When high triplet states are populated upon excitation by high-energy UV photons, the role of photochemical reactions in the relaxation of triplet states increases. In this case, some compounds have the quantum yield of the photochemical reaction equal to unity [5].

The triplet-triplet energy transfer from the T_n levels of luminophores to molecules of the environment was studied in detail in papers [6, 7]. It was shown in these papers that the efficiency of the $T_n \rightarrow T_m$ energy transfer for molecules with completely saturated bonds in matrices did not exceed $\sim 10^{-3}$. The energy-transfer efficiency is treated in this case as a fraction of molecules that irreversibly imparted their energy to molecules of the environment. The intersystem crossing to a singlet state was observed so far only for few aromatic compounds [8, 9], the quantum yield of the process being no more than 10^{-4} .

The population of the T_1 state decreases after excitation of molecules into the triplet-triplet absorption band either due to intersystem crossing to the singlet state followed by the $S_1 \rightarrow S_0$ fluorescence or nonradiative internal conversion or due to the $T_n \rightarrow T_m$ energy transfer to matrix molecules. Therefore, the problem of an external controlling of the T_1 -state population of molecules consists in a search for molecules with the high quantum yield of $T_n \rightarrow S_1$ intersystem crossing ($\sim 0.1 - 1.0$) and matrices with the high efficiency of the $T_n \rightarrow T_m$ energy transfer.

Studies of the properties of triplet states of fluorescein halogen derivatives in polyvinyl alcohol films showed that these molecules relax after photoexcitation mainly due to the $T_n \rightarrow S_1$ intersystem crossing. The quantum yield of this process varies from 0.11 for dibromofluorescein to 1.0 for erythrosine [10–12]. Depending on the intensity of an external controlling signal, the lowest triplet-level population can change because of intersystem crossing to the singlet state approximately by 50%. Such a variation in the triplet state population results in a reliably detected photochromic effect. In polymer matrices, where the efficiency of energy transfer from high triplet levels of dye molecules to the matrix molecules is high, the lowest triplet-level population will decrease due to the competition between intersystem crossing to the singlet state and the $T_n \rightarrow T_m$ energy transfer. In such matrices, the T_1 -state population was reduced by 90% with the help of controlling pulses [13].

3. Experimental

The experimental setup that we used for studying photochromism of samples consisted of two single-pulse lasers. The radiation from the first laser (Nd³⁺:YAG, $\lambda_1 = 532$ nm, the pulse duration $\tau = 10$ ns, and the energy $E = 30$ J) was

used to populate the S_1 state of dye molecules (process 1 in Fig. 1). After the time interval sufficient for the formation of triplet molecules due to the $S_1 \rightarrow T_1$ intersystem crossing (process 2), a sample was excited by a light pulse from the second laser (a dye laser, $\lambda_2 = 580 - 650$ nm, $\tau = 10$ ns, $E = 5$ mJ or a ruby laser, $\lambda_2 = 694$ nm, $\tau = 30$ ns, $E = 70$ mJ) into the $T_1 \rightarrow T_n$ absorption band (process 4). The induced absorption and luminescence of dye molecules (processes 6, 7, and 8) were detected through an MDR-41 monochromator with a FEU-84 photomultiplier. The experimental data were collected, accumulated and preliminary processed with an automated setup including a PC and a CAMAC crate with the transient-response front duration of 300 ns.

Photochromic samples were doped polymer films of polyvinyl alcohol (PVA), polyvinyl butyral, polymethyl methacrylate (PMMA) and others. We have chosen these polymers because of their different ability to accept the energy transferred from high triplet levels of dye molecules. The polymer films were doped with xanthene dyes – fluorescein derivatives: erythrosine, Bengal rose, diiodofluorescein, and eosin. The concentration of dye molecules was 10^{-4} mol L⁻¹. The films were prepared by the casting from a solution (polymer-dye-solvent) on a glass or metal plate. After the solvent evaporation, a solid dye-doped film was formed. The film thickness was of about 30 μ m in most experiments.

Fig. 2 shows the $S_0 \rightarrow S_1$ absorption spectra and the long-wavelength parts of the induced $T_1 \rightarrow T_n$ absorption spectra of dyes in PVA films. One can see that our radiation sources correspond to the necessary requirements: the first laser excites dye molecules to the S_1 state, whereas the second laser excites only dye molecules in the triplet state.

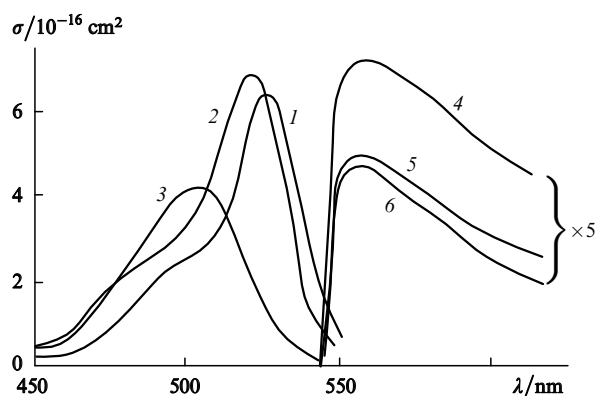


Figure 2. The $S_0 \rightarrow S_1$ (1–3) and $T_1 \rightarrow T_n$ (4–6) absorption spectra of xanthene dyes: erythrosine (1, 4), eosin (2, 5), and diiodofluorescein (3, 6). The $T_1 \rightarrow T_n$ absorption cross sections are multiplied by five (σ is the absorption cross section of dye molecules).

Fig. 3a shows a fragment of the decay curve for the induced $S_0 \rightarrow S_1$ bleaching of erythrosine in the PVA film upon two-photon excitation demonstrating the modulation of the sample transmission. After the termination of the pulse from the first laser, the concentration of dye molecules absorbing light at the operating wavelength decreases, resulting in an increase in the intensity of the probe light. The probe beam was produced by an incandescent KGM-100 lamp equipped with appropriate optical filters. The pulse from the second laser depletes triplet levels of dyes due

to the efficient $T_n \rightarrow S_1$ intersystem crossing, which is manifested as a step twofold decrease in the intensity of light transmitted through the sample.

Fig. 3b shows a fragment of the decay curve of the thermally induced delayed fluorescence of erythrosine in PMMA upon two-photon excitation. One can see that upon excitation by the second laser, the luminescence intensity increases almost by two orders of magnitude, and after the laser pulse termination the concentration of molecules in the triplet state decreases approximately by 70%. This is caused by the $T_n \rightarrow S_1$ intersystem crossing followed by the $S_1 \rightarrow S_0$ fluorescence and efficient $T_n \rightarrow T_m$ energy transfer to polymer molecules. Fluorescence induced by excitation of dye molecules in the triplet state coincides in this curve in its shape and duration with the laser pulse (this signal is recorded only partially in the fragment). This example demonstrates that, along with transmission of a photochromic material, the intensity of its luminescence also can be controlled.

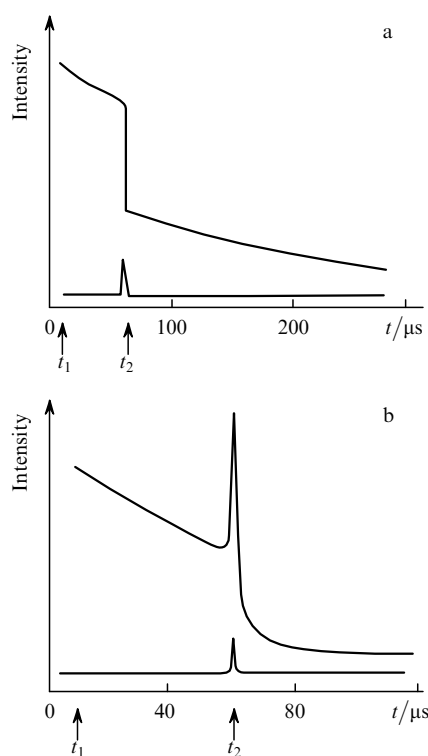


Figure 3. Fragments of the decay curves of the induced $S_0 \rightarrow S_1$ bleaching of eosin in the PVA film (a) and of the thermally induced delayed fluorescence of erythrosine in PMMA (b) upon two-photon excitation (t_1 is the instant of the first pulse termination, t_2 is the instant of the second pulse onset).

4. Basic parameters of photochromic materials

The basic parameters of physical photochromic materials are the spectral sensitivity of initial and photoinduced forms of the material, quantum yields of the direct and reverse phototransformations, the time of production and the lifetime of the photoinduced form, and the rates of transitions from the excited state to the ground state [1]. Our experimental results give information on these parameters.

The spectral sensitivity of photochromic materials is determined by the $S_0 \rightarrow S_1$ absorption spectrum and the induced $T_1 \rightarrow T_n$ absorption spectrum of dye molecules.

These spectra are presented in Fig. 2.

The triplet-state quantum yields of xanthene dyes in PVA films are 0.71 for eosin, 0.80 for diiodofluorescein, and 1.0 for Bengal rose and erythrosine [14]. The quantum yields ϕ_{TS} of the reverse $T_n \rightarrow S_1$ intersystem crossing measured by us for these dyes are 0.28, 0.72, 0.73, and 1.0, respectively. For the first three dyes, the quantum yield ϕ_{TS} in PVA can be increased by adding to PVA the molecules containing heavy halogen atoms [12, 13]. Fig. 4 shows the dependences of the quantum yield of the $T_n \rightarrow S_1$ intersystem crossing on the concentration of LiI in PVA films.

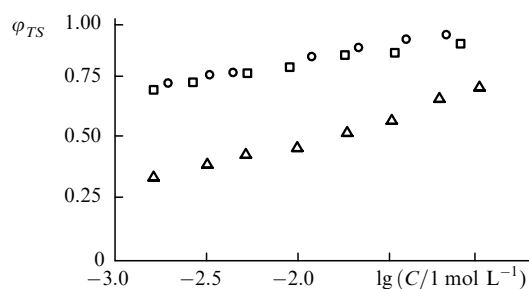


Figure 4. Dependences of the quantum yield of the $T_n \rightarrow S_1$ intersystem crossing of the LiI concentration in PVA films for Bengal rose (\circ), diiodofluorescein (\square), and eosin (\triangle).

The formation time of the triplet states is determined by the rate constant of the $S_1 \rightarrow T_1$ intersystem crossing. The corresponding rate constants are between $1.1 \times 10^8 \text{ s}^{-1}$ for eosin and $2.6 \times 10^8 \text{ s}^{-1}$ for erythrosine [14]. Therefore, the excited-state formation time is $\sim 1 - 10 \text{ ns}$. The lifetime of the photoinduced form depends on the triplet-state lifetime of dye molecules and, in the absence of triplet-state quenchers, lies between 0.7 and 5 ms. The triplet-state lifetime of dye molecules was measured from the decay of phosphorescence or induced triplet-triplet absorption.

The lifetime of high electronic states of polyatomic molecules is of the order of $10^{-12} - 10^{-11} \text{ s}$ [15, 16], while the lifetime of the S_1 state of the dyes studied here is $\sim 10^{-9} - 10^{-8} \text{ s}$ [14]. Therefore, when nanosecond ($\sim 10 - 20 \text{ ns}$) controlling pulses are used, the switching time of the system is limited by the pulse duration, whereas in the case of picosecond controlling pulses, the switching time is limited by the S_1 -state lifetime.

5. Conclusions

The efficient $T_n \rightarrow S_1$ intersystem crossing in fluorescein halogen derivatives makes it possible to change strongly the concentration of triplet states upon pulsed excitation of the dye molecules into the $T_1 \rightarrow T_n$ triplet-triplet absorption band. A rapid variation in the triplet-state population can be used for the development of controllable photochromic materials.

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