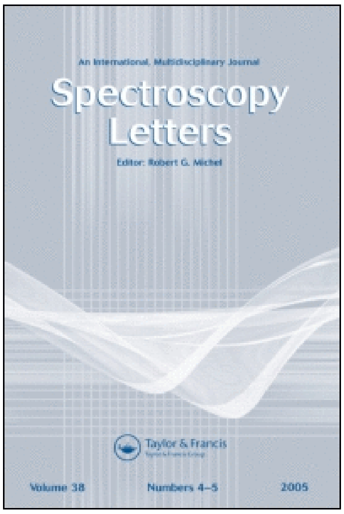

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EXCIMER FORMATION OF DIBENZOYLMETHANATOBORON DIFLUORIDE DURING PHOTOLYSIS IN POLYMER FILMS

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EXCIMER FORMATION OF DIBENZOYLMETHANATOBORON DIFLUORIDE DURING PHOTOLYSIS IN POLYMER FILMS

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ABSTRACT

Photochemical behavior of polyethylene, polystyrene and polymethylmethacrylate films containing dibenzoylmethanatoboron difluoride was investigated. It was observed that during UV irradiation of polyethylene films the monomer fluorescence of the complex ($\lambda_{max} = 450$ nm) transforms into excimer fluorescence ($\lambda_{max} = 535$ nm).

Key Words: Dibenzoylmethanatoboron difluoride; Luminescence; Excimer

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INTRODUCTION

Photochemical and fluorescent properties of light-transformation materials have been extensively studied, since these complexes can be used as luminescent and laser materials of good quality. However, most of these polymers often show low photostability over time[1]. Our previous results indicate that dibenzoylmethanatoboron difluoride (BF_2DBM) as luminescent additive to polymers is a prospective object of investigation in this regard[2]. Photochemical properties of BF_2DBM solutions were described in detail[3,4] but photochemical behavior of this compound in the polymeric matrices was studied in the case of its adducts with Lewis bases only[5].

In this work the photochemical behavior of dibenzoylmethanatoboron difluoride in the polymer series (polyethylene(PE), polystyrene(PS) and polymethylmethacrylate (PMMA)) was investigated.

EXPERIMENTAL

BF_2DBM was prepared according to the procedure described earlier[6]. The polyethylene films were prepared by extrusion. The polystyrene and polymethylmethacrylate films were prepared from solutions containing polymer and BF_2DBM in toluene poured onto a glass plate and dried (see Table 1).

The luminescence spectra of the films were recorded on an SDL-1 spectrometer. A DRSh-250 mercury lamp served as a source of excitation. The measurements were carried out at 300 K. Photolysis of the films was performed by exposing the samples to the nonfiltered light of DRT-250 mercury lamp and monochromatic light ($\lambda_{ex} = 365$ nm). The light flux intensity ($\lambda_{ex} = 365$ nm) measured using a ferrioxalate actinometer[7] was $2.75.10^{15}$ quantum/s; the distance from the lamp to the sample was 20 cm.

Table 1. The Conditions of Films Formation

Film	Polymer	C (BF_2DBM), mole/g	t, °C
I	PE	$1{,}9 \cdot 10^{-6}$	140
II	PS	$1{,}6 \cdot 10^{-4}$	20
III	PS	$1{,}8 \cdot 10^{-3}$	60
IV	PMMA	$3{,}5 \cdot 10^{-5}$	20
V	PMMA	$2{,}6 \cdot 10^{-4}$	60

RESULTS AND DISCUSSION

The fluorescence spectrum of BF_2DBM in polyethylene (the film **I**, Table 1) has a wide band with the maximum at 450 nm coinciding with the fluorescence band of the diluted BF_2DBM solutions and assigned to the monomer fluorescence of this complex. At UV irradiation of the film **I** this peak gradually decreases over time and thereafter disappears. Simultaneously, a new broad emission band with a peak at 535 nm appears and its intensity increases (see Figs. 1 and 2). It is identical to the fluorescence spectrum of crystalline BF_2DBM and could be attributed to excimer fluorescence[8].

In PS and PMMA films with low concentration of BF_2DBM (films **II**, **IV**) fluorescence spectra of the complex represent wide bands with maxima at 440 nm and 460 nm, respectively, that could be attributed to monomer fluorescence. The fluorescence intensity of this band decreases at UV irradiation over time (Figs. 3, 4). Unlike the film **I**, new emission bands are not observed in spectra at photolysis the films **II**, **IV**.

In the fluorescence spectra of nonirradiated PS and PMMA films with high concentration of BF_2DBM (films **III**, **V**) the bands of monomer fluorescence ($\lambda_{max} = 450$ and $\lambda_{max} = 460$ nm) and excimer fluorescence ($\lambda_{max} = 515$ and $\lambda_{max} = 535$ nm) were observed. Intensity of monomer fluorescence considerably decreases at irradiation. At the same time, excimer

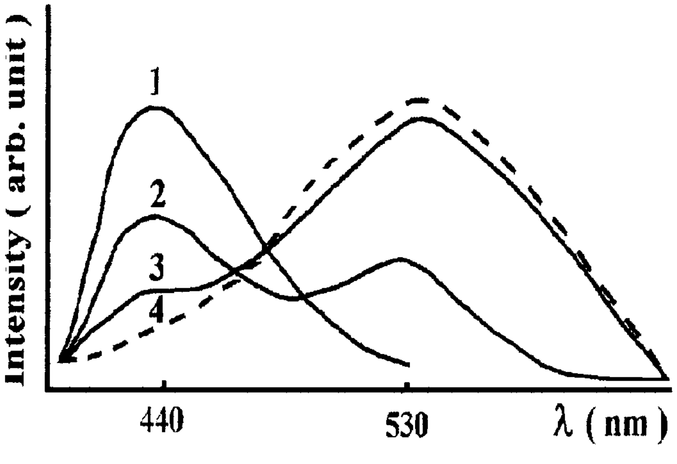

Figure 1. Time evolution of the luminescence spectrum of BF_2DBM (film **I**) during UV irradiation (h): 1-0; 2-0.33; 3-0.75; 4-1.

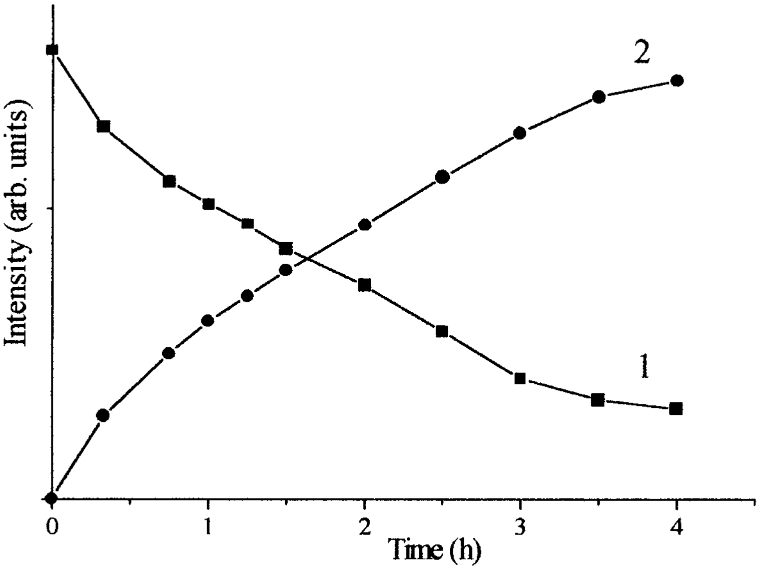

Figure 2. Intensity of the luminescence of the film **I** vs. the time of UV irradiation (1–monomer emission; 2–excimer emission).

emission, unlike the film **I**, not only increases but also gradually decreases. Thus, experimental results have shown that the photochemical behavior of BF_2DBM in polymer matrices depends on the polymer nature.

It is known[7] that the excited state can be deactivated as a result of several processes: i) radiative transitions (luminescence), ii) intra- and intermolecular non-radiative transitions, iii) photochemical reactions. All the above processes are characteristic for photochemical behavior of BF_2DBM in the films **II**–**V**. However, photochemical behavior of BF_2DBM in the film **I** is more interesting: beside above-mentioned ways for the excitation energy dissipation, a part of absorbed energy is used for excimer formation. The blue fluorescence of the nonradiatied film **I** shows that the BF_2DBM molecules are either non-coplanar or the distance between these are more than 3,6 Å. It is known, that existence of coplanar aromatic molecules with distance between these planes 3.0–3.6 Å to induces excimer formation[9]. According to the X-ray data BF_2DBM molecules are coplanar with distance between these 3.6 Å[8]. It could be suggested that Van der Waals forces between BF_2DBM non-coplanar molecules increase at photoexcitation. More intensive interaction between adjacent excited and unexcited molecules induces contingence and parallel orientation of these molecules.

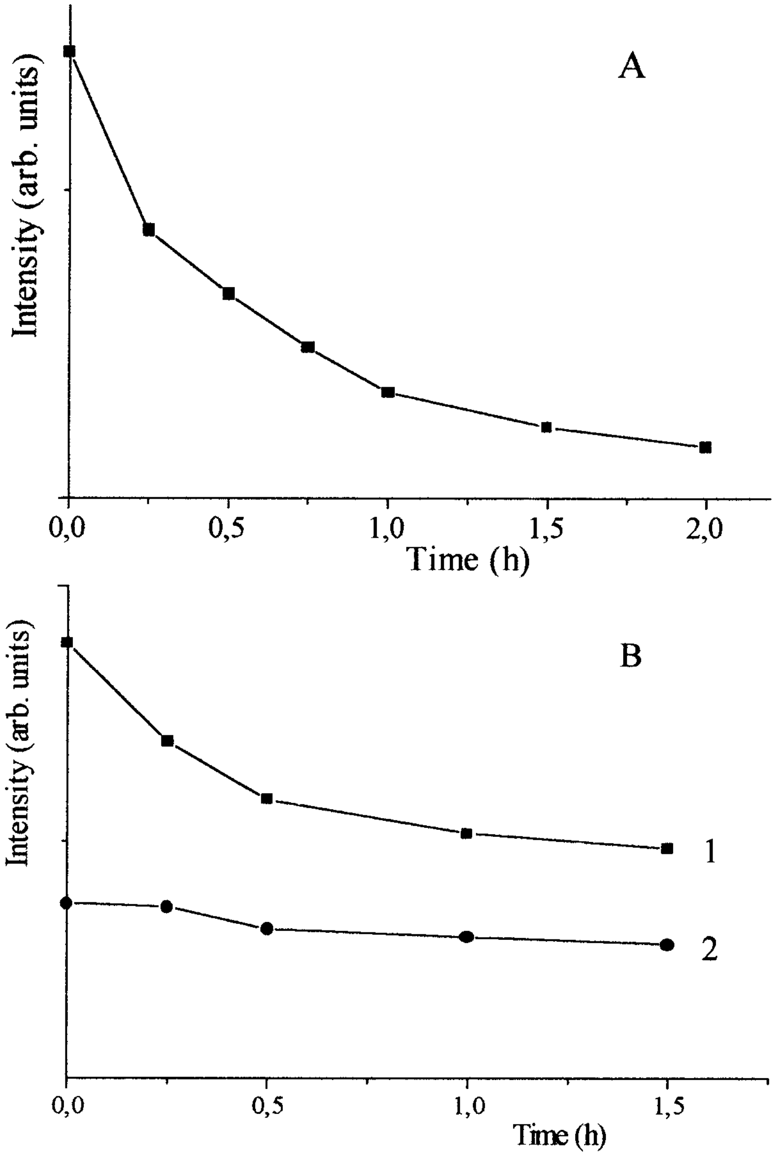

Figure 3. Intensity of the luminescence vs. the time of UV irradiation (A)-film **II**; (B)-film **IV** (1–monomer emission; 2–excimer emission).

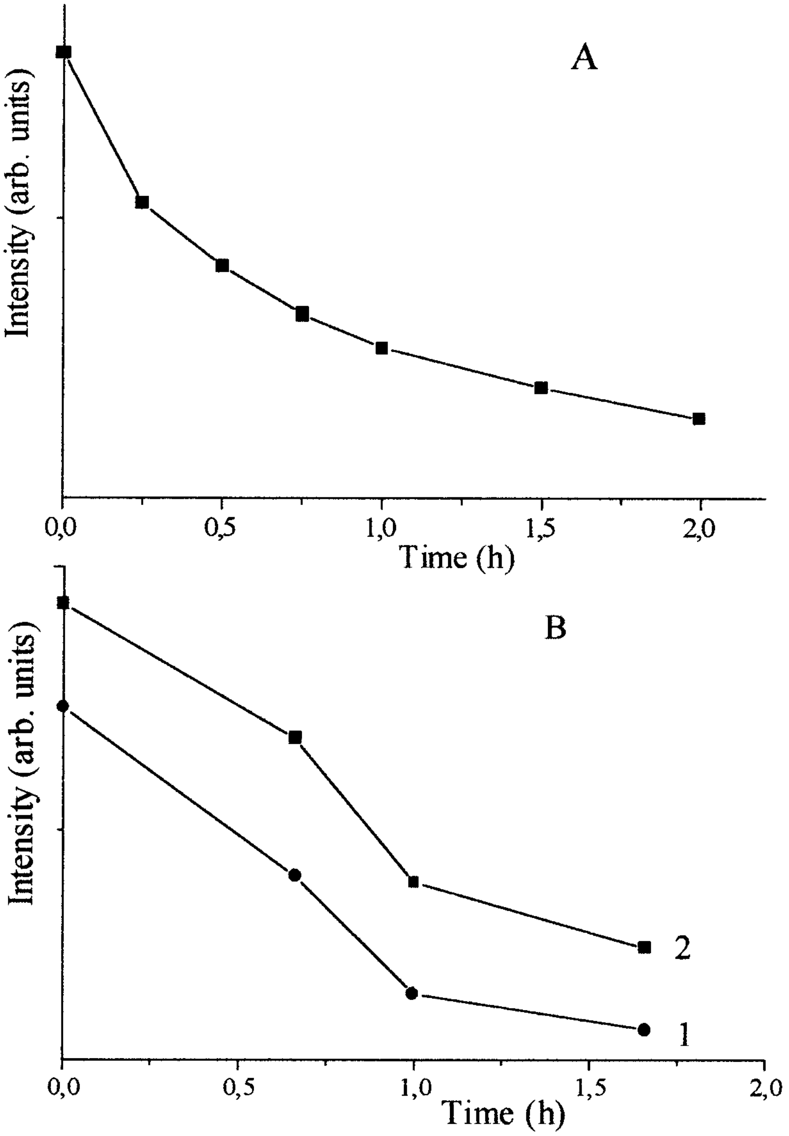

Figure 4. Intensity of the luminescence vs. the time of UV irradiation (A)-film **III**; (B)-film **V** (1–monomer emission; 2–excimer emission).

As a result, an excimer center is formed and fluorescence with $\lambda_{max} = 535\,nm$ appears.

The inert nature of polyethylene and low solubility of the complex in PE as compared with PS and PMMA apparently causes higher efficiency of the process of excimer formation during UV irradiation.

Thus, the performed comparative study of photochemical behaviour of BF_2DBM in polymers has shown that during photolysis the excimer formation occurs in polyethylene and does not occur in polystyrene and polymethylmethacrylate.

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