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Luminescent and Photochemical Properties of Light-Transforming Polymeric Materials

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Abstract—Light-transforming polymeric materials were obtained based on polymethylacrylate and high-pressure polyethylene activated by ytterbium(III) β-diketonates with various ligands and possessing intensive luminescence in the spectral range of 900–1100 nm. The study of the photochemical behavior of the polymers by the luminescent spectroscopy and stationary photolysis methods has revealed that the polymer compositions containing heteroligand ytterbium(III) dibenzoylmethanates or thenoyltrifluoroacetonates and triphenylphosphine oxide show high operational properties (an intensive luminescence and photostability).

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Ytterbium(III) compounds can be used as transformers of ultra-violet radiation to near infrared radiation, which is important for solving biomedical problems [1]. These transformers can find application for increasing UV spectral sensitivity of silicon receivers having a maximum of spectral sensitivity in the near infrared region and as luminescent labels in fluoroimmunoassay [2]. The synthesis of ytterbium(III) coordination compounds and the study of their physicochemical properties are described in detail in [2–4]. The physicochemical properties of polymeric compositions luminescing in the IR region and used in laser technique and medicine have been studied insufficiently.

It seems topical to measure and study fluorescent characteristics and photochemical behavior of polymer materials with luminescent characteristics in the infrared region (900–1100 nm). To obtain such polymeric materials, it is necessary to study photochemical behavior of heteroligand ytterbium(III) β-diketonates with nitrogen- and phosphorus-containing neutral ligands in high-pressure polyethylene and polymethylacrylate. Earlier we have described in detail the luminescence of crystalline ytterbium(III) β-diketonates with various ligands [5]. The photochemical behavior of ytterbium(III) compounds with various ligands in a polymeric matrix was not considered.

The present paper is devoted to the study of luminescence and photolysis of ytterbium(III) β-diketonates with various ligands in polymeric matrices: high-pressure polyethylene and polymethylacrylate.

We have prepared polymer compositions consisting of the following coordination compounds: $YbL_3 \cdot 2X$, where L is a dicarbonyl compounds [hexafluoroacetylacetone (**I**), dibenzoylmethane (**II**), thenoyltrifluoroacetone (**III**), benzoylacetone (**IV**)]; X is diphenylguanidine (a), 2,2'-bipyridine (b), triphenylphosphine oxide (c), 1,10-phenathroline (d), and a polymer is high-pressure polyethylene and polymethylacrylate. Luminescent properties and photochemical behavior of the polymers activated by coordination compounds were studied.

The common property of the synthesized ytterbium(III) complex compounds is a good solubility in polymethylacrylate. Polymethylacrylate was used because it is transparent and is easily processed. The solubility of these compounds is 0.5–2 g in 100 ml of a 5% polymethylacrylate solution in chloroform and 8 mg per 1 g of polyethylene.

The synthesized polyethylene and polymethylacrylate films activated by ytterbium(III) β-diketonates luminesce in the near IR range (900–1100 nm). Luminescence spectra of polymer films are more diffuse than the luminescence spectra of crystalline individual coordination compounds. In this case the character of the spectrum and the intensity of luminescence, and also the half-width of a luminescence maximum do not

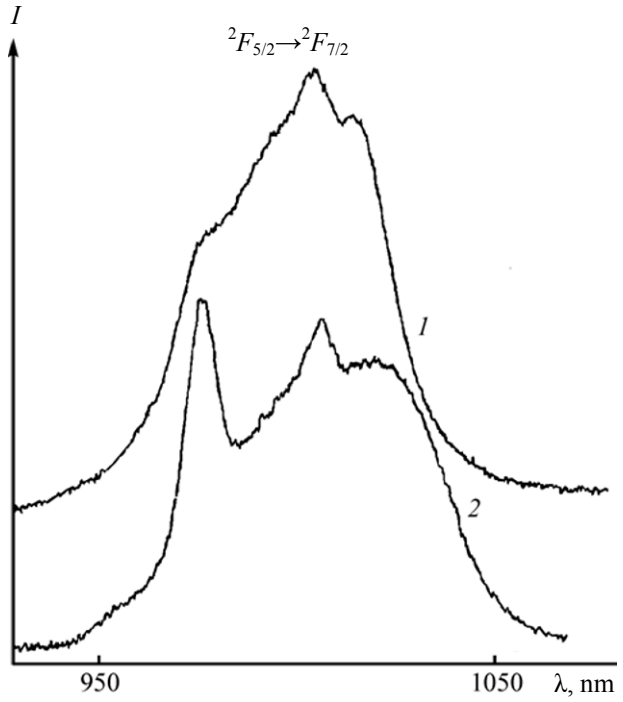

Fig. 1. Luminescence spectra of: (*1*) $[Yb(C_5HO_2F_6)_3]\cdot 2(C_6H_5)_3PO$ (**Ib**) and (*2*) $[Yb(C_{15}H_{12}O_2)_3]\cdot 2(C_6H_5)_3PO$ (**IIb**) in high-pressure polyethylene.

undergo significant changes, which points to the fact that the compounds do not dissociate on dissolution and the structure of luminophores dispersed in polymeric matrices is retained (Fig. 1).

Luminescence spectra of polymeric films activated by ytterbium(III) compounds contain structured bands including two-three components with the centre of gravity at approximately 1000 nm. Luminescence intensities of the activated polymeric materials and initial complexes are comparable. Ytterbium(III) β-diketonates used for the activation of polymer films have more intensive luminescence (2–3-fold) than similar neodymium(III) β-diketonates, which exceeds the intensity of initial ytterbium(III) nitrate practically by an order of magnitude.

To study the photochemical behavior, we have chosen polymeric compositions activated most intensively by luminescing ytterbium(III) β-diketonates, dibenzoylmethanates (**II**), thenoyltrifluoroacetonates (**III**), and benzoylacetonates (**IV**), with nitrogen- (a, b, d) and phosphorus-containing (c) neutral ligands [6]. The effect of irradiation duration (λ 350–650 nm) on their fluorescent properties was studied. The photoinduced degradation of luminescent characteristics of polymer compositions was monitored by the variation

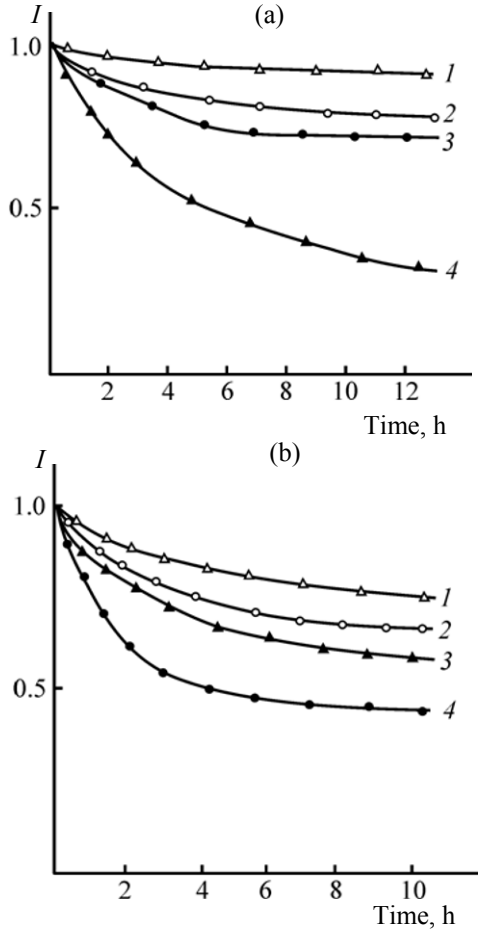

Fig. 2. Dependence of luminescence intensity of the Yb^{3+} ion in a polymeric composition on the UV irradiation time. (a) in polymethylacrylate: (*1*) $[Yb(C_{15}H_{12}O_2)_3]\cdot 2(C_6H_5)_3PO$ (**IIc**), (*2*) $[Yb(C_8H_6F_3O_2S)_3]\cdot 2C_{18}H_{15}PO$ (**IIIc**), (*3*) $[Yb(C_{15}H_{11}O_2)_3]\cdot 2C_{10}H_8N_2$ (**IIb**), (*4*) $[Yb(C_5HF_6O_2)_3]\cdot 2(C_6H_5)_3PO$ (**Ib**); (b) in high-pressure polyethylene: (*1*) $[Yb(C_{15}H_{12}O_2)_3]\cdot 2(C_6H_5)_3PO$ (**IIb**), (*2*) $[Yb(C_8H_6F_3O_2S)_3]\cdot 2C_{18}H_{15}PO$ (**IIIc**), (*3*) $[Yb(C_{15}H_{11}O_2)_3]\cdot 2C_{10}H_8N_2$, (*4*) $[Yb(C_5HF_6O_2)_3]\cdot 2(C_6H_5)_3PO$ (**Ic**).

of the integrated luminescence intensity of the head line of the ytterbium(III) ion $^2F_{5/2}$–$^2F_{7/2}$ transition on the UV irradiation duration.

Ytterbium(III) β-diketonates are highly photostable in a polymeric matrix (high-pressure polyethylene and polymethylacrylate). Under the irradiation by unfiltered light of a mercury lamp the ytterbium(III) luminescence intensity in polymer materials activated by the majority of $YbL_3\cdot 2X$ complex compounds slightly decreases (Fig. 2). The most photostable are the polymer materials activated by ytterbium(III) dibenzoylmethanates and thenoyltrifluoroacetonates with triphenylphosphine oxide. Photostability of ytterbium(III) complex compounds in polymethylacrylate is higher

than in polyethylene, which seems to be connected with their inclusion in a polymer: they are dissolved in polymethylacrylate, and are entered mechanically into polyethylene with great losses of the compounds. The luminescence intensity of the polymer compositions activated by the specified compounds decreases by 5-65% after a 10 h irradiation. The photostability of the polymer materials doped with these ytterbium(III) compounds appeared to be close to the photostability of the initial crystalline ytterbium(III) β-diketonates with various ligands.

Thus, the fulfilled comparative study points to high operational properties (intensive luminescence in the near IR range and photostability) of the polymer compositions containing heteroligand ytterbium(III) dibenzoylmethanates and thenoyltrifluoroacetonates with triphenylphosphine oxide.

EXPERIMENTAL

Doped polyethylene films were obtained by a pressing method. For this purpose samples of ytterbium(III) β-diketonates with various neutral ligands prepared by the procedure [7] were carefully mixed with a powder of high-pressure polyethylene and pressed on a hydraulic press at 140°C. To prepare polymer polymethylacrylate films, ytterbium(III) coordination compounds were dissolved in a 5% solution of polymethylacrylate in chloroform, and the polymer was deposited on a glass substrate and dried at a room temperature.

Luminescence spectra were recorded on an SDL-1 diffraction spectrometer at 300 K. The source of excitation was a DRSh-250 mercury lamp. The scale of wavelengths of the SDL-1 spectrometer was verified by lines of a helium-neon source and a mercury doublet at 576 and 579 nm.

The accelerated ageing of polymer films doped by ytterbium(III) compounds with various ligands was carried out by the irradiation with unfiltered light of a DRSh-250 mercury lamp within 20 h. The luminescence spectra of the polymers were recorded on an SDL-1 spectrometer with a FEU-62 photo multiplier in the range of 850–1100 nm. The luminescence was excited by a wide band in the spectral range of 350-650 nm isolated by SZS-23 and SZS-26 optical filters using xenon (DKsSH-130) and mercury (DRSh-250) lamps.

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