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Photochemical Behavior of Lanthanide-Containing Polymer Materials

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Abstract—Light-transforming polymer materials activated by compositions based on the mixed-ligand europium carboxylates and anthranilic acid exhibiting an intense luminescence in the spectral region 400–700 nm are prepared. The photolysis of the polymer materials is investigated. For the obtained compositions the flaring of intensity of luminescence of europium ion and anthranilic acid was detected.

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Luminescent europium compounds are widely used as activators of light-transforming materials, which are employed in medicine and agriculture [1–3]. These light-transforming polymers exhibit luminescence in the range 580–700 nm. However, the use of only the europium compounds as luminophors in the known compositions does not allow to cover the whole range of photosynthetically active radiation, thus decreasing the effectiveness of the electron transport in photosystems. Therefore, the preparation and investigation of new modifications of polymer materials possessing luminescence in the blue and red regions of the spectrum (luminescence in the range 400–700 nm), which is more favorable for plant growing, is a state-of-the-art problem.

Earlier, we have described in detail the effect of flaring for crystalline europium carboxylates with 1,10-phenanthroline and 2,2'-dipyridyl [4].

In the present paper we have studied the photochemical behavior of the compositions consisting of europium complexes, organic luminophor, and high-pressure polyethylene. New compositions were prepared consisting of complex $Eu(L)_3 \cdot nD \cdot xH_2O$ and anthranilic acid (C_6H_6NCOOH), where L is the anion of trifluoroacetic, *o*-toluic, cinnamic acid, D is 1,10-phenanthroline, with the ratio of the reacting components 1:0.5–6.

Polyethylene films activated with the synthesized europium complexes possess luminescence in the red region upon UV irradiation. The spectra of luminescence of the obtained films are more diffuse than those of the individual coordination compounds with neutral ligands in the crystalline state but are identical to them, which is indicative of retention of the structure of luminophors dispersed in the polyethylene matrix (Fig. 1a).

The spectrum of luminescence of polyethylene film containing only anthranilic acid at 300 K consists of a wide band with a maximum at 430 nm (blue luminescence) caused by π*-π-transitions of anthranilic acid (Fig. 1b).

The spectra of the polymer materials activated with the mixed-ligand europium carboxylates and anthranilic acid are represented by superposition of the lines of luminescence of the components. According to the data of fluorescent microscopy, the prepared polymer materials show the heterophase character of distribution of the luminescent particles of the luminophors used in the high pressure polyethylene: The blue luminescence of the anthranilic acid and the red luminescence of europium complexes is observed [5]. Such distribution of compounds in the high pressure polyethylene is due to poor solubility of these compounds in low polar solvents. The luminescence spectra of the polymer compositions consist of a broad band with the maximum at 430 nm and separate bands of the magnetic dipole $^5D_0$–$^7F_1$ and electric dipole $^5D_0$–$^7F_2$ Eu(III) transitions with the maxima at 595 and 615 nm, respectively (Fig. 1b).

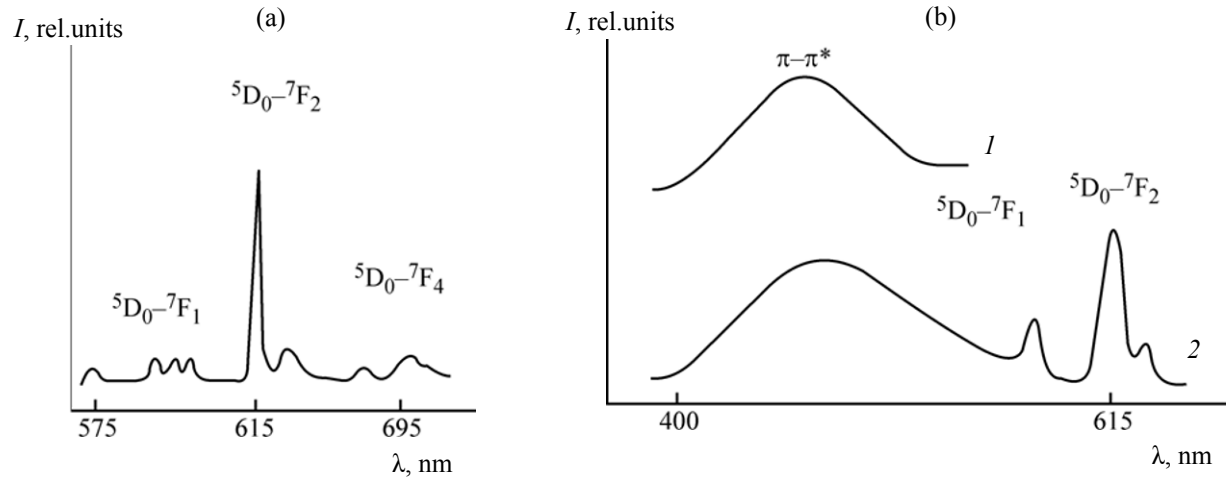

Fig. 1. Spectra of luminescence: (a) $Eu(CF_3COO)_3 \cdot 2C_{12}H_8N_2 \cdot H_2O$, (b) (*1*) anthranilic acid and (*2*) [$Eu(CF_3COO)_3 \cdot 2C_{12}H_8N_2 \cdot H_2O$ + C_6H_6NCOOH] in high-pressure polyethylene. $C_{12}H_8N_2$ is 1,10-phenanthroline.

At 1:0.5–2 molar ratio of the $Eu(L)_3 \cdot nD \cdot xH_2O$ and C_6H_6NCOOH the highest intensity of the luminescence of europium in the studied system is observed, and the additives are the most uniformly distributed in polyethylene (see the table). A significant increase in the concentration of the anthranilic acid in the polymer composition up to the ratio 1:6 leads to the decrease of the europium luminescence intensity.

We have studied the effect of the duration of the UV irradiation (λ 364 nm) on the fluorescent properties of the materials. The photoinduced degradation of the luminescence characteristics of the polymer compositions was followed by the change of integral intensities of the luminescence of europium(III) and anthranilic acid. The performed analysis of the photochemical behavior of compositions [$Eu(L)_3 \cdot 2C_{12}H_8N_2 \cdot xH_2O$ + C_6H_6NCOOH] has shown that for the molar ratio of the components of 1:0.5–3 the increase in intensity of luminescence is observed not only for europium but for anthranilic acid as well. Thus, after 15 h irradiation of the composition [$Eu(L)_3 \cdot 2C_{12}H_8N_2 \cdot xH_2O$ + C_6H_6NCOOH] (molar ratio 1:0.5–3) the intensity of luminescence of europium(III) increased by 70–90% (Fig. 2a).

Dependence of relative luminescence of Eu^{3+} ion and anthranilic acid (C_6H_6NCOOH) on the molar ratio of luminophors in the compositions

Composition	Ratio	I_{lum} (Eu^{3+})	I_{lum}, % (C_6H_6NCOOH)
$Eu(CF_3COO)_3 \cdot 2C_{12}H_8N_2 \cdot H_2O$ +	1:0.5	100	76
C_6H_6NCOOH	1:1	68	84
	1:3	32	91
	1:6	25	100
$[Eu(C_7H_7COO)_3 \cdot C_{12}H_8N_2]_2$ +	1:0.5	100	65
C_6H_6NCOOH	1:1	75	81
	1:3	43	95
	1:6	34	100
$Eu(C_8H_7COO)_3 \cdot 2\ C_{12}H_8N_2 \cdot H_2O$ +	1:0.5	100	62
C_6H_6NCOOH	1:1	62	79
	1:3	33	94
	1:6	28	100

Earlier we have found that the effectiveness of flaring of the luminescence of europium ion in its mixed-ligand carboxylates occurs in parallel with the increase in the concentration of the 1,10-phenanthroline radical-anion [4]. It is known that the molecules of 1,10-phenanthroline [6, 7] in complexes may exist both in neutral and in the radical-anion state. According to quantum-chemical calculations [6–8], the molecule of 1,10-phenanthroline has two comparable in energy low-lying π*-orbitals [$a_2(\chi)$ and $b_1(\psi)$] capable to play the role of the acceptors of the excess negative charge. Analysis of the ESR spectra and comparison of them with the results of quantum-chemical calculations of the electron density distribution allowed us to define unambiguously the ground state of the phenanthroline radical-anion as $^2B_1$, with the energy gap between the $a_2(\chi)$ and $b_1(\psi)$ orbitals being ~ 0.036 eV.

As said above, the sensibilization of the luminescence of anthranilic acid upon the UV irradiation of the polymer material is observed. The intensity of luminescence of anthranilic acid after 15 h increased

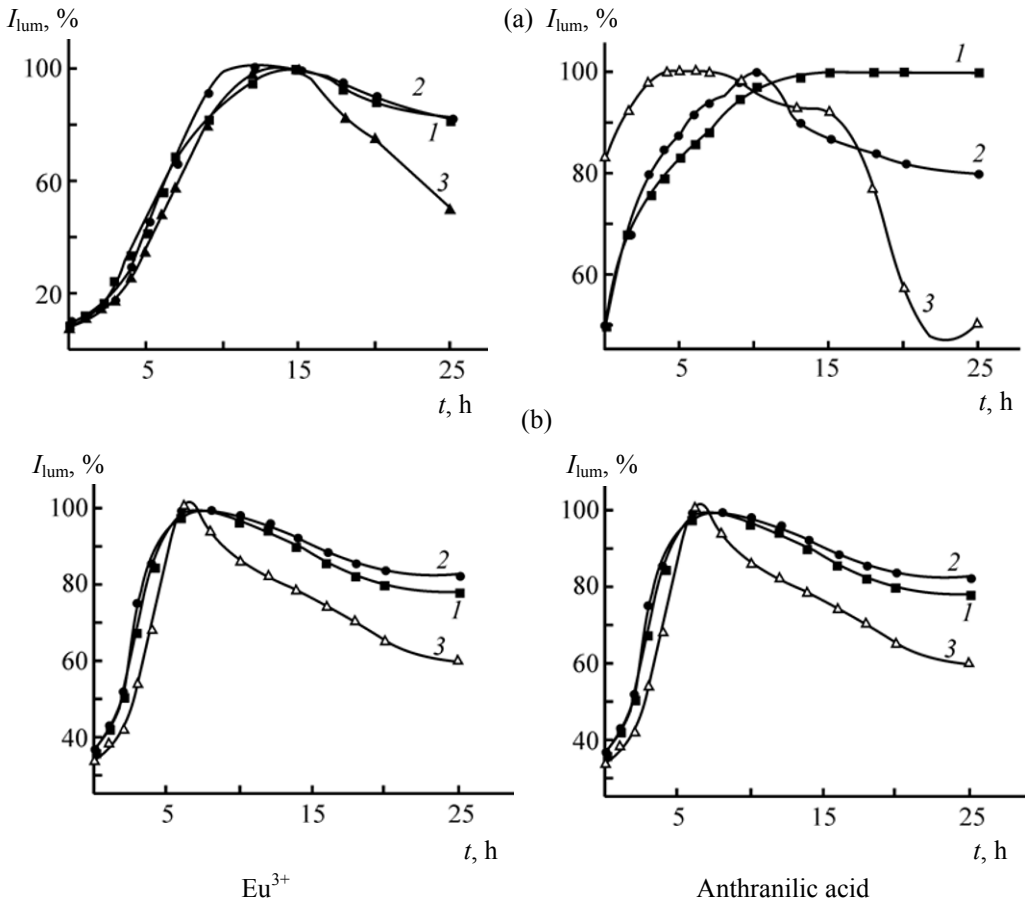

Fig. 2. Dependence of intensity of luminescence for compositions (a) $[Eu(CF_3COO)_3 \cdot 2C_{12}H_8N_2 \cdot H_2O + C_6H_6NCOOH]$ and (b) $[Eu(C_8H_7COO)_3 \cdot 2C_{12}H_8N_2 \cdot H_2O + C_6H_6NCOOH]$ in high-pressure polyethylene on the time of UV irradiation for molar ratio: (*1*) 1:05, (*2*) 1:3, and (*3*) 1:6.

by 20–50% (Fig. 2b). Further irradiation (20 h) practically does not change the intensity of the luminescence of europium(III) and anthranilic acid.

The increase in the content of anthranilic acid in the composition results in a decrease of sensibilization of its luminescence. Thus, at the molar ratio of the components $Eu(L)_3 \cdot 2C_{12}H_8N_2 \cdot xH_2O : C_6H_6NCOOH$ = 1:3 the intensity of the luminescence of anthranilic acid increased after the UV irradiation only by 17–25%, whereas at the ratio of 1:6 the intensity of the luminescence is decreased.

To understand the increase in the intensity of luminescence of anthranilic acid upon photolysis we have performed a comparative analysis of the excitation spectra of the compositions prepared at different molar ratio. The luminescence excitation spectra were registered at 300 K both at the maximum of the luminescence bands of europium ion (λ 595 nm) and at the maximum of the luminescence bands of anthranilic acid (λ 400 nm). In the spectrum of anthranilic acid in the high-pressure polyethylene a number of bands with the maxima at 230, 252, 274, 312, and 340 nm is observed (Fig. 3, curve *1*). The spectrum of excitation of the nonirradiated composition $[Eu(CF_3COO)_3 \cdot 2C_{12}H_8N_2 \cdot H_2O + C_6H_6NCOOH]$ (molar ratio 1:6) at λ_{lum} 595 nm consists of a series of intense bands caused by electron transitions of europium ion; at λ_{lum} 400 nm it contains a series of wide intense bands caused by electron transitions of anthranilic acid with the maxima at 225, 252, 274, 310, and 335 nm (Fig. 3, curve *3*). The transition bands of anthranilic acid at 335 and 252 nm are most intense and comparable to each other. At lower concentrations of anthranilic acid in the composition (molar ratio of the components 1:0.5–3), a redistribution of intensities of the bands of

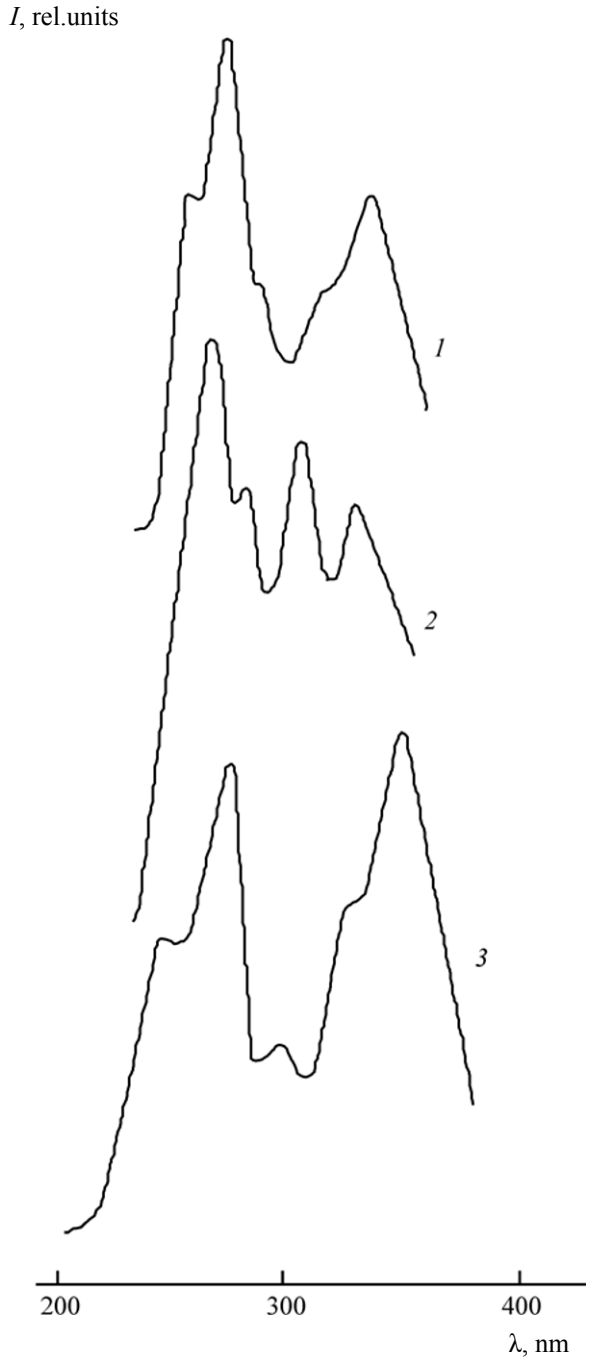

Fig. 3. Luminescence excitation spectra: (*1*) C_6H_6NCOOH (λ_{lum} 400 nm); (*2*) $[Eu(CF_3COO)_32C_{12}H_8N_2{\cdot}H_2O + C_6H_6NCOOH]$ (1:0.5); and (*3*) $[Eu(CF_3COO)_3{\cdot}2C_{12}H_8N_2{\cdot}H_2O + C_6H_6NCOOH]$ (1:6).

anhthranilic acid in the excitation spectrum is observed so that the bands with the maxima at 250 and 303 nm become most intense (Fig. 3, curve *2*).

The irradiation of the composition $[Eu(L)_3{\cdot}2C_{12}H_8N_2{\cdot}xH_2O + C_6H_6NCOOH]$ (1:0.5–3) by the UV

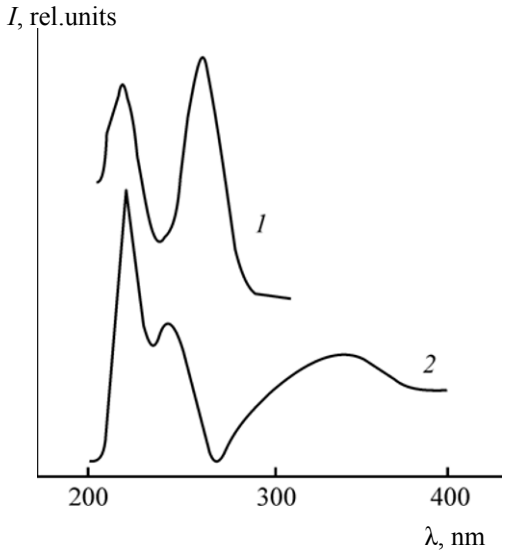

Fig. 4. Absorption spectra of (*1*) 1,10-phenanthroline and (*2*) anthranilic acid in ethanol ($c = 10^{-4}$ M).

light causes changes in the intensities of the bands of electron transitions of anthranilic acid in the excitation spectrum so that the intensity of the band at λ 315 nm increases.

According to the absorption spectra, the singlet levels of 1,10-phenanthroline lie higher than the singlet levels of anthranilic acid (Fig. 4) that suggests the possibility of energy transfer from the levels of the generated radical-anion of phenanthroline to the levels of anthranilic acid upon photolysis.

The above analysis of the photochemical behavior has shown that the duration of the "flaring" effect for the obtained compositions is longer than in the polymer materials activated only by europium carboxylates [4]. This may be due to the fact that in the composition with the optimal ratio of the luminophors (1:1) the luminescent particles have the smallest size (1.5–2.5 μm) and are the most uniformly distributed [5]. Another reason for the prolonged photostability of the polymer composition is the presence of organic luminophor, anthranilic acid, which is a good UV light absorber [9]. By absorbing the UV light, the anthranilic acid stabilizes the luminescence of europium compounds.

Therefore, the performed comparative studies show that photochemical behavior of the obtained polymer compositions is determined by the molar ratio of the components. The photochemical stability of the polymer materials doped with compositions of the compounds is higher than that of the original complexes.

EXPERIMENTAL

Doped polyethylene films were prepared by the pressing method. For this, a specimen of the mixed-ligand europium carboxylates prepared by the procedures described in [10–12] were thoroughly mixed with the powder of the high-pressure polyethylene and pressed on a hydraulic press at 140°C.

For preparation of the luminescent polymer compositions, the polyethylene powder, the mixed-ligand europium compounds, and the anthranilic acid in the molar ratio 1:0.5–6 (the mixture of dry luminophors and high-pressure polyethylene) were thoroughly mixed in a mortar and pressed on a hydraulic press at 140°C.

The luminescence spectra were registered on a SDL-1 diffraction spectrometer at 300 K. The DRSh-250 mercury lamp served as the excitation source. The error in the wave number measurements for the $^5D_0$–^7F_j transitions (j = 0–4) does not exceed ±2.0–3.0 cm^{-1} (the number of measurements no less than 5). The scale of the wavelength of the SDL-1 spectrometer was tested against the lines of the helium-neon source and the doublet of mercury at 576 and 579 nm.

Accelerated aging of the polymer films doped with the europium complex and an organic luminophor was performed using nonfiltered light of the DRT-250 mercury lamp (mercury lines 254, 313, 334, 365, and 405 nm). The light flow intensity (λ_{excit} 365 nm) measured by the use of ferrioxalate actinometer was 2.75×10^{15} quanta/s. Distance between the lamp and the sample was 20 cm. The process of photodecomposition was monitored by the dependence of the luminescence intensity of the head line of the $^5D_0$–$^7F_2$ electric dipole transition of europium ion on the time of irradiation with the UV light. The polyethylene samples were irradiated for 25 h.

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