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Luminescent and Photochemical Properties of the Lanthanide-Containing Polymer Materials

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Abstract—The light-transforming polymer materials have been obtained based on the mixed europium cinnamates, cinnamic acid, and high density polyethylene. The materials exhibit an intensive luminescence in the range of 400–700 nm. The photostability of the materials has been higher than that of polymer materials activated solely with europium compounds. The photolysis of the luminescent polymers has been studied. For the obtained polymer compositions the build-up of europium ion and cinnamic acid luminescence has been observed.

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The luminescent europium compounds are widely used as activators of light-transforming polymer materials that are in applied in medicine and agriculture [1–3]. Such light-transforming polymers exhibit luminescence at 580–700 nm. However, the use in the known compositions of europium compounds as the only luminophor does not overlap the whole range of photoactive irradiation, and thus the efficiency of the electron transport in the photoactive systems is reduced. Thus, the preparation and study of the modified polymer materials showing luminescence in the blue and red spectral ranges (400–700 nm), favoring the plants growth, are important.

Previously, we described in detail the build-up of the europium ion and anthranilic acid luminescence in polymeric compositions [4].

In this paper we report on the luminescent and photochemical properties of the polymeric compositions containing europium complexes, organic luminophor cinnamic acid, and high density polyethylene. The compositions were prepared from $Eu(C_8H_7COO)_3\cdot nD\cdot xH_2O$ and cinnamic acid (C_8H_7COOH), with D being 1,10-phenanthroline ($C_{12}H_8N_2$) and 2,2'-dipyridyl ($C_{10}H_8N_2$) in the molar ratio of 1:(0.5–2).

At 300 K, the luminescence spectrum of the polyethylene film containing only cinnamic acid consists of a broad band with the maximum at 450 nm (light blue luminescence) due to π*–π transition of the cinnamic acid (Fig. 1, curve *1*).

The polyethylene films activated with the prepared europium complexes possessed red luminescence at UV irradiation. The luminescence spectra were more diffuse than those of the individual crystalline complexes, however no other changes were observed,

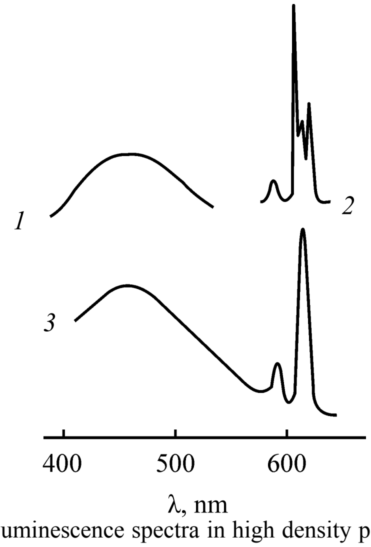

Fig. 1. Luminescence spectra in high density polyethylene: (*1*) C_8H_7COOH, (*2*) $Eu(C_8H_7COO)_3\cdot 2C_{12}H_8N_2\cdot H_2O$, and (*3*) $[Eu(C_8H_7COO)_3\cdot 2C_{12}H_8N_2\cdot H_2O + C_8H_7COOH]$.

thus proving that the structure of the luminophors was preserved upon dispersion in the polyethylene matrix (Fig. 1, curves *2* and *3*).

Spectral characteristics of the polymer materials activated with the mixed europium cinnamates and cinnamic acid were merely a superposition of the individual components bands (Fig. 1, curve *3*).

The effect of the duration of UV irradiation (λ = 364 nm) on the materials properties was studied. The integral intensity of Eu(III) ion and cinnamic acid luminescence was monitored.

In the case of [$Eu(C_8H_7COO)_3{\cdot}2C_{10}H_8N_2H_2O$ + C_8H_7COOH] composition we observed the photo-induced build-up of europium ion luminescence. Upon UV irradiation during 10 h, the luminescence intensity was up by 25–80%. The highest build-up of europium luminescence was observed after 6 h of UV irradiation. Simultaneously, the C_8H_7COOH luminescence intensity decreased (Fig. 2a).

The analysis of photochemical behavior of the [$Eu(C_8H_7COO)_3{\cdot}2C_{12}H_8N_2{\cdot}H_2O$ + C_8H_7COOH] composition revealed that at the components molar ratio of 1:(0.5–2) the increase of europium luminescence intensity was accompanied with build-up of cinnamic acid luminescence. For example, after 6 h irradiation of the [$Eu(C_8H_7COO)_3{\cdot}2C_{12}H_8N_2{\cdot}H_2O$ + C_8H_7COOH] composition the intensity of europium luminescence was up by 80–85% (Fig. 2b). As seen from Figs. 2a and 2b, the addition of organic luminophor to polymeric material led to the enhanced photostability of europium luminescence as compared with the

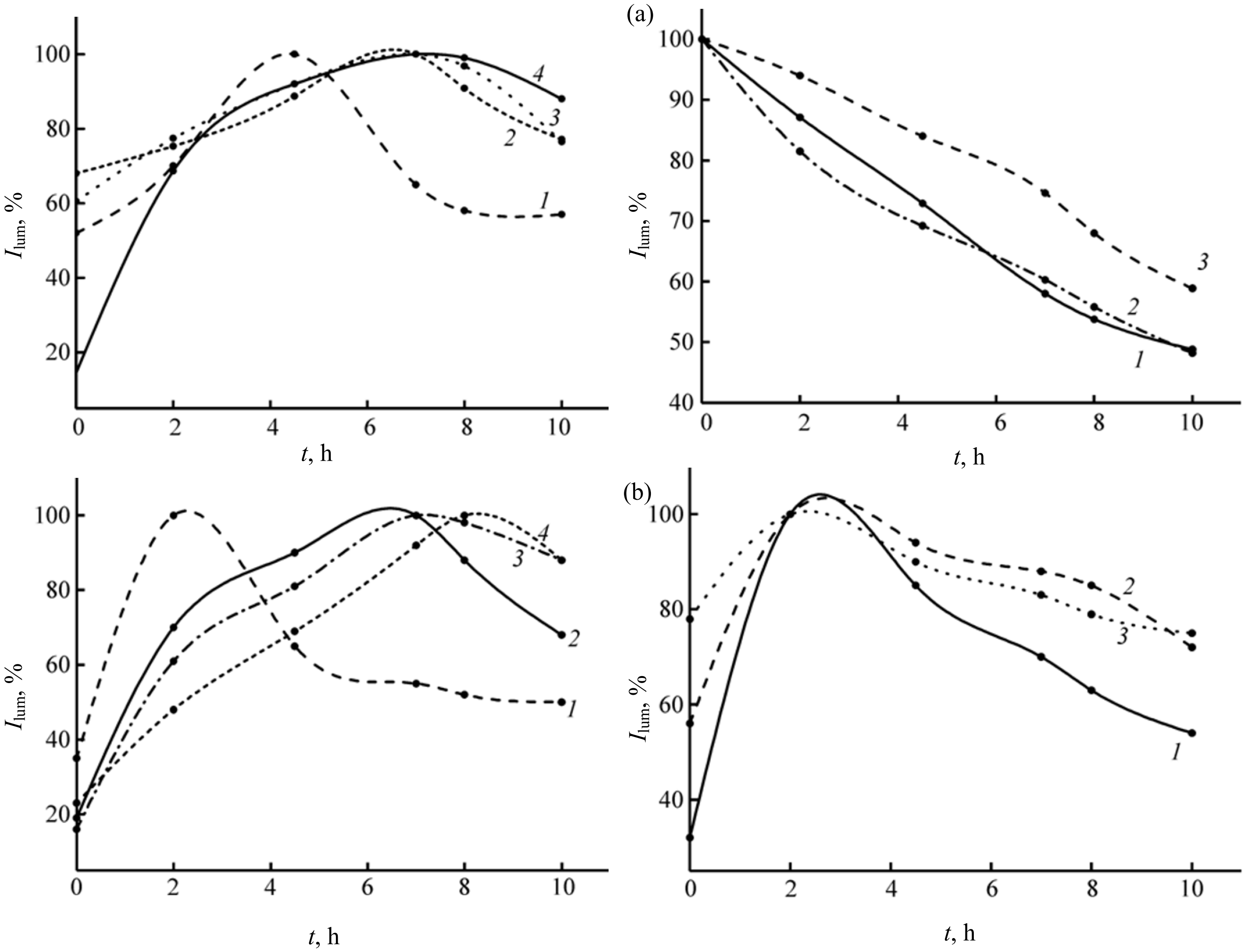

Fig. 2. Intensity of luminescence of the compositions (a) [$Eu(C_8H_7COO)_3{\cdot}2C_{10}H_8N_2H_2O$ + C_8H_7COOH] and (b) [$Eu(C_8H_7COO)_3{\cdot}2C_{12}H_8N_2{\cdot}H_2O$ + C_8H_7COOH] in high density polyethylene as a function of UV irradiation time at various molar ratios: (*1*) 1:0, (*2*)1:05, (*3*) 1:1, and (*4*) 1:2.

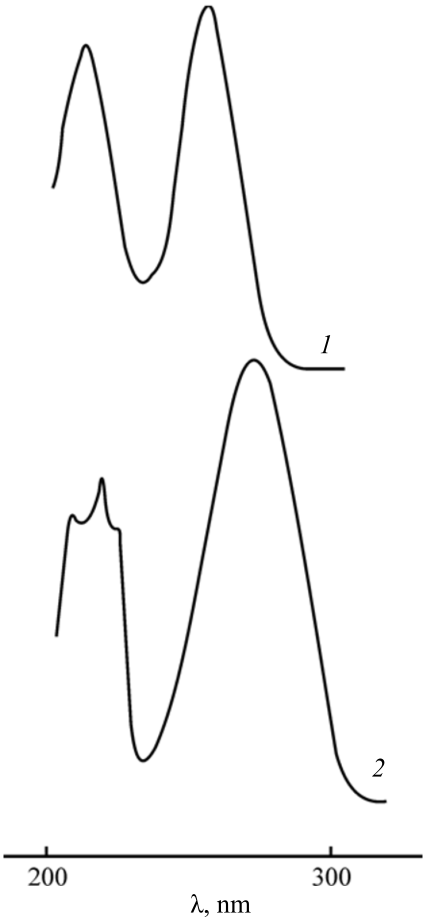

Fig. 3. Absorption spectra of (*1*) $C_{12}H_8N_2$ and (*2*) C_8H_7COOH in ethanol ($c = 10^{-4}$ mol L^{-1}).

materials containing only europium cinnamate additives [5]. The reason for higher photostability was the presence of cinnamic acid; absorbing UV radiation efficiently [6] it stabilized europium compounds luminescence.

Previously, we found that the luminescence build-up efficiency of europium in mixed-ligand carboxylates was in line with the increase in the content of anion-radicals of 1,10-phenanthroline and 2,2'-dipyridyl [5]. It is known that the complexes of 1,10-phenanthroline [7, 8] and 2,2'-dipyridyl [9–12] can contain their neutral molecules as well as anion-radical forms. According to the quantum-chemical calculations [7, 8, 13], in 1,10-phenanthroline molecule there are two close low-energy π*-orbitals, [$a_2(\chi)$ и $b_1(\psi)$], capable of accepting the excessive negative charge. The ESR spectra studies in combination with the information on the electron density distribution (as obtained from the quantum-chemical calculations) determined 1,10-phenanthroline anion-radical ground state as $^2B_1$, the energy difference between $a_2(\chi)$ and $b_1(\psi)$ orbitals being about 0.036 eV. Quantum-chemical studies of 2,2'-dipyridyl molecule found the only low-energy vacant molecular orbital of b_1 symmetry. Upon formation of the anion-radical, the negative charge should be accumulated on that orbital, as confirmed by the computations and the ESR studies of the diluted solutions of anion-radical complexes of dipyridyl [13].

As was stated above, UV irradiation of the polymeric materials led to the build-up of cinnamic acid luminescence. Its intensity grew up by 20–70% within 3 h (Fig. 2b). Further irradiation (10 h) led to the weakening of cinnamic acid luminescence. The highest amplitude of the change was observed in the case of composition with the components molar ratio of 1:0.5.

The enhancement of cinnamic acid luminescence upon photolysis was explained by comparison of the absorption spectra of cinnamic acid and 1,10-phenanthroline. According to the spectra, the singlet levels of 1,10-phenanthroline were located somewhat higher than the singlet levels of cinnamic acid (Fig. 3) thus pointing at the possibility of energy transfer from phenanthroline anion-radical to cinnamic acid upon photolysis.

Thus, we observed that the photochemical behavior of polymeric compositions was determined by the ratio of the components. It was found that the photostability of the prepared modified materials was higher than that of the initial complexes.

EXPERIMENTAL

The modified polyethylene films were prepared by moulding. To do so, mixed europium carboxylates prepared as described in [14], were thoroughly blended with high density polyethylene and moulded with hydraulic press at 140°C. The polymeric compositions containing mixed europium complexes and cinnamic acid were prepared similarly, from mixture of dry powders of the europium complex, cinnamic acid (molar ratio of 1:0.5 to 1:2), and high density polyethylene.

Luminescence spectra were registered with SDL-1 diffraction spectrometer at 300 K. The excitation source was DRSh-250 mercury lamp. The accuracy of determination of the wavenumber of $^5D_0$–^7F_j transition bands (j = 0–4) was ±2.0–3.0 cm^{-1} (no less than 5 measurements were run). The spectrometer scale was calibrated according to He–Ne source lines and to mercury doublet at 576 and 579 nm.

The accelerated ageing of the polymeric films modified with europium complex and organic luminophor was performed under the non-filtered light of DRT-250 mercury lamp (mercury bands at 254, 313, 334, 365, and 405 nm). The irradiation intensity (λ_{ex} = 365 nm) was 2.75×10^{15} imp s^{-1} as measured with ferrioxalate actinometer. The distance from the lamp to the sample was 20 cm. The photodegradation process was monitored by the luminescence intensity of the $^5D_0$–$^7F_2$ transition of europium as function of UV irradiation duration. Polyethylene samples were subjected to 10 h ageing.

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