ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 12, pp. 2436–2438. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © I.V. Kalinovskaya, A.N. Zadorozhnaya, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 12, pp. 2020–2022.

Luminescent and Photochemical Properties of Polyethylene Activated with Europium and Yttrium Compounds

I. V. Kalinovskaya[a] and A. N. Zadorozhnaya[b]

[a] *Institute of Chemistry, Far Eastern Branch, Russian Academy of Sciences, pr. 100-letiya Vladivostoka 159, Vladivostok, 690022 Russia*
e-mail: kalinovskaya@ich.dvo.ru

[b] *Pacific State Medical University, Vladivostok, Russia*

Received March 6, 2014

Abstract—Light-transforming materials have been prepared based on europium cinnamate, yttrium nitrate, and high-pressure polyethylene, and their luminescent as well as photochemical properties have been studied. The prepared polymers have exhibited strong luminescence at 400–700 nm. Photolysis of the prepared luminescent materials has been studied.

Keywords: lanthanides, polymer material, luminescence, photolysis

DOI: 10.1134/S1070363214120147

Luminescent europium compounds are widely used for activation of light-transforming polymer materials used in medicine and agriculture [1–5]. The europium-activated materials usually show luminescence at 580–700 nm. As this range does not completely cover the photosynthetic active radiation, the efficiency of electron transport in the photosystems is reduced. Therefore, the development and study of new polymer materials showing luminescence over a wider spectral range (400–700 nm) are desirable.

This report extends a series of earlier studies dealing with luminescent and photochemical properties of polymer materials containing several luminescent sites: heteroligand europium(III) complexes and an organic luminophor (anthranilic or cinnamic acid) [6, 7]. In the cases of several compositions, efficient build-up of europium(III) ion and anthranilic acid luminescence was revealed by stationary photolysis studies.

In this work we prepared new polymer materials based on high-density polyethylene, containing polymeric europium(III) cinnamate $[Eu(C_8H_7COO)_3]_n$ and yttrium nitrate $Y(NO_3)_3{\cdot}6H_2O$. We expected that these materials would luminesce over a wide spectral range because the applied additives possessed blue [yttrium(III) nitrate, Fig. 1a] as well as red [europium(III) cinnamate, Fig. 1b] luminescence.

Polyethylene films activated solely with yttrium(III) nitrate hexahydrate showed bright bright-blue luminescence: the emission spectrum contained a broad band with a maximum at 430 nm (300 K).

As expected, the materials modified with a mixture of $[Eu(C_8H_7COO)_3]_n$ and $Y(NO_3)_3{\cdot}6H_2O$ luminophors emitted radiation over a wider wavelengths range (Fig. 2) as compared with polyethylene activated with the individual compounds of Eu(III) and Y(III). Luminescence spectra of the polymer materials contained the less resolved bands as compared to spectra of the individual compounds of europium(III) and yttrium(III).

Relative intensity of luminescence of Eu^{III} and Y^{III} ions as function of the luminophors molar ratio in the polyethylene matrix

$[Eu(C_8H_7COO)_3]_n : Y(NO_3)_3{\cdot}6H_2O$, mol/mol	$I_{lum}(Eu^{3+})$, %	$I_{lum}(Y^{3+})$, %
2 : 1	89	81
1 : 1	100	100
1 : 2	44	88

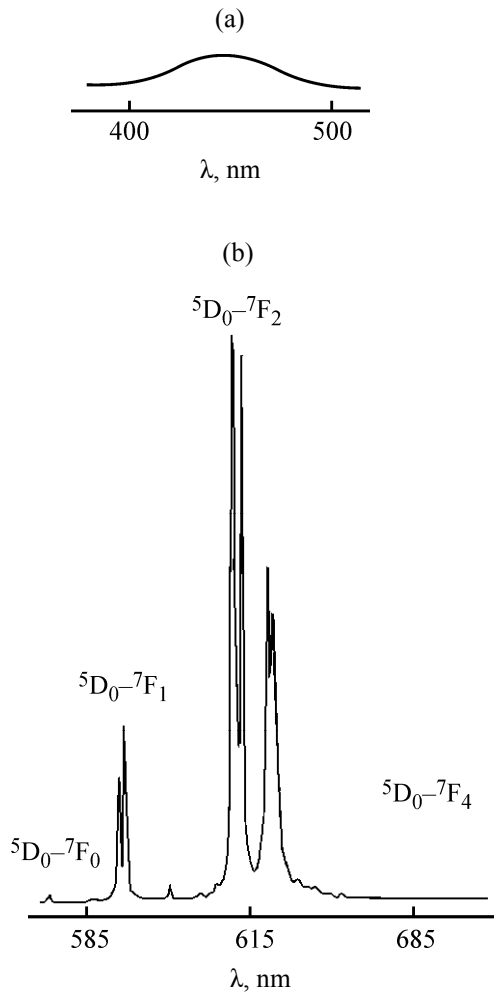

Fig. 1. Luminescence spectra of (a) yttrium(III) nitrate hexahydrate and (b) europium(III) cinnamate.

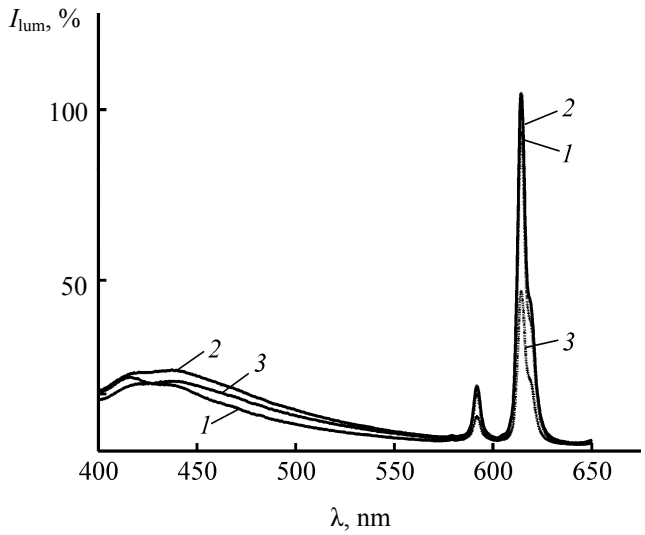

Fig. 2. Luminescence spectra of polyethylene activated with a mixture of $[Eu(C_8H_7COO)_3]_n$ and $Y(NO_3)_3 \cdot 6H_2O$ at the luminophors molar ratio of (*1*) 2 : 1, (*2*) 1 : 1, and (*3*) 1 : 2.

However, the emission spectrum of polyethylene activated with the mixture of europium cinnamate and yttrium nitrate was a superposition of emission bands of the individual components, thus confirming the preservation of initial structure of the disperse luminescent compounds.

Luminescence spectra of the polymer compositions contained a broad band with maximum at 430 nm [emission by yttrium(III) nitrate] and narrower bands assigned to magnetic-dipole $^5D_0$–$^7F_1$ (595 nm) and

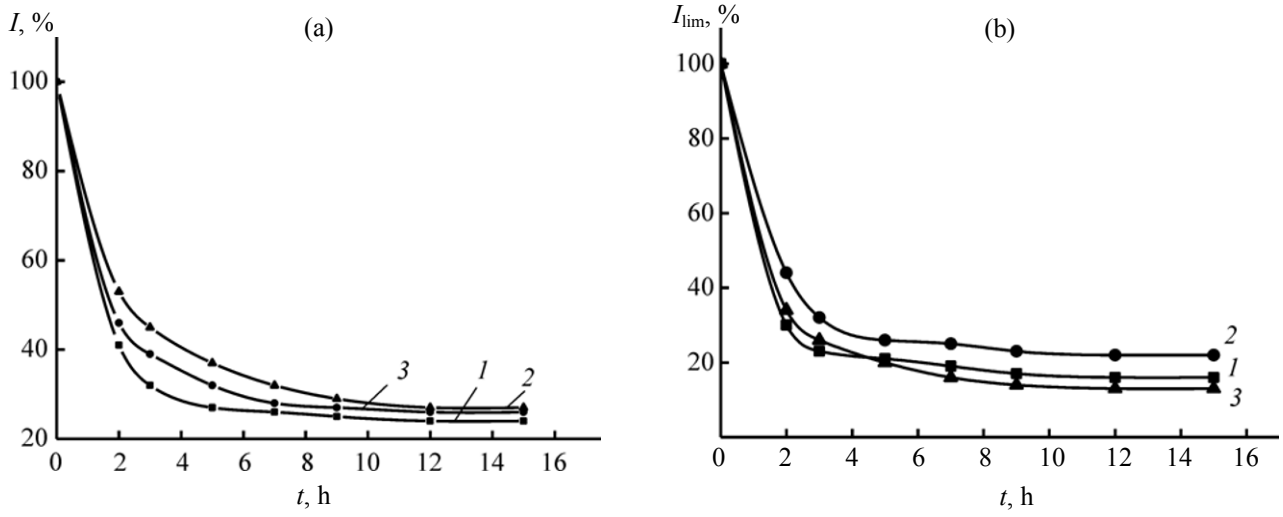

Fig. 3. Intensity of luminescence of polyethylene activated with a mixture of the luminophors: (a) Eu(III) and (b) Y(III) luminescence at the $[Eu(C_8H_7COO)_3]_n$:$Y(NO_3)_3 \cdot 6H_2O$ molar ratio of (*1*) 2 : 1, (*2*) 1 : 1, and (*3*) 1 : 2.

electron-dipole $^5D_0$–$^7F_2$ (615 nm) transitions of europium(III). Relative intensity of luminescence at varied ratio of the luminophors $[Eu(C_8H_7COO)_3]_n$:$Y(NO_3)_3 \cdot 6H_2O$ is shown in the table; the strongest luminescence was observed at equimolar ratio of the activating additives.

The influence of duration of UV irradiation on the photophysical properties of polyethylene activated with a mixture of europium(III) and yttrium(III) compounds was studied by means of stationary photolysis. The change of integral intensity of the activating ions luminescence evidenced the photoinduced degradation of the luminescent properties of the composites.

We found that irradiation with non-filtered light of mercury lamp led to a decrease in the luminescence intensity of Eu(III) and Y(III) incorporated into polyethylene matrix, the reduction being of 50–60% within two hours (Fig. 3). The composite with equimolar ratio of the luminophors showed the highest photoresistance. The composites prepared at the luminophors ratio of 2 : 1 and 1 : 2 were less stable, due likely to the concentration quenching of the activators luminescence.

EXPERIMENTAL

The luminescent composites were prepared as follows. Powders of polyethylene, europium(III) cinnamate, and yttrium(III) nitrate were thoroughly mixed in a mortar and pressed with a hydraulic press at *P* 50 atm and 140°C. The luminophors molar ratio was of 1 : 2, 1 : 1, and 2 : 1. The fraction of the luminophors in the material was 0.5 wt %, and the film thickness was 0.1 mm.

Luminescence spectra were recorded with a Shimadzu RF-5000 spectrofluorimeter at 293 K, λ 365 nm.

The accelerated aging of the composite polymer films was induced by non-filtered light of a DRT-250 mercury lamp (mercury lines at 254, 313, 334, 365, and 405 nm) during 10 h. The light flux intensity (λ_{ex} 365 nm) as measured with ferric-oxalate actinometer was of 2.75×10^{15} imp/s. The distance between the lamp and the specimen was 20 nm. Photolysis process was monitored via tracking intensity of the activators luminescence.

REFERENCES

1. Karasev, V.E., *Vestn. Dal'nevost. Otd. Ross. Akad. Nauk*., 2002, no. 3, p. 52.
2. Ostakhov, S.S., Kuznetsov, S.I., Murinov, Yu.I., Leplyanin G.V., and Kazakov, V.P., *Vysokomol. Soed., Ser. B*, 1995, vol. 37, no. 3. S. 523.
3. Raida, V.S., Koval', E.O., Ivanickii, A.E., Andrienko, O.S., and Tolstikov, G.A., *Plast. Massy*, 2001, no. 12, p. 38.
4. Pogreb, R., Whyman, G., Musin, A., Stanevsky, O., Bormarshenko, Y., Stenklar, S., and Bormarshenko, E., *Mater. Lett*., 2006, vol. 60, no. 15, p. 1911. DOI: 10.16/matlet.2005.12.048.
5. Pogreb, R., Finkelshtein, B., Shmukler, Y., Bormarshenko, E., *Polym. Adv. Technol*., 2004, vol. 15, no. 7, p. 414. DOI: 10.1002/pat.488.
6. Kalinovskaya, I.V. and Zadorozhnaya, A.N., and Karasev, V.E., *Russ. J. Gen. Chem*., 2013, vol. 83, no 10, p. 1906. DOI: 10.1134/S1070363213100186.
7. Kalinovskaya, I.V. and Zadorozhnaya, A.N., and Karasev, V.E., *Russ. J. Phys. Chem. A*, 2008, vol. 82, no. 12, p. 2392. DOI: 10.1134/S0036024408120327.