



Influence of the gamma irradiation on photoluminescence properties of DGMA doped with Eu^{3+} - β -diketonate complex

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Abstract

Diaquatrakis(thenoyltrifluoroacetate) europium(III) at 1% were doped in diglycidylmetacrylic resin (DGMA) and films were obtained in an PMMA matrix. Their luminescent properties, in the solid state are discussed. These systems were characterized by elemental analysis, thermogravimetry (TGA) and infrared spectroscopy (FTIR). Based on curve data, the thermal stability of DGMA:Eu(tta)₃ doped system (where tta = thenoyltrifluoroacetate) is similar to the polymer. The emission spectra of the Eu^{3+} complex doped in the DGMA recorded at 77 K exhibited the characteristic sharp bands arising from the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions ($J = 0-4$) of Eu^{3+} ion. Films containing DGMA: 1%Eu(tta)₃ system doped in PMMA matrix were prepared and irradiated at low dose of gamma radiation and showed a decreasing of luminescence intensity with increase of the radiation dose.

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1. Introduction

The luminescent properties of rare earth complexes with a variety of organic ligands have been reported in the last decade [1–4]. The employment of photoactive rare earth complexes in display technologies plays an important role in optical

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electronic devices [5,6] in parallel with the development of biodetection applications [7]. Recent researches have been developed to obtain novel luminescent materials within a silica matrix that hosts an anchored europium complex [8]. In the system containing rare earth ions the efficiency of energy transfer depends on the correlation of the relative positions of the triplet state (T) of ligands and the energy levels from the rare-earth ion. The triplet state of the ligand in the precursor is dependent of the substituent in the β -diketonate anion [9]. The advantage of the Eu^{3+} ion as emitter center is the presence of the single emission peak arising from $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transitions in C_{nv} , C_n , C_s and C_i symmetries and consequently provides a useful luminescent probe. If this transition exhibits more than one emission peak it indicates the existence of more than one site of symmetry. Additionally, the luminescence intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is not influenced by the chemical environment (allowed by the magnetic dipole mechanism) and thus it can be generally taken as reference [10]. Due to its hard acid character, rare earth ion has strong affinity to molecules containing oxygen as donor atoms. The influence of the acrylate polymers in the luminescence of Eu^{3+} complexes was reported [11]. The synthesis of the Eu^{3+} and Tb^{3+} ions doped in polyacrylate system is reported, which indicates the coordination between the dopant metal ion and the carboxylic anions, in the aqueous solution. In that work is reported the Eu^{3+} doped in acrylic polymer in the solid state [12].

In this article, we report the preparation and characterization of DGMA: $\text{Eu}(\text{tta})_3$ 1% system doped in PMMA matrix films that were irradiated at low doses of gamma radiation until 50 kGy. By the fact that the europium complex is stable and the cation is a highly efficient probe of the chemical vicinity, the results of irradiation on the PMMA matrix can be evaluated by changes in the luminescence properties of an doped system. The photoluminescence properties of these systems have been studied based on the excitation and emission spectra and luminescence intensity decay under irradiation conditions.

2. Experimental

2.1. Preparation of the polymer system doped with the Eu^{3+} - β -diketonate complex

The dyglycidylmetacrylic polymer used is originated from Ciba-Geigy (epoxy 505 g/equivalent). The Diaquatris(thenoyltrifluoroacetate) europium(III) complex was synthesized by the dissolution of europium chloride, $\text{EuCl}_3 \cdot 6(\text{H}_2\text{O})$, in water, according to the method described by Charles and Ohlmann [13]. The solid compound was filtered, washed with water and dried in vacuum desiccators over anhydrous calcium chloride, at room temperature. The Eu^{3+} ion content was estimated by complexometric titration with EDTA in methanol solution using xylenol orange as an indicator [14]. Elemental analysis of carbon and hydrogen were determined by the usual microanalytical procedures using a Perkin Elmer Model CHN 2400. The preparation of the luminescent polymeric materials was processed using the DGMA polymer and $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex as dopant.

The luminescent system containing the polymer doped with europium in 1, 5, 10, and 15, in percentages, were prepared by dissolving the polymer in methanol and mixing it with the required

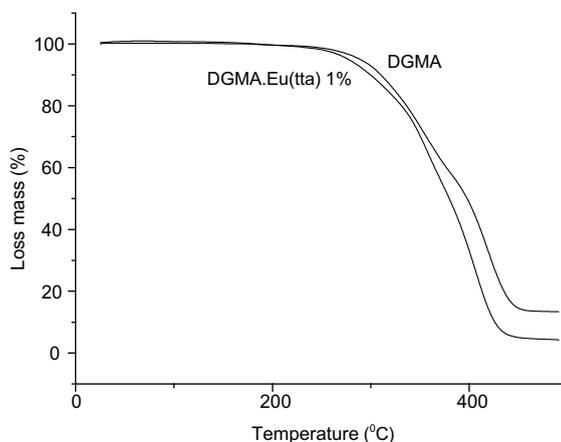


Fig. 1. TGA curves of the samples obtained at N_2 atmosphere 50 mL min^{-1} at heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ for the DGMA and DGMA: 1% $\text{Eu}(\text{tta})_3$ system.

amount of the luminescent Eu^{3+} -complex dissolved in acetone. The homogeneous solutions were heated at $40\text{ }^\circ\text{C}$ for 10 min and after that the solvent was evaporated at around $60\text{ }^\circ\text{C}$. The solid products were dried in vacuum desiccators over anhydrous calcium chloride at room temperature for a period of 12 h.

The solid product of DGMA 1% ($30.3 \pm 0.01\text{ mg}$) was mixed with PMMA ($3 \times 10^3 \pm 0.01\text{ mg}$) in acetone solution (20 mL). The mixture was casting in Pyrex recipient and left to dry. The Eu^{3+} ion

content in the films was estimated by complexometric titration with EDTA in methanol, and the Eu^{3+} complex concentration was 0.1 mg/g of PMMA. The film was cut of in slices that were irradiated and analyzed.

The excitation and emission spectra of the films were recorded on a SPEX Fluorolog-2 spectrofluorometer (model FL212) at room and liquid nitrogen temperature, using the front face mode. This apparatus was fully controlled by a DM3000F spectroscopic computer.

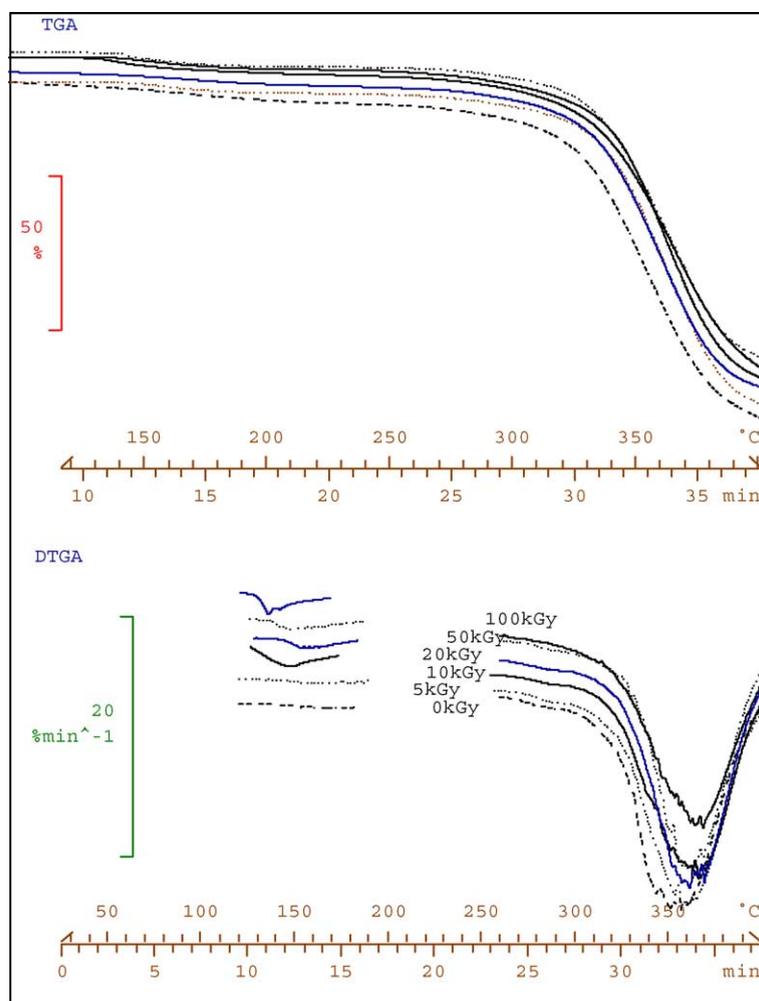


Fig. 2. TGA curves of the samples obtained at N_2 atmosphere 50 mLmin^{-1} at heating rate of $10\text{ }^\circ\text{Cmin}^{-1}$ for the PMMA/DGMA:1% $\text{Eu}(\text{tta})_3$ obtained after irradiation doses (in kGy): (a) 0; (b) 5; (c) 10; (d) 20; (e) 50 and (f) 100.

Irradiation took place in a ^{60}Co in Gammacell 220 from Inst. Eng. Atomic, Canadá, with 6917.4 CI activity, operating at 5.72 kGy/h. The applied radiation doses in the PMMA/DGMA: 1%Eu (tta)₃ were 0, 5, 10, 20 and 50 kGy. The emission spectra of these samples were recorded after irradiation in order to obtain information on the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions ($J=0-4$).

Thermogravimetric (TG) curves were obtained with an SDTA-822 thermobalance (Mettler Toledo), using samples about 10 mg in sapphire crucibles, under dynamic nitrogen atmosphere (50 mL min⁻¹), at heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) curves were obtained with a DSC-821 cell (Mettler Toledo) using an aluminum crucible with 5 mg of the sample, in a dynamic nitrogen atmosphere (50 mL min⁻¹) at a heating rate of 10 °C min⁻¹. The DSC apparatus was calibrated with In metal (m.p. 156.61 °C; $\Delta H = 28.4 \text{ J g}^{-1}$).

3. Results and discussion

The europium content was determined by complexometric titration with EDTA in methanol. The carbon and hydrogen contents were estimated by microanalytical procedures: The C, H and Eu³⁺ percentage values calculated/found for the complex are: [C: 33.52/33.85; H: 1.88/1.89; Eu: 12.51/11.30] in accordance with the general formula [Eu(tta)₃(H₂O)₂].

The TGA curves exhibited a main event of mass loss for the doped samples in the interval of 200–450 °C. The thermal decomposition profiles are similar to doped and undoped system sample and the temperature onset (Tonset) of thermodecomposition were around 282 °C for the DGMA resin and 274 °C for DGMA: 1% Eu(tta) as illustrated in Fig. 1. A film of PMMA prepared under the same conditions has a Tonset of 338 °C.

In the thermogravimetric analysis of DGMA: 1% Eu(tta) was verified absence of mass reduction in the temperature interval of 80–120 °C, interval in which the precursor losses the two water molecules. This fact indicates that the coordination of the Eu³⁺-complex into the polymer occurs via substitution of the water molecules.

The DGMA resin doped with 1% was mixed to PMMA in solution (99.0:1.0) to obtain the films by casting process. Films of PMMA/DGMA: 1%Eu (tta)₃ were irradiated in low doses of 5, 10, 20, 50 and 100 kGy. The TGA curves of the irradiated films show a main single event of mass loss for the samples (Fig. 2). The Table 1 shows the temperature onset of these events and the loss of mass in the interval 130–200 °C.

In this study the doped system with the [Eu(tta)₃(H₂O)₂] in the DGMA into PMMA resin irradiated shows thermal stability increase at low dose of irradiation, until 50 kGy, Table 1. The increase on the Tonset indicates the occurrence of cross-link in the matrix due to radiation mechanisms and in consequence the polymeric matrix increases in thermal stability. At 100 kGy the film presents a decrease of Tonset due to degradation products.

The excitation spectra of doped polymers (Fig. 3) were recorded in the range 250–500 nm, at 77 K, with emission monitored in the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition at 614 nm. The narrow absorption bands around 460 nm corresponding to the $^7\text{F}_0 \rightarrow ^5\text{D}_2$ transition. The broad bands in the range from 250 to 420 nm arising from the β -diketonate group are overlapped with those narrow bands from the Eu³⁺ ion [11].

The emission spectra of Eu-systems (Fig. 4) were recorded in the range of 500–750 nm under excitation at around 350 nm, at 77 K. These spectra show the emission bands corresponding to the electronic

Table 1
TGA data of the PMMA doped system under nitrogen atmosphere at heating rate of 10 °C min⁻¹

Sample	TGA	
	Onset (°C)	Mass loss (%) (130–200 °C)
PMMA	338.0	–
DGMA	282.0	–
DGMA: 1%Eu(tta) ₃	278.0	–
PMMA:DGMA: 1%Eu(tta) ₃ 0 kGy	336.5	3.73
PMMA:DGMA: 1%Eu(tta) ₃ 5 kGy	340.0	3.44
PMMA:DGMA: 1%Eu(tta) ₃ 10 kGy	343.5	3.80
PMMA:DGMA: 1%Eu(tta) ₃ 20 kGy	344.0	3.15
PMMA:DGMA: 1%Eu(tta) ₃ 50 kGy	345.0	2.91
PMMA:DGMA: 1%Eu(tta) ₃ 100 kGy	342.0	3.90

Results obtained in different radiation doses.

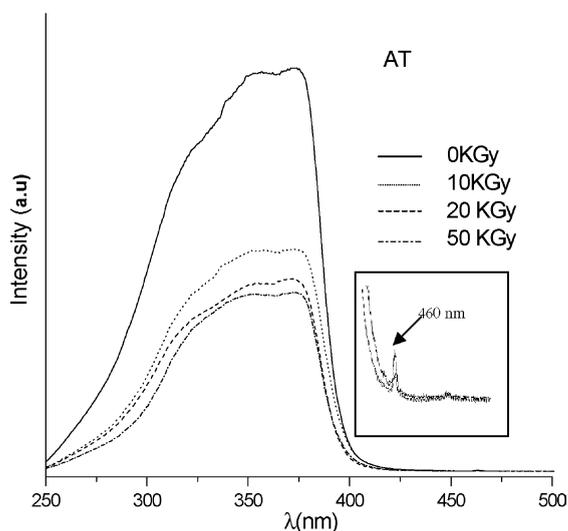


Fig. 3. Excitation spectra of the PMMA/DGMA: 1%Eu(tta)₃ system, under excitation at transition around 614 nm, obtained in the radiation doses (in kGy): (a) 0; (b) 5; (c) 10; (d) 20 and (e) 50.

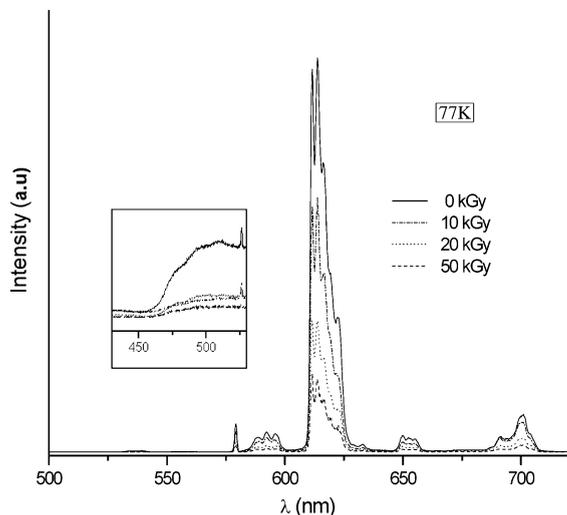


Fig. 4. Emission spectra of the PMMA/DGMA: 1%Eu(tta)₃ system with excitation at 350 nm (at 77 K) obtained after following radiation doses (in kGy): (a) 0; (b) 5; (c) 10; (d) 20 and (e) 50.

$^5D_0 \rightarrow ^7F_j$ transitions ($J = 0-4$) from the europium trivalent ion. The presence of the only one peak in the $^5D_0 \rightarrow ^7F_0$ transition indicates that the Eu^{3+} ion has only one chemical environment. The

$^5D_0 \rightarrow ^7F_2$ transition is hypersensitive to the ligand field since this transition is of forced electric dipole nature, while the intensity of the magnetic dipole $^5D_0 \rightarrow ^7F_1$ transition is not sensitive to the ligand field and it is generally taken as reference. In the case of the emission spectrum of the DGMA: 1%Eu(tta)₃ system, the broad bands at around 420–550 nm are attributed to the transitions from the organic part of the polymer overlapped with the transitions from the tta ligand [15]. It was verified that the luminescent intensities decrease with increasing of the radiation dose. The films of PMMA/DGMA: 1%Eu(tta)₃ system exposed to gamma-radiation showed variations, with the radiation dose, in the luminescence intensity.

4. Conclusion

The characterization of the DGMA: 1%Eu(tta)₃ system by TGA techniques indicated that the Eu^{3+} -complex precursor was immobilized in the polymer matrix by the Eu–O interaction when the complex is doped into the DGMA polymer. The thermal stability of those doped systems is similar to the polymer undoped. The film of PMMA/DGMA: 1%Eu(tta)₃ system that was submitted to gamma radiation degradation showed changes in the thermal stability and effects in the luminescence properties of rare earth ion. The luminescence intensity of dipolar $^5D_0 \rightarrow ^7F_j$ transitions of europium ($J = 0-4$) decreases with augment of the radiation dose (0, 5, 10, 20 and 50 kGy). This indicated that the irradiation on PMMA matrix produced degradation products, other than the cross link effect, acting as a filter for the luminescence intensity. Changes that improve the absorption property of the film consequently can quench the luminescent effect. This suggests to the material the possibility of application as optical marker of high efficiency in conditions of irradiation at low dose.

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