

Energy Transfer to Eu(III) in the Solid-State Low-Density Polyethylene–Poly(acrylic acid) and Low-Density Polyethylene–Fe₂O₃–Poly(acrylic acid) Matrices

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ABSTRACT: Ion exchange between H⁺ and Eu³⁺ and/or Tb³⁺ was studied in the material modified by *in situ* sorption and thermal polymerization of acrylic acid in low-density polyethylene (LDPE–PAA) and in the composite system LDPE–Fe₂O₃–PAA. Fluorescence spectroscopy showed evidence of Eu³⁺ and/or Tb³⁺ ion exchanges in these materials. The matrix LDPE–PAA after Eu(III) ion exchange presented luminescence (excitation 265 nm). This was explained by an energy-transfer process from the matrix LDPE–PAA to Eu³⁺ ions. The LDPE–PAA matrix after simultaneous Eu³⁺/Tb³⁺ ion exchange exhibited Eu³⁺ and Tb³⁺ ion luminescence (excitation 265 nm), confirming an energy-transfer process from LDPE–PAA to Eu³⁺ ions in LDPE–PAA–Eu³⁺–Tb³⁺ matrix. Fe₂O₃ in LDPE–Fe₂O₃–PAA quenched the matrix for excitation at 265 nm and no emission at the region 400 nm was observed. The luminescence of Tb³⁺ ions in the matrix LDPE–Fe₂O₃–PAA–Tb³⁺ (excitation 265 nm) was partially quenched by Fe₂O₃. However, a weak emission of Eu³⁺ ions was observed (excitation 265 nm) in the matrix LDPE–Fe₂O₃–PAA after simultaneous Eu³⁺ and Tb³⁺ ion exchanges, suggesting an energy transfer from Tb³⁺ to Eu³⁺ ions. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 919–931, 2000

Key words: polymer luminescence; energy transfer; poly(acrylic acid); ion exchange; ionomer

INTRODUCTION

Low-density polyethylene (LDPE) can be modified by *in situ* sorption and thermal polymerization of vinyl monomers in the matrix.¹ Kinetic studies on LDPE/poly(acrylic acid) (PAA) showed that the carboxylic groups of PAA are located mainly at the surface or at neighboring layers of the matrix,

in which a radical initiation reaction occurs mainly at the LDPE film surface or near to it and a propagation reaction proceeding subsequently into the bulk matrix.² A diffusion-free process for the acrylic acid (AA) thermal polymerization on LDPE films (thickness $\leq 200 \mu\text{m}$) was suggested.

The modification was also observed in an Fe₂O₃-doped LDPE matrix yielding LDPE–Fe₂O₃–PAA, LDPE–Fe₂O₃–poly(methyl methacrylate) (PMMA) and LDPE–Fe₂O₃–poly(4-vinylpyridine) (P4VP) materials.^{3,4} The Mössbauer spectra of these samples revealed AA interaction with iron(III) oxide particles, yielding acrylates, hydroacrylates, polyacrylates, and polyhydroacrylates.

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The incorporation of rare earth or lanthanide ions in suitable host materials has generated great interest in the past few years, because they can impart to those materials some valuable optical properties.⁵⁻⁷ Added to that, some materials can exhibit luminescence and other energy-transfer processes whose occurrence is related to interaction between neighboring lanthanide ions.⁸⁻¹¹ The ionic structures, especially the aggregation of lanthanide ions, is a key to some of the energy-transfer processes.

Some of the studies were performed on polymeric materials which contain carboxylic groups, yielding organic matrices with fluorescent functions.^{8,9,12,13} Also, a number of fluorescent probes have proved to be useful in the study of ionomer membrane systems. These studies have determined the relative equilibrium locations of cations and anions within the microphase-separated structure of the polymer with the purpose to establish the essential cause of superselectivity of those systems.¹⁴

Studies to determine whether the fluorescence behavior of the Tb(III) ion is sensitive to spatial relationship between ligating moieties in tactic polymers were realized.¹⁵ Isotactic and syndiotactic poly(methacrylic acid) were chosen to complex with the metal since they process a definite microstructure with respect to their ligating species. The binding efficiency of chelating species with the Tb(III) ion is strongly influenced by the tacticity of the coordination polymer.

The fluorescence of the europium ion added to the small number and sharp fluorescence peaks of this rare earth ion make it suitable for studies of the distribution of carboxylate groups of PAA in the LDPE matrix. The distribution of carboxylate groups of PAA in the LDPE matrix was studied

using Eu(III) and UO₂(II) ions as a probe.^{12,13} Simultaneous H⁺ ↔ Eu³⁺/UO₂²⁺ ion exchange in the LDPE-PAA matrix was investigated by fluorescence spectroscopy. No evidence of energy transfer from UO₂²⁺ to Eu³⁺ was observed and, consequently, no ionomer aggregate sites.¹³

In this work, we investigated the evidence of energy transfer to the europium(III) ion in the matrices LDPE-PAA and LDPE-Fe₂O₃-PAA after the sequential and simultaneous ion exchanges of terbium(III) and europium(III) ions, to elucidate ion aggregation in this ion-containing doped polymer.

EXPERIMENTAL

Materials

AA was supplied by the Aldrich Chemical Co. (Milwaukee, WI). Hydroquinone monomethyl ether (HMME) was supplied by Cia. Química Rhodia Brasileira (São Paulo, Brazil). It was purified by successive crystallization in acetone. Europium(III) oxide (Eu₂O₃) 99.99% and terbium oxide (Tb₄O₇) were supplied by the Alpha Inorganics Ventron Co. (Danvers, MA). Europium(III) chloride hexahydrate (EuCl₃ · 6H₂O) 99.99% and terbium (III) chloride hexahydrate (TbCl₃ · 6H₂O) 99.99% were supplied by Aldrich Chem. Co. Iron pentacarbonyl [Fe(CO)₅] was supplied by BASF (Frankfurt, Germany). LDPE sheets, *d* = 0.918 g/cm³, MI = 1.15 g/10 min, were donated by Poliolefinas (São Paulo, Brazil). All reagents were of analytical grade and they were used without further purification.

Methods

The sorption and *in situ* oxidation of Fe(CO)₅ in LDPE films (3 × 4 cm) followed the procedure

Table I Eu³⁺ and Tb³⁺ Ion Exchanges in LDPE-PAA Matrix

Sample (No.)	% PAA in LDPE Matrix	% Eu ³⁺ in LDPE-PAA Matrix	% Tb ³⁺ in LDPE-PAA Matrix
LDPE-PAA-Eu ³⁺ (S ₁)	4.9	11.2	—
LDPE-PAA-Tb ³⁺ (S ₂)	4.5	—	18.7
LDPE-PAA-Eu ³⁺ /Tb ³⁺ ^a (S ₃)	5.8	12.0	12.1
LDPE-PAA-Tb ³⁺ /Eu ³⁺ ^b (S ₄)	5.9	8.8	17.5
LDPE-PAA-Eu ³⁺ /Tb ³⁺ ^c (S ₅)	3.2	2.1	— ^d

^a Eu³⁺ followed by Tb³⁺ ion exchange.

^b Tb³⁺ followed by Eu³⁺ ion exchange.

^c (Eu³⁺ + Tb³⁺) simultaneous ion exchange.

^d Impossible to calculate.

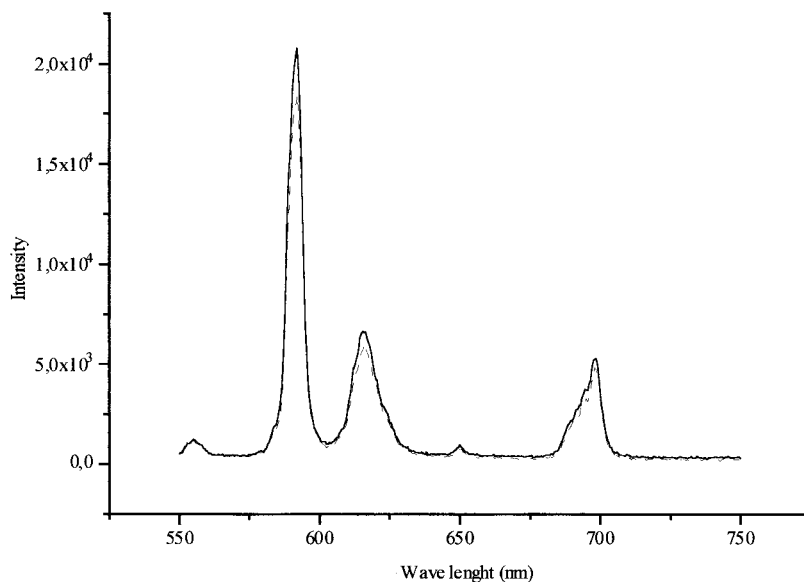


Figure 1 Fluorescence spectra of (—) 10 mM EuCl₃ · 6H₂O solution and (· · ·) EuCl₃ · 6H₂O solution after the Eu³⁺ ion exchange in LDPE-PAA (4.9% PAA). Excitation: 395 nm.

previously described.¹ The sorption and *in situ* thermal polymerization of AA (80% by unit volume of aqueous solution containing 350 or 500 ppm of HMME) in LDPE films (either plain or Fe₂O₃-doped) followed the method described in our previous work.^{1,3} The average film thickness

was 200 μm. The mass increase on LDPE films was obtained gravimetrically.²

The synthesis of EuCl₃ · 6H₂O and TbCl₃ · 6H₂O from Eu₂O₃ and Tb₄O₇ followed the method described in ref. 12. Europium or terbium ion exchange was carried out by immer-

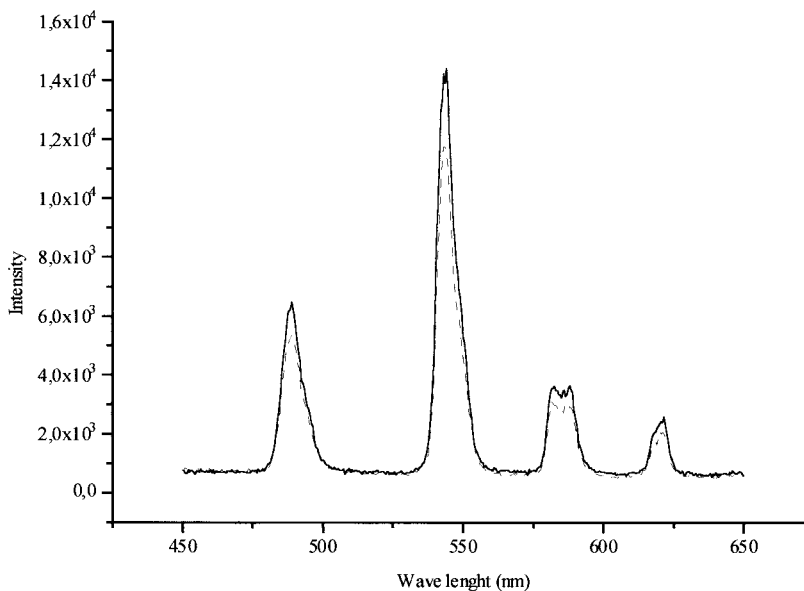


Figure 2 Fluorescence spectra of (—) 10 mM TbCl₃ · 6H₂O solution and (· · ·) TbCl₃ · 6H₂O solution after the Tb³⁺ ion exchange in LDPE-PAA (4.5% PAA). Excitation: 265 nm.

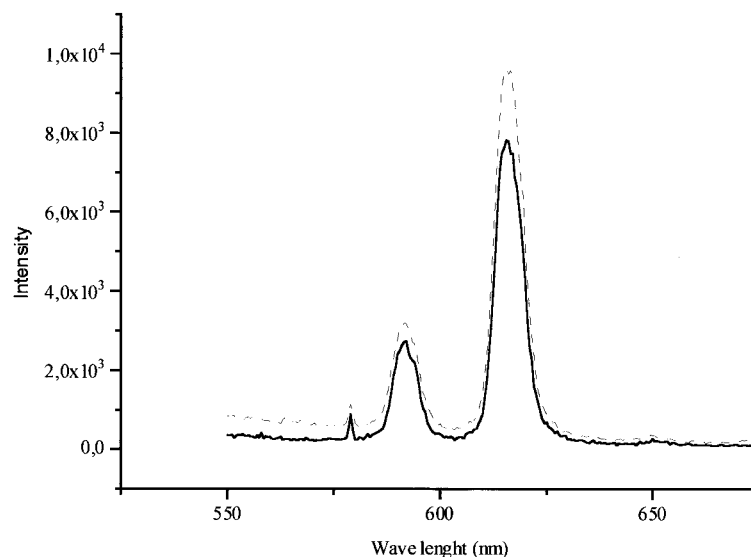


Figure 3 Fluorescence spectra of LDPE-PAA-Eu³⁺ matrix (S₁): 4.9% PAA; 11.2% Eu³⁺. Excitation: (a) (—) 395 nm; (b) (· · ·) 265 nm.

sion of the matrix into a 5–7 mL of 10 mM EuCl₃ or TbCl₃ solution at 60°C for 24 h. Simultaneous europium/terbium ion exchange in the matrix followed a similar procedure using 3 mL of each 10 mM EuCl₃ and TbCl₃ solution. The percent of ions in the solution after thermal treatment was calculated by the fluorescence spectra of the solution using the peak intensity at 591 nm or at 544 nm. The fluorescence intensity of the peak at 591 nm of a 10 mM EuCl₃ · 6H₂O solu-

tion or at 544 nm of a 10 mM TbCl₃ · 6H₂O solution was assumed to be 100%.¹² The fluorescence spectra of the EuCl₃ · 6H₂O and of the TbCl₃ · 6H₂O solutions were obtained in the region of 450–650 nm with excitation at 395 nm and at 265 nm, respectively.

The fluorescence spectra of the dehydrated LDPE-PAA and LDPE-Fe₂O₃-PAA matrices after ion exchange were obtained under the same conditions as described for the solution. For simul-

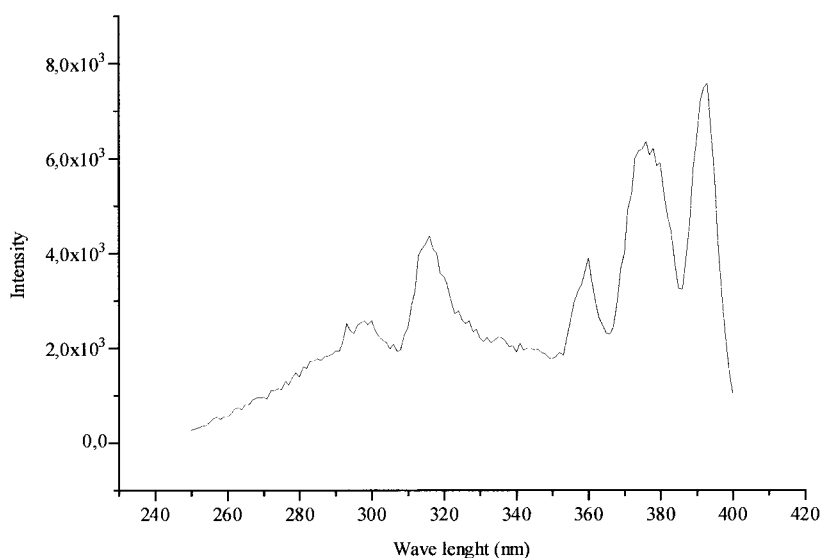


Figure 4 Excitation spectrum of LDPE-PAA-Eu³⁺ matrix (S₁): 4.9% PAA; 11.2% Eu³⁺. Emission: 616 nm.

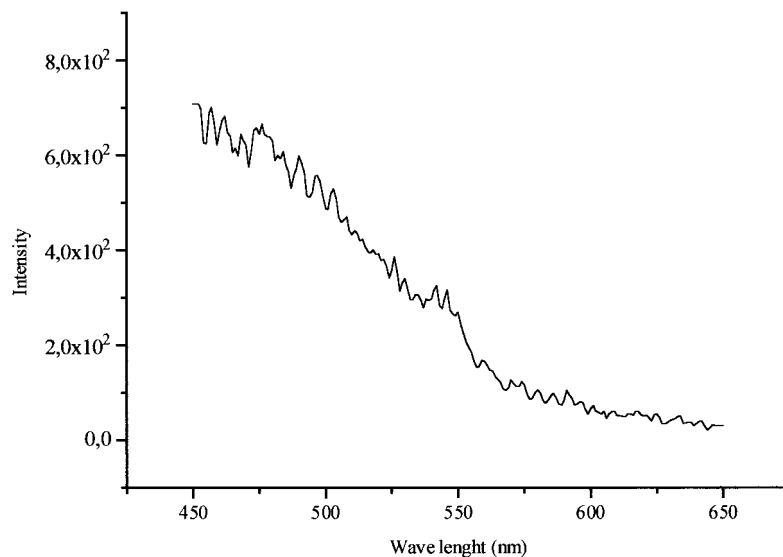


Figure 5 Fluorescence spectrum of LDPE-PAA matrix: 6.7% PAA. Excitation: 265 nm.

taneous Eu(III) and Tb(III) ion exchanges, the matrix was excited at 395 and 265 nm, respectively.

Measurements

The fluorescence spectra of the matrices and solution were obtained using a SPEX Fluorolog-2 attached to a Datamate and a multiprocessor. FTIR spectra were registered using a Michelson Bomem Hartmann & Braun, Serie MB, spectrophotometer.

RESULTS

LDPE-PAA After Eu³⁺ or/and Tb³⁺ Ion Exchange

Luminescence studies were realized in the matrix LDPE-PAA after Eu³⁺ or/and Tb³⁺ ion exchange. The characteristics data of the samples after ion exchange are given in Table I.

The samples were characterized by FTIR spectroscopy. A peak at 1770 cm⁻¹ (ν of the carbonyl group) and the absence of insaturation confirm

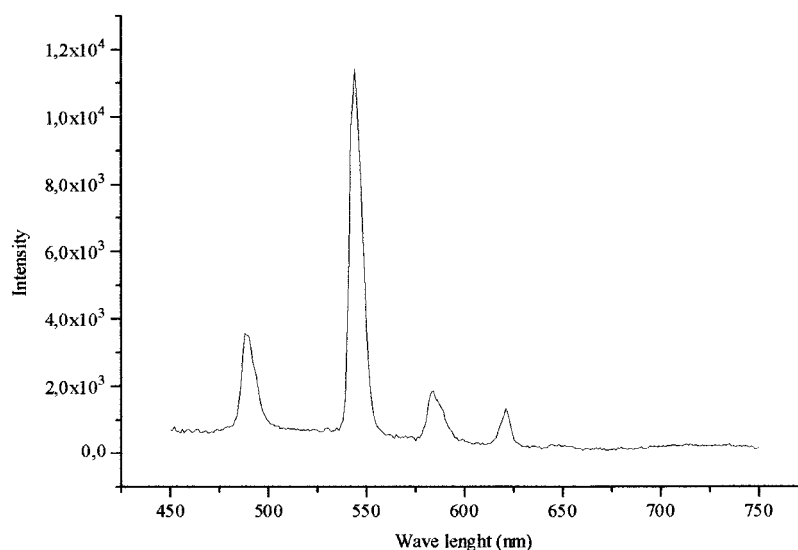


Figure 6 Fluorescence spectrum of LDPE-PAA-Tb³⁺ matrix (S₂): 4.5% PAA; 18.7% Tb³⁺. Excitation: 265 nm.

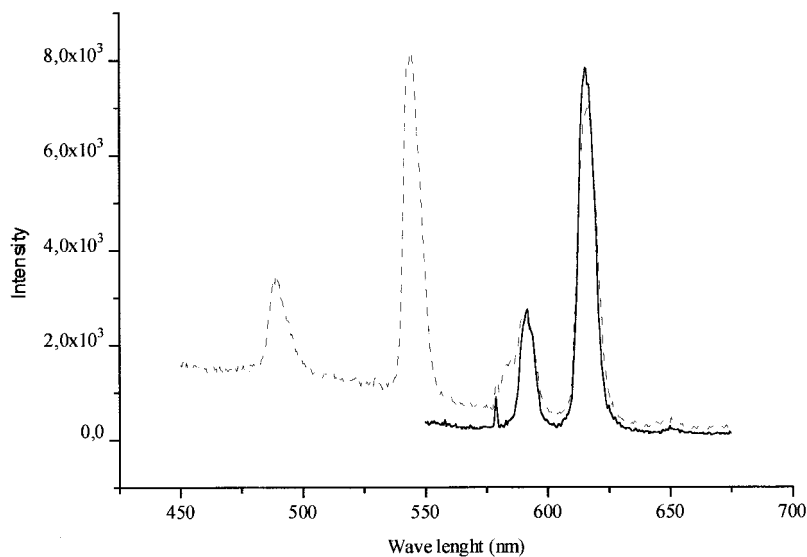


Figure 7 Fluorescence spectra of LDPE-PAA-Eu³⁺/Tb³⁺ matrix (S₃): 5.8% PAA; 2.0% Eu³⁺; 12.1% Tb³⁺. Excitation: (a) (—) 395 nm; (b) (· · ·) 265 nm.

the presence of PAA in the LDPE matrix. Also, the ion exchange in the matrices was evidenced by a peak at 1540 cm⁻¹, characteristic of carboxylate ion stretching.

The luminescence spectra (excitation at 395 nm) of the 10 mM EuCl₃ · 6H₂O solution before and after the Eu³⁺ ion exchanges in the LDPE-PAA (4.9% PAA, S₁) matrix showed three fluorescence intensity peaks characteristic of Eu³⁺ ions (Fig. 1). The two more intense lines are due to the transitions ⁵D₀ → ⁷F₁ (591 nm) and ⁵D₀ → ⁷F₂ (615 nm). The fluorescence intensity ratio between them was 3 : 1, confirmed by previous results.¹²

The luminescence spectra (excitation at 265 nm) of the 10 mM TbCl₃ · 6H₂O solution before and after the Tb³⁺ ion exchange in LDPE-PAA (4.5% PAA, S₂) are shown in Figure 2. The two more intense peaks characteristic of Tb³⁺ ions are due to the ⁵D₄ → ⁷F₆ (489 nm) and ⁵D₄ → ⁷F₅ (544 nm) transitions. The fluorescence intensity ratio between them was of 1 : 2.5. The percent of Eu³⁺ and Tb³⁺ ion exchanges in the matrices was estimated from the fluorescence intensity peaks at 591 nm and at 544 nm for Eu³⁺ and Tb³⁺ according description in the Method section.

The emission spectrum (excitation at 395 nm) of the dehydrated LDPE-PAA-Eu³⁺ matrix (S₁) was similar to that obtained in previous work¹² [Fig. 3(a)]. The ratio between the fluorescence

intensity peaks at 591 nm (⁵D₀ → ⁷F₁) and 615 nm (⁵D₀ → ⁷F₂), which are sensitive to the ligand media, changed and it was equal to 1 : 3 as previously observed.¹² This is evidence of interaction between Eu³⁺ and carboxylate groups in the LDPE-PAA matrix after ion exchange.^{12,13} The emission spectrum (excitation at 265 nm) of the same sample (S₁) is presented in Figure 3(b). The spectrum showed peaks characteristic of Eu³⁺ ion emission, although no excitation of Eu³⁺ ions at 265 nm in the matrix LDPE-PAA-Eu³⁺ would be expected (emission at 616 nm) (Fig. 4). However, the emission spectrum of the LDPE-PAA matrix (excitation at 265 nm) showed a broad emission band with maximum intensity at the vicinity of 400 nm (excitation region of Eu³⁺ ion) (Fig. 5). This fact suggests an energy transfer from the matrix LDPE-PAA to the Eu³⁺ ion.

Figure 6 shows the emission spectrum of the matrix LDPE-PAA-Tb³⁺ (S₂), with excitation at 265 nm. The spectrum shows peaks characteristic of Tb³⁺ ion emission in solution (Fig. 2). However, the ratio of fluorescence intensity of the peaks at 489 nm (⁵D₄ → ⁷F₆) and at 544 nm (⁵D₄ → ⁷F₅), which are sensitive to the nature of interactions in the media, was 1 : 3.5. The data confirm the interaction between Tb³⁺ ions and carboxylic groups in the LDPE-PAA matrix.

Figure 7(a) shows the emission spectrum of LDPE-PAA-Eu³⁺/Tb³⁺ (S₃), with excitation at

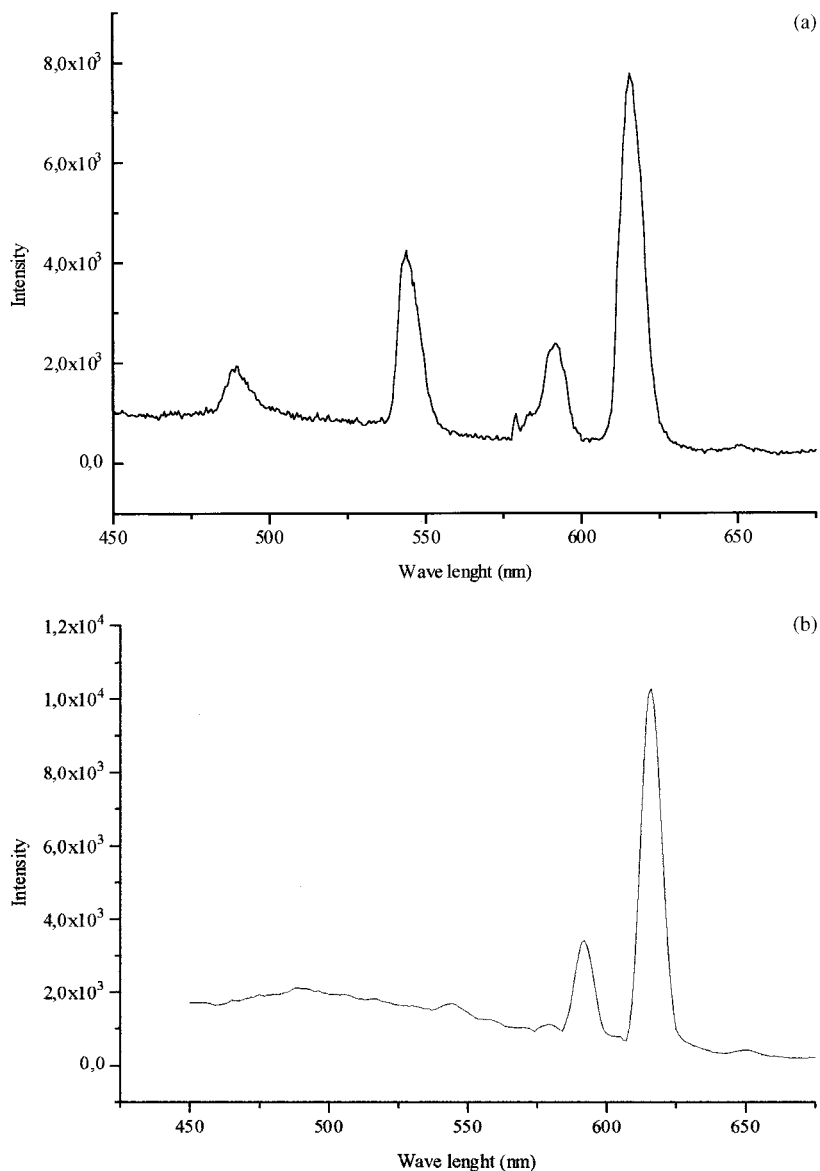


Figure 8 (a) Fluorescence spectrum of LDPE-PAA-Tb³⁺/Eu³⁺ matrix (S₄): 5.9% PAA; 17.5% Tb³⁺; 8.8% Eu³⁺. Excitation: 265 nm. (b) Fluorescence spectrum of LDPE-PAA-Tb³⁺/Eu³⁺ matrix (S₄): 5.9% PAA; 17.5% Tb³⁺; 8.8% Eu³⁺. Excitation: 395 nm.

395 nm. Its pattern is similar to that for LDPE-PAA-Eu³⁺ [Fig. 3(a)]. The emission spectrum of the same sample at excitation of 265 nm is shown in Figure 7(b). Intense fluorescence peaks due to Tb³⁺ ions (489 and 544 nm) were observed and also peaks at the emission region of Eu³⁺ ions (591 and 615 nm). They were similar to those observed for the emission spectrum of LDPE-PAA-Eu³⁺ (S₁) at same excitation region [Fig. 3(b)]. This fact reinforces the proposal of an energy-

transfer process from the matrix to the Eu³⁺ ions, although a probable contribution of energy from the Tb³⁺ ion to Eu³⁺ would not be discounted.

In this sample (S₃), a sequential ion exchange occurred in the matrix LDPE-PAA (5.8% of PAA). Initially, the Eu³⁺ ions had been exchanged followed by the Tb³⁺ ions. The amounts of both ions exchanged were similar (12.0% for Eu³⁺ and 12.1% for Tb³⁺) (Table I). This suggests an iden-

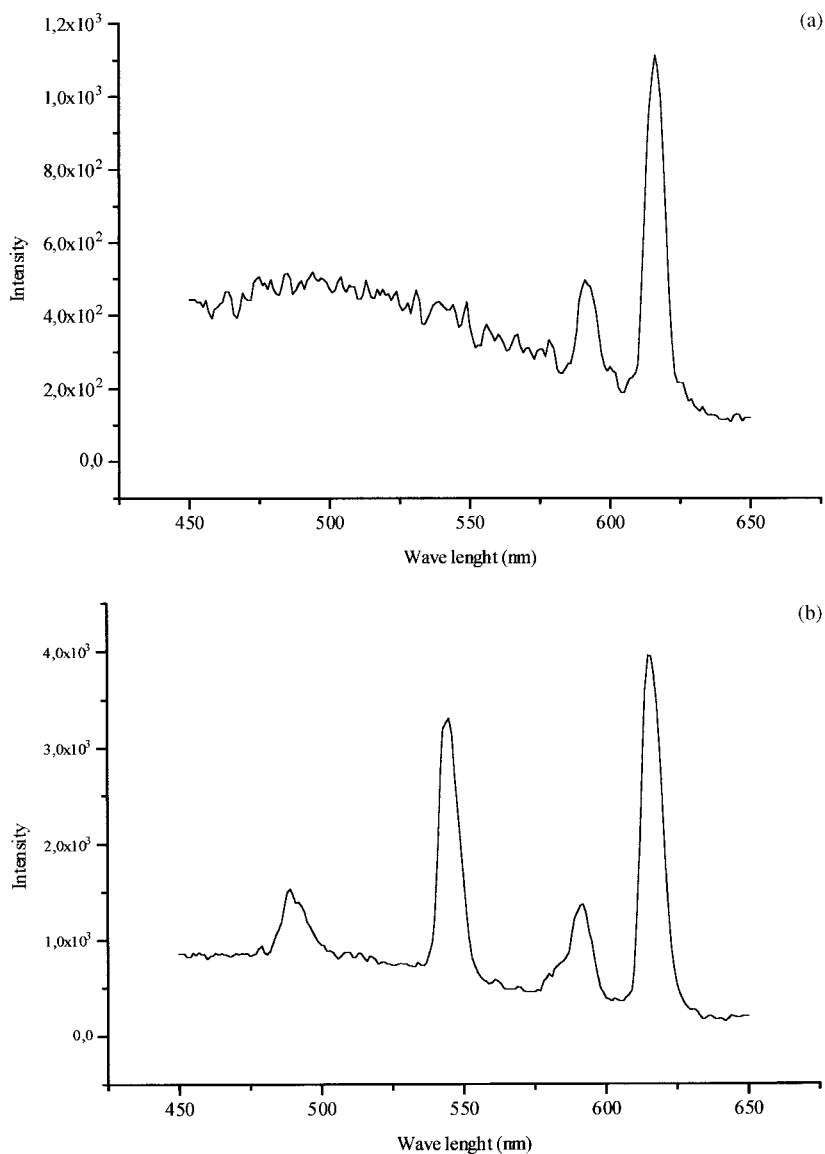


Figure 9 (a) Fluorescence spectrum of LDPE-PAA-Eu³⁺-Tb³⁺ matrix (S₅): 3.2% PAA; 2.1% Eu³⁺; percent Tb³⁺ ions impossible to calculate. Excitation: 395 nm. (b) Fluorescence spectrum of LDPE-PAA-Eu³⁺-Tb³⁺ matrix (S₅): 3.2% PAA; 2.1% Eu³⁺; percent Tb³⁺ ions impossible to calculate. Excitation: 265 nm.

tical apparent exchange rate for both ions in the matrix. The hydrated ionic radius of the ions probably does not interfere in the exchange.

Figure 8(a,b) shows the emission spectra of LDPE-PAA (5.9% of PAA) after sequential ion exchange in the matrix: The Tb³⁺ ion followed by the Eu³⁺ ion (S₄). The emission spectra for both excitations (at 265 and 395 nm) were similar to that observed in Figure 7. In the same way, energy transfer from the matrix to the Eu³⁺ ions was evidenced. The contribution of Tb³⁺ ions in this process also was not clear.

In this case, the amount of Tb³⁺ ions (17.5%), first exchanged, was higher than that of Eu³⁺ ions (8.8%), subsequently exchanged. As the ion-exchange procedure was realized in aqueous media, the hydrate ionic radius of these ions should be considered, which is bigger for the Tb³⁺ ions.¹⁶ So, the carboxylate sites of PAA on the matrix were first exchanged by Tb³⁺ ions remaining in those sites which do not present steric hindrance for the subsequent Eu³⁺ ion exchange.

Figure 9(a,b) shows the emission spectra for the matrix after simultaneous Tb³⁺ and Eu³⁺ ion

Table II Characteristics of the Samples Before and After Eu³⁺ or/and Tb³⁺ Ion Exchanges

Sample (No.)	% Fe ₂ O ₃ in LDPE Matrix	% PAA in LDPE-Fe ₂ O ₃ Matrix	% Eu ³⁺ in Matrix	% Tb ³⁺ in Matrix
LDPE-Fe ₂ O ₃ -PAA (S ₆)	0.2	0.4	—	—
LDPE-Fe ₂ O ₃ -PAA-Tb ³⁺ (S ₇)	0.3	0.4	—	3.3
LDPE-Fe ₂ O ₃ -PAA-Eu ³⁺ -Tb ³⁺ ^a (S ₈)	0.3	1.2	^b	31.6
LDPE-Fe ₂ O ₃ -PAA-Eu ³⁺ -Tb ³⁺ ^a (S ₉)	0.2	1.6	^b	^b

^a Simultaneous ion exchange.

^b Experimental difficulties for calculation.

exchange with excitations at 395 nm [Fig. 9(a)] and at 265 nm [Fig. 9(b)]. The spectra showed peak characteristics of Eu³⁺ ion emission (excitation at 395 nm) and of Tb³⁺ and Eu³⁺ ion emissions (excitation at 265 nm). These data again confirm the proposal of an energy-transfer process from the matrix to the Eu³⁺ ions.

LDPE-Fe₂O₃-PAA After Eu³⁺ or/and Tb³⁺ Ion Exchange(s)

Luminescence studies were done using the LDPE-Fe₂O₃-PAA matrices after Eu³⁺ or/and Tb³⁺ ion exchanges. The characteristics of the sample are shown in Table II.

It was impossible to calculate the amount of Eu³⁺ and Tb³⁺ ions in the samples S₈ and S₉ after ion exchange in the LDPE-Fe₂O₃-PAA matrix due to experimental difficulties. However, the presence of Eu³⁺ and Tb³⁺ ions in the samples (S₈ and S₉) was checked by FTIR spectra. A peak at 1591 cm⁻¹, characteristic of carboxylate groups (ν_{COO^-}), confirmed the ion exchange in the samples.

Figure 10(a,b) shows the UV-VIS spectra of Fe₂O₃ in the LDPE-Fe₂O₃-PAA (S₆) and in the LDPE-Fe₂O₃-PAA-Eu³⁺-Tb³⁺ (S₈) matrices. It was observed that iron(III) oxide absorbs in the region of 200–500 nm before and after ion exchange.

Figure 11(a,b) shows the emission spectrum of the matrix LDPE-Fe₂O₃-PAA (S₆) for excitation at 395 nm [Fig. 11(a)] and at 265 nm [Fig. 11(b)]. For excitation at 395 nm, a broad emission peak shifted to the region 500–650 nm with a maximum at about 550 nm [Fig. 11(a)]. For excitation at 265 nm, no clear emission of the matrix was observed [Fig. 11(b)] as it was for the undoped matrix LDPE-PAA (Fig. 5). This was explained by the quenching effect of iron(III) oxide doped in

the matrix which absorbs at 265 nm [Figs. 10(a,b)].

Figure 12 shows the emission spectrum (excitation at 295 nm) of the LDPE-Fe₂O₃-PAA-Tb³⁺ matrix (S₇). A weak emission at 544 nm was identified as the transition ⁵D₄ → ⁷F₅ of the Tb(III) ion. The reduction of the emission signal was probably due to the quenching of the Tb(III) ion by the iron(III) oxide, which also acts as suppressor of the matrix.

The emission spectrum (excitation at 395 nm) of LDPE-Fe₂O₃-PAA after simultaneous Eu³⁺/Tb³⁺ ion exchange (S₉) is shown in Figure 13. A weak emission signal at 615 nm was identified as the transition ⁵D₀ → ⁷F₂ of the Eu³⁺ ion. In this case, the Eu³⁺ ion emission had been masked by the broad-band emission in the region 500–600 nm attributed to the LDPE-Fe₂O₃-PAA matrix.

Figure 14 shows the emission spectra (excitation at 265 nm) of sample S₉. An emission signal at 615 nm, characteristic of Eu³⁺ ion transition (⁵D₀ → ⁷F₂), and no clear emission due to the Tb³⁺ ion transition were observed. The weak broad emission of the matrix appears at 500–600 nm, so it does not interfere in the Eu³⁺ ion excitation process, as which occurred in the previous case of the LDPE-PAA matrix. The data suggest an energy transfer from Tb³⁺ to Eu³⁺ ions in the matrix LDPE-Fe₂O₃-PAA-Eu³⁺-Tb³⁺. In this case, the vicinity of the Eu³⁺ and Tb³⁺ ions can be proposed, making possible the ionic aggregate formation.

DISCUSSION

Previous investigation about the formation of ionic aggregations in LDPE-PAA material using Eu³⁺ and UO₂²⁺ ions as luminescence probes did

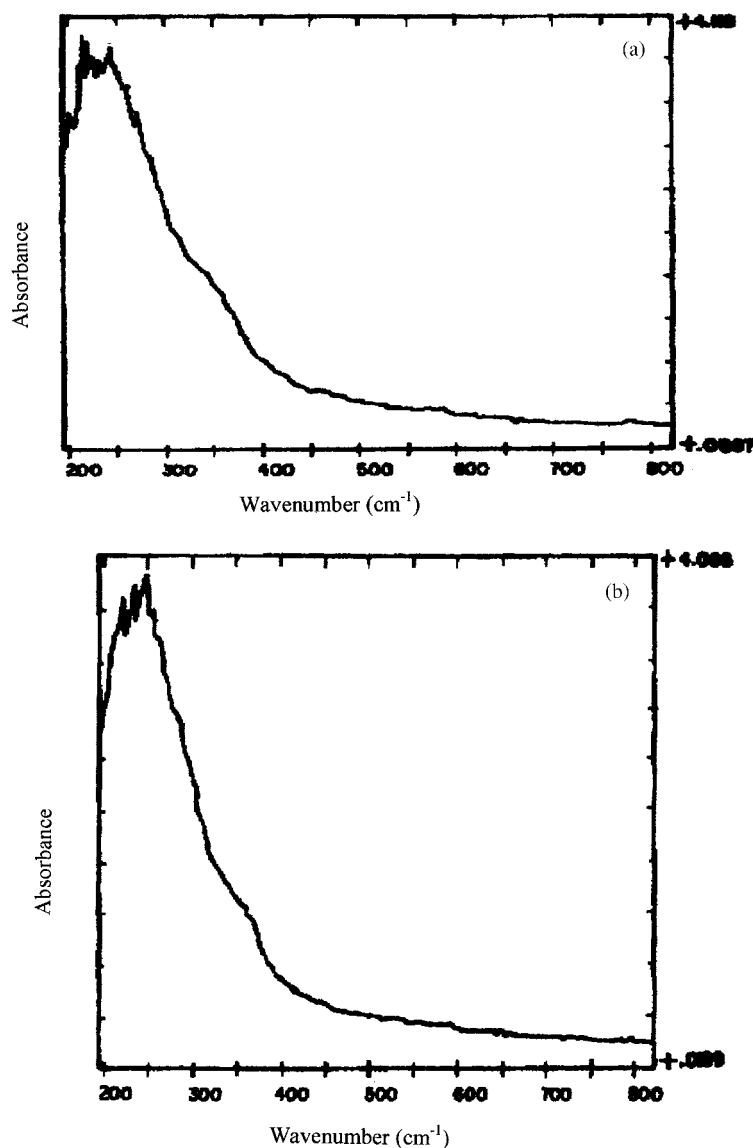


Figure 10 (a) Absorption spectrum in UV-VIS of LDPE-Fe₂O₃-PAA matrix (S₆): 0.2% Fe₂O₃; 0.4% PAA. (b) Absorption spectrum in UV-VIS of LDPE-Fe₂O₃-PAA-Eu³⁺-Tb³⁺ matrix (S₈): 0.3% Fe₂O₃; 1.2% PAA; 31.6% Tb³⁺.

not show any evidence of energy transfer from UO₂²⁺ to Eu³⁺ ions after the ion exchange in the modified matrix.¹³ The change of the UO₂²⁺ ion by the Tb³⁺ ion avoided effects due to ion charge. Also, better-resolved luminescence peaks are expected for the Tb³⁺ ions. Even so, evidence of energy transfer from Tb³⁺ to Eu³⁺ ions in the matrix LDPE-PAA after ion exchange has not been clear. However, the results have shown the energy-transfer process from the matrix (LDPE-PAA) to Eu³⁺ ions for excitation at 265 nm. It is

known from the literature that the polymer component (PAA) has shown luminescence.¹⁷ It acts as an energy donor to the Eu³⁺ ions by superposition of the emission spectrum region of the modified matrix and the absorption spectrum region of the Eu³⁺ ion, as observed.

The energy-transfer mechanism is not clear yet. Suggested is a direct one-step quenching mechanism of the excimer species (carbonyl groups from PAA and alkyl groups from LDPE matrix) to the acceptor (Eu³⁺ ion). The carbonyl

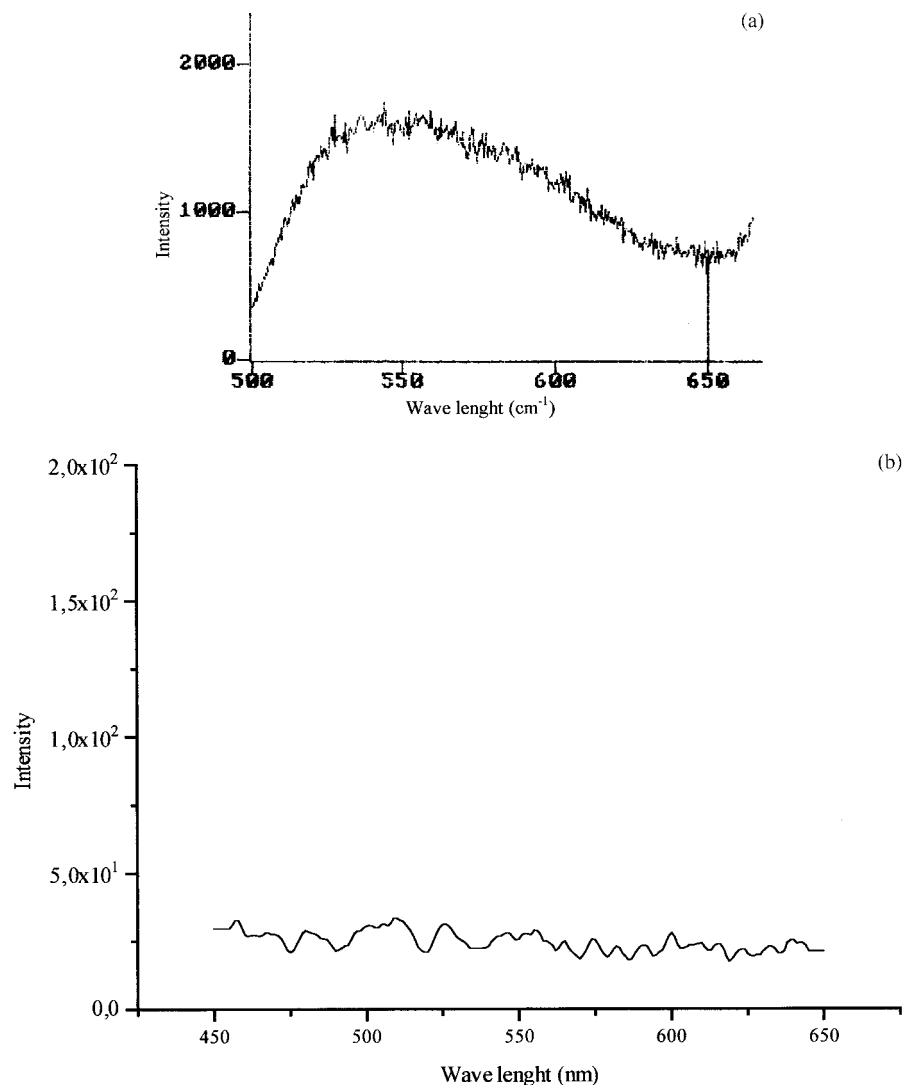
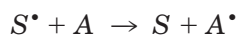


Figure 11 (a) Fluorescence spectrum of LDPE-Fe₂O₃ matrix (S₆): 0.2% Fe₂O₃; 0.4% PAA. Excitation: 395 nm. (b) Fluorescence spectrum of LDPE-Fe₂O₃ matrix (S₆): 0.2% Fe₂O₃; 0.4% PAA. Excitation: 265 nm.

groups from the side chain, which does not interact with the counterions (Eu³⁺ or/and Tb³⁺ ions) due to steric hindrance, are excited, transferring energy to the complex produced in the matrix (carboxylate group-counterion). According to the literature, the energy-transfer process can be observed if the distance between the complex species is in the range of 20–50 Å.¹⁷

So



where, S^{*} is the donor excited species (carbonyl chromophore from PAA or/and alkyl group from

the matrix); A, the acceptor species (complex carboxylate-Eu³⁺ counterion); S, the quenched donor species; and A^{*}, the excited acceptor species.

Clearly, the energy transfer from Tb³⁺ to Eu³⁺ ions in LDPE-PAA after the simultaneous Eu³⁺ and Tb³⁺ ions exchange was not observed. This may be explained by

- (i) steric hindrance during the ion exchange; or
- (ii) a mask effect of energy transfer from the matrix to Eu³⁺ ions (excitation at 265 nm).

Previous information on the iron(III)-doped modified matrix, LDPE-Fe₂O₃-PAA, showed the

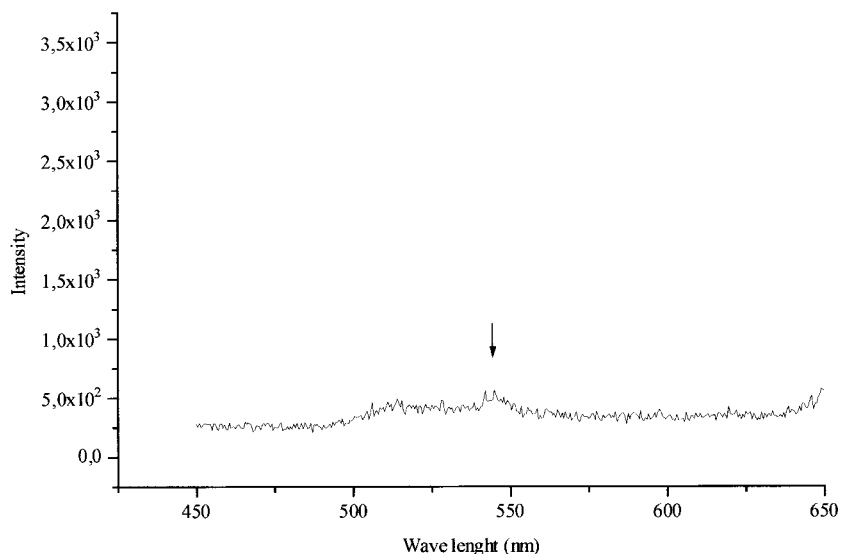


Figure 12 Fluorescence spectrum of LDPE-Fe₂O₃-PAA-Tb³⁺ matrix (S₇): 0.3% Fe₂O₃; 0.4% PAA; 3.3% Tb³⁺. Excitation: 265 nm.

encapsulation of Fe₂O₃ particles by PAA in the LDPE matrix.¹ The formation of hydroacrylates and acrylates in the surface of Fe₂O₃ particles become closer to the free carboxylic groups of PAA. Added to that, the quenching effect of iron(III) in the matrix, which shows a maximum absorption at about 265 nm, had avoided the

emission of the matrix and, consequently, the excitation of Eu³⁺ ions by energy transfer from the matrix as observed for the LDPE-PAA matrix. So, the Eu³⁺ ion emission (excitation at 265 nm) in the matrix LDPE-Fe₂O₃-PAA after simultaneous Tb³⁺ and Eu³⁺ ion exchange was assumed to be an energy-transfer process from Tb³⁺ to Eu³⁺ ions.

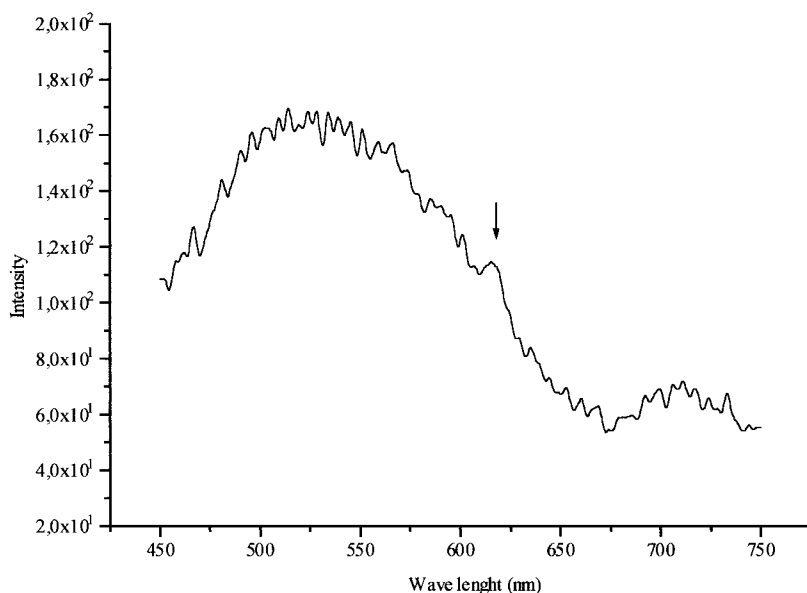


Figure 13 Fluorescence spectrum of LDPE-Fe₂O₃-PAA-Eu³⁺-Tb³⁺ matrix (S₉): 0.2% Fe₂O₃; 1.6% PAA. Excitation: 395 nm.

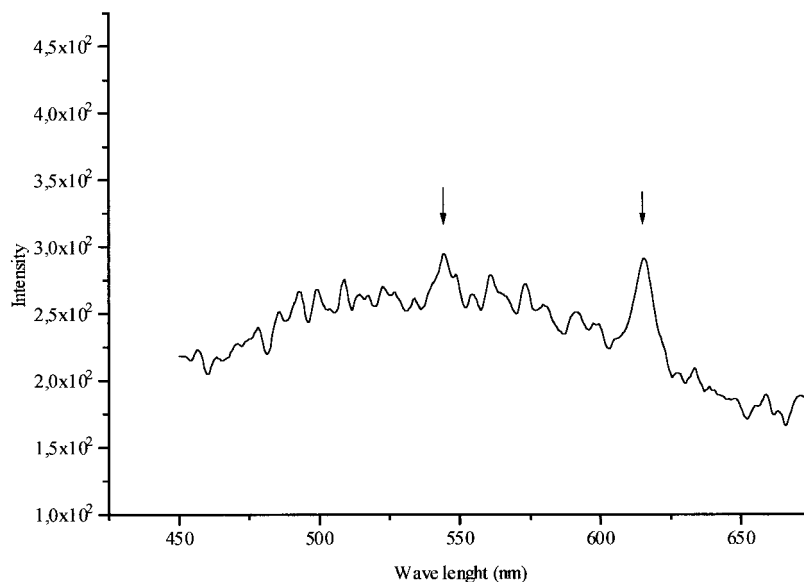


Figure 14 Fluorescence spectrum of LDPE-Fe₂O₃-PAA-Eu³⁺-Tb³⁺ matrix (S₉): 0.2% Fe₂O₃; 1.6% PAA. Excitation: 265 nm.

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