Enhancement of the Luminescent Intensity of the Novel System Containing Eu^{3+}-β-Diketonate Complex Doped in the Epoxy Resin

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ABSTRACT: Photoluminescent properties of the europium tris(thenoyltrifluoroacetonate) dihydrate [Eu(TTA)$_3$(H$_2$O)$_2$] incorporated in epoxy resin in the solid state are reported. The polymeric Eu^{3+} complex and the precursor compound were characterized by elemental analysis, thermogravimetry (TG), differential scanning calorimetry (DSC), infrared spectroscopy, nuclear magnetic resonance (NMR), and electronic spectroscopy. Due to efficient energy transfer from the polymer to the rare earth ion, the polymer phosphorescence intensity was observed to decrease with an increase of the Eu^{3+} ion concentration. High values of the Ω_2 intensity parameter were obtained, reflecting the hypersensitive character of the $^5D_0 \to {}^7F_2$ transition and indicating that the Eu^{3+} ions are in a highly polarizable chemical environment. This is consistent with systems containing epoxy resin that generally show a higher value for the Ω_4 parameter as a consequence of the difference in the basicity of the oxygen donor from the polymer. Lifetime measurement (τ = 0.442 ms) suggests that the Eu^{3+} luminescence has a higher efficiency than in the case of hydrated compound (τ = 0.260 ms). The emission quantum efficiency shows higher luminescence for the polymer containing 1% of Eu^{3+}-β-diketonate complex. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2716–2726, 2002

Key words: epoxy resin; europium; luminescence; diketonate complex

INTRODUCTION

The epoxy resins are a class of materials characterized by a chemical structure containing two or more epoxy groups or oxirane rings per molecule. The widely used epoxy resins are prepared from the reaction of epichlorohydrin with a dihydroxy compound such as bisphenol-A (Fig. 1). The epoxy structure of the diglycidyl ether of bisphenol-A (DGEBA) can be cured by a variety of crosslinking agents known as hardeners or catalysts that promote self-polymerization.[1] These kinds of resin are largely used in areas such as coatings, encapsulates, and composite materials.[2,3] The literature describes the improvement of physical properties as stabilization against photodegradation,[4] for example, by the incorporation of the methacryloyl moiety in the epoxy resin.[5]

The luminescent properties of rare earth complexes with various organic ligands are reported in the literature.[6–14] The europium ion has advantageous luminescent properties for the complex,[15] as follows: (a) narrow emission bands (f–f
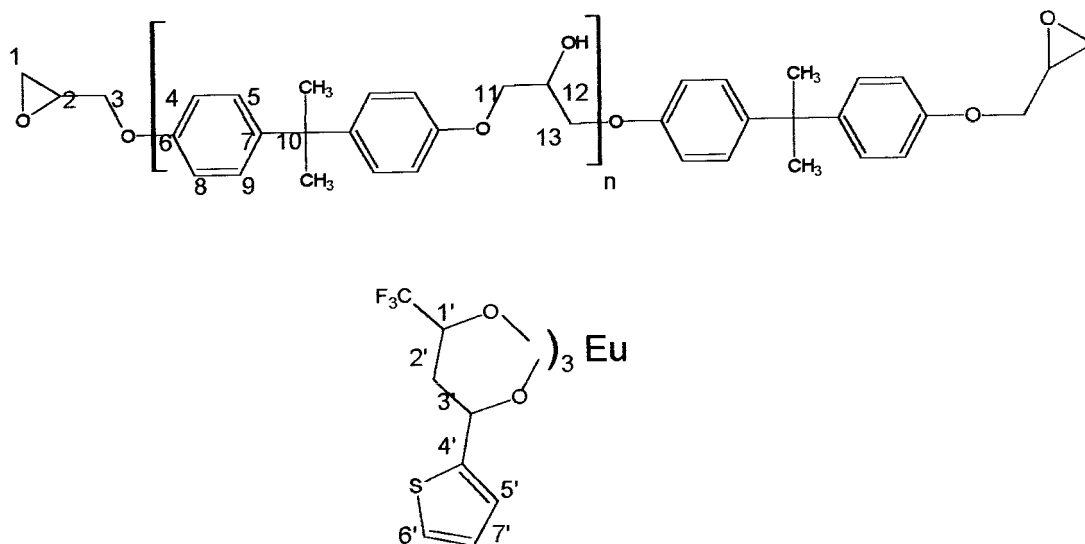

Figure 1 Molecular structures related to the resin and the europium complex.

transitions forbidden by Laporte rule) leading to monochromatic red emission color; (b) the main excited state is the emitting $^5D_0$ level separated around 12,000 cm^{-1} from the ground terms ^7F_J (J = 0 up to 6); (c) the totally symmetric shape of the $^5D_0$ and $^7F_0$ levels evidencing that the Eu^{3+} ion occupies identical site symmetries of the type C_s, C_n, or C_{nv}. This requisite facilitates the interpretation of the optical data and provides information on the eventual existence of more than one site symmetry being occupied by the Eu^{3+} ion; (d) the $^5D_0 \rightarrow {}^7F_1$ Stark level is usually taken as a reference transition[6] because it is allowed by magnetic dipole, and consequently, the intensity of this transition is not considerably altered by the perturbing ligand field; (e) long lifetimes of the emitting $^5D_0$ level (ms); and (f) large Stokes shift.

The rare earth ion as a hard acid has strong preference for negatively charged atom in the following order: fluorine, oxygen, nitrogen, or sulfur. This justifies the facilities to rare earth ions to bind with water, β-diketonates, carboxylates, nitrates, fluoride, perchlorates, sulfoxides, N-oxide, and other ligands.[9–14,16] The rare earth ions have low electronegativity and strong oxophilicity that allows the metal to coordinate to the oxiranic oxygen of an epoxy ring. These trivalent metal ions present large ionic radii (1.160–0.870 Å, CN = 8) and the chemical environment can alter their coordination sphere.[17] These facts allow modifying structures in the epoxide network.

Some studies of synthesis and spectroscopic properties of polymer doped with rare earth

ions,[18–22] for example, the combination of polyethylene glycol with europium or terbium ions, was verified in presence and absence of 2,2'-bipyridine. In these systems, an increase in the luminescence intensity and decay time was observed when increasing the polymer concentration.[18] In the example of the poly(acrylic acid) doped with Eu^{3+} ion, a decrease of the polymer phosphorescent intensity with an increase of the Eu^{3+} concentration was shown, owing to the complex formation.[19]

The photoluminescence study of Eu^{3+} complexes with β-diketonate anion (TTA$^-$) was increased in this last decade because of its high luminescence.[6–10] These complexes can be seen as light conversion molecular devices, assuming the term antenna effect, to denote the efficiency in the sequence of absorption, energy-transfer, and emission involving distinct absorbing and emitting components.[10] Consequently, this system is promising in potential applications as optical markers, optical sensors, fluoroimmunoassays, and clinical area.

The great advantage of the use of europium tris-(thenoyltrifluoroacetonate) dihydrate [Eu(TTA)$_3$-(H$_2$O)$_2$] precursor compound as doping in polymeric host matrices is the high luminescence, owing to the energy transfer efficiency via triplet state (T) of the TTA ligand to emitting $^5D_0$ level of the trivalent europium ion. This TTA$^-$ anion acts as an excellent bidentate chelating agent that protects the rare earth ion of other water molecules by the chelating effect.[6] In addition, there is the possibility of increasing the luminescence ef-

ficiency of this β-diketonate complex by partial substitution of water molecules coordinated by a polymer that will act as a sensitizer in the chelate complex.[22]

In the present study, we have reported the synthesis, characterization, and luminescent properties of the Eu^{3+}-β-diketonate precursor compound when doped in the epoxy resin at a ratio of 1, 5, and 10 in mass percentages. The goal of the study was to obtain information about the photoluminescent behavior of the polymer doped 1, 5, and 10% w/w of Eu^{3+}-β-diketonate complex.

EXPERIMENTAL

Synthesis of the Eu^{3+}-β-Diketonate and Eu Complex Polymer System

The hydrated compound complex was prepared by the method described by Charles and Ohlmann.[23] The difference was that the complex solution was heated at about 60°C for a period of 12 h to eliminate the possible formation of the trihydrated complex. The solid was purified with acetone and dried in vacuum desiccators over anhydrous calcium chloride at room temperature overnight. The Eu^{3+} content was estimated by complexometric titration with EDTA, where the compound was dissolved in methanol by using xylenol orange as an indicator. The carbon, hydrogen, and sulfur contents were determined by usual microanalytical procedures using elemental analyzer CHN 2400 model (Perkin–Elmer, USA).

The epoxy resin is a diglycidyl ether of bisphenol-A (Araldite GT 7004) obtained from Ciba-Geigy with epoxy 720 g/equiv. In the preparation of the luminescent polymeric material, Eu^{3+}-β-diketonate, doped into the epoxy resin, was utilized in the mass ratios of 1, 5, and 10% (w/w) of Eu^{3+} complex to epoxy resin where the solid europium-hydrated precursor was dissolved in acetone. The epoxy resin was also dissolved in acetone and added to the solution of the Eu^{3+}-β-diketonate in each specific mass ratio. These solutions were heated at 60°C (about 15 min) and stirred until complete evaporation of the solvent to obtain the solid product. The three compounds of Eu^{3+}-β-diketonate doped in epoxy resin were identified as polymer 1%, polymer 5%, and polymer 10%.

Measurements

Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were obtained with a TG-50 thermobalance (Shimadzu) by using platinum crucibles with 2 mg of the sample, under dynamic air atmosphere (50 mL min^{-1}), at heating rate of 10°C min^{-1}. Differential scanning calorimetry (DSC) curves were obtained with a DSC-50 cell (Shimadzu) by 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 system was calibrated with indium (mp 156.6°C; ΔH = 28.54 Jg^{-1}).

The infrared absorption spectra of the solid samples were measured in the range 4000–400 cm^{-1} in KBr pellets by using a Bomem model MB102 FTIR spectrophotometer.

The NMR spectra were recorded in an Avance DPX spectrophotometer operating at 300 MHz. The ^{1}H-NMR was calibrated with tetramethysilane (TMS) as internal standard and the ^{13}C-NMR with the solvent peak of deuterated acetone [δ_C 2.04 ppm of $(CD_3)_2CO$ as internal standard].

The excitation and emission spectra of the powdered samples were performed in a SPEX Fluorolog-2 spectrofluorometer, model FL212 system, double-grating 0.22 m SPEX 1680 monochromators, 450 W Xenon lamp, as an excitation source using the front face mode. This apparatus was fully controlled by a DM3000F spectroscopic computer. The lifetime measurements were recorded at room and nitrogen liquid temperature by using the phosphorimeter (SPEX 1934D) accessory coupled with the spectrofluorometer.

RESULTS AND DISCUSSION

The europium percentage in the hydrated precursor was determined by complexometric titration with EDTA in methanol solution. The C, H, and S contents were determined by microanalytical procedures. The percentages found/calculated are C: 33.61/33.85; H: 1.88/1.89; 12.30/11.30; Eu^{3+}: 17.45/17.85, respectively. These results are consistent with the general formula [Eu(TTA)$_3$-(H$_2$O)$_2$].

The TG data from [Eu(TTA)$_3$(H$_2$O)$_2$] showed one first event in the range of 90–120°C with a mass loss of 4.3% corresponding to the water molecules in the hydrated complex that corroborated with the microanalytical procedures. The anhydrous compound is thermally stable until 190°C. The TG curves obtained under oxidative atmosphere of air showed a decrease of the temperature onset of oxidation to the doped polymeric system, indicating a thermal stability lower than
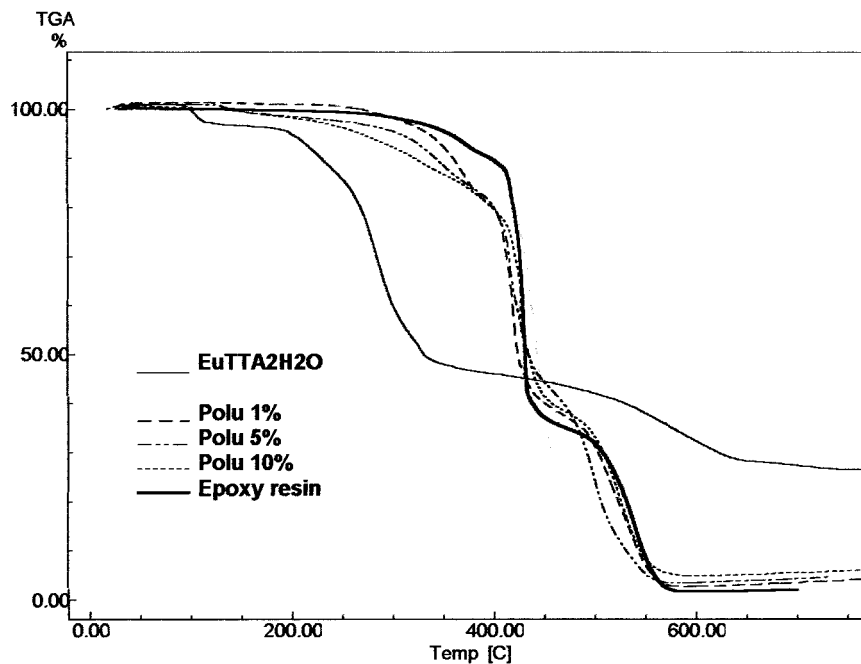
(a)
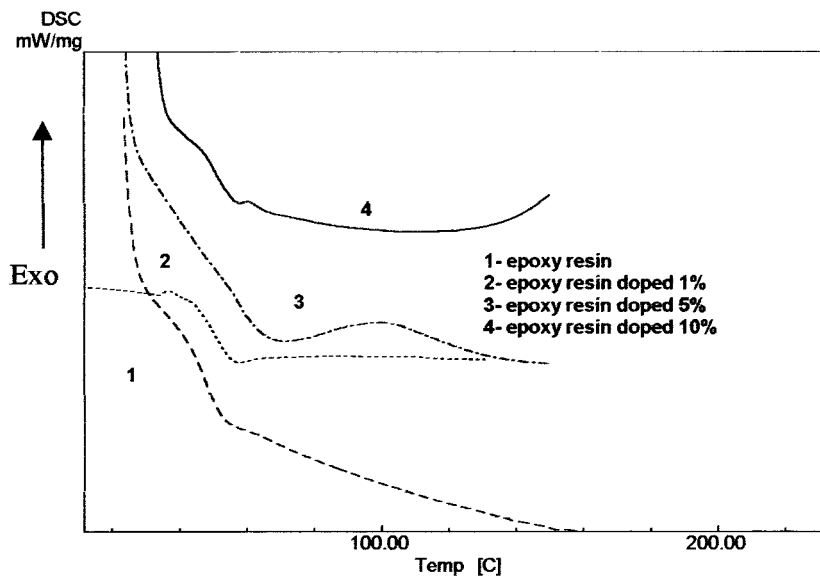
(b)

Figure 2 Thermal analysis curves of the epoxy resin (free) and doped with 1, 5, and 10% $[Eu(TTA)_3(H_2O)_2]$, at a heating rate of 10°C/min; (a) TG data recorded in air dynamic atmosphere; (b) DSC data recorded in dynamic atmosphere of nitrogen. Displacement of glass transition (T_g) from 43°C of original resin to 46, 54, and 58 for 1, 5, and 10% doped polymers, respectively.

that of nondoped polymeric samples [Fig. 2(a)]. The thermogravimetric data show that the epoxy resin is more resistant in terms of oxidative thermal degradation than those polymeric samples doped with Eu^{3+}-β-diketonate (Table I), indicating that an introduction of the europium complex into the resin decreases its thermal stability. On the other hand, the doped polymers are stable until 270°C as t_{onset} of degradation. The TG/DTG data of the polymer Eu^{3+} complex show absence

Table I   Temperature of Onset of Mass Loss (T_{onset}) and Glass Transition (T_g) of the Doped Samples Compared to the Original Polymer at a Heating Rate of 10°C/min

Species	T_{onset} (°C) in Air	T_g (°C)
Epoxy resin	372	43.0
Polymer, 1%	329	48.0
Polymer, 5%	306	54.0
Polymer, 10%	272	58.0

of the loss mass event in the range of 90–130°C, suggesting that the interaction between the Eu^{3+} complex and polymer occurs via replacement of the water molecules in the coordination compound.

It is noted that the loss mass of this system in the interval temperature of 200 to 590°C occurs with the TTA and resin degradation. According to Figure 2(a), the degradation was observed accelerating with the increase in the Eu^{3+} complex concentration (1, 5, and 10%). On the other hand, it is verified that at 590°C the residual solid was produced and above this temperature there is no mass loss.

The DSC results in Figure 2(b) showed a displacement of glass transition (T_g) from 43°C of the original resin to 46, 54, and 58°C for the 1, 5, and 10% doped in polymer, respectively. The Eu^{3+} ion in complex is coordinated to epoxy resin changing the T_g temperature.

The IR spectra of samples of the polymer Eu^{3+} complex presented a large complexity of peaks. The peaks related to the H_2O vibrational modes in the $[Eu(TTA)_3(H_2O)_2]$ complex were attributed at 3500–3200 cm^{-1} (ν_s and ν_{as} OH) and at 1630–1600 cm^{-1} (HOH bending).[6,24] In the case of the polymer complex system, the absence of these bands cannot be confirmed because of strong absorptions of the resin part in those regions. In the examination of the IR spectral data of the polymer doped with Eu^{3+}-β-diketonate complex, the characteristics peaks at 1138 cm^{-1} attributed to $\nu_{as}(CF_3)$ and 933 cm^{-1} of $\nu(C=C + C=O)$ were verified, indicating the presence of TTA^- in the polymer complex. The epoxy resin peak at 950 cm^{-1} that was attributed to $\delta_{ax,ass}$ (COC) of oxirane ring in the original resin was displaced to 900 cm^{-1}, suggesting an interaction between the Eu^{3+} ion and the ether oxygen oxirane group, probably with substitution of the water molecules in the complex.[20]

The ^{1}H-NMR results were attributed according to ref. [25]. The spectrum of the original resin presents epoxy ring protons, H (—OCH—) occurring at δ 2.77 ppm and H (—OCH$_2$—) at 2.82 ppm. The doped polymer shows displacement of those protons. The H (—OCH$_2$—) was displaced to δ 3.11 ppm, and the H (—OCH—) was displaced to δ 3.08 ppm, as illustrated in Figure 3(b). This fact suggests the interaction of the trivalent europium ion with the oxygen atoms of the epoxy rings.

The ^{13}C-NMR data of the epoxy resin are presented in Table II. The carbon atoms of the aromatic ring showed typical absorption at 144.0, 129.5, and 114.7 ppm. The oxirane ring showed peaks at 50.6 ppm C (—CH—) and C (—CH$_2$—) at 44.2 ppm. The C atom of the secondary alcohol occurs at 69.3 ppm. The methyl group of the bisphenol occurs at 31.1 ppm and the carbon atoms of —CH$_2$O— at 70.0 and 70.1 ppm.

The ^{13}C-NMR spectra of the Eu^{3+}-β-diketonate precursor showed carbon atoms of the thiophene ring at 135.9, 127.0, and 124.4 ppm; C (—CF$_3$—) at 95.6 ppm; C (—CH$_2$—) at 52.3 ppm; and C (—C=O) at 163.3 ppm of the TTA^- group.

The ^{13}C-NMR spectra of the doped polymer (10%) showed small peaks of the complex at 124.4, 127.0, and 135.9 ppm attributed to the thiophene ring, as illustrated in Figure 3(a). In addition, these data show peaks characteristic of the diglycidyl ether indicated by the C's of aromatic ring (at 144.0, 128.5, and 114.8 ppm) and C (—CH$_2$O—) group at 70.15 and 70.0 ppm. It was also observed that the peaks related to the C from the oxirane ring at 50.6 ppm C (—CH—), 44.2 ppm (—CH$_2$—), and of the bisphenol were detected at 31.37 ppm C (—CH$_3$). These NMR results indicate the presence of the Eu^{3+}-diketonates and epoxy resin species in combined form. It is important to report that the ^{1}H-NMR data were also obtained to the epoxy resin doped with 1 and 5%, confirming the same displacements.

Figure 4 shows the excitation spectra of the epoxy resin doped with Eu^{3+} complex in the ratio 1, 5, and 10 in percentage, which were recorded in the range of 250 to 500 nm at nitrogen liquid temperature. The excitation was monitored at 612.6 nm, corresponding to the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition. The narrow absorption band around 460 nm ($^7F_0 \rightarrow {}^5D_2$ transition) verified for all doped samples is characteristic of f $\leftrightarrow$ f transitions of the rare earth ion. On the other hand, the high-intensity bands in the range of 270–450 nm are typical of the thenoyltrifluoroacetonate enveloped with the $^7F_0 \rightarrow {}^5G_6, {}^5H_4, {}^5L_6$ transitions from Eu^{3+} ions. It is observed in Fig-
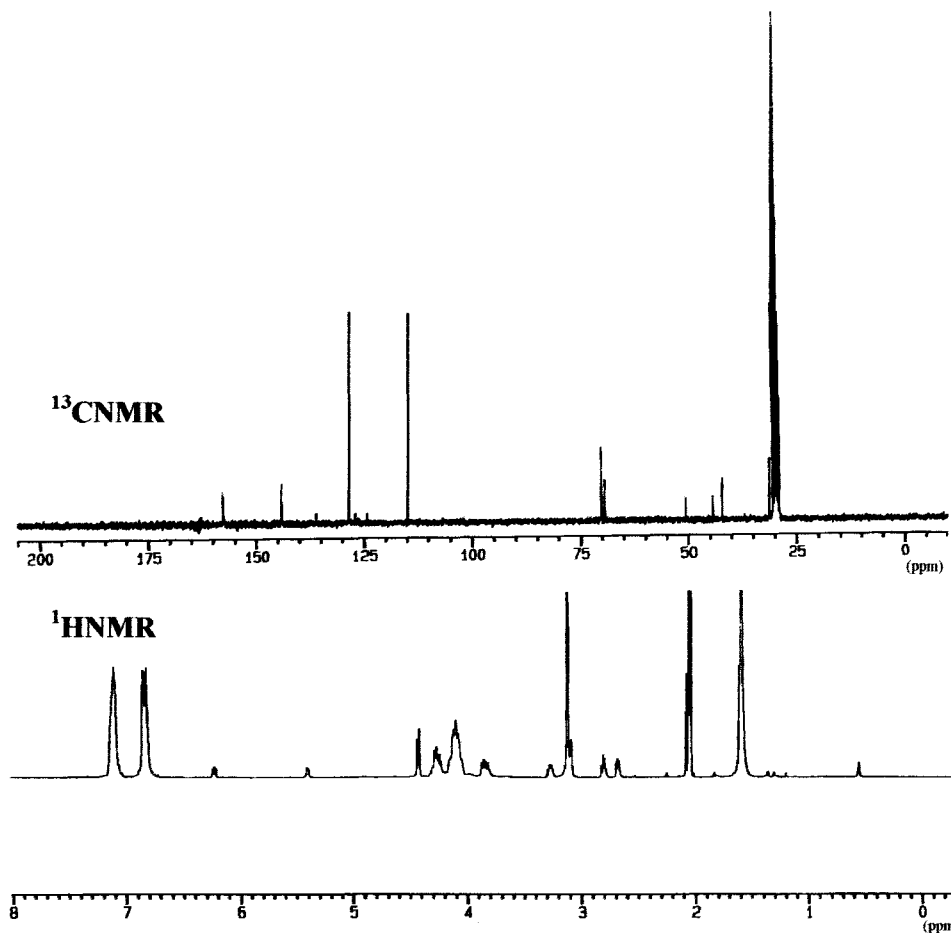
Figure 3 ^{1}H- and ^{13}C-NMR spectra of the epoxy resin doped with 10% of Eu^{3+}-β-diketonate complex.

ure 4 that an increase in the absorption intensities of these bands increases the europium complex concentration in the polymer in a ratio of 1, 5, and 10%.

Figure 5(a) shows the emission spectra of the polymer doped with [Eu(TTA)$_3$(H$_2$O)$_2$] in 1, 5 and 10% recorded in the range of 420–720 nm by monitoring the excitation around 394 nm at 77 K. Their profile bands are the same at room temperature, but the resolution observed is higher at lower temperature. This fact confirms that no significant structural change occurs at low temperature. According to the $^5D_0 \rightarrow {}^7F_0$ transition about 579 nm [Fig. 5(a)], no splitting is noted when perturbed by the polymer and TTA anion (ligand field) around Eu^{3+} ion, which suggests the existence of only one site symmetric to the rare earth ion. The hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition around 615 nm, forced electric dipole transition, is more intense than $^5D_0 \rightarrow {}^7F_1$ (magnetic dipole-allowed transition), indicating that the

Eu^{3+} ion is not found in a site symmetry with inversion center. Comparing qualitatively the three spectral profiles of doped polymers in the range of 560 up to 720 [Fig. 5(a)], the increase of the luminescent intensity with the increase of the percentage (1, 5, and 10%) of the doped polymers is noted.

The inset of Figure 5(a) presents the polymer broad band around 475 and $^5D_1 \rightarrow {}^7F_J$ transitions ($J = 0$, 1, and 2) from Eu^{3+} ion in the range of 457–525 nm at 77 K. It is observed that a decrease of the polymer band intensity with the increasing concentration of the precursor Eu^{3+} complex became more intense with the $^5D_1 \rightarrow {}^7F_{0,1,2}$ transitions. It is also observed in the inset spectra that one deflection around 460 nm for all species is due to self-absorption of the $^7F_0 \rightarrow {}^5D_2$ transition in these polymeric systems (see Fig. 4).

According to the luminescence data of the precursor, hydrated [Fig. 5(b)] and doped polymer [Fig. 5(a)] was verified that the splitting of the

Table II   NMR Data from the Eu Complex, the Epoxy Resin, and the Epoxy Resin Doped with the Eu Complex

	H (δ ppm)	C (δ ppm)	Doped Epoxy Resin (^{1}H δ ppm)	Doped Epoxy Resin (^{13}C δ ppm)
CH$_2$ (1)	2.82	44.41	3.11	44.40
CH (2)	2.77	50.60	3.08	50.60
CH$_2$ (3)	4.28; 4.08	70.18; 70.06	4.28	70.17; 70.04
CH$_2$ (11)				
CH (4)	6.85	114.83	6.85	114.81
CH (8)				
CH (5)	7.12	128.47	7.12	128.45
CH (9)				
C (6)	—	157.7	—	157.0
C (7)	—	144.0	—	144.0
C (10)	—	42.26	—	42.24
CH (12)	3.8	69.34	3.8	69.3
CH$_3$	1.61	31.4	1.60	31.6
OH	4.41	—	4.40	—
CH (13)	4.08	—	4.40	—
CF$_3$	—	95.6	—	No
CO (1′)	—	163.0	—	No
CH$_2$ (2′)	4.36	52.3	No	52.3
CO (3′)	—	163.0	—	No
C (4′)	—	136.0	—	136.0
C (5′)	7.09	124.4	7.04	124.4
C (6′)	6.18	127.0	6.18	127.0
C (7′)	5.3	124.4	5.3	124.4

No, not observed.

hypersensitive $^5D_0 \rightarrow {}^7F_2$ transitions are very different. This indicates that the Eu^{3+} ions are found in distinct chemical environments in the three species.

The experimental intensity parameters, Ω_2 and Ω_4, were determined from the emission spectra of the Eu^{3+} ion by using the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ transitions, respectively, and estimated according to [26]:

$$A_{0J} = \frac{4e^2\omega^3}{3\hbar c^3} \chi \sum_\lambda \Omega_\lambda \langle {}^7F_J \| U^{(\lambda)} \| {}^5D_0 \rangle^2 \quad (1)$$

where $\lambda = 2$ and 4; A_{0J} is the coefficient of spontaneous emission; χ is the Lorentz local field correction term that is given for $\chi = n(n^2 + 2)^2/9$ with the refraction index $n = 1.5$; and $^7F_J \| U^{(\lambda)} \| {}^5D_0{}^2$ are the reduced matrix elements whose values are 0.0032 and 0.0023 to $J = 2$ and 4, respectively.[27] The coefficient of spontaneous emission, A, in eq. (1), is obtained by summing the values of the A_{0J} corresponding to $^5D_0 \rightarrow {}^7F_J$ transitions and each value of the A_{0J} coefficient, with $J = 2$ and 4, was determined by taking the magnetic dipole allowed

$^5D_0 \rightarrow {}^7F_1$ transition as reference, because of its intensity to be considered insensitive to ligand environment. The emission spontaneous coefficient, A_{01}, is given by the expression $A_{01} = 0.31 \times 10^{-11}(n)^3(\nu_{01})^3$ and its value is estimated[10] to be about 50 s^{-1}.

The intensity spectroscopic parameters, Ω_2 and Ω_4, are presented in Table III. The values of the Ω_2 parameters of the Eu^{3+} complexes doped in polymer increase following the order: $1 < 5 < 10$ in percentage (27.7, 33.8, and 35.4, respectively). This suggests that the interaction of metal–polymer increases with the concentration of Eu^{3+} ion, but is not linear, reflected through the high value of the Ω_2 parameter. Therefore, the highest value of the Ω_2 is observed to the system with 10% in concentration reflecting the higher hypersensitive behavior of the $^5D_0 \rightarrow {}^7F_2$ transition. This can be explained in terms of the steric effect and strong interaction of the negative charge (oxygen) in the polymer with the metal ion, suggesting that the Eu^{3+} ion is in a highly polarizable chemical environment.
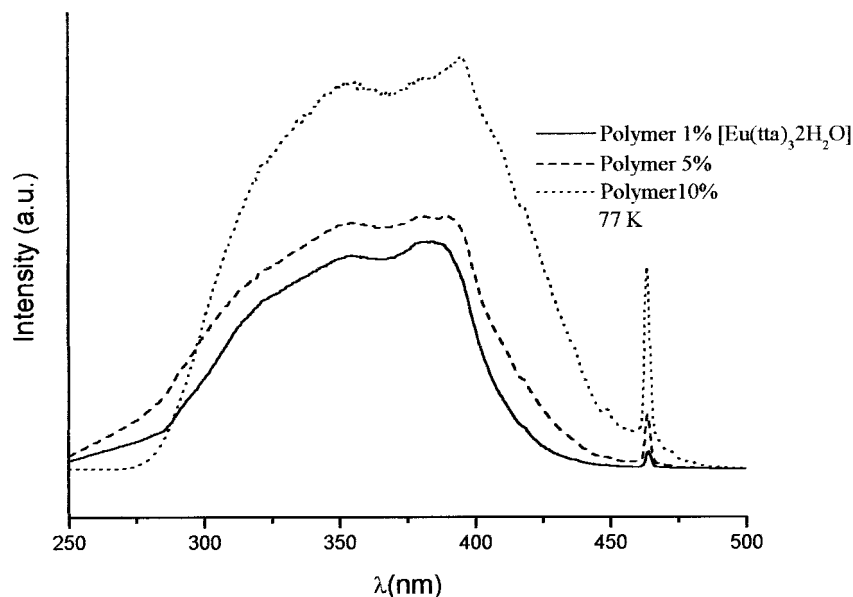
Figure 4   Excitation spectra of the epoxy resin doped with [Eu(TTA)$_3$(H$_2$O$_2$)] complex, at nitrogen liquid temperature, under excitation at hypersensitive transition around 614 nm in the following concentrations: (a) polymer 1%; (b) polymer 5%; and (c) polymer 10%.

According to the Ω_4 parameters, in Table III, $\Omega_4 = 4.6$ to the precursor compound compared with ($\Omega_4 \sim 10$) of doped polymer species, proving a perturbation of the chelate effect of the TTA anion ion on the Eu^{3+} ion by the steric factors of the diglycidyl ether on the chelate structure of the TTA ligands. In this case, it does not hinder the epoxy resin to bind to the europium ion.

Table III presents the lifetimes (τ) of the ^{5}D$_0$ emitter state of the precursor compound and Eu^{3+}-diketonates doped in the epoxy resin measured at room temperature. The decay curves show only a single exponential, suggesting that there is no other depopulation channel for the emitting ^{5}D$_0$ level. By comparing the lifetimes between the hydrated precursor with those of doped polymer, an increasing in the lifetimes of these systems is observed, as expected, from the nonradiative decay channel, owing to vibronic coupling of the water molecules in the [Eu(TTA)$_3$(H$_2$O)$_2$] complex.

The lifetime (τ), nonradiative ($A_{n\text{rad}}$), and radiative (A_{rad}) rates are related through the following equation:[10]

$$A_{\text{tot}} = \frac{1}{\tau} = A_{\text{rad}} + A_{n\text{rad}} \qquad (2)$$

The emission quantum efficiency (η) of the emitting ^{5}D$_0$ state were determined by using

$$\eta = \frac{A_{\text{rad}}}{A_{\text{rad}} + A_{n\text{rad}}} \qquad (3)$$

where the nonradiative contributions in eq. (2) are obtained by $A_{n\text{rad}} = A_{\text{tot}} - A_{\text{rad}}$. The radiative rates A_{rad} in eq. (2) are evaluated from the relative intensities of emission spectra by summing over the radiative rates A_{0J} arising from ^{5}D$_0 \rightarrow$ ^{7}F$_J$ Stark levels ($J = 0$–4).

As shown in Table III, the 1% polymer presents a smaller A_{tot} value than the hydrated precursor and the two other doped systems because of the smaller value of the nonradiative contribution ($A_{n\text{rad}} = 1229$ s^{-1}). The similar values of decay rates for the 5 and 10 (%) doped species indicated concentration quenching of luminescence also reflected in the quantum efficiency values determined by eq. (3). The doped polymer (1, 5, and 10%) present higher quantum efficiency values than hydrated precursor compound, proving that the polymeric matrices act as a sensitizer, reinforcing the energy transfer from the TTA ligand to the Eu^{3+} ion in these systems.

The R_{02} intensity parameter that is the ratio between the intensities of the ^{5}D$_0 \rightarrow$ ^{7}F$_0$ and ^{5}D$_0$ $\rightarrow$ ^{7}F$_2$ transitions was determined for the precursor compound and for the polymer-based complexes (Table III). The R_{02} parameter may give information on the J-mixing effect associated with the ^{5}D$_0 \rightarrow$ ^{7}F$_0$ transition, as described in
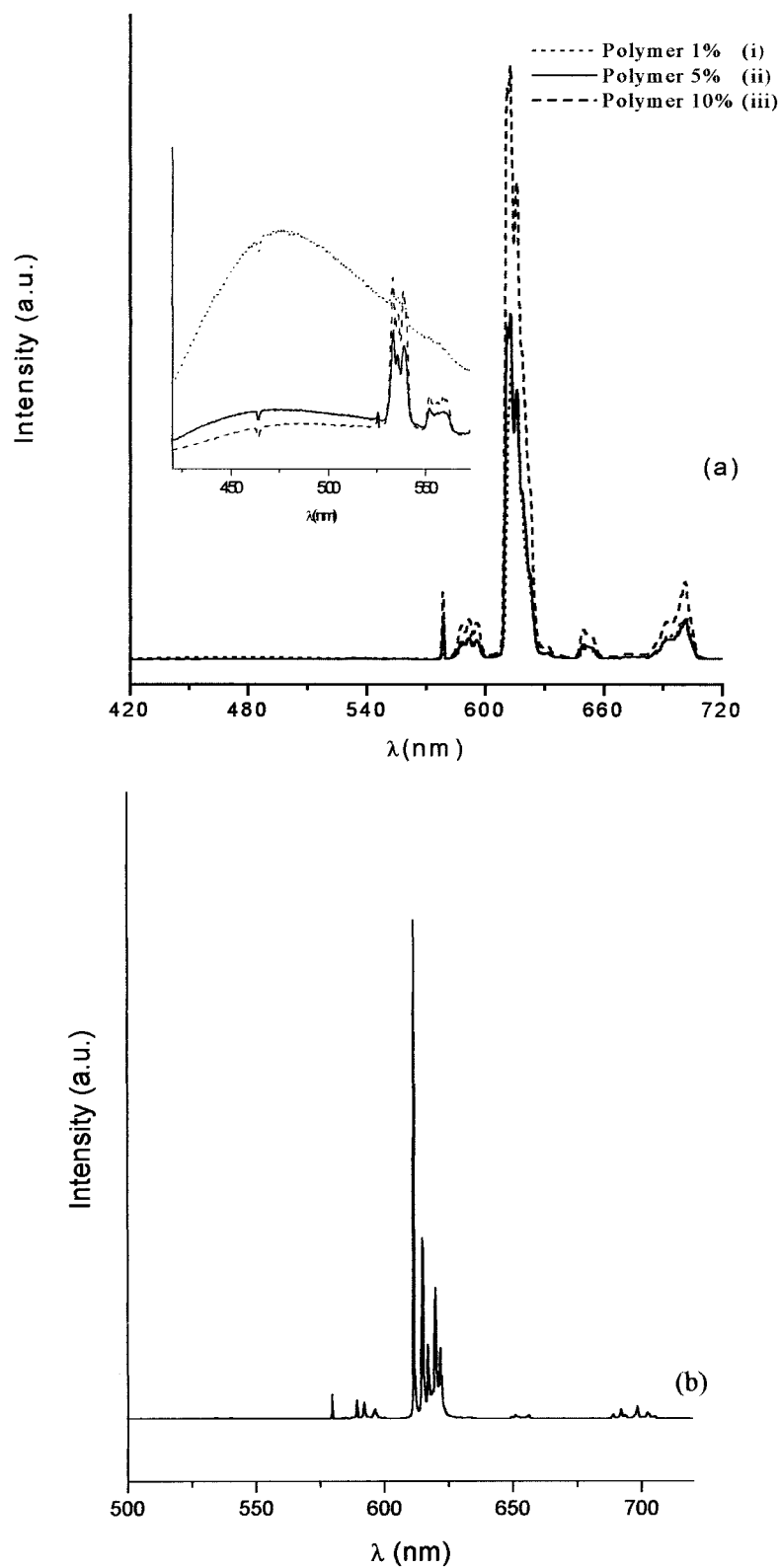
Figure 5   (a) Emission spectra of the epoxy resin doped with Eu^{3+} complex, at 77 K, with excitation in $^7F_0 \rightarrow {}^5L_6$ from the Eu^{3+} ion around 394 nm in the following concentrations: (i) polymer 1%; (ii) polymer 5%; and (iii) polymer 10%. The insert shows a zoom of the $^5D_1 \rightarrow {}^7F_J$ levels ($J = 1, 2,$ and 3) in the range of 420–570 nm; (b) emission spectra of the $[Eu(TTA)_3(H_2O)_2]$ at 77 K.

Table III Photoluminescent Data of the Polymer Doped with the [Eu(TTA)$_3$(H$_2$O)$_2$] Complexes in the Ratio of 1, 5, and 10%, in Solid State, Experimental Intensity Parameters (Ω_2, Ω_4, R_{02}), Lifetimes (τ), Emission Coefficient, and Quantum Efficiency (η) Were Obtained at Room Temperature

Compounds	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	R_{02}	A_{rad} (s^{-1})	A_{nrad} (s^{-1})	A_{tot} (s^{-1})	τ (ms)	η (%)
[Eu(TTA)$_3$(H$_2$O)$_2$]	33.0	4.6	0.013	923	2923	3846	0.260	29.0
Polymer, 1%	27.7	10.3	0.005	1034	1229	2263	0.442	45.7
Polymer, 5%	33.8	9.3	0.011	1206	1949	3155	0.317	38.2
Polymer, 10%	35.4	9.9	0.011	1262	1913	3175	0.315	39.5

detail in ref. [27]. This effect is mainly due to the mixing between the $^7F_2$ manifold and the $^7F_0$ level through the rank two components of the environment chemical around the rare earth ion. We note the same R_{02} values obtained for the 5 and 10% polymer-based complexes (twice higher than the one observed for the 1% polymer complex).

CONCLUSION

The polymer doped with 1, 5, 10% of Eu^{3+}-β-diketonate complex were prepared and characterized by nuclear magnetic resonance (NMR), vibrational and electronic spectroscopy, DSC, TGA, and elemental analysis. The results demonstrated that the doped polymer is absent of water molecules, indicating the interaction of the oxygen from oxirane group with the metal ion of the Eu^{3+}-β-diketonate complex.

The highest value of the Ω_2 parameter for the 10% doped polymer indicates the higher hypersensitive behavior of the $^5D_0 \rightarrow {}^7F_2$ transition and a highly polarizable chemical environment around the Eu^{3+} ion. On the other hand, the Ω_4 values in the polymers suggested a perturbation of the chelate effect (TTA) due to steric factors.

The higher lifetimes of the emitting $^5D_0$ Stark level in the Eu^{3+} complex doped in polymer is associated with the absence of the water molecules in these systems. The similar values obtained for all the decay rates (A_{rad}, A_{nrad}, and A_{tot}) of the 5 and 10% complexes indicate the existence of concentration quenching of luminescence in these systems. The doped polymers present higher quantum efficiency values than [Eu(TTA)$_3$(H$_2$O)$_2$] complex, substantiating that the epoxy resin acts as a sensitizer reinforcing the energy transfer to the rare earth ion.

Finally, we note that the epoxy resin acts as an antenna absorbing energy that is then efficiently transferred to the Eu^{3+} energy levels, which shows enhancement of the luminescence intensity of the novel system.

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