

Characterization and Photoluminescence Properties of Diglycidyl Methacrylic Resin Doped with the Eu^{3+} - β -Diketonate Complex

D. F. Parra,¹ A. Mucciolo,² D. G. Duarte,¹ H. F. Brito,² A. B. Lugão¹

¹Centro de Química e Meio Ambiente, IPEN/CNEN, Avenida Lineu Prestes, 2242, Butantã, São Paulo-SP, Brazil

²Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, Caixa Postal 26077, 05599-970, São Paulo/SP, Brazil

Received 22 October 2004; accepted 23 May 2005

DOI 10.1002/app.23116

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Triaquatris(acetyl acetonate)europium(III) [$\text{Eu}(\text{acac})_3$] at 1, 5, 10, and 15% was doped in diglycidyl methacrylic (DGMA) resin, and their luminescent properties in the solid state are reported. These systems were characterized with elemental analysis, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and Fourier transform infrared spectroscopy. On the basis of TGA data, the thermal stability of the DGMA/ $\text{Eu}(\text{acac})_3$ x% system was similar to that of the polymer, except at the highest concentration (15%). The DSC results indicated that the new systems were chemically stable and underwent the cure process before decomposition. The emission spectra of the Eu^{3+} /

acetyl acetonate complex doped in DGMA, recorded at 298 and 77 K, exhibited the characteristic bands arising from the $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions ($j = 0-4$). The luminescence intensity decreased with an increasing precursor concentration in the doped polymer. The system doped at a low concentration (1% Eu^{3+} complex) presented more luminescence efficiency than those doped at 5, 10, and 15%. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 406–412, 2006

Key words: europium complex; acetyl acetonato; photoluminescence; dgma resin

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 electronic devices,^{5,6} in parallel with the development of biodetection applications.⁷ Recent research has been conducted to obtain novel luminescent materials within a silica matrix that hosts an anchored europium complex.⁸ In a system containing rare-earth ions, the efficiency of energy transfer depends on the correlation of the relative positions of the triplet state of the ligand and the energy levels from the rare-earth ion. The triplet state of the ligand in the precursor is also dependent on the molecular structure of the β -diketonate derivatives.⁹ The advantage of using the Eu^{3+} ion as an emitter center is the presence of the single band arising from $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transitions in any chemical environment, and

so it provides a useful diagnostic probe for europium-ion coordination heterogeneity. If this transition exhibits more than one emission peak, it indicates the existence of more than one site symmetry. Additionally, the luminescence intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is almost independent from the chemical environment (allowed by the magnetic dipole mechanism), and so it can be used as a reference transition. The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is hypersensitive to the chemical environment around the Eu^{3+} ion, which can give information about the coordination sphere.¹⁰ The rare-earth ion, because of its hard acid character, has a strong affinity for organic molecules containing oxygen as a donor atom. Polymers containing the acrylic group have donor atoms to coordinate with the rare-earth ion via doping into the polymer matrix. The influence of the polymer matrix on the luminescence of Eu^{3+} complexes has been reported.¹¹ The synthesis of Eu^{3+} and Tb^{3+} ions doped in poly(acrylic acid) has been reported and shows evidence of coordination between the dopant ion and the carboxylic anions in an aqueous solution. In this work, Eu^{3+} doped in an acrylic polymer in the solid state is reported.¹² Materials based on an acrylic polymer doped with europium complexes show unique properties that may be used to develop special devices.

Correspondence to: D. F. Parra (duclercp@iq.usp.br).

Contract grant sponsor: Fundação de Amparo à Pesquisa do Estado de São Paulo.

Contract grant sponsor: Conselho Nacional de Desenvolvimento Científico e Tecnológico.

TABLE I
TGA and DSC Data of the DGMA:Eu(acac)₃ System Under a Nitrogen Atmosphere at a Heating Rate of 10°C/min

Sample	TGA		DSC	
	Onset (°C)	Loss mass/residue (%; 65–650°C)	Exothermic cure event (°C)	Endothermic melting event (°C)
Resin	274	97.5/2.5	—	65.7
DGMA/Eu(acac)1%	273	97.5/2.5	182.6–248.0	63.5
DGMA/Eu(acac)5%	281	93.0/7.0	165.2–239.0	63.9
DGMA/Eu(acac)10%	279	91.0/9.0	151.1–222.0	63.3
DGMA/Eu(acac)15%	254	90.2/9.8	161.8–229.2	62.8

In this article, we report the preparation and characterization of triaquatris(acetyl acetonate)europium(III) [Eu(acac)₃] at 1, 5, 10, and 15% that was doped in diglycidyl methacrylic (DGMA) resin and their luminescent properties in the solid state. The photoluminescence properties were studied on the basis of the excitation and emission spectra and luminescence decay curves. The thermal analysis data of the DGMA/Eu(acac)*x*% system (*x* = 1, 5, 10, or 15) are discussed.

EXPERIMENTAL

The DGMA polymer was obtained from Ciba–Geigy (Guarulhos, Brazil) (505 g of epoxy/equiv). The Eu(acac)₃ complex was synthesized through the dissolution of europium chloride, EuCl₃ · 6(H₂O), in water, the addition of acetyl acetone in ethanol in a 1:3M ratio (Eu/acac), and the addition of concentrated ammonium hydroxide until the pH was approximately 6, at which point the Eu-β-diketonate complex precipitated.¹³ The solid compound was filtered, washed with water, and dried in vacuum desiccators over anhydrous calcium chloride at room temperature. The Eu³⁺-ion content was estimated by complexometric titration with EDTA in a methanol solution with xylenol orange as an indicator.¹⁴ Elemental analyses of carbon and hydrogen were determined with the usual microanalytical procedures with a PerkinElmer model CHN 2400 instrument. The luminescent polymeric materials were processed with the DGMA polymer and the prepared Eu(acac)₃(H₂O)₃-complex precursor.

The luminescent system containing the polymer doped with europium in 1, 5, 10, and 15% concentrations was prepared through the dissolution of the polymer in methanol and mixing with the required amount of the luminescent Eu³⁺ complex dissolved in acetone. The homogeneous solutions were heated at 40°C for 10 min, and after that, the solvent was evaporated around 60°C. The solid products were dried in vacuum desiccators over anhydrous calcium chloride at room temperature for 12 h.

The infrared spectra of the solid samples were recorded in the range of 4000–400 cm⁻¹ at a concentration of 1% in KBr pellets. They were recorded at room

temperature with a Bomem model MB102 Fourier transform infrared (FTIR) spectrophotometer.

The excitation and emission spectra of the powdered samples were recorded on a SPEX Fluorolog-2 spectrofluorometer (model FL212) at room temperature and the temperature of liquid nitrogen with the front face mode. This apparatus was fully controlled by a DM3000F spectroscopic computer. The luminescence decay curves were recorded at room temperature with a SPEX 1934D phosphorimeter accessory (SPEX Industries, Inc., Edison, NJ, USA) coupled with the spectrofluorometer.

Thermogravimetric curves were obtained with an SDTA-822 thermobalance (Mettler–Toledo, Switzerland) with samples of about 2 mg in sapphire crucibles under a dynamic nitrogen atmosphere (50 mL/min) at a heating rate of 10°C/min. Differential scanning calorimetry (DSC) curves were obtained with a DSC-821 cell (Mettler–Toledo) with an aluminum crucible with 5 mg of the sample under a dynamic nitrogen atmosphere (50 mL/min) at a heating rate of 10°C/min. The DSC apparatus was calibrated with In metal (mp = 156.61°C, Δ*H* = 28.4 J/g).

RESULTS AND DISCUSSION

The CH elemental analysis and complexometric europium test of the precursor showed values [C, 38.32/38.55; H, 4.88/4.96; and Eu, 32.51/32.52 (found/calculated)] in agreement with the general formula Eu(acac)₃(H₂O)₃. The thermogravimetric analysis (TGA) curves (Fig. 1) showed a single event of loss mass for the four doped samples in comparison with the DGMA resin. The thermal decomposition profiles of the doped system were similar to that of the undoped sample. Table I reports the temperature onset of these events and the decrease in the mass as a percentage. The results showed that the DGMA resin and the polymer doped with 1% Eu-complex precursor had the same thermal stability. The onset temperature increased by 7 and 5°C with 5 and 10% precursor, respectively. On the other hand, the onset temperature decreased around 20°C at the level of 15%, and this indicated some pertur-

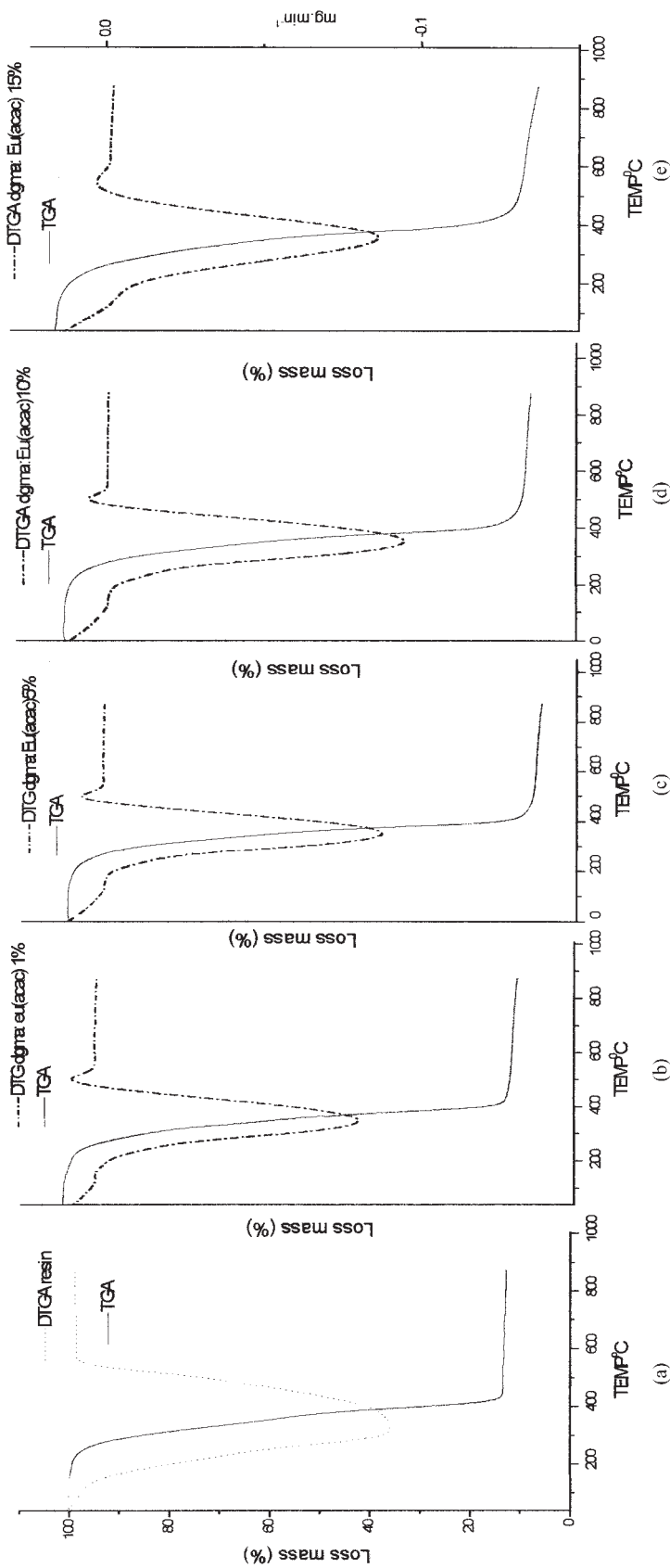


Figure 1 TGA curves of samples obtained in an N₂ atmosphere (50 mL/min) at a heating rate of 10°C/min for DGMA/Eu(acac)_x with the following concentrations (w/w): (a) x = 0, (b) x = 1, (c) x = 5, (d) x = 10, and (e) x = 15.

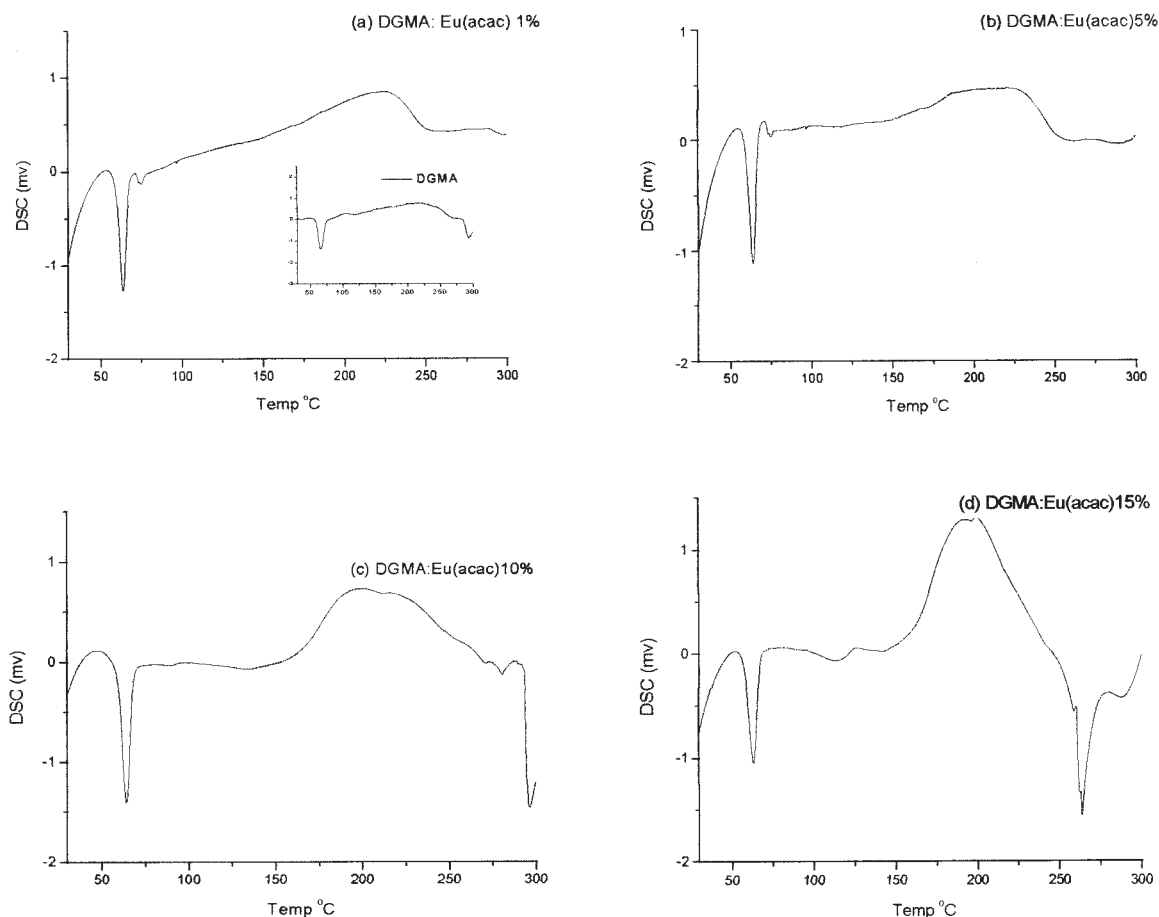


Figure 2 DSC curves of DGMA/Eu(acac) x % systems obtained in an N_2 atmosphere (50 mL/min) at a heating rate of $10^\circ\text{C}/\text{min}$: (a) $x = 0$ and 1, (b) $x = 5$, (c) $x = 10$, and (d) $x = 15$.

bation of the thermal stability of the doped system at this concentration.

A residue content with an inorganic composition around 450°C and an absence of mass reduction in the temperature interval of 80 – 120°C , in which the precursor lost the three water molecules, were verified. This fact indicated that the coordination of the Eu^{3+} complex to the polymer occurred via substitution of the water molecules.

The DSC curves (Fig. 2) of the doped DGMA/Eu(acac) x % systems ($x = 1, 5, 10$, or 15%), obtained in an N_2 atmosphere (50 mL/min) at a heating rate of $10^\circ\text{C}/\text{min}$, indicated one small displacement of the melting point of the resin, suggesting a small plasticizer effect of the doping in the polymer.

An exothermic event was observed in the temperature interval of 150 – 248°C and was attributed to the cure of the polymer due to the presence of the precursor complex, in which the Eu^{+3} ion could act as a cure-promoter agent to improve self-polymerization of the diglycidyl acrylic resin. A similar effect was observed with the epoxy resin when the doped systems had been synthesized with $\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_3$ at 1, 5, and 10% in diglycidylether of

bisphenol A (DGEBA) resin.¹⁵ In contrast, the epoxy resin (DGEBA) doped with the $\text{Eu}(\text{acac})_3(\text{H}_2\text{O})_3$ complex at 1 and 5% presented typical curves of degradation processes starting around 180°C , instead of one cure event.¹⁵ In this work, a different behavior was verified when the $\text{Eu}(\text{acac})_3(\text{H}_2\text{O})_3$ complex was coordinated to the DGMA polymeric matrix. This fact suggested that the new system containing DGMA resin was thermally more stable, and this permitted the cure process before decomposition. The DSC curve of DGMA shown in the inset of Figure 2(a) indicates no event of cure, whereas the DGMA/Eu(acac) $_3 \cdot (\text{H}_2\text{O})_3$ 15% system exhibited one strong exothermic event followed by a decomposition event [Fig. 2(d)].

Figure 3 shows the infrared spectra of DGMA and the doped system recorded in a spectral range of 500 – 1850 cm^{-1} . The infrared spectrum of DGMA shows a presence at 1728 cm^{-1} attributed to the $\text{C}=\text{O}$ bond stretching vibrations of the carboxyl group and a doublet at 1453 and 1494 cm^{-1} attributed to the $-\text{CH}_2-$ deformation and bending vibrations of the $>\text{CH}-\text{CO}-$ group. The doublet at 1175 and 1107 cm^{-1} was due to $\text{C}-\text{O}$ stretching

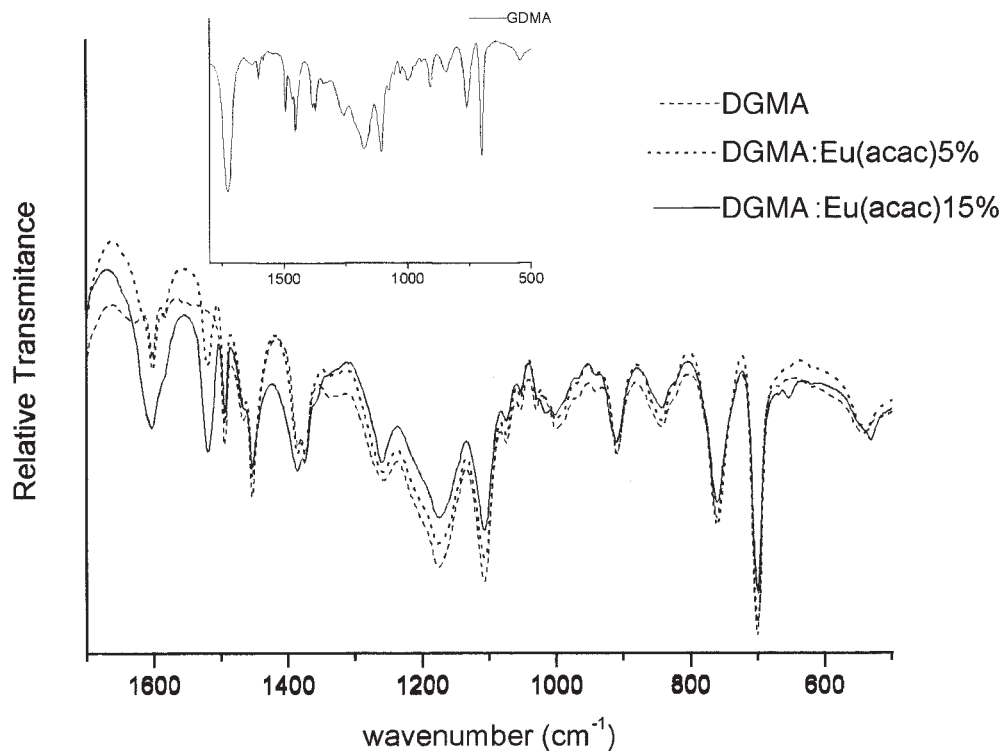


Figure 3 Infrared spectra of doped systems of DGMA/Eu(acac)₃ with 5 and 15% concentrations and the undoped polymer.

coupled with O—H in-plane bending of the carboxyl group.^{12,16,17} In the case of doped samples (5 and 15%), a new band was observed at 1547 cm⁻¹. The band at 1602 cm⁻¹ was attributed to the C=O bond stretching vibrations of the carboxyl group of

the acetyl acetonate group; its intensity increased with the enhancement of the doping concentration. The intensity peaks at 1175 and 1107 cm⁻¹ decreased because of the loss of the acid hydrogen as a result of coordination of the europium ion to the

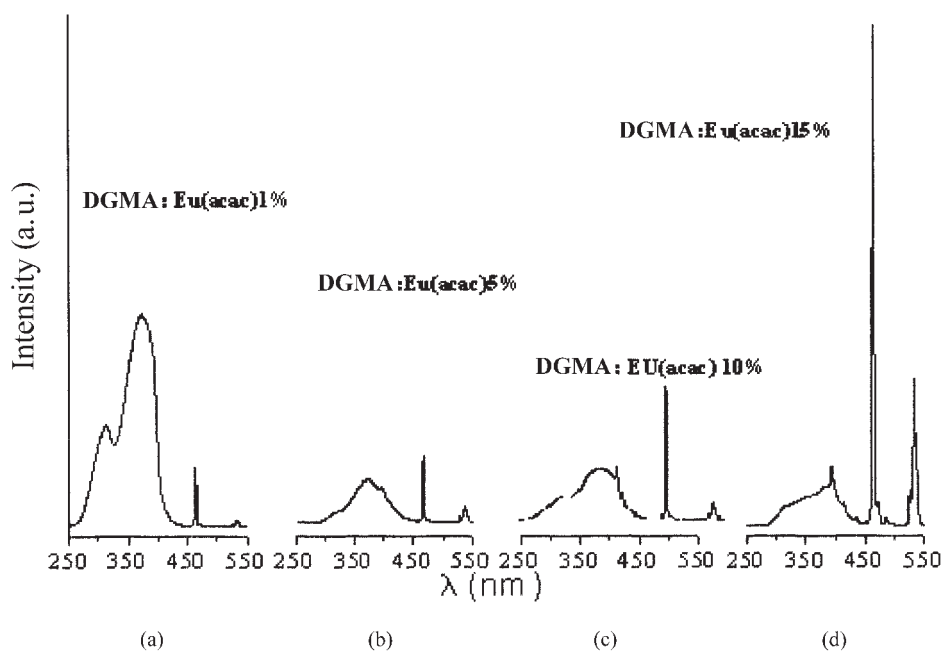


Figure 4 Excitation spectra of DGMA/Eu(acac)*x*% systems with the following concentrations: (a) *x* = 1, (b) *x* = 5, (c) *x* = 10, and (d) *x* = 15 (λ = wavelength).

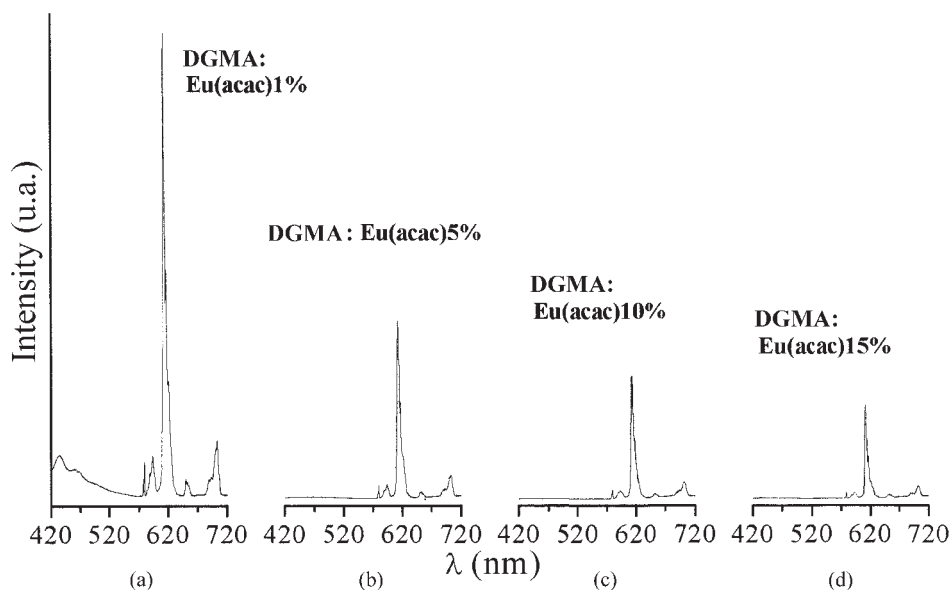


Figure 5 Emission spectra of DGMA/Eu(acac) x % systems with the following concentrations: (a) $x = 1$, (b) $x = 5$, (c) $x = 10$, and (d) $x = 15$ (λ = wavelength).

oxygen atom of the carboxyl group. The coordination of the oxygen was confirmed by the reduction of the intensity band at 1728 cm^{-1} of the C=O bond stretching vibrations of the carboxyl group.¹²

The excitation spectra of the doped polymers (Fig. 4) were recorded in the range of 250–550 nm at 77 K, with the emission monitored in the hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition at 612 nm. The narrow absorption bands around 393, 460, 525, and 579 nm were characteristic transitions of the europium ion corresponding to the $^7\text{F}_0 \rightarrow ^5\text{L}_6$, $^7\text{F}_0 \rightarrow ^5\text{D}_2$, $^7\text{F}_0 \rightarrow ^5\text{D}_1$, and $^7\text{F}_0 \rightarrow ^5\text{D}_0$ transitions, respectively. The intensity absorption of the f -intraconfigurational transition increased with the augmentation of the doping concentration in the following order: $1 < 5 < 10 < 15\%$. The broad bands in the range from 260 to 410 nm, arising from the β -diketonate group, overlapped with those narrow bands from the Eu^{3+} ion attributed to the $^7\text{F}_0 \rightarrow ^5\text{D}_4$, $^7\text{F}_0 \rightarrow ^5\text{L}_7$, and $^7\text{F}_0 \rightarrow ^5\text{D}_3$ transitions.¹¹

The emission spectra (Fig. 5) were recorded at 77 K in the range of 420–720 nm under excitation around 393 nm. These spectra show the emission bands corresponding to the electronic $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions ($J = 0-4$) from the europium ion. The presence of only one peak in the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition indicates the degree of Cnv, Cn, and Cs symmetries in the local chemical environment of the Eu^{3+} ions. The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is hypersensitive to the ligand field strength because this transition has an electric dipole nature, whereas the intensity of the magnetic dipolar $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is not sensitive to the ligand field strength and is generally taken as a reference. In the case of the emission spectrum of the DGMA/Eu(acac) $_3$ 1% system, the broad bands

around 420–520 nm were attributed to the transitions from the organic part of the polymer overlapped with the transitions from the acetyl acetate ligand. It was verified that the luminescent intensities decreased with an increasing Eu^{3+} -complex concentration doped into the polymer in the following order: $15 < 10 < 5 < 1\%$. The quenching of luminescence in the systems was observed when the concentration of the Eu^{3+} complex was increased.

CONCLUSIONS

The characterization of the DGMA/Eu(acac) $_3x\%$ system by the FTIR, TGA, and DSC techniques indicated that the Eu^{3+} -complex precursor was immobilized in the polymer matrix by the Eu—O interaction when the complex was doped into the DGMA polymer. The thermal stability of the systems was similar to that of the polymer, except at the highest concentration (15%), at which the onset temperature of decomposition decreased around 20°C ; this indicated some perturbation of the thermal stability of the doped system at this concentration. According to the DSC results, the new system [DGMA/Eu(acac) $_3$] was thermally stable and underwent a cure process before decomposition. The luminescent intensity decreased with increasing precursor concentration in the doped polymer. The system doped at a low concentration (1% Eu^{3+} complex) presented more luminescence efficiency than those at 5, 10, and 15%.

References

1. Kido, J.; Okamoto, Y. *Chem Rev* 2002, 102, 2357

2. Sá, G. F.; Malta, O. L.; Donegá, M. C.; Simas, A. M.; Longo, R. L.; Santa-Cruz, P. A.; Silva, E. F. *Coord Chem Rev* 2000, 96, 165.
3. Bunzli, J. C. G.; Piguet, C. *Chem Rev* 2002, 102, 1897.
4. Brito, H. F.; Malta, O. L.; Menezes, J. F. S. *J Alloys Compd* 2000, 300, 336.
5. Klein, D. L.; Roth, R.; Lim, A. K. L.; Alivisatos, A. P.; McEuen, P. L. *Nature* 1997, 389, 699.
6. Carlos, L. D.; Videira, A. L. L. *Chem Phys Lett* 1997, 264, 57.
7. Bruchez, M.; Moronne, M., Jr.; Gin, P.; Weiss, S.; Alivisatos, A. P. *Science* 1998, 281, 2013.
8. Soares-Santos, P. C. R.; Nogueira, H. I. S.; Félix, V.; Drew, M. G. B.; Ferreira, R. A. S.; Carlos, L. D.; Trindade, T. *Chem Mater* 2003, 15, 100.
9. Buono-Core, G. E.; Li, H.; Marciniak, B. *Coord Chem Rev* 1990, 9, 55.
10. Malta, O. L.; Brito, H. F.; Menezes, J. F. S.; Gonçalves Silva, F. R.; Donega, M. C.; Alves, S., Jr.; de Andrade, A. V. M. *J Lumin* 1997, 75, 255.
11. Parra, D. F.; Brito, H. F.; Matos, J. R.; Dias, L. C. *J Appl Polym Sci* 2002, 83, 2716.
12. Rosendo, A.; Flores, M.; Córdoba, G.; Rodríguez, R.; Arroyo, R. *Mater Lett* 2003, 57, 2885.
13. Wang, S.; Wang, W.; Qian, Y. *Mater Res Bull* 2000, 35, 2057.
14. Lyle, S. J.; Rahman, M. M. *Talanta* 1963, 10, 1177.
15. Parra, D. F.; Mucciolo, A.; Brito, H. F.; Thompson, L. C. *J Solid State Chem* 2003, 171, 412.
16. Hu, H.; Saniger, J.; Garcia-Alejandre, J.; Castano, V. M. *Mater Lett* 1991, 12, 281.
17. Dong, J.; Ozaki, Y.; Nakashima, K. *J Polym Sci Part B: Polym Phys* 1997, 35, 507.