

Calorimetric investigations of luminescent films polycarbonate (PC) doped with europium complex $[\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2]$

Pedro Lima Forster · Ademar Benevolo Lugao ·
Hermi Felinto Brito · Duclerc Fernandes Parra

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Abstract Polymers doped with rare earth complexes are advantaged in film production for many applications in the luminescent field. In this luminescent polycarbonate (PC) films doped with diaquatris(thenoyltrifluoroacetate)europium(III) complex $[\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2]$ were prepared and their calorimetric and luminescent properties in the solid state are reported. The thermal behavior was investigated by utilization of differential scanning calorimetry (DSC) and thermogravimetry (TG). Due of the addition of rare earth $[\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2]$ into PC matrix, changes were observed in the thermal behavior concerning the glass transition and thermal stability. Characteristic broadened narrow bands arising from the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ transitions ($J = 4-0$) of Eu^{3+} ion indicate the incorporation of the Eu^{3+} ions in the polymer. The luminescent films show enhancement emission intensity with an increase of rare earth concentration in polymeric matrix accompanied by decrease in thermal stability.

Keywords Luminescent films · Polycarbonate · Rare earths · Thenoyltrifluoroacetate · Thermal behavior

Introduction

Rare earth β -diketonate complexes are of particular interest, since these complexes show intense luminescence [1]. In the luminescent field, Eu^{3+} is the rare earth ion is the most investigated. The main advantage of use Eu^{3+} as luminescence probe to study the composition of the first coordination sphere is the non-degeneracy of the ${}^5\text{D}_0$ and ${}^7\text{F}_0$ levels. In the Eu^{3+} complexes energy is primarily transferred from the ligand triplet to the ${}^5\text{D}_0$ level from which luminescent transitions to the ground state manifold ${}^7\text{F}_J$ ($J = 0-4$) are observed in the red spectral region. The most intense transition of Eu^{3+} is the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition, corresponding to a red emission band at 615 nm [2].

Built materials that combine simple methods of synthesis and high luminescent properties became more attractive in the last years. Luminescent systems based on rare earths doped into polymeric matrices have been explored for many researches [3–7] and have been interesting due to the combination of unique spectroscopic properties from rare earth complexes associated to physical and chemical properties intrinsic properties from polymers. Nowadays, there is continuous interest in the potential applications of rare earth complexes to obtain high luminescent materials for fluorescent labels, organic light-emitting diodes (OLEDs), biological imaging and sensor devices [2–12].

Polycarbonate (PC) has excellent properties for example optical properties as high clarity, transparency and ratio of refractive indices, low water absorption, exceptional impact resistance, toughness and high glass transition temperature (T_g) in the range of 413–428 K. Whereas below of T_g PC retain their properties differentially than other amorphous thermoplastics that are brittle and stiff. The presence of benzene rings and quaternary carbon

P. L. Forster (✉) · A. B. Lugao · D. F. Parra
Chemistry and Environmental Centre, Institute of Energetics and Nuclear Researches, National Commission of Nuclear Energy, IPEN/CNEN-SP, Prof. Lineu Prestes, Av., 2242, CEP 05508-000, São Paulo, SP, Brazil
e-mail: plforster@usp.br

H. F. Brito
Department of Fundamental Chemistry, Chemistry Institute, University of São Paulo, Av. Prof. Lineu Prestes, 748, CEP 05508-000, São Paulo, SP, Brazil

atoms on the polymeric structure make PC to forms bulky and stiff chains that enhance rigidity.

In this work luminescent films of PC doped with di-aquatrakis(thenoyltrifluoroacetate)europium(III) complex $[\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2]$ were prepared and their calorimetric and luminescent properties in the solid state are reported. The ratio of the complex $[\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_3]$ were 1, 2, 5 and 7% (mass/mass).

Experimental

Materials

The PC sample is originated from Bayer (Germany) (Makrolon[®] 2458), cylindrically cut granules (diameter 2–3 mm, length 2–3 mm) with glass transition temperature of 412 K.

The rare earths complex $[\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2]$ was prepared by addition of europium chloride aqueous solution to TTA ligand in ethanol solution 1:3 molar ratio followed by addition of concentrated ammonium hydroxide around pH ~ 7 .

The luminescent system containing the polymer doped with europium complex in percentages were prepared by dissolving the polymer in tetrahydrofuran (THF) and mixing it with the required amount of the luminescent Eu^{3+} complex dissolved in acetone. The homogeneous solutions were heated at 313 K for 10 min and the solvent was evaporated at around 333 K.

Measurements

Thermogravimetric curves (TG) were obtained with an SDTA-822 thermobalance (Mettler Toledo) using samples at about 5 mg in sapphire crucibles under dynamic nitrogen atmosphere (50 mL min^{-1}), heated from 298 to 923 K at heating rate of 10 K min^{-1} in inert (N_2) and/or oxidative atmospheres. Heat flow curves were obtained using a Differential Scanning Calorimeter, model DSC822e (Mettler Toledo) under nitrogen atmosphere, at a heating rate of 10 K min^{-1} , in the 253–493 K temperature range. The differential scanning calorimetry (DSC) apparatus was calibrated with In ($\text{mp} = 429.61 \text{ K}$, $\Delta H = 28.4 \text{ J g}^{-1}$).

The excitation and emission spectra of the samples in form of films were recorded at room temperature in SPEX Fluorolog-2 spectrofluorimeter, model FL212 system, double grating 0.22 SPEX monochromators, 450 W Xenon lamp as excitation source.

Elemental analysis of carbon and hydrogen were determined by the usual microanalytical procedures using a PerkinElmer Model CHN 2400.

Results and discussion

Elemental analysis

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 Eu percentage values calculated/found for the complex were: [C: 33.85/33.52; H: 1.89/1.88; Eu: 17.85/17.16] in agreement with the $[\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2]$ general formula.

Luminescent properties

Polymers are interesting matrix for rare earths β -diketonate complexes owing to synthesis facility, and the possibility to

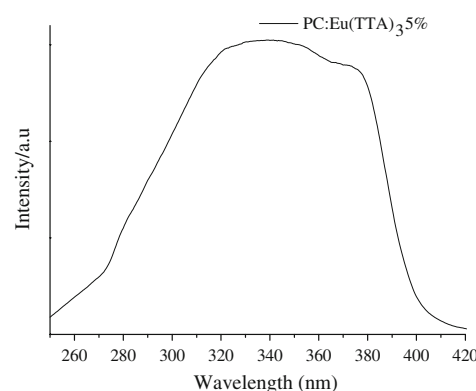


Fig. 1 Excitation spectrum of PC:Eu(TTA)₃ complex at 615 nm emission wavelength at room temperature

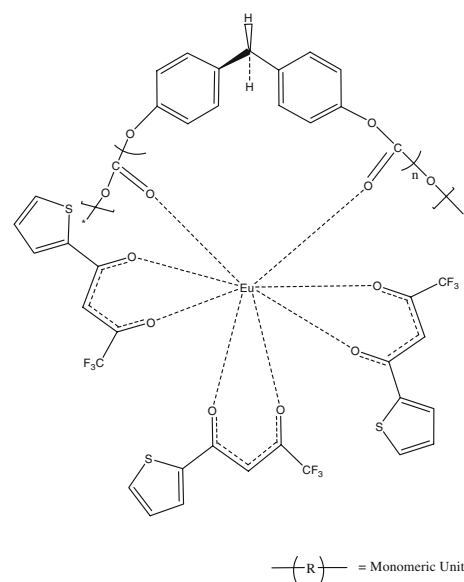


Fig. 2 A schematic structure of rare earth complex $\text{Eu}(\text{TTA})_3$ doped into polycarbonate matrix

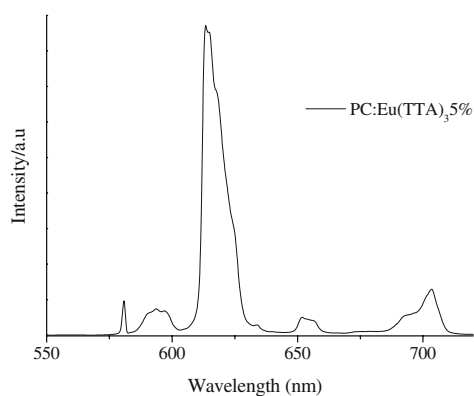
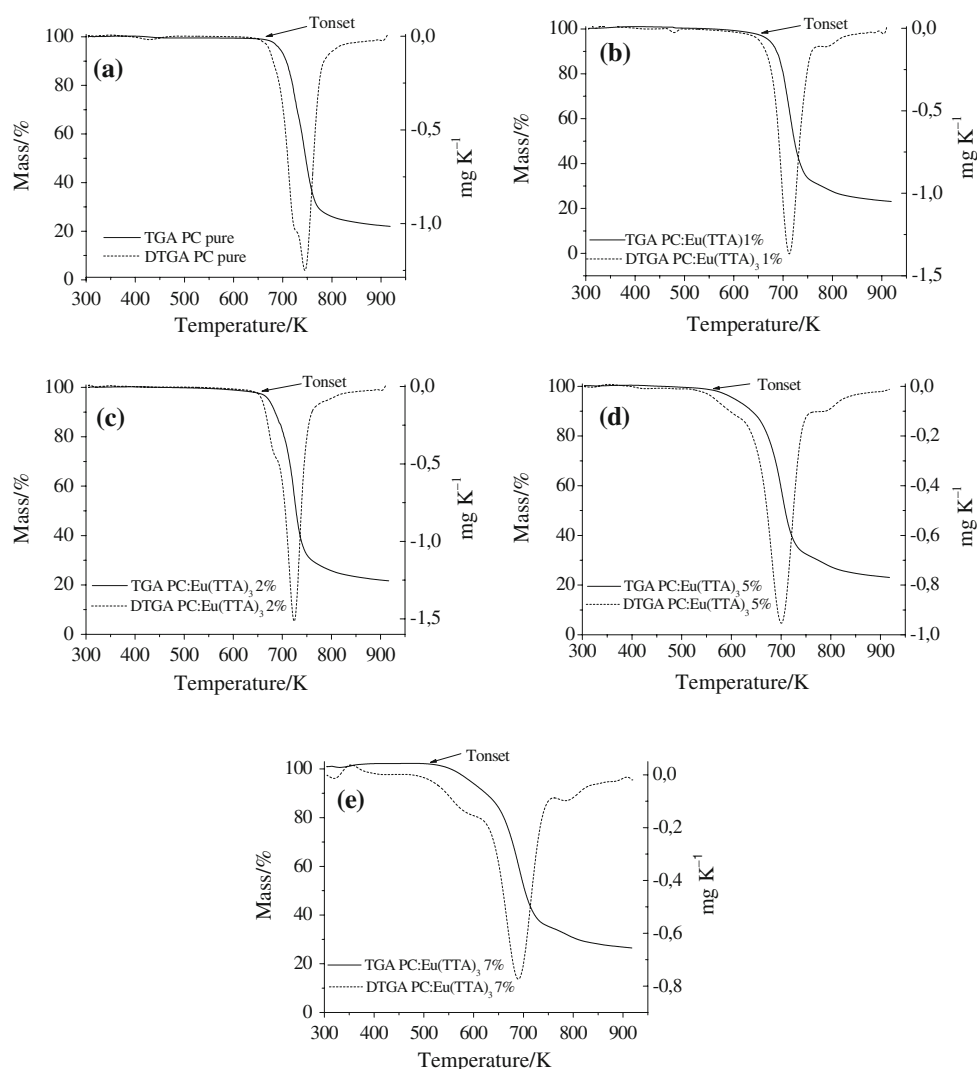


Fig. 3 Emission spectrum of PC:Eu(TTA)₃ with ratio 5%, excitation at 350 nm wavelength at room temperature

absorb light and channels it to the europium(III) ion. The incorporation of luminescent material consists in the use of one polymer matrix and the luminescent complex as doping agent.

Fig. 4 Thermal decomposition of doped systems PC:Eu(TTA)₃ x% where **a** x = 0, **b** x = 1, **c** x = 2, **d** x = 5, and **e** x = 7



The excitation spectrum of doped polymers (Fig. 1) was recorded in the 250–420 nm range at 298 K (room temperature) with emission monitored at 615 nm corresponding to the hypersensitive $^5D_0 \rightarrow ^7F_2$ transition. The spectral region of 280–420 nm was assigned by an intense broadband attributed to the thenoyltrifluoroacetate ligand enveloped with the narrow bands from Eu^{3+} ions of the schematic structure represented in Fig. 2.

The emission spectrum in Fig. 3 was recorded in the range 550–720 nm at 298 K (room temperature) under excitation of 350 nm. The characteristic polymer emission band is absent suggesting an efficient intramolecular energy transfer from polymer to the rare earth ion evidencing that polymer acts as co-sensitizer in the luminescent system.

The emission spectrum of the PC:Eu(TTA)₃ 5% system exhibits broadened bands arising from excited 5D_0 state to ground 5F_J states ($J = 0-4$) of Eu^{3+} ion while the narrow bands are typical of the precursor complex in the emission

Table 1 TG data of the PC:Eu(TTA)₃ systems under a nitrogen (N₂) atmosphere and heating rate 10 K min⁻¹

System	Onset (K)	Mass loss/residue (%)
Polycarbonate	661.0 ± 0.5	77/23
PC: Eu(TTA) ₃ 1%	648.0 ± 0.5	77/23
PC: Eu(TTA) ₃ 2%	644.0 ± 0.5	76/24
PC: Eu(TTA) ₃ 5%	560.0 ± 0.5	75/25
PC: Eu(TTA) ₃ 7%	512.0 ± 0.5	73/27

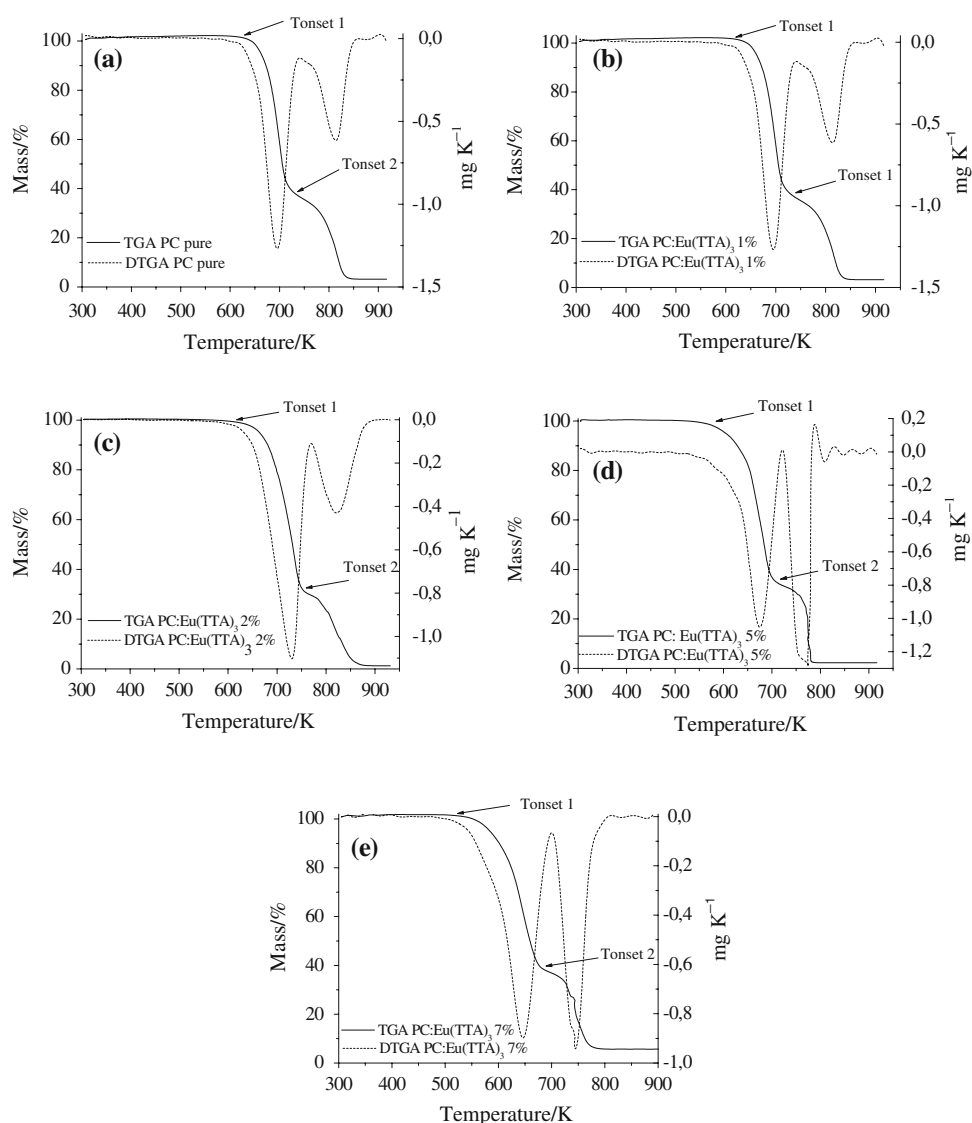
spectrum. This difference between complex precursor and the complex doped into the polymer is due to inhomogeneous line broadening of the intraconfigurational 4f-transitions, effect of the interaction between polymer and europium ion.

Thermogravimetric analysis

Thermogravimetric analysis (TG) was used to measure the mass loss of the sample. The measurement was obtained by raising the temperature at a steady rate until the system is substantially decomposed. The knowledge of thermodynamic properties is essential to understand mechanisms of chemical synthesis of the complexes and concerning theoretical research in rare-earth science and technology for relevant applications [13].

The thermal degradation curves (under N₂ atmosphere) showed a single mass loss event for the four doped PC systems: Eu(TTA)₃ in comparison to PC resin (Fig. 4). The curve profiles of doped systems are similar to that of undoped system. Table 1 shows the onset temperature values of these events and reported the mass loss in

Fig. 5 Thermoxidative decomposition of doped systems PC:Eu(TTA)₃ x% where **a** x = 0, **b** x = 1, **c** x = 2, **d** x = 5, and **e** x = 7



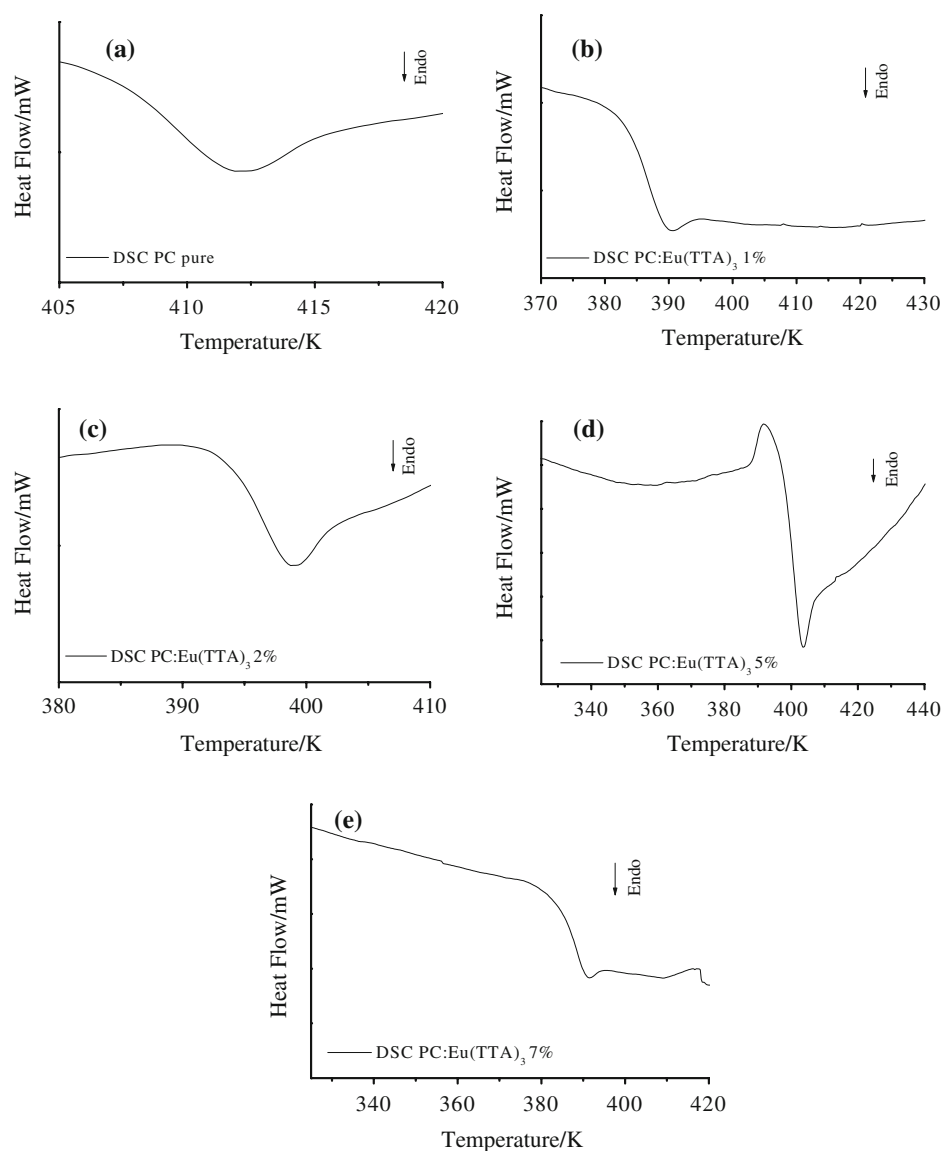
percentage. The results report that PC:Eu(TTA)₃ 1 and 2% systems show that their onset temperatures decreased by 13 and 16 K, respectively. The intense decrease of 103 and 140 K were observed for the 5 and 7% of doping, respectively, and it reports some perturbation of thermal stability of doped systems on this concentration.

The thermal degradation curves (in O₂ atmosphere) showed two loss mass events for the four doped polycarbonate:Eu(TTA)₃ systems in comparison to PC resin (Fig. 5). The curve profiles of doped systems are similar to that of undoped system. The corresponding thermo-gravimetric data are collected in Table 2.

Table 2 TG data of the PC:Eu(TTA)₃ systems under a oxygen (O₂) atmosphere and heating rate of 10 K min⁻¹

System	Tonset 1 (K) (O ₂)	Tonset 2 (K) (O ₂)	Mass loss/residue (%)
Polycarbonate	621.0 ± 0.5	732.0 ± 0.5	97/2
PC: Eu(TTA) ₃ 1%	617.0 ± 0.5	736.0 ± 0.5	96 /3
PC: Eu(TTA) ₃ 2%	609.0 ± 0.5	754.0 ± 0.5	98/2
PC: Eu(TTA) ₃ 5%	572.0 ± 0.5	709.0 ± 0.5	97 /2
PC: Eu(TTA) ₃ 7%	514.0 ± 0.5	681.0 ± 0.5	94/5
Eu(TTA) ₃ (H ₂ O) ₂	336.0/508.0 ± 0.5	695.0 ± 0.5	54/45

Fig. 6 DSC curves of PC:Eu(TTA)₃ x% systems obtained in an inert (N₂) atmosphere at a heating rate of 10 K min⁻¹: x = 0 (a), 1% (b), 2% (c), 5% (d), and 7% (e)



The results indicate that PC:Eu(TTA)₃ systems show similar profile to that of PC but are less resistant to oxidation. The onset temperatures decrease as consequence of some perturbation of thermal stability of doped systems at each concentration.

The TG/DTG measurements of doped systems PC:Eu(TTA)₃ showed absence of the mass loss event associated to the complex [14–16] and was observed as a single step event in the 363–403 K temperature range of the hydrated complex. This fact indicates the interaction between the complex Eu(TTA)₃ and PC via replacement of two water molecules by coordination of Eu³⁺ with oxygen of the carbonyl C=O polymer groups. It was observed that thermal and thermoxidative degradation are accelerated by the increasing concentration of Eu(TTA)₃ complex, but, in other hand, it could be observed that thermal stability of Eu(TTA)₃ was increased in the polymer matrix.

Glass transition changes

The DSC curves in Fig. 6 show the displacement of glass transition (T_g of the PC) from 412 to 390, 398, 402 and 390 K for doped systems of PC:Eu(TTA)₃ 1, 2, 5 and 7%, respectively. These results show decrease in the glass transition in the doped systems. In the coordination between the Eu(TTA)₃ complex and the PC, the complex acts with plasticizer effect between the polymer chains.

Conclusions

The PC:Eu(TTA)₃ doped systems show similar thermal profiles in comparison to the PC resin. Increasing Eu(TTA)₃ complex concentration on the doped polymeric system thermal and thermoxidative degradation are accelerated compared to the thermal behavior of PC. In the other hand polymeric matrix protected the rare earth complex raising the thermal stability of doped system PC:Eu(TTA)₃ in comparison with thermal behavior of rare earth complex. The coordination proposed between Eu(TTA)₃ and PC occurs via interaction Eu–O by substitution of two water molecules.

This coordination also may explain the phenomenon of increasing the emission intensity, since water molecules acts as suppressor of luminescence. Plasticizer effect in the polymer was also consequence of the rare earth complex interaction.

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