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Highly luminescent polycaprolactone films doped with diaquatris (thenoyltrifluoroacetonate)europium(III) complex

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ABSTRACT

In this work we report the preparation, characterization, thermal and luminescence properties of highly luminescent polycaprolactone (PCL) polymer films incorporated with diaquatris(thenoyltrifluoroacetonate)europium(III) complex $[Eu(tta)_3(H_2O)_2]$ (doping concentration at 1, 2, 5, 10 and 15 wt%). Thermogravimetry analysis (TGA) showed no weight loss in the range of 323–473 K for the polymeric systems, suggesting that the interaction between the polymer matrix and the Eu^{3+}-complex occurs when the carbonyl groups along the polymer backbone substitute the water molecules in the complex precursor. Differential scanning calorimetry (DSC) showed no significant changes in T_m for the film samples, however crystallinity is affected by non combined complex in the polymer chains. The changes in the curve-fitted FTIR spectral areas for each component peak are gradually changed with the increase of doping concentration. The displacement of the C–O for the β-diketonate complex to new positions in PCLE systems provide good evidence that the metal ion is coordinated through the oxygen atoms deriving from PCL. The observation of characteristic emission bands arising from the $^5D_0 \rightarrow {}^7F_J$ transitions ($J=0$–4) dominated by the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition at around 614 nm of Eu^{3+} ion indicates the incorporation of the Eu^{3+} ions in the system corroborating with the CHN and IR data. Luminescence quenching is observed, with the film of 5% doping concentration of the Eu^{3+} complexes showing the highest luminescence intensity among all samples.

1. Introduction

The lanthanide β-diketonate complexes are widely used in the development of luminescent materials for exhibiting monochromatic emission in applications such as optical markers [1], optoelectronic devices [2], luminescent signages [3] and biological labels [1–4]. These features are due to the strong energy absorption in the UV region by organic ligands and the non-radiative intramolecular ligand-to-Ln^{3+} ion energy transfer with subsequent emission in the visible region. The advantages of photoluminescent properties of Ln^{3+} complexes are the presence of narrow emission bands arising from the 4f–4f transitions, long lifetimes and large Stoke shifts [2,3]. Numerous interesting luminescent systems were developed using coordination compounds of trivalent lanthanide ions, usually those containing Eu^{3+} and Tb^{3+} ions owing to their energy level structures.

In order to obtain strong luminescent intensities, Ln^{3+} ions need a cleverly designed environment consisting of organic ligands with chromophoric groups to absorb efficiently light and subsequently populate the excited states of Ln^{3+} ions via energy transfer. Besides, it is important the absence of water molecules coordinated to the lanthanides ion where the ligands act as protecting shell to minimize non-radiative de-activation [5].

One of the most investigated lanthanide β-diketonates is the diaquatris(thenoyltrifluoroacetonate)europium(III) $[Eu(tta)_3(H_2O)_2]$ as precursor of luminescent materials [6]. In the Eu^{3+}–tta complexes, the energy is transferred from the ligand triplet state (T_1) to the $^5D_{0,1}$ excited level followed by radiative decay to the ground state manifold ^7F_J ($J=0$–4) of europium ion. The strongest emission intensity is the $^5D_0 \rightarrow {}^7F_2$ hypersensitive transition centered around 614 nm, corresponding to its characteristic monochromatic-red emission [5]. The tta^- group acts not only as the antenna in the energy transfer processes, but also an excellent bidentate chelating ligand that prevents the lanthanide ion from binding with other water molecules.

However, the use of $[Eu(tta)_3(H_2O)_2]$ complex is greatly limited

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by its poor thermodynamical performance. Moreover, the efficiency of Eu^{3+} emission is sensitive to the vibronic coupling between the emitting 4f levels and vibrational modes of the O–H oscillators of coordinated water molecules in the hydrated complex. One of the methods to enhance the overall thermal stability and luminescent properties of the Ln^{3+}-β-diketonate-based devices may be through the design of systems combining lanthanide complexes with polymers (e.g. polymethylmethacrylate and polycaprolactone) [3,7–9].

Nonetheless, conventional polymers are inappropriate for applications in which plastics are used for short periods and then disposed. In these cases, plastics often soiled by biological substances can be attractive for specific applications [9]. Polycaprolactone (PCL) is a hydrophobic semi-crystalline aliphatic polyester, commercially available, biodegradable and with low crystallization temperature. Having linear planar zigzag structure as polyethylene (PE), its mechanical properties are comparable with many other polymers that enlarge its field of applications.

The low glass transition temperature T_g (−60 °C) reveals its nature as a soft polymer with high main-chain flexibility, a characteristic which is unique among polyesters. In addition, PCL can be enzymatically degraded by microorganisms when disposed in bioactive environments. Its polymer chains may also be broken down by nonenzymatic processes such as chemical hydrolysis. Moreover, the carbonyl groups along with PCL carbon-chain can interact with Ln^{3+} ions and subsequently replace water molecules in hydrate lanthanide complexes resulting in overall enhancement of physical and chemical properties. Improvements in the emission characteristics, such as emission quantum efficiency and lifetimes, can be also expected with PCL polymer films doped with $[Eu(tta)_3(H_2O)_2]$ complex (PCLE).

In this work, a series of PCLE films were prepared and their thermal and luminescence properties in the solid state were investigated. To the best of our knowledge, this is the first time photophysical studies of systems containing PCL polymer and trivalent europium β-diketonate complexes are reported.

2. Experimental

The $[Eu(tta)_3(H_2O)_2]$ complex was prepared by the method previously reported [6]. The PCLE-*x*% luminescent systems (x=1, 2, 5, 10 and 15%) were prepared by dissolving 0.3 g PCL polymer in 60 mL chloroform, then mixing it with the required amount of the luminescent Eu^{3+} complex dissolved in 5 mL of acetone. The homogeneous solution was cast onto a Petri dish and heated at around 60 °C until total evaporation of solvents. The obtained films were then cut in slices and analyzed in film form.

The infrared absorption spectra of film samples were recorded in the range of 4000–400 cm^{-1} by using a Thermo Nicolet model 6700 FTIR spectrophotometer. Curve-fitting analysis of FTIR spectra of different PCLE systems were estimated quantitatively in the 1800–1550 cm^{-1} region by a curve-fitting algorithm with a mixed Gaussian–Lorentzian function [10]. The best curve-fitting procedure analysis depends on the positions and intensities of the components of the contour, substantial attention was paid to obtaining the best possible fit with the minimum number of component bands. The relative proportion of a component was computed to be the fractional area of the corresponding peak, divided by the sum of areas of all the peaks.

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 20–220 °C temperature range. The differential scanning calorimetry (DSC) apparatus was calibrated with in element (mp=156.46 °C, ΔH=28.4 J g^{-1}).

Thermogravimetric analysis (TGA) 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 25 to 750 °C, at heating rate of 10 °C min^{-1} in N_2 inert atmosphere.

PXRD was performed in the reflection mode on a Rigaku diffractometer Mini Flex II (Tokyo, Japan) operated at 30 kV voltage and a current of 15 mA with CuKα radiation (λ=1.5418 Å).

The excitation and emission spectra of luminescent films were recorded at room temperature in a SPEX Fluorolog-2 spectrofluorimeter, model FL212, double grating 0.22 m SPEX monochromators, and a 450 W Xenon lamp as the excitation source. Luminescence decay curves of the Eu^{3+} complex doped in PCL polymer films were measured using the SPEX 1934D phosphorimeter accessory attached to the 150 W pulsed xenon lamp.

3. Results and discussion

The precursor complex used diaquatris(thenoyltrifluoroacetonate) europium(III) $[Eu(tta)_3(H_2O)_2]$ has XRD reported in Fig.1. Three sharp diffraction peaks at 2θ angles of 5.4, 16.3 and 22.1, 29.6 can be observed in the XRD pattern of $[Eu(tta)_3 \cdot (H_2O)_2]$ prepared, indicating a product with good crystallinity form.

As shown in the IR absorption spectra (Fig. 2) of the PCL polymer and PCLE-*x*% (x: 1, 2, 5, 10 and 15%) films, the C=O absorption peaks at 1725 cm^{-1} can be assigned to the crystalline portion of PCL pristine, and a shoulder peak can be observed at 1736 cm^{-1} which is assigned to the amorphous phase.

The characteristics peaks at 1138 cm^{-1} attributed to $\upsilon_{as}(CF_3)$ and 933 cm^{-1} υ(C=C+C=O) for the Eu^{3+} complex are also identified in the PCLE films, indicating the presence of tta^- in the luminescent system (Fig. 2). The absorption bands related to the H_2O vibrational modes in the $[Eu(tta)_3(H_2O)_2]$ complex are found at 3500–3200 cm^{-1}(υ_s and υ_{as} OH). However, in the case of the doped polymer films, these bands are not observed, indicating the absence of H_2O molecules in the obtained PCLE films, possibly due to the interaction between the carbonyl groups in PCL and the Eu^{3+} ion, which had substituted the initially coordinated H_2O of the luminescent complex.

The IR spectral region of 1800–1550 cm^{-1} was selected due to C=O absorption sensitive changes in this region. The changes in the curve-fitted FTIR (Fig. 3) shows the peak positions of the amorphous and the crystalline fixed at 1738 and 1727 cm^{-1}, respectively [10]. IR peaks position and area gradually changed with the increase of doping concentration. When the doping

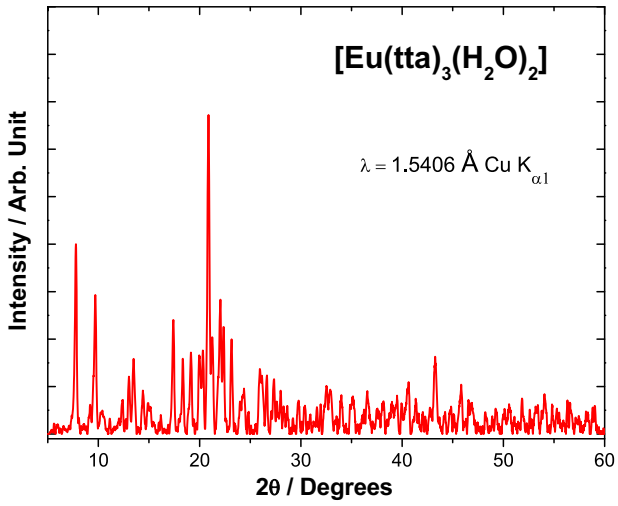

Fig. 1. Powder X-ray diffraction pattern of $[Eu(tta)_3(H_2O)_2]$.

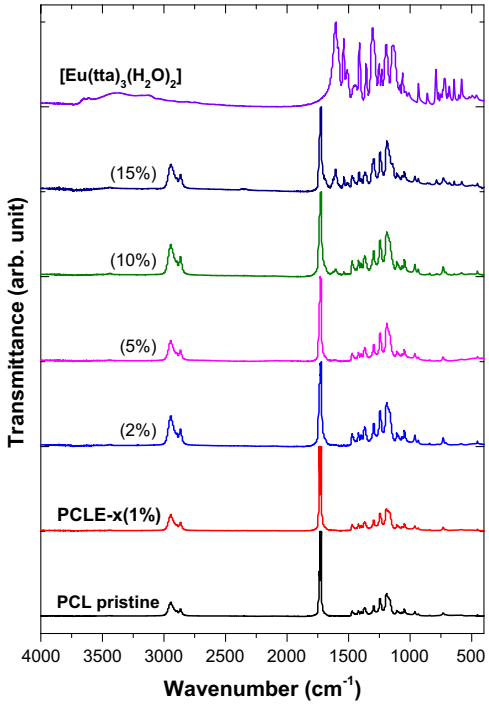

Fig. 2. FTIR absorption spectra of PCLE-*x*% (*x*=1, 2, 5, 10 and 15), $[Eu(tta)_3(H_2O)_2]$ precursor complex and PCL pristine polymer.

concentrations are above 5%, it was observed displacement of the C=O stretching band from 1605 cm^{-1} for the β-diketonate complex to positions at 1699, 1718 and 1696 cm^{-1} in PCLE 5, 10 and 15, respectively. This result indicates that the metal ion is coordinated through the oxygen atoms from PCL. The peak positions of contribution of C=O of PCL are also modified due to the doping

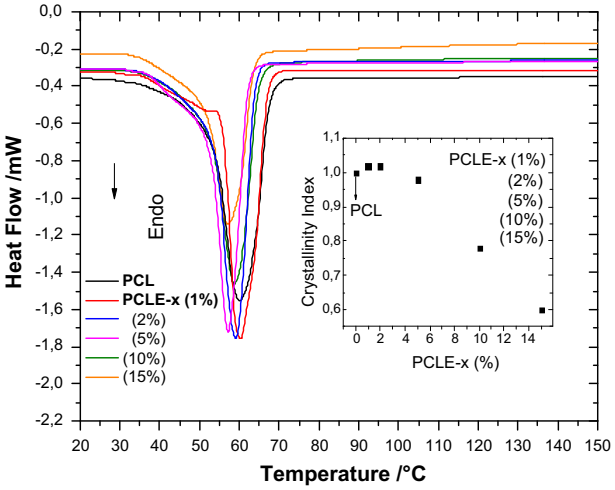

Fig. 4. DSC curves of PCLE-*x*% films registered under inert atmosphere (N_2) at a heating rate of 10 °C min^{-1}. Inset shows the crystallinity index of the luminescent systems.

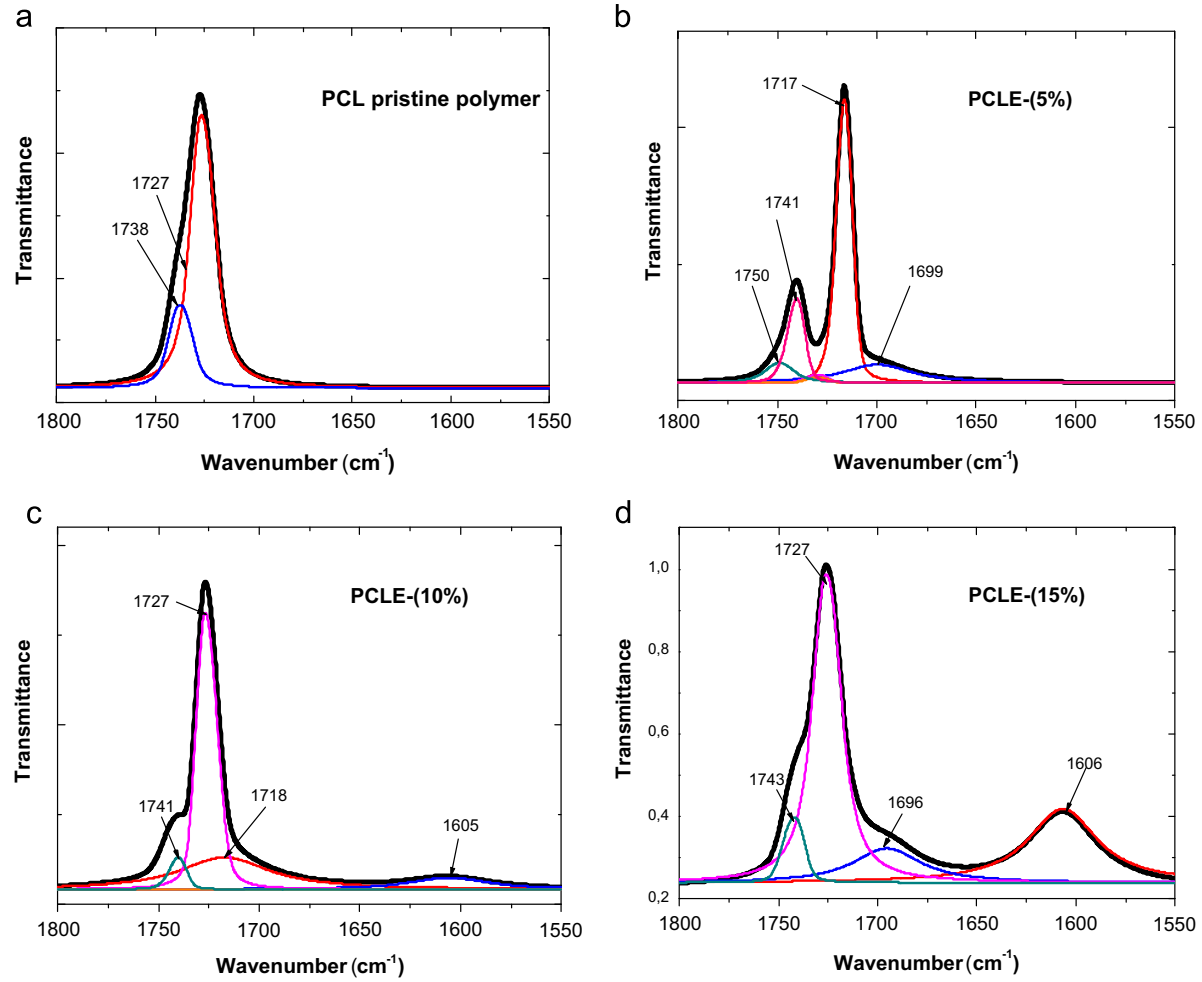

Fig. 3. Curve-fitted profiles for the PCLE samples from the IR spectra in the range 1800–1550 cm^{-1}. (a) PCL; (b) PCLE-5%; (c) PCLE-10% and (d) PCLE-15%.

process. In the cases of 10 and 15%, an absorption band around 1606 cm^{-1} deriving from of β-diketone appears, indicating the excess of complex (not coordinated with the polymer) on the PCLE systems.

The differential scanning calorimetry (DSC) technique was applied in order to verify the second melting temperature (T_{m2}) of the PCLE-*x*% materials in the film form. Compared with the undoped PCL polymer, the T_{m2} temperatures of the doped PCLE-*x*% systems show a decreasing trend from 60 to 57 °C with increasing doping percentage from 1% to 15% (Fig. 4). Meanwhile, the DSC curves of all doped films exhibit similar profiles. Calculated from the area of their respective DSC peaks, the ratio of the enthalpy of fusion between the PCLE-*x*% system per enthalpy of the undoped PCL film can be considered as the crystallinity index of the systems. The results reveal that the crystallinity of the PCL polymer is affected by the doping process. In the cases of complex containing more than 5% the crystallinity decreases as shown in the inset of Fig. 4 attributed to complex not coordinated in the polymer chain that restrain the crystallite formation.

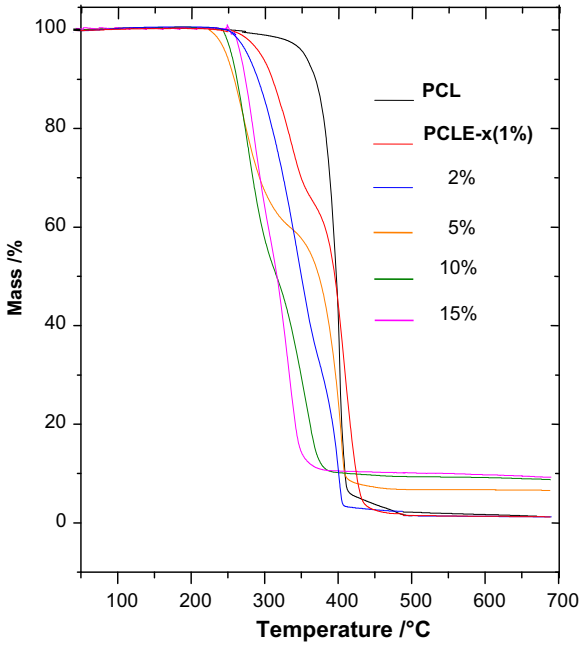

Fig. 5. Thermal decomposition curves of PCL polymer and PCLE-*x*% films where *x*=0, 1, 2, 10 and 15% registered in the temperature range of 323–973 K, under nitrogen atmosphere.

The normalized thermogravimetric curves for the PCL and PCLE-*x*% (*x*=1, 2, 5, 10 and 15) are shown in Fig. 5. The onset temperature of decomposition (T_{onset}) decreases from 375 °C for polycaprolactone to 325, 310, 295 and 280 °C with the increase of the Eu^{3+}-complex doping concentration at 1, 2, 5, 10 and 15%, respectively. In addition, compared to the one-step decomposition profile of undoped PCL, it is identified two weight-loss events for the luminescent PCLE systems (Fig. 5). The result suggests that (1) the ligand decomposition of the $Eu(tta)_3$ dopant, normally below 200 °C for Eu^{3+} complex and (2) the main chain scission of the PCL polymeric host, at higher temperature (~375 °C). The TG data of PCLE 15% decomposition show one event of mass loss, which may attributed to overlap of ligand decomposition and main chain scission of polymeric matrix.

Another interesting information that can be obtained from the TGA curves is that in the temperature interval from 50 to 200 °C no weight-loss event is observed, corroborating with the IR data that water molecules of the hydrated complex precursor are absent after the doping reaction. Confirming these results, a molecular structure of the PCLE systems is suggested and illustrated in Fig. 6. The coordination sites originally occupied by the H_2O molecules in the complex precursor are replaced by the oxygen atoms of the carbonyl group of the PCL polymer, comprising a protective environment around the Eu^{3+} ions that prevents it from multiphonon relaxation induced by coupling with the O–H oscillators.

3.1. Photoluminescence investigation

Fig. 7 shows the excitation spectra (monitoring the most intense $^5D_0 \rightarrow {}^7F_2$ transition at 614 nm) of the PCLE samples. All spectra display a broad absorption band in the range of 250 to 400 nm, which may result from the overlap of the electronic transitions of the tta ligand and the polymeric matrix. The excitation spectrum of $[Eu(tta)_3(H_2O)_2]$ complex shows narrow absorption bands assigned to the $^7F_0 \rightarrow {}^5D_2$ (~465 nm), $^7F_0 \rightarrow {}^5D_1$ (~530 nm) and $^7F_0 \rightarrow {}^5D_0$ (~578 nm) transitions of metal ion and broad absorption bands of the $S_0 \rightarrow S_1$ transition of tta ligand. On the other hand, in the excitation spectra of doped materials PCLE-*x*% (*x*=1, 2, 5, 10 and 15%) present very strong absorption bands (Fig. 7) arising from organic systems (polymer and tta). These data indicate that the Eu^{3+} ion are mainly excited via an effective sensitization process involving the

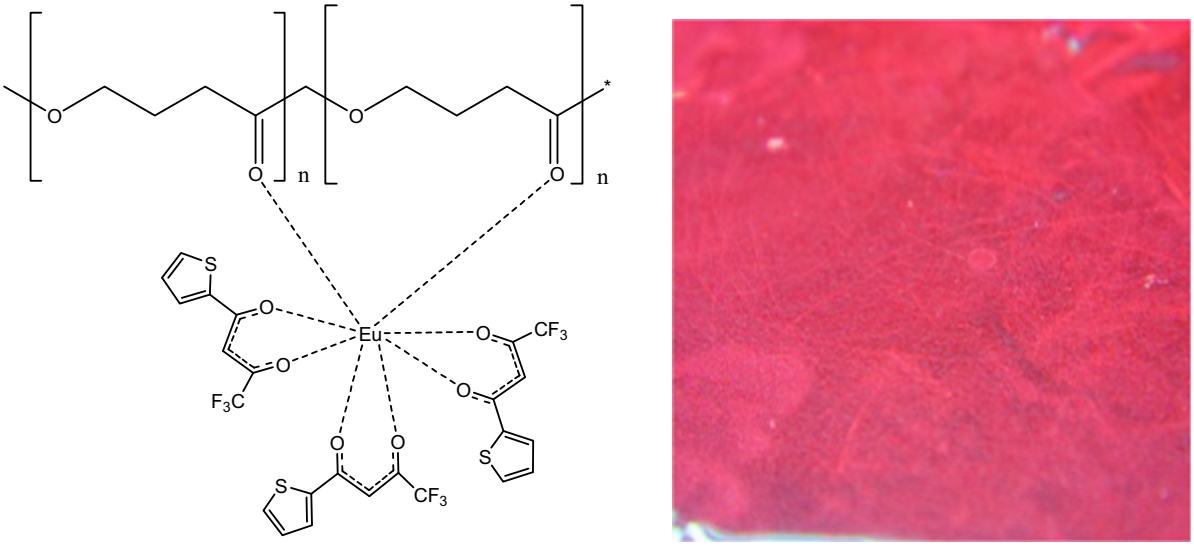

Fig. 6. A schematic illustration of the molecular structure of PCLE luminescent system and the PCLE-5% film photo.

polymer and tta ligand excited states, rather than by direct excitation centered in 4f–4f transitions. Moreover, the incorporation of the complex into the PCL polymer results in an improvement of the luminescence sensitization process.

The emission spectra of the doped PCLE-*x*% polymer films were recorded at ~298 K in the range of 420–750 nm upon excitation at 370 nm (Fig. 8). The characteristic narrow bands arising from the intraconfigurational $^5D_0 \rightarrow {}^5F_J$ transitions (J=0–4) of Eu^{3+} ion are observed, with dominant hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition around 614 nm in the whole spectral range, which indicates that the Eu^{3+} ion is located in an symmetry site without inversion center. It was also observed the broadened emission peaks of the $^5D_0 \rightarrow {}^7F_J$ transitions in the emission spectra of the doped polymer materials that can be explained by a non-homogeneity of Eu^{3+} sites due to the polymer structures [11,12]. One of the effects of a distribution of different symmetry sites occupied by the RE^{3+} ion is to produce the inhomogeneous line broadening. The absence of the broad emission bands of tta^- ligand in the blue/green region suggests an efficient intramolecular energy transfer between organic moiety and the europium ion.

The emission intensity, (I), taken as the integrated intensity (S) of the $^5D_0 \rightarrow {}^7F_J$ (J=0–4) emission curve, is given by [13]

$$I_{i\rightarrow j} = \hbar\omega_{i\rightarrow j} A_{i\rightarrow j} N_i \approx S_{i\rightarrow j} \quad (1)$$

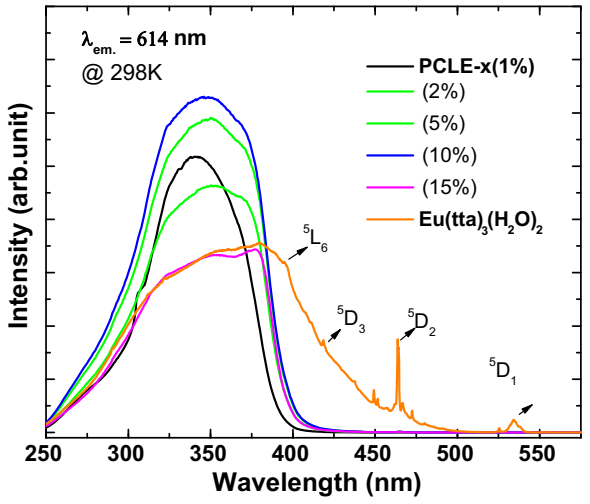

Fig. 7. Excitation spectra of PCLE-*x*% (x=1, 2, 5, 10 and 15) and complex [Eu(tta)$_3$(H$_2$O)$_2$] recorded at 298 K under emission at 614 nm.

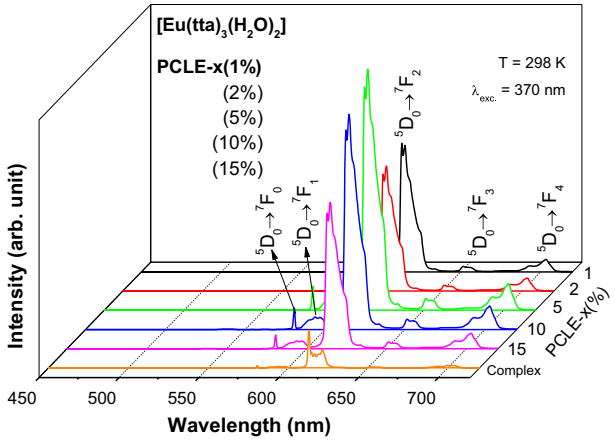

Fig. 8. Emission spectra of PCLE-*x*% (x=1, 2, 5, 10 and 15) recorded at 298 K under excitation at 370 nm.

where i and j are the initial $^5D_0$ and final levels ^7F_J (J=0–4), respectively, $\hbar\omega_{i-j}$ is the transition energy, A_{i-j} is the Einstein coefficient of spontaneous emission, and N_i is the population of the emitter $^5D_0$ level. The $^5D_0 \rightarrow {}^7F_5$ and $^5D_0 \rightarrow {}^7F_6$ transitions were neglected as they are not experimentally detected.

Since the emission intensity of the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition is almost insensitive to the chemical environments around the Eu^{3+} ion, it is considered as a reference. Then, the experimental coefficients of spontaneous emission, A_{0-J}, were determined by the following equation [14].

$$A_{0\lambda} = A_{01}\left(\frac{S_{0\lambda}}{S_{01}}\right)\left(\frac{\nu_{01}}{\nu_{0\lambda}}\right) \quad (2)$$

where υ_{0-1} and υ_{0-J} are the baricentres of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_J$ transitions, respectively. Lifetime (τ), radiative (A_{rad}) and non radiative (A_{nrad}) rates are related through the equation:

$$A_{tot} = \frac{1}{\tau} = A_{rad} + A_{nrad} \quad (3)$$

where A_{rad} can be obtained by summing over the radiative rates A_{0-J} for each $^5D_0 \rightarrow {}^7F_J$ transition $A_{rad} = \Sigma A_{0-J}$. Assuming that only non radiative and radiative processes are essentially involved in the depopulation of the $^5D_0$ state, η, can be expressed as:

$$\eta = \frac{A_{rad}}{A_{rad} + A_{nrad}} \quad (4)$$

The value of the emission quantum efficiency of $^5D_0$ level for the doped polymer materials (η=40–62%) are higher than for the [Eu(tta)$_3$(H$_2$O)$_2$] complex (η=29%) (Table 1). This result indicates the absence of multiphonon relaxation due to OH groups of water molecules in the doped polymer materials. Besides, when we compare the PCLE-*x*% (x=1, 2, 5, 10 and 15).

According to Krishna Rao et al. [15], if an ion is chemically bonded to the polymer chains, the type of chemical interaction between the both, ion and the polymer chain and the distribution of metal ion along the polymer chains will strongly influence the optical properties of the materials obtained, differently from the complex precursor non-coordinated. Consequently, it is suggested that the polymer matrix acts as a co-sensitizer to improve the energy transfer from the tta^- ligand to the Eu^{3+} ion in these systems, improving the emission quantum efficiency (η).

The R_{02} intensity parameter (Table 1) is the ratio between the intensities of the $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_2$ transitions for the PCLE systems in comparison with europium β-diketonate complex. The high R_{02} values (0.011–0.013) are similar to precursor complex (0.013) in all PCLE systems, showing a considerable intensity mixture of the J's states. This effect is mainly due to the mixing between the $^7F_2$ manifold and the $^7F_0$ level though the rank-two components of the ligand field [1,16].

Table 1
Emission quantum efficiencies (η), lifetimes (τ), radiative (A_{rad}), non-radiative (A_{nrad}) and total (A_{tot}) emission coefficient rates R_{02} for the PCLE-*x*% samples and the [Eu(tta)$_3$(H$_2$O)$_2$] complex.

Luminescent system	A_{rad} (s^{-1})	A_{nrad} (s^{-1})	A_{tot} (s^{-1})	τ (ms)	R_{02}	η (%)
PCL:Eu(tta)$_3$ 1%	863	1265	2128	0.470	0.011	40
PCL:Eu(tta)$_3$ 2%	869	990	1859	0.538	0.012	47
PCL:Eu(tta)$_3$ 5%	840	995	1835	0.545	0.013	46
PCL:Eu(tta)$_3$ 10%	868	868	1736	0.576	0.012	50
PCL:Eu(tta)$_3$ 15%	918	568	1486	0.673	0.012	62
[Eu(tta)$_3$(H$_2$O)$_2$][a]	1110	2923	3846	0.260	0.013	29

[a] Ref. [6].

4. Conclusions

Unprecedented highly luminescent polycaprolactone films doped with Eu (tta) complex was successfully prepared and characterized. In general, the polymeric systems presented enhancement in mechanical and thermal properties due to the interaction between Eu^{3+} ions and the polymer carbon-chain. The interaction between the PCL polymer matrix and Eu^{3+} complex occurs via replacement of the water molecules in the first coordination shell of the Eu^{3+} ion.

Crystallinity of the PCL polymer was affected by the doping process that restrains the polymeric crystallites formation in concentration higher than 5% of the complex. In the systems of complex 10% and 15%, a FTIR peak deriving from the β-diketone appears, indicating excess of complex on PCLE system that is corroborated with the decrease in the crystallinity of the systems owing to non-coordinated ion in the polymer chains.

The luminescence behaviors of the polymer films show significant improvement in comparison to the complex precursor, suggesting their promising applications as optical markers.

Acknowledgments

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References

[1] H.F. Brito, O.L. Malta, M.C.F.C. Felinto, E.E.S. Teotonio, in: J. Zabicky (Ed.), Patai Series: The Chemistry of Metal Enolates, John Wiley & Sons Ltd., Chichester, England, 2009, pp. 131–184 , Chapter 3.
[2] K. Binnemans, Chem. Rev. 109 (2009) 4283.
[3] L.D. Carlos, R.A.S. Ferreira, V. De Zea Bermudez, S.J.L. Ribeiro, Adv. Mater. 21 (2009) 509.
[4] J.C.G. Bünzli, C. Piguet, Chem. Rev. 102 (2002) 1897.
[5] G.F. de Sá, O.L. Malta, C. de Mello Donega, A.M. Simas, R.L. Longo, P.A. Santa-Cruz, Coord. Chem. Rev. 196 (2000) 165.
[6] O.L. Malta, H.F. Brito, J.F.S. Menezes, F.R. Gonçalves, E. Silva, S. Alves Jr., F.S. Farias Jr., A.V.M. De Andrade, J. Lumin. 75 (1997) 255.
[7] S. Faulkner, S.J.A. Pope, B.P. Burton-Pye, Appl. Spectrosc. Rev. 40 (2005) 1.
[8] J. Rocha, L.D. Carlos, F.A.A. Paz, D. Ananias, Chem. Soc. Rev. 40 (2011) 926.
[9] J. Kai, M.C.F.C. Felinto, L.A.O. Nunes, O.L. Malta, H.F. Brito, J. Mater. Chem. 21 (2011) 3796.
[10] M. Bradley, Curve Fitting in Raman and IR Spectroscopy: Basic Theory of Line Shapes and Applications Application Note: 50733 Thermo Scientific, Thermo Fisher Scientific, Madison, WI, USA, 2006.
[11] A.V.S. Lourenço, C.A. Kodaira, E.M. Ramos-Sanchez, M.C.F.C. Felinto, H. Goto, M. Gidlund, O.L. Malta, H.F. Brito, J. Inorg. Biochem. 123 (2013) 11.
[12] O.L. Malta, L.D. Carlos, Quim. Nova 26 (2003) 889.
[13] L.U. Khan, H.F. Brito, J. Hölsä, K.R. Pirota, D. Muraca, M.C.F.C. Felinto, E.E. S. Teotonio, O.L. Malta, Inorg. Chem. 53 (2014) 12902.
[14] S. Biju, R.O. Freire, Y.K. Eom, R. Scopelliti, J.C.G. Bünzli, H.K. Kim, Inorg. Chem. 53 (2014) 8407.
[15] K.S.V. Krishna Rao, H.-G. Liu, Y.-I. Lee, Appl. Spectrosc. Rev. 45 (2010) 409.
[16] H.-G. Liu, X.-S. Feng, K. Jang, S. Kim, T.-J. Won, S. Cui, Y.-I. Lee, J. Lumin. 127 (2007) 307.