

Preparation, Characterization, and Spectroscopic Properties of PC/PMMA Doped Blends: Study of the Effect of Rare-Earth Doping on Luminescence, Quenching Rate, and Lifetime Enhancement

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Optical properties of highly transparent blends formed by bisphenol A polycarbonate (PC) and poly(methyl methacrylate) (PMMA) and doped with either europium(III) thenoyltrifluoroacetone hydrate [Eu(TTA)₃-hydrate] or terbium(III) acetylacetonate hydrate [Tb(ACAC)₃-hydrate] were studied. From the absorption/emission spectra (200 to 800 nm), percolation limits of less than 0.4 wt/wt% for Eu and above 0.7 wt/wt% for Tb were found. Lifetimes for 20/80 and 60/40 Tb-doped blends were from 1.0 to 1.5 ms, respectively, about 5 times longer than for a similar blend prepared with Langmuir–Blodgett film. For blends doped with Eu, the lifetimes were from 0.4 to 0.8 ms, almost double that for the pure complex. The results indicated interactions between the PC/PMMA blends and the rare-earth ion complex. Particularly, photoluminescent spectra evidenced the incorporation of the Eu³⁺ and Tb³⁺ ions into the blend, with quenching observed near 1.0 wt/wt%, except for the 20/80 blend doped with Eu ion, in which luminescence increased to 5 wt/wt %.

1. Introduction

The past decade has seen increasing interest in doped or codoped materials for laser development, including transparent vitroceraamics,¹ phosphor materials based on metal complexes as well as luminescent concentrators for solar cells,^{2,3} electro-optical devices dependent on polarizing emitters,⁴ and other devices such as planar light emitters⁵ and blue-shifted emitters.⁶ There is also great interest in optical telecommunication amplifiers, where light is used to transport information, and optical gain is always welcomed.⁷ Rare-earth (RE)-doped inorganic crystals are suitable materials for this purpose and a wide variety of other applications. However, some of them may present serious limitations in terms of their mechanical properties, processability, and chemical and physical stability. In addition, they show limited solubility, and their pure complexes can absorb moisture from the air and form clusters, resulting in luminescence quenching at relatively low concentrations.

These factors make the pure complexes highly promising for photophysical applications, but limit their practical use. In order to overcome these shortcomings, RE ions are usually synthesized with appropriate ligands that make it possible to incorporate them into organic, inorganic, or hybrid organic/inorganic matrices. Zeolites,⁸ mesoporous materials,^{9–11} sol–gel silica or organically modified silicates (ORMOSIL),^{12–14} and polymers¹⁵ are the most common hosts, and have been investigated in recent years. The proper incorporation of an RE complex into organic polymers represents an ideal and extremely versatile approach to generate such hybrid materials.

It is known that for RE ions, shielding of the electrons from the 4f shell partially filled and surrounded by completely filled 5s and 5p shells may confer special optical properties. Trivalent RE ions with a partially filled 4f shell have energy levels of equal parity, so that electric dipole transition is forbidden by Laporte's rule. This group includes terbium (Tb), europium (Eu), and erbium (Er), among other trivalent RE ions. For a solid with some energy levels represented by quantum levels labeled by odd-parity wave functions, the existence of a small degree of overlapping makes the transition unlikely to occur. For this reason, the cross sections for absorption and emission for these RE ions are small, resulting in longer lifetimes on the order of milliseconds. The degenerate 4f levels may be split by a local electric field around the RE ion, by means of the Stark effect. However, the shielding effect of 5s and 5p on the 4f levels may result in a small-magnitude split, and therefore, narrow emission lines are expected, as well as a small bias from the host material on the emission wavelength.¹⁶

Eu(III) and Tb(III), two of the most important elements among the lanthanides, with β -diketones (or other ligands that can absorb and transfer energy to the central metal) provide very strong luminescence due to increased absorbability.^{17–20} Because of the narrow f–f transition, good sensitization of Eu³⁺ and Tb³⁺ luminescences can be achieved through the antenna effect,¹⁷ where the absorbing energy is efficiently transferred to the ions. Europium(III) thenoyltrifluoroacetate hydrate [Eu(TTA)₃-hydrate] and terbium(III) acetylacetonate hydrate [Tb(ACAC)₃-hydrate] are used as RE sources in polymeric matrices. They show luminescent properties due to the energy transfer between their ligand triplet state and the emitter ⁵D₀ level of Eu³⁺ and also between the emitter ⁵D₄ level of Tb³⁺. Moreover, thenoyltrifluoroacetate and acetylacetonate anions

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act as chelates, protecting the RE ion from water molecules,²¹ and thus increasing luminescence efficiency.^{22,23}

Materials based on acrylic polymeric systems, either pure or modified with inorganic salts, show unique properties that have been used to develop special devices. Doping polymeric blends with RE ions results in very narrow emission bands, raising the possibility of obtaining stable luminescent materials. This allows their application as luminescent probes and sensors, since the structural properties of these materials are predominantly determined by the local configuration in the behavior of the cation.^{23–25}

Blends of bisphenol A polycarbonate (PC) and poly(methyl methacrylate) (PMMA) have been reported.^{26–30} Viville³¹ showed that PC/PMMA blends are partially miscible due to the formation of an $n-\pi$ complex between the PMMA ester group and the phenyl ring of PC. Agari et al.²⁶ reported miscible PC/PMMA blends obtained by casting, in a single-phase system under low critical solution temperature. Kyu and Saldanha²⁷ discussed the effect of the solvent on the morphology of PC/PMMA films prepared by casting, suggesting that the morphology is mostly controlled by the competition between a phase-separation phenomenon and solvent-induced crystallization. Many authors have discussed the phase behavior of PC/PMMA blends, based on the preparation method and on the nature of the solvent.^{30,32} Two procedures can be used to prepare PC/PMMA blends using tetrahydrofuran (THF) as a solvent. In one procedure, the solvent is removed by heating the polymer solution in the 48–60 °C range,^{27,29,33,34} and in the other, the solvent is removed by precipitation using a nonsolvent.^{34,35} As a polymer matrix, PMMA has attracted particular interest for its low optical absorption, refractive index tailorability with molecular weight, high resistance to UV radiation, simple synthesis, and low cost. It also has been considered to form a quasi-cross-linked structure through strong dipole–dipole interactions, which prevent it from crystallizing, and is regarded as a transparent glass. Furthermore, acrylic polymers exhibit excellent optical properties (good transparency), excellent resistance for outdoor applications, and good compatibility with additives and plasticizers. However, the use of the pure PMMA has some practical disadvantages, e.g., its brittleness and high water absorption. Many efforts have been made to circumvent these drawbacks through copolymerization and polymer blending. A homogeneous polymer mixture contributes to the performance of PMMA without loss in transparency. Among a number of PMMA blends studied for miscibility, PMMA with PC is one of the most thoroughly investigated blends, due to the excellent properties of PC, including outstanding ductility, low water absorption, and high glass transition temperature.

Here we report the investigation of the spectroscopic and luminescent properties of blends formed by PC and PMMA doped with different amounts of the RE complexes, Eu(TTA)₃-hydrate and Tb(ACAC)₃-hydrate, and the influence of the β -diketonate ligand on the photoluminescence properties and energy-transfer processes of these compounds. The interaction between the RE complexes and the blend was studied through photoacoustic spectroscopy (PAS), photoluminescent (PL) spectroscopy, the ⁵D₄ emission lifetime for Tb(III), and the ⁵D₀ emission lifetime for Eu(III).

2. Experimental Section

2.1. Sample Preparation. PC (64 000 g·mol⁻¹, Aldrich) and PMMA (120 000 g·mol⁻¹, Aldrich) were used as received. Distilled THF (Merck) and hexane (Chemco) were used as solvents. Eu(TTA)₃-hydrate, formula Eu(C₈H₅F₃O₂S)₃·2H₂O

(Aldrich) and Tb(ACAC)₃-hydrate, formula Tb(C₅H₇O₂)₃·xH₂O (Aldrich, hereafter called) were used as received.

PC/PMMA blends were prepared as previously described.³⁶ The blends were prepared as a powder by the precipitation method. Weighed polymer fractions (20/80 and 60/40 PC/PMMA in %) were dissolved in THF at room temperature, homogenized for 24 h, and prepared by slowly pouring the mixture into a beaker containing hexane under vigorous stirring. The white precipitate formed was filtered, repeatedly washed with hexane, and dried in a vacuum oven at 85 °C for 48 h. Doped PC/PMMA blends were prepared using the same procedure, and by adding 0.5, 1, 2, 4, 8, 16% (w/w) of Eu(TTA)₃-hydrate and 0.5, 1, 2, 4, 8, 16, 20% (w/w) of Tb(ACAC)₃-hydrate to the polymer solution. After the solution was poured into hexane, the yellowish precipitate formed was treated similarly. To prepare the samples, the precipitate was pressed using a stainless-steel mold (0.8 cm diameter and 500 μ m thick) at 155° for 15 min at 80 Pa.

2.2. Physical Measurements. A homemade photoacoustic (PA) cell was used in the PAS measurements, and the samples were illuminated with a modulated monochromatic light beam from a source. A photoacoustic spectrometer, with a Brüel–Kjaer microphone coupled to the PA cell and lock-in amplified detection running at 21.2 Hz, was used in all experiments.

The PL spectroscopy measurements were carried out at room temperature using a monochromatized Xenon arc lamp and a monochromator coupled with a photodiode detector for setting the 400–800 nm range and recording the luminescence emission signal. Lifetime decay measurements of terbium and europium main emitting levels were obtained by a IBH-Horiba-Jobin-Yvon 5000U time resolved fluorescence system equipped with picoseconds photon detection module (TBX-04) under lighting from a Xenon flash lamp, monochromatized at 325 nm.

3. Results and Discussion

The photoacoustic UV–vis spectra of the blends doped with RE ions were obtained in the 200–500 nm range at 21 Hz, 3.16 mm slit, light from a Xenon arc lamp at 800 W, normalized, and subtracted from the calibration sample base spectrum (pure PC/PMMA). Figure 1 shows the photoacoustic signal related to the (a) terbium and (b) europium complexes, respectively. Shoulders in the 260–400 nm range were assigned to interactions between the RE complexes and the PC/PMMA matrix. The data presented in insets were fitted with the scaling law of the percolation theory $I_{\max} = c(f - f_p)^t$, where I_{\max} is the maximum intensity PA signal, c is a constant, t is a critical exponent, f is the percentage of the RE ion, and f_p is the percentage of the ion at the percolation threshold. By fitting the experimental data to the plot of $\log(I_{\max})$ versus $\log(f - f_p)$, it was possible to estimate the system percolation threshold (Table 1).

The PL spectroscopy measurements were recorded at room temperature with excitations generated by a Xenon arc lamp monochromatized at 322 and 340 nm for Tb(ACAC)₃-hydrate and Eu(TTA)₃-hydrate, respectively, with the emissions from these doped blends analyzed by an Oriel monochromator with a holographic grating of 1200 lines/mm and detected at 12 Hz by a photodiode detector coupled to the analyzer exit. Figures 2 and 3 show the PL spectra for the terbium and europium complexes, respectively, including their insets, which show spectra integrated areas for different concentrations of the RE ions in each fraction of the PC/PMMA blends.

The PAS results show that the I_{\max} of doped blends with 2% Tb ion was 0.71% for the 20/80 and 0.47% for the 60/40 blends,

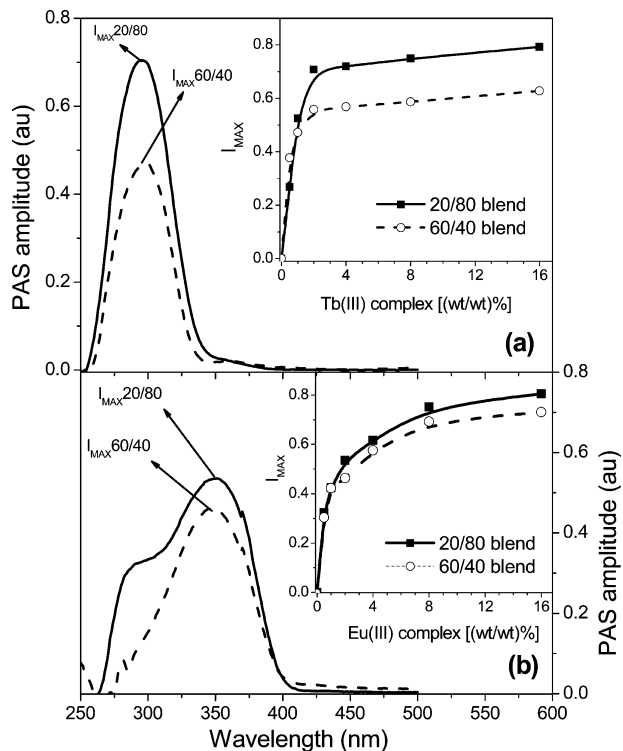


Figure 1. UV-vis photoacoustic spectra of 20/80 and 60/40 PC/PMMA blend fractions doped with 2% of (a) Tb(ACAC)₃-hydrate and (b) Eu(TTA)₃-hydrate. Inset: Maximum-intensity PA signal as a function of the RE doping content.

TABLE 1: Blend Percolation Threshold Data^a

blend + RE complex	f_p (wt/wt %)	t	R
20/80 + Tb	0.694	0.078	0.873
60/40 + Tb	0.909	0.102	0.998
20/80 + Eu	0.378	0.195	0.995
60/40 + Eu	0.381	0.185	0.992

^a t = critical exponent; f_p = percentage at the percolation threshold, R = correlation coefficient.

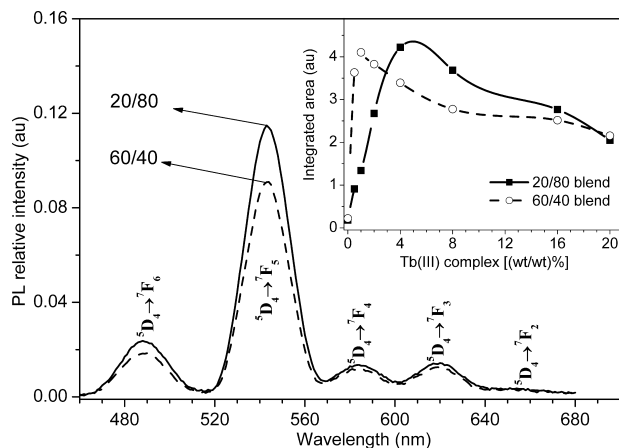


Figure 2. PL emission spectra of PC/PMMA blend fractions doped with 4% Tb(ACAC)₃-hydrate. Inset: Integrated area PL signal as a function of the Tb doping content.

whereas, for the blends with 16% Eu ion doping, the I_{\max} was 0.54% for the 20/80 blends and 0.46% for the 60/40 blends. These results also suggest that there was a more efficient energy transfer between the ligand and the rare earth, with the 20/80 blends having a higher PAS signal intensity than the 60/40 blends for any concentration of rare earth added to the

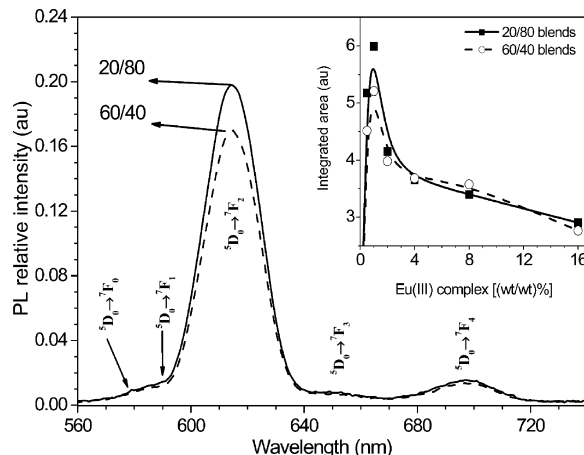


Figure 3. PL emission spectra of PC/PMMA blend fractions doped with 1% Eu(TTA)₃-hydrate. Inset: Integrated area PL signal as a function of the Eu doping content.

PC/PMMA matrix. These results are consistent with the PL outputs of the blends, indicating a more homogeneous distribution of RE ions and resulting in a higher PA signal for blends with lower Tb(ACAC)₃-hydrate and Eu(TTA)₃-hydrate contents (Figures 2 and 3, respectively). These features also corroborate the preferable location of the RE complex within the PC phase.^{36,37}

In samples containing Tb³⁺, spectral data showed five emissions in the range 460–680 nm due to the Tb³⁺, which are assigned to $^5D_4 \rightarrow ^7F_j$ ($j = 2, 3, 4, 5, 6$) transitions, the $^5D_4 \rightarrow ^7F_5$ (543 nm) being the strongest relative emission intensity and $^5D_4 \rightarrow ^7F_2$ (650 nm) the weakest. Five typical Eu³⁺ luminescence peaks in the range of 560–740 nm emissions appear at 578 nm ($^5D_0 \rightarrow ^7F_0$), 590 nm ($^5D_0 \rightarrow ^7F_1$), 614 nm ($^5D_0 \rightarrow ^7F_2$), 652 nm ($^5D_0 \rightarrow ^7F_3$), and 698 nm ($^5D_0 \rightarrow ^7F_4$), with the strongest peak at 614 nm and the 7F_0 transitions appearing superimposed as one broad band.

The emission bands shown for the PL data corresponding to Tb³⁺ and Eu³⁺ are all inhomogeneously broadened, suggesting a statistical distribution of different sites available for both in the polymeric matrix.^{17,24,25,36,38,39} The PL spectra also allowed us to assess the emission quenching, which can occur for two main reasons: first, a typical ion concentration quenching can be observed in the insets in Figures 2 and 3,^{24,37–39} showing a higher relative intensity of light output for a lower ion concentration in the blends; second, a higher PL signal output for a lower PC concentration, suggesting a PC killer-like effect (probably due to the phenyl ring) on the ester group in the organic antenna.

The luminescent decay and fitted curves (not shown), with emission monitored at $^5D_4 \rightarrow ^7F_5$ for Tb(III) and $^5D_0 \rightarrow ^7F_2$ for Eu(III), were adjusted with a first-order exponential decay function. The lifetime (τ , decay time) of the 5D_4 and 5D_0 emitting level of the decay curve of the doped blends are shown in Table 2. By comparing the values obtained for the precursor complex and the doped blends, increasing lifetimes were observed for the polymeric systems. The observed increase in decay time must be related to the substitution of ligand groups from the polymeric matrix for the water molecules at the RE ions coordination shell.^{23,39} The higher the increase in the amount of complex, the lower the observed lifetime decay. In general, lower decay rates for more highly doped blends indicate luminescence quenching, which is also reflected in the PL signal output.^{37,39} Hence, these results showed that a saturation effect

TABLE 2: Time-Resolved PL Data for Blends Doped with Tb(ACAC)₃-hydrate and Eu(TTA)₃-hydrate

doping ratio (% RE)	Tb(III)		Eu(III)	
	τ_{exp}^a (ms) 20/80	τ_{exp} (ms) 60/40	τ_{exp} (ms) 20/80	τ_{exp} (ms) 60/40
0.5	1.089	1.137	0.569	0.511
1.0	1.239	1.184	0.655	0.493
2.0	1.178	1.173	0.793	0.477
4.0	1.169	1.126	0.728	0.463
8.0	1.154	1.108	0.661	0.467
16.0	1.157	1.136	0.653	0.443
20.0	1.147	1.126	***	***
pure complex ^b	—	—	0.288	—
LB film ^c	0.245	—	0.486	—

^a τ_{exp} = experimental lifetime. ^b Data taken from Parra et al.³⁹^c Data taken from Zhang et al.⁴⁰

occurs at higher RE concentrations when the PMMA amount is increased, for both ions presented.

4. Conclusion

The RE complexes Tb(ACAC)₃-hydrate and Eu(TTA)₃-hydrate doping polymeric blends show good luminescence characteristics, based on electronic transitions of the ions. PAS data showed absorption bands of the ions in both fractions of the PC/PMMA blends, providing a percentage at the percolation threshold, related to the maximum-intensity PA signal as a function of the ion-doping content. PL spectra indicate that the emission is sensitive to an increase of the ion concentration and it almost quenches blends, showing a preferable location of the RE complexes in the PC phase and corroborating the PAS data. Finally, we note that the polymeric matrix also acts as an antenna, absorbing energy that is then efficiently transferred to the Tb³⁺ and Eu³⁺ energy levels, with the ensuing enhancement of the luminescence intensity of the novel system. On the basis of these results, a series of new RE complexes could be designed and synthesized to optimize the luminescent properties of these lanthanide ions, and to generate secondary colors by codoping amounts.

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