Synthesis and Luminescence Properties of Novel Eu-Containing Copolymers Consisting of Eu(III)−Acrylate−*β*-Diketonate Complex Monomers and Methyl Methacrylate

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Received February 22, 2000. Revised Manuscript Received May 22, 2000

Luminescent Eu-containing copolymers were synthesized through the copolymerization of Eu−complex monomers containing β-diketones with methyl methacrylate and characterized by FT-IR, UV−vis, XPS, GPC, TGA, and DSC. All these Eu copolymers are fully soluble in common organic solvents and can be cast into transparent, uniform, thin films with good mechanical flexibility and thermal stability. The Eu−copolymer luminophores exhibited intense red light at 615 nm under UV excitation at room temperature, which is attributed to the $^5D_0 \rightarrow ^7F_2$ transition of Eu(III) ions. The luminescence intensities, lifetimes and monochromaticities, $\eta(^5D_0 \rightarrow ^7F_2/^5D_0 \rightarrow ^7F_1)$, of the Eu−copolymers are much higher than that of the corresponding Eu−complex monomers as well as Eu−complex/PMMA blends. Energy transfer processes and microenvironment effects were found to contribute to the improvement of the luminescence properties of the Eu−copolymers. A study of the dependence of emission intensities of the Eu−copolymers on the Eu content showed that the emission intensities increased nearly linearly with increasing Eu content, and no significant emission concentration quenching phenomenon was observed at the Eu content of 0−6.38 mol %. This indicates that the Eu−complex units in the Eu−copolymers are very uniformly bonded to the polymer chain, which is in good agreement with the result of polymer structure analysis.

Introduction

Luminescent rare earth complexes, particularly europium β-diketonates, have been intensively studied with respect to applications for luminescence and as laser materials[1−5] since the first successful laser action in europium β-diketonate was reported by Lempicki and Samelson in 1963.[6] Recently, rare earth complexes have attracted considerable attention for organic electroluminescent (EL) devices[7−11] as well as for optical microcavity emitters[12,13] owing to their inherent extremely sharp emission bands and potentially high internal quantum efficiency. However, there are three major problems in using small rare earth complexes. The first is that rare earth complexes are unstable in organic solution and tend to dissociate into lower complex forms.[14] The second is that most rare earth complexes usually contain inner-coordinated water molecules, leading to low luminescence quantum efficiency because the coordinated H_2O molecules can effectively quench the luminescence by the nonradiative dissipation of energy on the high-energy O−H vibrations.[15] The third is that it is often not possible to form vacuum-vapor deposited films due to the nonvolatile nature of rare earth complexes.[16,17] Vacuum-vapor deposition is known

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10.1021/cm000158i CCC: $19.00

to be a suitable method for forming uniform thin films with metal complexes.

Upon inheriting the advantages of both the luminescence characteristics of rare earth ions and the material properties of plastics, rare earth metal-containing polymers have also attracted attention in the past decade.[18−21] In comparison with small molecular weight rare earth complexes, besides the advantage of the desired mechanical flexibility, polymer-based rare earth luminescent materials can be solution or fused processable, which is more attractive for optical and electronic applications. Furthermore, the dissociation may be minimal in the solid polymer complexes, where rare earth complex units should be, to a certain extent, locked into a specific configuration due to the synergistic effects of metal complexes with polymers.[18] Okamoto and co-workers have synthesized a series of rare earth metal-containing polymers and studied their luminescence properties, even demonstrating the probability of laser action.[18,22−24] However, most rare earth metal-containing polymers reported so far were prepared by direct reaction of the polymer ligands with rare earth ions. Although this synthetic methodology is simple, the polymer luminophores usually show serious emission concentration quenching due to the occurrence of ionic aggregates even at low rare earth content.[22] In addition, the microenvironment of each rare earth ion is very different and complicated, which makes the elucidation of the luminescence properties difficult.[25]

Up to now few rare earth metal-containing polymers were synthesized by the copolymerization of rare earth metal-containing monomers and organic monomers,[18] which are expected to be intensely luminescent materials because it may avoid forming ionic aggregates by means of designing appropriate rare earth-containing monomers in the polymer systems. In view of the excellent luminescence properties and potential commercial applications of the latter polymer systems, it is important and necessary to simplify the synthetic procedures and further improve the luminescence properties of rare earth metal-containing polymers.

In this paper, we present a simple synthetic approach to construct a series of highly efficient luminescent Eu-containing polymers. The first luminescent Eu−complex monomers without coordinated water molecules were designed and synthesized through the reaction of europium isopropoxide with β-diketone and acrylic acid, then Eu-containing copolymers were prepared by the copolymerization of Eu−complex monomers with methyl methacrylate (MMA). The luminescence properties of the Eu−copolymers and monomers were investigated in detail in solution and solid states. The energy transfer processes and the influence of polymer conformation will be discussed.

Experimental Section

Measurements. Microanalyses for C and H were conducted on a Carbon-Erba 1106 model elemental analyzer. Eu content was determined by EDTA titration after the Eu(III) ions in the complexes were dissociated with 10% hydrochloric acid. FT-IR spectra were recorded on a Nicolet Magna 750 spectrometer by dispersing samples in KBr disks. Thermogravimetric analysis (TGA) was carried out on a DuPont Thermal Analyst 2100 system with a TGA 2950 thermogravimetric analyzer under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) was run on a DuPont DSC 2910 module in conjunction with the DuPont Thermal Analyst system at a heating rate of 10 °C min^{-1} in air. The glass transition temperatures were taken as the midpoint of the change in slope of the baseline. Gel permeation chromatography (GPC) analysis was conducted with a Shimadzu LC-6A HPLC system using polystyrene as standard and THF as the eluent. X-ray photoelectron spectroscopy (XPS) spectra were obtained using a VG Scientific ESCALAB 220I-XL photoelectron spectrometer with binding energy values refered to C_{1s} (284.6 eV). Absorption spectra were recorded with a Shimadzu UV-2201PC spectrophotometer. Luminescence spectra were performed with a Hitachi F-3000 spectrophotometer. Luminescence lifetimes were measured on a laser-induced fluorescence spectrophotometer assembled for this purpose. The samples were excited by the 355 nm outputs of a pulsed neodymium laser, the pulse duration being ∼10 ns. The resulting emission was monitored at 615 nm by a WDG30 grating monochromator and detected by a Tektronix TDS 620B oscilloscope.

Materials. Eu_2O_3 (99.99%) was purchased from the Yaolong Non-Ferrous Co. Ltd. and used without further purification. Acetylacetone (acac) was redistilled before use. Benzoylacetone (BA), dibenzoylmethane (DBM), and thenoyltrifluoroacetone (TTA) were recrystallized from ethanol. Acrylic acid (AA) and methyl methacrylate (MMA) were purified according to standard procedures. 2,2′-Azoisobutyronitrile (AIBN) was recrystallized twice from ethanol. 2-Propanol and benzene were distilled over sodium. Other chemicals were analytical grade and used without further purification.

Synthesis of Eu−Acrylate−β-Diketonate Complex Monomers, Eu(TTA)$_2$AA. Anhydrous europium chloride (1.29 g, 5.0 mmol), which was prepared from Eu_2O_3, hydrochloric acid, and ammonium chloride,[26] was dissolved in 20 mL of anhydrous 2-propanol and benzene (1:1) by heating in a 150 mL flask under N_2. To this stirred solution was added a solution of sodium isopropoxide (1.23 g, 15.0 mmol) in 20 mL of 2-propanol. The mixture was refluxed for 4 h (europium isopropoxide was synthesized) and then a solution of thenoyltrifluoroacetone (2.22 g, 10.0 mmol) in 20 mL of benzene was added dropwise. After refluxing for 2.5 h, a solution of acrylic acid (0.36 g, 5.0 mmol) in 10 mL of benzene was added. The reactive mixture was refluxed for another 2 h and cooled. The mixture was filtered and the residue was obtained from the filtrate after the solvent evaporated. The residue was washed five times with cyclohexane and dried under vacuum at room temperature for 24 h to give 2.53 g of a pale yellow product with a yield of 76%. The complex is fairly soluble in benzene, tetrahydrofuran (THF), ethanol, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). Mp: >250 °C. FT-IR (cm^{-1}): 3114, 1613, 1582, 1543, 1512, 1458, 1412, 1357, 1309, 1250, 1232, 1186, 1142, 1063, 935, 846, 789, 752, 720, 685, 640, 584, 498, 467. UV−vis (nm): 313, 332 (sh). Anal. Calcd for Eu(TTA)$_2$AA: C, 34.30; H, 1.67; Eu, 22.84. Found: C, 33.96; H, 1.78; Eu, 22.79.

Eu(acac)$_2$AA. The synthesis and purification were similar to the above procedures for Eu(TTA)$_2$AA, except that acety-

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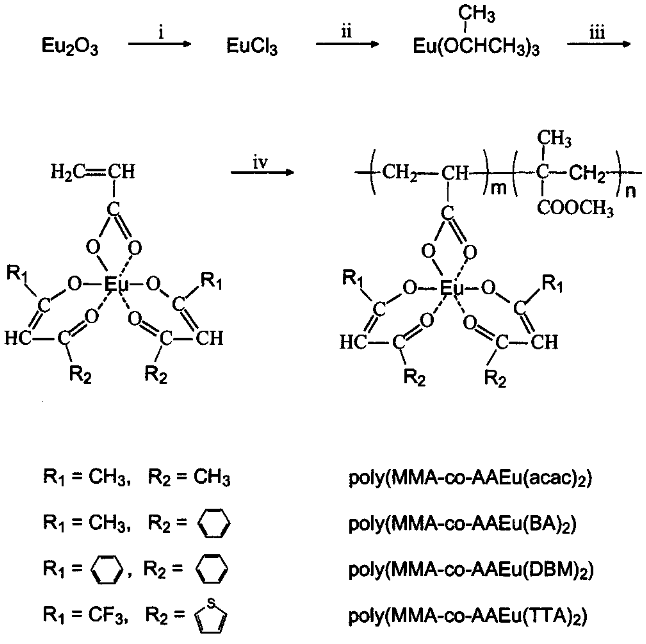
Scheme 1. Synthetic Route for the Eu-containing Copolymers[a]



[a] Reagents and conditions: (i) HCl/NH$_4$Cl; (ii) Na(O^{i}Pr)/^{i}PrOH/benzene; (iii) β-diketone/AA/^{i}PrOH/benzene; (iv) MMA/AIBN/DMF.

lacetone was used in place of thenoyltrifluoroacetone. Yield: 70%. Mp: >250 °C. FT-IR (cm^{-1}): 2958, 1589, 1522, 1437, 1385, 1265, 1192, 1020, 922, 764, 677, 658, 611, 532, 413. UV−vis (nm): 297. Anal. Calcd for Eu(acac)$_2$AA: C, 37.07; H, 4.07; Eu, 36.07. Found: C, 36.95; H, 4.01; Eu, 36.54.

Eu(BA)$_2$AA. The synthesis and purification were similar to the above procedures for Eu(TTA)$_2$AA, except that benzoylacetone was used in place of thenoyltrifluoroacetone. Yield: 75%. Mp: >250 °C. FT-IR (cm^{-1}): 3066, 2958, 1595, 1558, 1531, 1487, 1452, 1387, 1306, 1282, 1201, 1180, 1109, 1070, 1028, 962, 845, 764, 714, 688, 679, 559, 519, 413. UV−vis (nm): 311, 336 (sh). Anal. Calcd for Eu(BA)$_2$AA: C, 50.65; H, 3.88; Eu, 27.86. Found: C, 50.29; H, 3.97; Eu, 27.58.

Eu(DBM)$_2$AA. The synthesis and purification were similar to the above procedures for Eu(TTA)$_2$AA, except that dibenzoylmethane was used in place of thenoyltrifluoroacetone. Yield: 79%. Mp: >250 °C. FT-IR (cm^{-1}): 3060, 1597, 1552, 1522, 1479, 1456, 1442, 1311, 1286, 1221, 1178, 1066, 1024, 941, 783, 750, 717, 686, 608, 515, 470, 428. UV−vis (nm): 316, 341 (sh). Anal. Calcd for Eu(DBM)$_2$AA: C, 59.20; H, 3.76; Eu, 22.70. Found: C, 58.76; H, 4.03; Eu, 22.68.

Synthesis of Eu-Containing Copolymers Poly(MMA-*co*-AAEu(*β*)$_2$). The mixture of comonomer Eu−complex monomer and MMA (1.84 mol/L) in certain ratios, a small amount of initiator AIBN (6.09×10^{-3} mol/L), and solvent DMF was mixed and added into a glass polymerization tube. The homogeneous solution was degassed and sealed under vacuum. The polymerization was carried out by heating the sealed tube at 60 °C for 60 h. The viscous homogeneous solution was then dissolved in THF and poured into 200 mL of methanol with stirring. The resulting precipitate was redissolved in THF and reprecipitated in methanol twice and finally dried under vacuum at 50 °C for 24 h to afford powder polymers. The Eu content in the copolymers is in the range of 0.27−7.50 mol %. Poly(methyl methacrylate) (PMMA) was prepared using the same polymerization conditions for comparison.

Results and Discussion

Synthesis and Characterization of Eu-Containing Copolymers. The synthetic route for Eu−copolymers as outlined in Scheme 1 is very convenient. Eu−acrylate−β-diketonate complexes as monomers were synthesized by the reaction of europium isopropoxide with β-diketone (acac, BA, DBM, TTA) and acrylic acid in anhydrous organic solvents. In comparison with the water-phase synthetic approach using oxide as the starting material, this synthetic method utilizing highly reactive rare earth alkoxide in organic phase has the advantage of affording the desired complex without inner-coordinated water molecules, especially for preparing a rare earth−mixed ligands complex. Eu−copolymers were prepared by the radical copolymerization of the corresponding Eu−complex monomers with MMA using AIBN as an initiator in DMF. Eu−copolymers are fully soluble in common organic solvents such as chloroform, 1,2-dichloroethane, THF, benzene, and toluene and can be easily cast into transparent, uniform, thin films. The number-average molecular weights (M_n) and the polydispersity indexes (PDI) of the resulting polymers, as shown in Table 1, were measured by gel permeation chromatography (GPC) using THF as eluent and polystyrene as standard. The M_n and PDI of all Eu−copolymers are in the range of 53 700−72 600 and 4.79−5.96, respectively. However, the M_n values of all Eu−copolymers are smaller, and the PDI are larger than that of PMMA. It may be due to the lower polymerization reactivities of Eu−complex monomers than that of MMA. From the experimental data of the Eu(BA)$_2$AA−MMA polymerization system in DMF at 60 °C, the reaction ratios of MMA and Eu(BA)$_2$AA were 1.62 ± 0.01 and 0.056 ± 0.005, respectively.

The structures of all Eu−complex monomers and Eu−copolymers were confirmed by FT-IR, UV−vis, and XPS spectra. For example, for Eu(TTA)$_2$AA and poly(MMA-*co*-AAEu(TTA)$_2$), the spectra (not shown) could be interpreted as follows. The FT-IR spectrum of monomer Eu(TTA)$_2$AA shows that the C=O stretching vibration of free acrylic acid at 1702 cm^{-1} is absent and the typical antisymmetric and symmetric stretching vibrations of carboxylate at about 1582 and 1458 cm^{-1} appear. The C=O and C=C stretching vibrations of TTA in the complex are shifted to lower frequencies, from 1661 cm^{-1} of free TTA to 1613 cm^{-1} of coordinated TTA and from 1585 to 1543 cm^{-1}, respectively. Two weak bands at 498 and 467 cm^{-1} corresponding to the Eu−O stretching vibrations were observed.[27] These results suggest that the coordination bonds were formed between the Eu(III) ion and the ligands AA and TTA in the complex. However, the typical OH absorption at 3200−3500 cm^{-1} is undetectable, implying that there are no coordinated H$_2$O molecules in the complex, which is in good agreement with the result of the elemental analysis. This result verifies that the above-described synthetic method can easily afford the complex without coordinated water. It is very important to eliminate water molecules in complexes to obtain highly efficient luminescence rare earth complexes due to decreasing the deactivation of O−H oscillators.[15] The FT-IR spectrum of copolymer poly(MMA-*co*-AAEu(TTA)$_2$) is quite similar to that of PMMA as the Eu content, i.e., the content of the Eu−complex moiety in the copolymer, is low. However, as the Eu content is of up to 3.51 mol %, the C=O and C=C stretching vibrations of TTA in the copolymer were

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Table 1. Properties of the Eu-Containing Copolymers

polymer	MMA/Eu−monomer (mol)	Eu (%)	M_n	PDI	T_d (°C)	T_g (°C)
poly(MMA-*co*-AAEu(acac)$_2$)	MMA/Eu(acac)$_2$AA (50)	2.33	72 600	4.79	265	120
poly(MMA-*co*-AAEu(BA)$_2$)	MMA/Eu(BA)$_2$AA (50)	2.27	53 700	5.96	259	118
poly(MMA-*co*-AAEu(DBM)$_2$)	MMA/Eu(DBM)$_2$AA (50)	2.20	70 700	6.90	256	121
poly(MMA-*co*-AAEu(TTA)$_2$)	MMA/Eu(TTA)$_2$AA (50)	2.16	59 100	5.84	255	121
PMMA		0	137 200	3.17	237	104

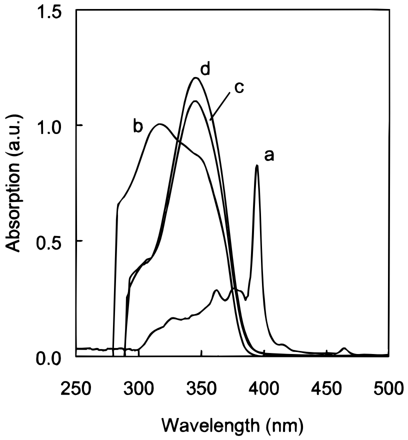

Figure 1. UV−visible absorption spectra of $EuCl_3$ (a), TTA (b), Eu(TTA)$_2$AA (c), and poly(MMA-*co*-AAEu(TTA)$_2$) (d).

Table 2. Data of the Binding Energies for Compounds

compound	$Eu_{3d5/2}$ (eV)	O_{1s} (eV)
TTA		533.2
$EuCl_3$	1137.0	
Eu(TTA)$_2$AA	1135.0	531.2
poly(MMA-*co*-AAEu(TTA)$_2$)	1134.8	531.2, 532.3

observed at 1615 and 1543 cm^{-1}, respectively. A series of absorption peaks at 1310, 791, and 582 cm^{-1} corresponding to the CF_3 vibrations of TTA were also found.

Figure 1 displays the UV−vis absorption spectra of $EuCl_3$, TTA, Eu(TTA)$_2$AA, and poly(MMA-*co*-AAEu(TTA)$_2$) in THF solution. In the UV−vis spectrum of $EuCl_3$, the maximum absorption is at 394 nm, which corresponds to the $^7F_0 \rightarrow ^5L_6$ transition of Eu (III) ion. The absorption spectrum of free TTA reveals the maximum absorption at 313 nm with a shoulder at 332 nm, which are assigned to the $\pi-\pi^*$ transitions of ketonic form and enol form of free TTA in THF, respectively. In comparison with $EuCl_3$ and free TTA, the main absorption band at 341 nm of Eu(TTA)$_2$AA may be attributed to the enol form of coordinated TTA, indicating the formation of a Eu(III)−TTA coordination structure through the dehydrogenation of the enol form of TTA. The absorption spectrum of poly(MMA-*co*-AAEu(TTA)$_2$) with the maximum absorption of 341 nm is quite similar to that of Eu(TTA)$_2$AA, which reveals that the absorption of the copolymer is mainly attributed to the ligand TTA, although the content of the Eu(TTA)$_2$AA moiety is much lower than that of MMA.

Table 2 gives the XPS data of several compounds. The binding energy of $Eu_{3d5/2}$ in Eu(TTA)$_2$AA and poly(MMA-*co*-AAEu(TTA)$_2$) is reduced by 2.0 and 2.2 eV, respectively, compared with that in $EuCl_3$. The O_{1s} binding energy of coordinated TTA in both Eu(TTA)$_2$AA and poly(MMA-*co*-AAEu(TTA)$_2$) is lower by 2.0 eV than that of free TTA. This is due to the increase of the negative charge of the oxygen atom in the coordinated TTA induced by the dehydrogenation of the enol form. The fact shows that the Eu(III) ion is coordinated with the oxygen atoms in both Eu(TTA)$_2$AA and poly(MMA-*co*-AAEu(TTA)$_2$).

The results of the FT-IR and UV−vis absorption spectra and XPS data reveal that Eu(TTA)$_2$AA moieties are directly bonded to the polymer backbone as an integrated unit and that the dissociation of AA and TTA groups is negligible during the copolymerization and purification processes.

Thermal Properties. The thermal stability of the Eu−copolymers was evaluated by means of DSC and TGA under air or nitrogen atmosphere. The thermal properties of the Eu−copolymers are presented in Table 1. All of the Eu−copolymers exhibited relatively good thermal stability compared with PMMA. The glass transition temperatures (T_g) and the starting temperatures of decomposition (T_d) of all the Eu−copolymers with Eu content $\sim$1.58 mol % are in the range of 118−121 and 255−265 °C, respectively, both of which are higher by above 14 and 18 °C than that of PMMA. This result indicates that the thermal stability and the T_g of the copolymers can be enhanced through introducing Eu−complex moieties into the polymer chains. Since the Eu(III) ion is quite large, it can attract more than six oxygen atoms, effectively cross-linking the chains through intra- and intermolecular coordination with the carbonyl oxygen of the MMA unit. This leads to the restriction of chain mobility of the polymers to enhance the T_g values.

Luminescence Properties. The luminescence properties of the Eu−copolymers and Eu−complex monomers as well as Eu−complex/PMMA blends directly obtained from the mixture solution of Eu−complex and PMMA in THF were investigated in detail. The excitation and emission spectra of all the samples in the solution (THF) and solid states were measured at room temperature. The excitation spectra of different Eu−copolymers, obtained by monitoring the emission of the Eu(III) ions at 615 nm, are quite similar, also similar to that of the corresponding Eu−complex monomers and Eu−complex/PMMA blends. The maximum absorption of all the samples occurred in the range of 340−455 nm, which varied greatly with the change of the β-diketone ligands and thus may be attributed to the $\pi-\pi^*$ transitions of the β-diketone ligands. This result indicates that the emission of the Eu−copolymers is mainly sensitized by the absorption of the β-diketone ligands in the UV region rather than directly by the Eu(III) ion absorption. The emission spectra of all the Eu−copolymers and corresponding Eu−complex monomers as well as Eu−complex/PMMA blends, excited at 345 nm, do not show significant differences and all exhibit the characteristic emissions of Eu(III) ions. As shown in Figure 2, six narrow emission peaks centered at 536, 581, 593, 615, 652, and 702 nm, assigned to the $^5D_1 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$, and $^5D_0 \rightarrow ^7F_4$ transitions, respectively, were observed for most samples both in the solution and solid states (but the $^5D_0 \rightarrow ^7F_0$ transition is

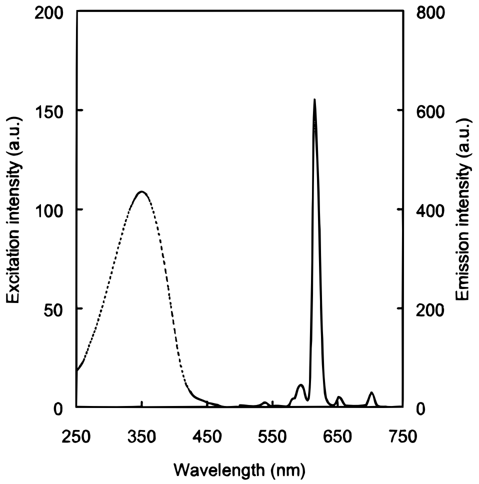

Figure 2. Emission (−) and excitation (- - -) spectra of a typical Eu−copolymer in THF solution.

undetectable in some solid samples). Among the peaks, the emission at 615 nm from the $^5D_0 \rightarrow {}^7F_2$ electrodipole transition is the strongest, suggesting low symmetry around the Eu(III) ion in the Eu−copolymers and monomers. Because the forbidden $^5D_0 \rightarrow {}^7F_2$ electrodipole transition is sensitive to the coordinative environment of Eu(III) ions,[28,29] the asymmetric microenvironment causes the polarization of the Eu(III) ion under the influence of the electric field of the surrounding ligands, which increases the probability for the electrodipole transition.[29] However, the luminescence properties such as the emission intensities, monochromaticities [η($^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$)], and lifetimes of different Eu−copolymers, monomers, and Eu−complex/PMMA blends vary greatly. The corresponding data of these luminescence properties are summarized in Table 3. In comparison with the data of $EuCl_3$, the emission intensities of both Eu−copolymers and monomers were enhanced several hundred times, even up to 1634 times, which indicates that there exists an effective intramolecular energy transfer from the β-diketone ligand to the Eu(III) ion in the Eu−complex unit. Accompanyingly, the monochromaticities were also apparently enhanced from 0.92 to 34.1, especially for Eu−copolymers, due to the lower symmetry around Eu(III) ion in Eu−copolymers and monomers. The emission intensities of the Eu−copolymers were found to depend strongly on the substituents of the β-diketone ligands, increasing with the β-diketone ligands in the order acac < BA < DBM < TTA. The order is identical for Eu−complex monomers and Eu−complex/PMMA blends. The efficiency of the intramolecular energy transfer was very sensitive to the energy levels of the triplet-state of the ligand. It is known that the lowest triplet-state levels of the β-diketones decrease slightly in the order acac > BA > DBM > TTA. Obviously, the closer the triplet-state levels of the β-diketones to the resonance energy level of Eu(III) ion, the more efficient the intramolecular energy transfer.

It is more interesting to note that the luminescence intensities, monochromaticities, and lifetimes of all the Eu−copolymers both in the solution and solid states are much higher than that of the corresponding Eu−complex monomers and Eu−complex/PMMA blends with the same Eu content, whereas the luminescence intensities and monochromaticities of the Eu−complex/PMMA blends are very close to that of the corresponding Eu−complex monomers. The improvement of the luminescence properties of Eu(III) ions in the Eu−copolymers may be mainly due to the special chemical environments of the Eu−complex units in the polymers, not in the PMMA matrix. It is well-known that the self-polymerization ability of the Eu−complex monomer is very low in the $Eu(BA)_2AA$−MMA polymerization system because the reaction ratio of the Eu−complex monomer is much smaller than that of MMA. In this system, the resulting copolymer may be a block copolymer consisting of several successive MMA moieties and an Eu−complex moiety. That is, the Eu−complex units are uniformly dispersed in the polymer backbone. As a result, every Eu−complex unit should be surrounded by the soft chain consisting of MMA units, like being enclosed in cages. Thus, the interaction between the Eu−complex units is very weak under this conformation. Consequently, the probability of emission quenching is reduced and the quantum efficiency is enhanced accordingly. Moreover, the coordination stability of the Eu−complex unit in the copolymer is improved because the coordination degree of the unsaturated Eu−complex unit is satisfied through the intra- and intermolecular coordination, which results in the decrease of nonradiative decay rate of the excited levels of Eu(III) ion and the increase of the luminescence lifetime. In addition, the Eu−complex units can be twisted by the surrounding polymer chain. This may further lower the symmetry of the Eu(III) ion and consequently enhance the $^5D_0 \rightarrow {}^7F_2$ transition and improve the monochromaticities of Eu−copolymers. Considering the above results, it is concluded that the highly luminescence properties of the Eu−copolymers are caused by their special conformations. However, for the Eu−complex/PMMA blend system, the emission intensity is not noticeable improved by the PMMA matrix compared with Eu−complex monomers; the matrix may only play a role as a solid solvent for diluting Eu−complex monomers.

The dependence of emission intensities of poly(MMA-*co*-$AAEu(TTA)_2$) and Eu−complex/PMMA blend films on the Eu content is displayed in Figure 3. In the Eu−complex/PMMA blend, the emission intensity increases with the increase of Eu content and reaches its maximum at 2.71 mol % and then exhibits typical emission concentration quenching on further increasing Eu content. This quenching phenomenon may be caused by the deactivation of the $^5D_0$ or $^5D_1$ state through electrostatic multipolar interaction or by the exciton migration via the Förster dipole−dipole mechanism in solid complexes.[30,31] When the content of Eu−complex doped in PMMA matrix is small, the probability of energy migration via diffusional collision of the Eu−complex should be small. But at high content of the complex, the aggregates of the complex often occur in the solid matrix. Under this condition, the exciton migration process may be a dominant effect accounting for emis-

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Table 3. Luminescence Properties of the Eu−Copolymers and Monomers as Well as the Eu−Complex/PMMA Blends at 615 nm in the Solution and Solid States

compound	relative intensity		$\eta(^5D_0 \rightarrow {}^7F_2/^5D_0 \rightarrow {}^7F_1)$		lifetime (μs), solid
	solution	solid	solution	solid	
poly(MMA-*co*-AAEu(acac)$_2$)	174	278	9.13	11.2	600
poly(MMA-*co*-AAEu(BA)$_2$)	565	734	12.5	15.7	560
poly(MMA-*co*-AAEu(DBM)$_2$)	783	801	14.8	20.4	500
poly(MMA-*co*-AAEu(TTA)$_2$)	1634	1540	17.2	34.1	540
Eu(acac)$_2$AA	33		3.94	5.87	260
Eu(BA)$_2$AA	117		4.83	7.04	100
Eu(DBM)$_2$AA	186		4.93	7.53	220
Eu(TTA)$_2$AA	453		8.34	9.68	91
EuCl$_3$	1		0.92		
Eu(acac)$_2$AA/PMMA	61	52	4.28	3.24	
Eu(BA)$_2$AA/PMMA	198	220	5.43	5.78	
Eu(DBM)$_2$AA/PMMA	304	350	6.11	6.54	
Eu(TTA)$_2$AA/PMMA	438	882	8.73	9.07	
EuCl$_3$/PMMA		1		0.97	

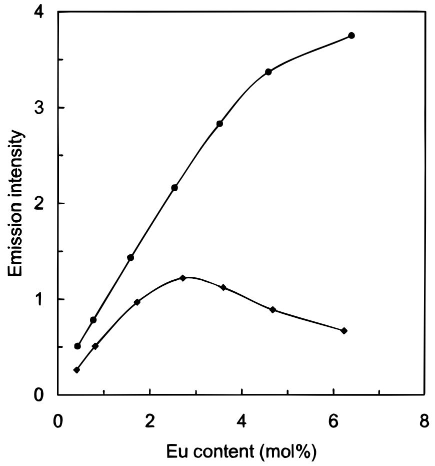

Figure 3. Dependence of the emission intensities of poly(MMA-*co*-AAEu(TTA)$_2$) (●) and Eu(TTA)$_2$AA/PMMA blend (◆) on the Eu content.

sion concentration quenching. In striking contrast, the emission intensity of poly(MMA-*co*-AAEu(TTA)$_2$) increases linearly with increasing Eu content within 3.51 mol %, and no significant emission concentration quenching phenomenon is observed at a Eu content of up to 6.38 mol %. As mentioned above, the Eu−complex units are uniformly dispersed in the polymer backbone and are surrounded by the polymer chain. This special conformation reduces the ligand interaction and decreases the exciton migration, which results in the decrease of the probability of the emission concentration quenching.

In our experiment, the obtained luminescence decay curves of Eu−copolymer films at 615 nm are well-described in terms of a single-exponential function within the experimental errors and the luminescence lifetimes, τ, of the Eu(III) $^5D_0$ level of different Eu−copolymers are almost identical as well, which suggests that all Eu(III) ions are experiencing a similar chemical microenvironment in copolymers.[30,32] For interpreting the energy transfer processes, the typical luminescence decay curves of the Eu(III) $^5D_0$ and $^5D_1$ levels in poly(MMA-*co*-AAEu(TTA)$_2$) are illustrated in Figure 4. It was found that both the $^5D_0$ and $^5D_1$ levels can accept instantaneously the energy transferred from the ligands, then the accepted energy of the $^5D_1$ level decays fast with a lifetime on the order of 0.7 μs, and simultaneously, the energy of the $^5D_0$ level increases further with the same lifetime of 0.7 μs, which indicates that the latter part of the obtained energy of the $^5D_0$ level comes from the $^5D_1$ level through nonradiative decay. Finally, the energy of the $^5D_0$ level decays with a lifetime of 540 μs (not shown in Figure 4) and emits a red light of 615 nm. Obviously, an efficient intramolecular energy transfer from the ligands to Eu(III) ions is crucial to the enhancement of luminescence quantum efficiency, and the long luminescence lifetime is also of importance. As shown in Figure 4 and Table 3, the great improvement of the luminescence properties for Eu−copolymers

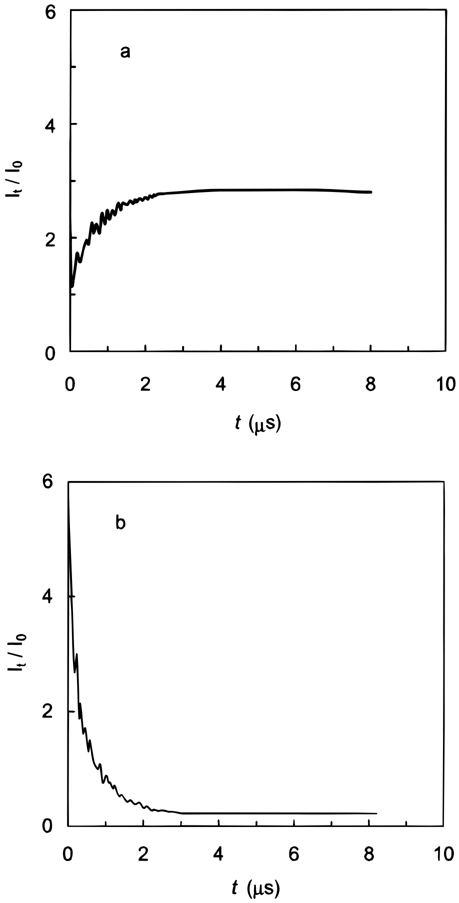

Figure 4. Luminescence decay curves of the Eu(III) $^5D_0$ level (a) and $^5D_1$ level (b) in poly(MMA-*co*-AAEu(TTA)$_2$).

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is just due to the existence of the efficient intramolecular energy transfer from the triplet-state level of the ligands to the $^5D_0$ and $^5D_1$ levels of Eu(III) ions in the Eu−copolymers. In addition, the longer luminescence lifetime of the Eu−copolymers compared to the Eu−complex monomers also accounts for this result.

Conclusions

A novel series of Eu-containing copolymers was synthesized by the direct copolymerization of Eu−complex monomers containing β-diketones with methyl methacrylate. The copolymers containing luminescent Eu−complex units have a great advantage over Eu−complex-doped polymers in constructing the desired conformation to sensitize the Eu(III) emission, in which the Eu−complex units are very uniformly bonded to the polymer chain and are surrounded by the polymer chain. Another advantage is that the Eu−copolymers are fully soluble in common organic solvents and can be cast into transparent, thin films with good mechanical flexibility and thermal stability, compared with small rare earth complexes. The Eu−copolymer luminophores exhibited intense red light at 615 nm, corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu(III) ions under UV excitation. The luminescence intensities, lifetimes, and monochromaticities [$\eta(^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1)$] of the Eu−copolymers are much higher than that of the corresponding Eu−complex monomers and Eu−complex/PMMA blends. The improvement of the luminescence properties for Eu−copolymers was attributed to the efficient intramolecular energy transfer from the triplet-state level of the ligands to the $^5D_0$ and $^5D_1$ levels of Eu(III) ions as well as the microenvironment effects. The dependence of emission intensities of Eu−copolymers on the Eu content showed that the emission intensities increased with increasing Eu content and no significant emission concentration quenching phenomenon was observed in the range of 0−6.38 mol %, which may be due to the great decrease of the exciton migration via diffusional collision of the Eu−complex units. Furthermore, the luminescence intensities of the Eu−copolymers were found to depend strongly on the substituents of the β-diketone ligands, increasing with the β-diketones in the order acac < BA < DBM < TTA.

Acknowledgment. This work was financially supported by the National Science Technology Board, Republic of Singapore, and the Natural Science Foundation of Fujian Province, People's Republic of China.

Supporting Information Available: FT-IR spectra of Eu(TTA)$_2$AA, poly(MMA-*co*-AAEu(TTA)$_2$) and PMMA, and the DSC thermograms of the Eu−copolymers and PMMA. This material is available free of charge via the Internet at http://pubs.acs.org.

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