

Synthesis and Fluorescent Properties of Europium–Polymer Complexes Containing Naphthoate and 1.10-Phenanthroline Ligands

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ABSTRACT: Highly fluorescent Eu–polymer complexes were synthesized through copolymerization of EuPhen(Nap)₂AA with methyl methacrylate or styrene and their luminescent properties were investigated. The Eu–polymer luminophores showed intense red emission under UV excitation, and the emission intensities were much stronger than that of the EuPhen(Nap)₂AA complex. Typical relationships between emission intensity and Eu content in copolymers exhibited some extent of concentration quenching in our studies. However, ⁵D₀ lifetime results suggested that the concentration quenching phenomena cannot be accounted for by deactivation of the ⁵D₀ state through exchange and multipolar interactions. Ligand energy migration along or crosspolymer chains can interpret the emission concentration quenching phenomena reasonably. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1405–1410, 1997

Key words: rare earth; fluorescence; polymer complex; exciton migration

INTRODUCTION

In recent years, there has been a growing interest in the luminescent properties of rare earth metal-containing polymers because of their potential use in fluorescence and laser systems.^{1–3} Okamoto et al. have synthesized copolymers containing coordination groups and studied the fluorescent properties of the complexes.^{4–6} Although these materials are very useful in connecting with their optical applications. There are, however, problems associated with this approach: first, the polymer complexes prepared by direct reaction of the polymer ligands with rare earth ions usually have an ionic aggregation nature, resulting in weak fluorescence of polymer luminophores;^{7,8} second, the microscopic environment of rare earth ions is very complicated, which make the elucidation of the

fluorescent properties difficult.⁹ From a practical standpoint, it is desirable that the polymer complex yields a true solution and that ionic clusters be absent. The use of prefunctionalized ligand leads to excellent homogeneous fluorescent polymer materials,¹⁰ but this method both increases the complexity of synthesis and limits the choice of coordination ligands that can be attached to the polymer chains, and as a result made the use of polymer luminophores uneconomical. For this reason, the key to the development of polymer–rare earth fluorescent materials is to synthesize homogeneous fluorescent polymer complexes under easy and mild conditions. In this article, the highly fluorescent Eu–polymer complexes were first synthesized through copolymerization of a Eu–acrylate–di(naphthoate)–phenanthroline complex with methyl methacrylate or styrene. Compared with previously reported works, this article reported a unique and simple way to obtain fluorescent polymer complexes by synthesizing a mixed ligand complex monomer, because many

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low molecular ligands are at hand and mild reaction conditions are easy to adjust. The copolymers synthesized by this method exhibit intense Eu^{3+} typical fluorescence even at low Eu content. Furthermore, these polymer luminophores can be cast into clear thin films with good thermal and moisture stable properties, which is important in optical application. Up to now, there has been little study on the synthesis and fluorescent properties of this kind of polymer complex, and energy transfer process has hardly been considered.

EXPERIMENTAL

Materials

Eu_2O_3 (99.99 wt %) was purchased from Shanghai Non-Ferrous Metals Limited and used without further purification. Styrene, acrylic acid, and methyl methacrylate were purified before use. 2,2-Azoisobutyronitrile (AIBN) was recrystallized twice from methanol (m.p. = 103°C). Other chemicals were analytical grade.

Measurement Techniques

Absorption spectra were recorded on a UV-240 spectrophotometer. TG measurements were carried out using a DU Pont 1090 thermal analyzer. FTIR spectra were recorded on a Nicolet Magna 550 FTIR spectrometer. Excitation and emission spectra were measured on Hitachi MPF-4 spectrophotometer equipped with an automatic compensation and procalibration system and powder samples were used for this purpose. Fluorescence lifetime measurement was carried out with a Nd:YAG pumped tunable dye laser ($\lambda_{\text{ex}} = 353.3$ nm, pulse duration is 7 ns).

Eu–Acrylate–Di(naphthoate)–Phenanthroline complex ($\text{EuPhen}(\text{Nap})_2\text{AA}$)

Dissolving 12.9 mmol acrylic acid (AA), 21.4 mmol naphthoic acid (Nap), and 21.4 mmol phenanthroline (Phen) in 100 mL 70% ethanol aqueous solution. Then 80 mL freshly prepared $\text{Eu}(\text{OH})_3$ aqueous suspension (10.3 mmol) was slowly dropped in under constant stirring. The flocculent precipitate initially formed was stirred continuously for half an hour, then filtered, washed repeatedly with 20% ethanol aqueous solution and dried under vacuum at room temperature for 24 h. The complex is fairly soluble in benzene,

sparkingly soluble in alcohol, but highly soluble in dimethylformamide. The IR spectrum of the complex showed the characteristic absorption at 1518 cm^{-1} for phenanthroline ring vibration and 990, 910 cm^{-1} for vinyl moiety. The C=O stretching bands of free naphthoic acid at 1678 cm^{-1} and acrylic acid at 1724 cm^{-1} are essentially absent in the complex. The strong bands at 1548 cm^{-1} , 1410 cm^{-1} correspond to the antisymmetric and symmetric stretching vibrations of coordinated COO^- moiety. The absence of absorption bands in the region of 3200–3500 cm^{-1} indicated that there are no coordinated water or hydroxy group in the complex. The C, H, and N contents of the complex determined by elemental analysis are C: 59.8%, H: 3.5%, N: 3.9%, Eu content determined by ICP is 20.1%. The calculated values for $\text{EuPhen}(\text{Nap})_2\text{AA}$ are C: 59.85%, H: 3.35%, N: 3.75%, Eu: 20.38%. The above experimental results suggested that the reasonable formula for complex is $\text{EuPhen}(\text{Nap})_2\text{AA}$.

Copolymers of $\text{EuPhen}(\text{Nap})_2\text{AA}$ with Styrene (I) and Methyl Methacrylate (II)

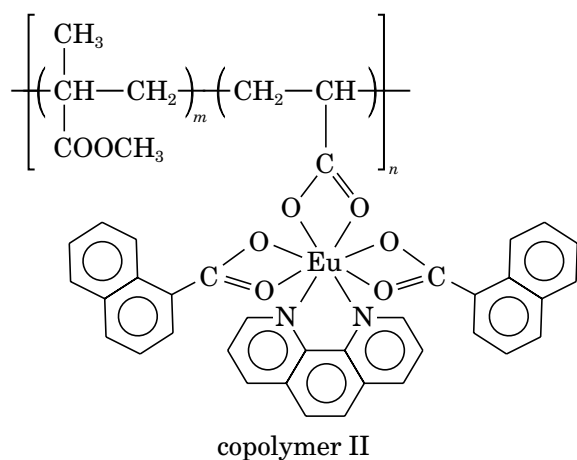
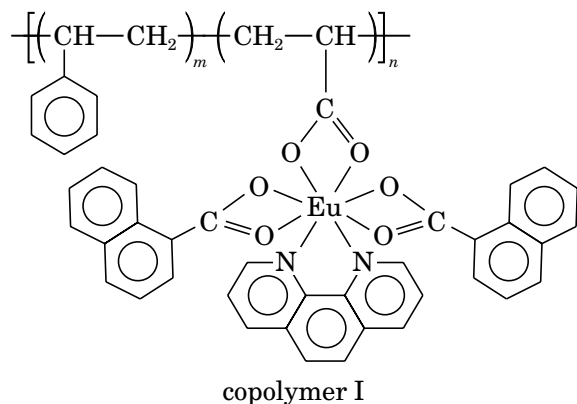
The copolymerizations of $\text{EuPhen}(\text{Nap})_2\text{AA}$ with styrene and MMA were carried out in methanol solutions. The amount of styrene or MMA in the feed was 4 g. The ratios of $\text{EuPhen}(\text{Nap})_2\text{AA}$ to the comonomers were in the range of 1.5–15 wt %. The concentration of the complex in the methanol was kept as a constant: 0.3 g/mL. Under such conditions, essentially homogeneous copolymerization occurred when the conversion limit was controlled within 35%. The typical procedure was described as follows: 0.3 g $\text{EuPhen}(\text{Nap})_2\text{AA}$ was dissolved in 1 mL methanol and mixed with 4 g styrene, the homogeneous solution was placed in a tube and AIBN (0.5 wt %) was added. The solution was degassed by three freeze–thaw cycles under vacuum, then sealed and heated in oil bath at 60°C for 3 h. The viscous homogenous solution was then dissolved in THF and purified by reprecipitating the solution with methanol, and dried under vacuum at 60°C for 2 days. The detail information about copolymerization conditions and experiment results are summarized in (Table I).

Molecular weight was determined by GPC with polystyrene standards used for calibration and THF as eluent. The number-average molecular weight (M_n) of copolymer **I** and **II** does not show apparent changes with the change of Eu content. For copolymer **I**, M_n is in the range of 8.8×10^4 to 9.6×10^4 . M_n of copolymer **II** is in the range of 5.8

Table I Yields of Copolymers and Eu Content in Copolymers under Given Conditions: Styrene and MMA in the Feed: 4 g; AIBN Content: 0.5 wt %; Time of Reaction: 3 h; Reaction Temperature: 60°C

EuPhen(Nap) ₂ AA Content in the Feed (g)	Yield of Copolymers (wt %)		Eu Content in Copolymers (wt %)	
	Copolymer I	Copolymer II	Copolymer I	Copolymer II
0.07	31.8	—	0.10	—
0.10	31.1	26.3	0.26	0.18
0.15	30.6	26.0	0.48	0.32
0.20	29.8	25.5	0.73	0.56
0.30	30.0	24.5	1.28	0.98
0.40	28.2	23.6	1.51	1.52
0.50	26.5	22.8	1.93	1.78
0.60	23.8	—	2.28	—
0.70	—	20.3	—	2.20
0.80	—	19.2	—	2.80

$\times 10^4$ to 6.6×10^4 . Eu content in both copolymer systems is in the range of 0.1–2.8 wt %. The copolymers can be shown schematically as:



RESULTS AND DISCUSSION

Eu-containing copolymers are highly soluble in CHCl_3 , THF, etc., and can be easily cast into

transparent thin films. Both elemental analysis results and Eu content in each copolymer sample interpreted the mol ratio of Eu : Phen to be 1 : 0.92 and 1 : 0.93 for copolymer I and II, respectively. The infrared spectrum of copolymer I (Eu content, 2.28 wt %) showed that the C=O stretching vibrations of poly(acrylic acid) at 1700 cm^{-1} and free naphthoic acid at 1678 cm^{-1} are essentially absent. The OH typical absorption at $3200\text{--}3500 \text{ cm}^{-1}$ is also undetectable. The typical antisymmetric and symmetric stretching vibrations of carboxylate at 1548 and 1410 cm^{-1} and ring vibration of phenanthroline at 1518 cm^{-1} cannot be well identified. These bands are buried under the aromatic ring vibrations and C—H bending vibrations of PS occur at 1610 , 1583 , 1493 , and 1452 cm^{-1} owing to the relatively low content of EuPhen(Nap)₂AA moiety. All the above experimental results illustrated that EuPhen(Nap)₂AA moiety attaches to the polymer backbones as a whole and the dissociation of AA, Phen, and Nap groups is negligible during the copolymerization, and thereafter the purification processes. In considering the good solubility of EuPhen(Nap)₂AA in methanol, few free EuPhen(Nap)₂AA monomers can still stay in the copolymers through precipitating from THF into methanol. The above results also suggested that with one of the coordinate ligand linked to the polymer chains directly, the EuPhen(Nap)₂AA moiety is much uniformly dispersed in PMMA or PS matrices, which is important in optical applications. TGA analysis showed that both copolymers have a good thermal stability, and there is no weight loss up to 320°C .

Figure 1 shows the UV absorption spectra of

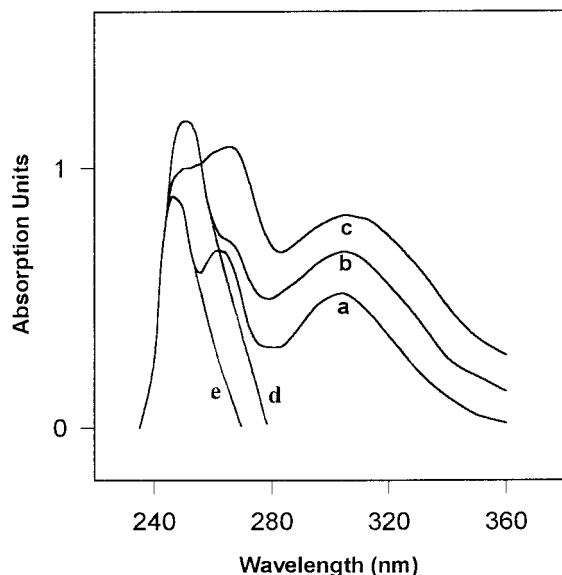


Figure 1 Absorption spectra of (a) EuPhen(Nap)₂AA; (b) copolymer II; (c) copolymer I; (d) PS; (e) PMMA; in THF solvent.

copolymers in THF solution. The absorption spectra of different Eu-polymer complexes are very similar and exhibit a superposition of absorption bands characteristic of EuPhen(Nap)₂AA complex and pure PS or PMMA. The absorption due to phenanthroline ligand at 266 nm is buried under the phenyl π - π^* absorption of PS at 260 nm. The absorption at 326 and 308 nm due to phenanthroline and at 296 nm from naphthoate group do not appear separately; a very broad shoulder band appears in this region.

Figure 2 shows the emission and excitation spectra of EuPhen(Nap)₂AA monomer and copolymer I and II. The excitation spectra of copolymers and EuPhen(Nap)₂AA, obtained by monitoring 615 nm emission intensity of Eu³⁺, are quite similar. They all feature a broad excitation band at 320 nm, with intensity dropping slowly in the range of 280–350 nm. A comparison of the absorption spectra (Fig. 1) with the excitation spectra of copolymers shows reasonable overlap between the naphthoate and phenanthroline absorption in the UV region with the strong absorption in the excitation spectra. The excitation bands corresponding to the absorption of PMMA and PS for copolymers were also observed. The above results suggested that the emission of Eu³⁺ in EuPhen(Nap)₂AA is mainly sensitized by naphthoate and phenanthroline π - π^* transitions, whereas that of polymer complexes are sensitized not only by ligands absorption but by the polymer

matrices absorption at 240–260 nm. The emission spectra of copolymers and complex monomer, excited at 320 nm, do not show significant differences and all exhibit ligand-sensitized emission typical of Eu³⁺. The assignment of observed bands to appropriate f-f transitions is straightforward. The line corresponding to the ⁵D₀-⁷F₀ transition at 580 nm was also detected for the Eu-polymer complexes, suggesting a low symmetric binding site around Eu³⁺.

In our experiment, the emission intensity of Eu³⁺ is greatly enhanced upon copolymerization. The emission intensity of copolymer II at Eu content 1 wt % is comparable with that of Eu(TTA)₃ and is about eight times that of EuPhen(Nap)₂AA complex under 365 nm excitation. Then what is the main effect contributing to the enhancement of Eu³⁺ emission in polymer complex? The binding sites in both copolymers and EuPhen(Nap)₂AA complex are quite similar. Each Eu³⁺ ion coordinates with six oxygen atoms of bidentate cyclic carboxylic groups and two nitrogen atoms of phenanthroline, forming an eight-coordinate inner sphere. The only difference between the copolymers and complex monomer lies in that: in copolymers, the EuPhen(Nap)₂AA molecule links to the polymer main chains and uniformly dispersed into the polymer matrices. Under this condition, the mean distance between two Eu³⁺ ions may be larger than that of the complex. Exciton migration had been used to interpret rare earth emission quenching in solid complexes.^{11,12} In the EuPhen(Nap)₂AA complex, ligand excitation energy migration is evident when the sample containing 1% Eu³⁺, (Eu_{0.01}Gd_{0.99})Phen(Nap)₂AA, is excited at 320 nm. No significant emission from the ligand at about 440 and 556 nm is observed, while sharp Eu³⁺ emission is dominant, indicating that only small amounts of Eu³⁺ traps are needed to quench the ligand fluorescence. This condition is possible when energy transfer among ligand states is rapid.¹³ In copolymers, the large distance between two EuPhen(Nap)₂AA moieties means that all intermolecular energy transfer processes would be slow, and as a result, a much greater part of excitation is transferred to Eu³⁺ under UV radiation. The exciton migration process can be further confirmed by the following experiment.

Typical relationships between fluorescence intensity and Eu content in copolymer I and II are shown in Figure 3. In the copolymer II system, the emission intensity increases with increasing Eu content and reaches a maximum at 2.2 wt %. The copolymer I system exhibits typical emission

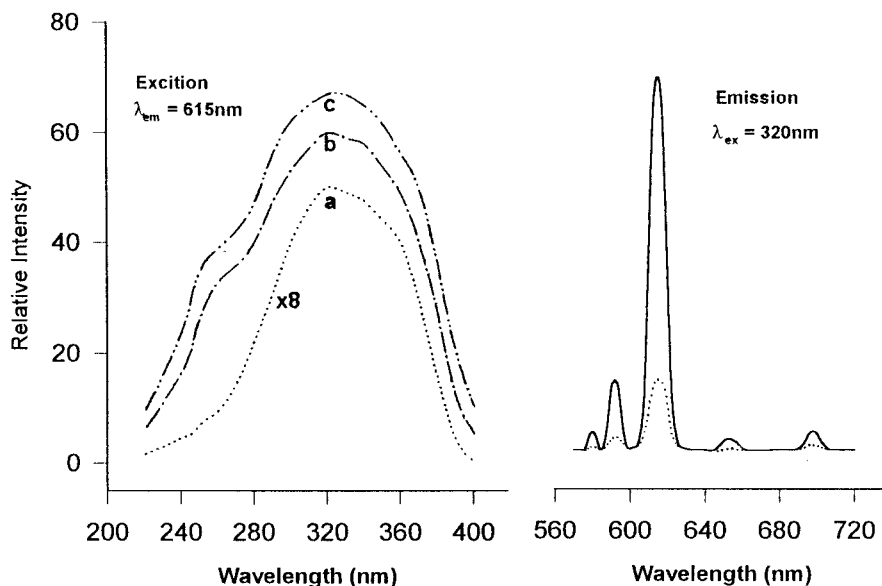


Figure 2 Excitation spectra of (a) $\text{EuPhen}(\text{Nap})_2\text{AA}$; (b) copolymer **II**; (c) copolymer **I**; Emission spectra of $\text{EuPhen}(\text{Nap})_2\text{AA}$ (\cdots), and copolymers at Eu^{3+} content 1 wt % ($-$).

concentration quenching and has a maximal emission intensity at 1.5 wt %. The mechanism corresponding to electrostatic multipolar interaction had been used to explain the concentration quenching phenomena in RE- β -diketone chelates doped PMMA matrix.¹⁴ It was shown that quenching through electrostatic multipolar interaction will cause a decrease in the $^5\text{D}_0$ lifetime. However, in our experiment, concentration quenching cannot be accounted for by deactivation of $^5\text{D}_0$ state through exchange or multipolar interactions, because the lifetimes for the $\text{EuPhen}(\text{Nap})_2\text{AA}$ complex and copolymers of different Eu content are almost identical (about 1.2 μs). Van Uitert have demonstrated that Eu^{3+} self-quenching by multipolar interaction is much more efficient for the $^5\text{D}_1$ state than for the $^5\text{D}_0$ state.¹⁵ But quenching through the $^5\text{D}_1$ state should have a low efficiency in the copolymer systems owing to the relative larger distance between Eu^{3+} ions and the short lifetime nature of the $^5\text{D}_1$ state. The tendency of exciton migration along the polymer chain thereby enhancing the probability that the excitation will encounter a quencher was first confirmed by Cozzens and Fox.¹⁶ In the exciton migration process, ligand triplet state T_1 can be easily quenched by paramagnetic species (e.g., O_2) or intrinsic traps of the polymer, the polymer matrix itself participated both as an acceptor of energy from exciton and as a medium for the triplet energy migration.¹⁷ In copolymer **I** of 2.28 wt %, the

concentration quenching phenomenon is apparent. If energy migration is the reason for concentration quenching in this copolymer, then it follows that dispersing the polymer into organic solvents should hinder the migration process and enhance the emission intensity. This was verified by the apparently enhanced emission intensity of freshly precipitated copolymer **I** (2.28 wt %) con-

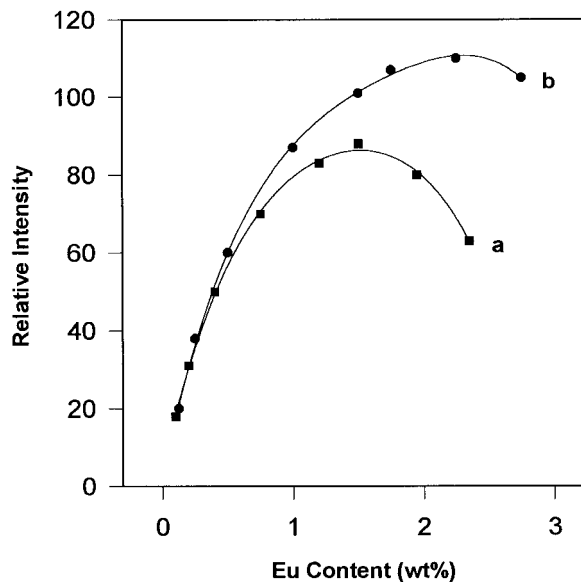


Figure 3 Relationship between fluorescence intensity and Eu^{3+} content in (a) copolymer **I**; (b) copolymer **II**.

taining methanol. As depicted in Figure 3, both copolymer I and copolymer II show concentration quenching, with the former being more efficient. This phenomenon suggested that ligand exciton migration is favoured when ligands coupling caused by Coulomb electrostatic interactions is strong.¹⁸ An exciton migration process that competes with the ligand to metal energy transfer process is negligible in low Eu content polymer complexes and becomes more apparent with increasing Eu content. It is argued that it is the very energy migration process, along or across polymer chains, that enhances the probability that the exciton will encounter a quencher and consequently causes Eu emission concentration quenching.

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