

Copolymers of Styrene with a Quaternary Europium Complex

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ABSTRACT: A complex of Eu^{3+} , benzoate (BA), acrylate (AA), and 1,10-phenanthroline (Phen) was synthesized in this work. The structure of $\text{Eu}(\text{BA})_2(\text{AA})(\text{Phen})$ was characterized with elemental analysis, FTIR, and UV spectroscopy. Copolymers containing rare earth complex were prepared via the copolymerization of $\text{Eu}^{3+}(\text{BA})_2(\text{AA})(\text{Phen})$ with styrene. Semitransparent, luminescent polymer materials with high fluorescent intensity were obtained. The as-synthesized materials were further characterized by means of IR and UV spectra, which indicated that they were copolymers instead

of blends. The fluorescence spectra of the copolymers revealed the intense UV absorption characteristics of the rare earth complex present in the materials, as long as only a small portion of the complex was incorporated into the copolymers. Moreover, thermal analysis showed that the copolymer had excellent heat stability. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1506–1510, 2006

Key words: copolymerization; fluorescence

INTRODUCTION

Rare earth (RE) ions, containing abundant emission spectra, have been extensively used in inorganic and organic luminophores as effective luminescent sources. However, RE inorganic materials have some problems, such as poor processibility and high cost. The stability of RE organic hydrone complexes is also low. Such disadvantages restrict the application of RE luminophores in some areas. RE organic polymers, possessing the distinctive optical, electrical, and magnetic properties of RE ions and the excellent material functions of polymers, are a new type of functional material and have potential use in the fields of photoluminescence, electroluminescence, lasers, and solar-energy conversion systems.^{1,2} Although most RE organic polymers can be prepared directly by the reaction of RE ions with coordination groups of polymer main chains, there are problems associated with this approach. First, the RE content is difficult to quantitatively control; second, the reaction system usually has ionic aggregation, which results in weak fluorescence

of polymer luminophores; and third, the coordination structures of different RE ions have greater differences, their microscopic environment is very complicated, and this makes the elucidation of the fluorescent properties difficult.^{3–5} The use of a prefunctionalized ligand has led to excellent homogeneous fluorescent polymer materials.⁶ However, 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, makes the use of polymer luminophores uneconomical. One of the approaches for addressing this problem is to prepare RE organic polymers through the copolymerization of RE complex monomers with conventional monomers (e.g., styrene). In this work, we aimed to synthesize a quaternary complex containing high polymerization activity and intense luminescent properties with the europium ion (Eu^{3+}), in conjunction with benzene carboxylic acid, acrylic acid (HAA), and the neutral ligand 1,10-phenanthroline (Phen). In the following steps, highly fluorescent Eu-containing polymers were synthesized through the copolymerization of the complex with styrene.

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EXPERIMENTAL

Materials

Eu_2O_3 (99.9 wt %) was purchased from Shanghai Yuelong Nonferrous Metals, Ltd. Styrene and HAA were purified before use. 2,2-Azoisobutyronitrile (AIBN) as

TABLE I
Yields of the Copolymers and Eu Content in the Copolymers

| Eu(BA) ₂ (AA)(Phen) content in the feed (g) | Yield of the copolymers (wt %) | Eu content in the copolymers (wt %) |
|--|--------------------------------|-------------------------------------|
| 0.10 | 71.59 | 0.75 |
| 0.20 | 62.50 | 1.23 |
| 0.30 | 54.02 | 1.55 |
| 0.40 | 48.54 | 1.78 |

Conditions: Styrene in the feed = 2 g; AIBN content = 0.6 wt %; time of reaction = 8 h; reaction temperature = 70°C.

an initiator was recrystallized twice from ethanol. Other chemicals were analytical-grade.

Characterization techniques

The content of Eu³⁺ in the complex and the polymer was determined by ethylenediaminetetraacetic acid (EDTA) titration; the contents of carbon, hydrogen, and nitrogen were determined with an Elementar Vario EL III elemental analyzer (Germany). IR spectra were recorded on a Nicolet Magna 550 FTIR spectrophotometer (Tokyo, Japan), absorption spectra were recorded with a Varian Cary UV-500 spectrophotometer (Palo Alto, CA), fluorescence spectra were obtained with a Hitachi F-4 spectrophotometer (Tokyo, Japan), and thermogravimetric analysis was carried out with a TGA-SDTA851E thermal analyzer (Switzerland); the heating rate was 10°C/min, and the measurements were performed in the air atmosphere.

Dissolution of EuCl₃ in ethanol

A calculated weight of Eu₂O₃ was dissolved in excess concentrated hydrochloric acid and evaporated to near dryness, and then ethanol was added to the crystal.

Eu-benzoate (BA)-acrylate (AA)-Phen

HAA (13 mmol), 20 mmol of benzoic acid (HBA), and 10 mmol of Phen were dissolved in a 70-mL 95% ethanol aqueous solution. Then, 50 mL of an EuCl₃-ethanol aqueous solution (10 mmol) was slowly dropped into the previous solution with constant stirring. The pH of the mixture solution was adjusted to pH 6.5 with an ethanol solution of NaOH (2M), and the mixture was stirred at 70°C for 4 h, filtered, washed repeatedly with a 20% ethanol aqueous solution, and dried *in vacuo* at 50°C for 6 h.

Copolymerization of Eu(BA)₂(AA)(Phen) with styrene

The copolymerization of Eu(BA)₂(AA)(Phen) with styrene was carried out in a dimethyl sulfoxide (DMSO)

solution. The amount of styrene in the feed was 2 g. The ratios of Eu(BA)₂(AA)(Phen) to the monomers were in the range of 5–20 wt %. The DMSO solutions were 7 mL. Under such conditions, essentially homogeneous copolymerization occurred. The typical procedure can be described as follows: 0.1 g of Eu(BA)₂(AA)(Phen) was dissolved in 7 mL of DMSO and mixed with 0.7 g of styrene and 0.006 g of AIBN, and then the homogeneous solution was placed in a tube. The solution was degassed and filled with N₂ and then was sealed and heated in a water bath at 70°C for 15 min. The other 1.3 g of styrene and 0.006 g of AIBN were injected into the tube next, and the tube was placed in a water bath at 70°C for 8 h. The viscous, homogeneous solution was then dissolved in tetrahydrofuran (THF), purified by the reprecipitation of the solution with methanol, and dried *in vacuo* at room temperature for 1 day. Detailed information about the copolymerization conditions and experimental results are summarized in Table I.

RESULTS AND DISCUSSION

Characterization of the Eu complexes

The C, H, and N contents of the complex, determined by elemental analysis, were as follows: C, 52.62%; H, 3.51%; and N, 3.92%. The Eu content, determined by EDTA titration, was 22.37%. The calculated values for the complex were as follows: C, 52.49%; H, 3.47%; N, 4.22%; and Eu, 22.93%. The IR spectra of the complex and Phen (Fig. 1) showed that the stretching vibration of Phen at 1620 cm⁻¹ and the bent vibrations at 854 and 739 cm⁻¹ were shifted to lower frequencies at 1610, 849, and 721 cm⁻¹, respectively, and indicated that Phen had coordinated with the Eu ion. The C=O stretching bands of free HBA at 1685 cm⁻¹ and HAA at 1724 cm⁻¹ were essentially absent in the complex. The strong bands at 1570 and 1430 cm⁻¹ corresponded to the antisymmetric and symmetric stretching vibrations of COO⁻¹ and confirmed that the two acids had

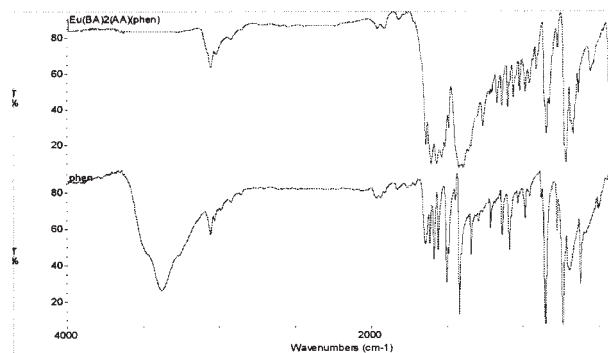


Figure 1 IR spectra of Phen and Eu³⁺(BA)₂(AA)(Phen) complexes.

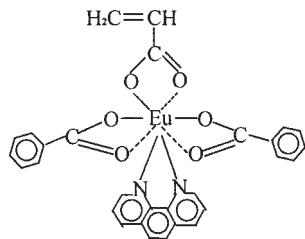


Figure 2 $\text{Eu}^{3+}(\text{BA})_2(\text{AA})(\text{Phen})$.

coordinated with the Eu ion. The absence of absorption bands in the region of $3200\text{--}3500\text{ cm}^{-1}$ indicated that there was no coordinated water or hydroxyl group in the complex. In addition, the stretching vibration of $\text{Eu}\text{--O}$ at 428 cm^{-1} also showed the formation of a coordinate bond. These experimental results suggest that a reasonable formula for the complex is $\text{Eu}(\text{BA})_2(\text{AA})(\text{Phen})$. The complex is shown schematically in Figure 2.

Structure of the copolymers

Before the structure of the Eu-containing copolymers is revealed, Table I lists the conversions of the copolymerization under various conditions as well as the Eu contents in the resulting copolymers. Table II further details the results obtained from gel permeation chromatography (GPC) measurements. The molecular weight was determined by GPC with polystyrene (PS) standards for calibration and with THF as an eluent. The number-average molecular weight of the copolymer did not show apparent changes with the change in the Eu content. Table II shows that the molecular weight of the copolymers was slightly lower and that the distributed width index was higher than that of PS; this may be attributed to the easier end of the complex monomer free radicals. The copolymers are shown schematically in Figure 3.

It was possible for $\text{Eu}(\text{BA})_2(\text{AA})(\text{Phen})$ to homopolymerize, copolymerize, or not polymerize in the copolymerization system of this complex and styrene. However, it was proved that the homopolymerization of the complex could not take place because of its extremely low self-polymerization activity. Moreover,

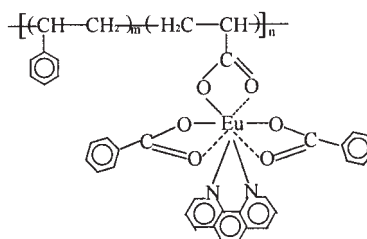


Figure 3 $\text{Eu}^{3+}(\text{BA})_2(\text{AA})(\text{Phen})\text{-}co\text{-PS}$.

if the complex had been simply mixed or blended in the PS matrix, the high amount of the complex should have been detectable by an analysis of the Eu content in methanol after the purification or precipitation of the copolymer because the unbound complex (i.e., the complex was not copolymerized) dissolved well in methanol. However, this was not the case, and only a few complex chains were detected. Therefore, the complex was indeed copolymerized with the styrene monomer, and this led to a stable copolymer that prevented the complex from being leached out.

The structure of the Eu-containing copolymers was also investigated by an analysis of their IR and UV spectra. Figure 4 shows that the primary IR spectrum of the copolymer was similar to that of the PS homopolymer, except for several weak characteristic absorptions of the complex. This suggests that the IR spectrum of the copolymer mostly reflected the characteristic absorptions of the PS structure when the complex monomer content was relatively low. The $\text{C}=\text{O}$ stretching vibrations of poly(acrylic acid) at 1724 cm^{-1} and free HBA at 1685 cm^{-1} were essentially absent. The typical antisymmetric and symmetric stretching vibrations of carboxylate at 1570 and 1430 cm^{-1} and the ring vibration of Phen at 1518 cm^{-1} could not be well identified. These bands were probably buried under the aromatic ring vibrations. $\text{C}\text{--H}$ bending vibrations of PS shifted to 1610 , 1583 , 1493 ,

TABLE II
Molecular Weights and Distributions of the Copolymers and PS

| Eu^{3+} content (%) | $M_n/10^5$ | $M_w/10^5$ | α |
|------------------------------|------------|------------|----------|
| 0 | 1.81 | 8.04 | 4.78 |
| 0.41 | 1.22 | 6.56 | 5.62 |
| 0.78 | 1.15 | 6.12 | 5.89 |

M_n = number-average molecular weight; M_w = weight-average molecular weight; α = molecular weight distributing.

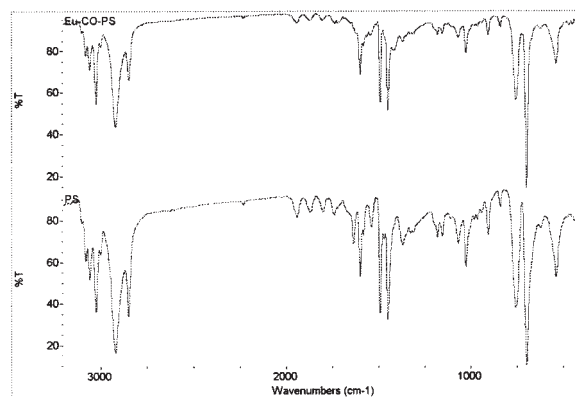


Figure 4 IR spectra of $\text{Eu}\text{-}co\text{-PS}$ and PS.

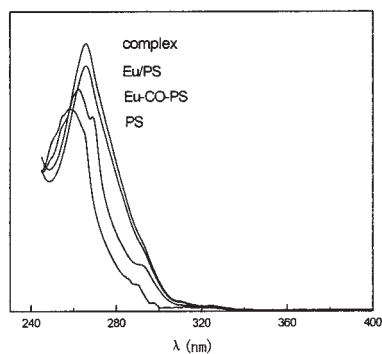


Figure 5 UV spectra of the complex, Eu/PS, Eu-co-PS, and PS.

and 1452 cm^{-1} because of the comparatively low content of the complex monomer. Moreover, there was a stretching vibration of Eu—O at 420 cm^{-1} . All the experimental results suggested that the complex monomers were well attached to the polymer backbones and formed an entire entity. Because of the good solubility of the copolymers in THF and $\text{Eu}(\text{BA})_2(\text{AA})(\text{Phen})$ in methanol, few free $\text{Eu}(\text{BA})_2(\text{AA})(\text{Phen})$ could still remain in the copolymers. The aforementioned results also illustrated that with one of the coordinate ligand linked to the polymer chains directly, the complex monomer was very uniformly dispersed in the PS matrices, and this is important in optical applications.

Figure 5 shows the UV absorption spectra of $\text{Eu}(\text{BA})_2(\text{AA})(\text{Phen})$, PS, a mixture of the complex with PS (Eu/PS), and copolymers (Eu-co-PS) in THF solutions. The absorption spectra of different Eu-co-PS samples were very similar and exhibited a superposition of absorption bands characteristic of $\text{Eu}(\text{BA})_2(\text{AA})(\text{Phen})$ and PS. Eu-co-PS had an intense absorption band at 262 nm, which exhibited the π -electron transition of phenyl in styrene and the corresponding redshift due to the formation of the utmost conjugated system after the nitrogen atom of Phen and the oxygen atom of HBA were attached to Eu ions. This increased the electron delocalization and facilitated the excitation of the π electron of phenyl. Moreover, the absorption at 269 nm of Eu-co-PS was close to that at 266 nm of the complex, and this reflected the characteristic absorption of the complex due to the $\pi \rightarrow \pi^*$ transition of the Phen ring.⁷ Again, the weak absorption might be attributed to the low Eu content. The absorption spectrum of the mixture of the complex with PS was similar to that of the complex, confirming that the complex monomer in Eu-co-PS brought stable coordination and indeed copolymerized with styrene instead of being simply blended in PS.

Thermal properties of the copolymers

Eu-co-PS with different Eu^{3+} contents were expected to have similar thermal stability. Therefore, thermal analysis was only performed for Eu-co-PS containing 1.78 wt % Eu^{3+} . The results, shown in Figure 6, indicated that the initial decomposition temperature of the copolymer was 303°C , which was higher than that of PS. The slight increase in the decomposition temperature suggested that the complex structure improved the stability of Eu-co-PS. This probably occurred because Eu^{3+} in Eu-co-PS created potential crosslinking due to the coordination effect and induced intramolecular or intermolecular association. As a result, the stability of Eu-co-PS was improved. Eu-co-PS decomposed sharply, and the weight decreased distinctly in the range of $320\text{--}390^\circ\text{C}$. In this temperature range, the loss should mainly have occurred in the structure units of styrene. The weight loss was also evident between 390 and 450°C and was mostly caused by the loss of the complex structure units. However, the decomposition temperature was higher than that of the complex monomer, which began to lose weight at 270°C , suggesting that the stability of the complex structure units was enhanced after it was incorporated into Eu-co-PS chains.

Fluorescence properties of the copolymers

Figure 7 shows an emission spectrum of Eu-co-PS. The emission excited at 340 nm did not show significant differences and exhibited the ligand-sensitized emission typical of Eu^{3+} . The assignment of the observed bands to appropriate f-f transitions was straightforward. In our experiment, the Eu content in Eu-co-PS of $\text{Eu}(\text{BA})_2(\text{AA})(\text{Phen})$ was maintained at the same level, that is, 1.78%. Even at such a low content, Eu-co-PS emitted visual and intense red fluorescence, whereas the PS homopolymer could not emit any color fluorescence at the same excitation wavelength. Moreover,

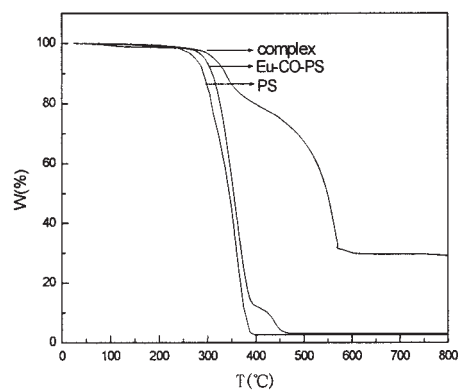


Figure 6 Thermogravimetric curves of the complex, PS, and Eu-co-PS.

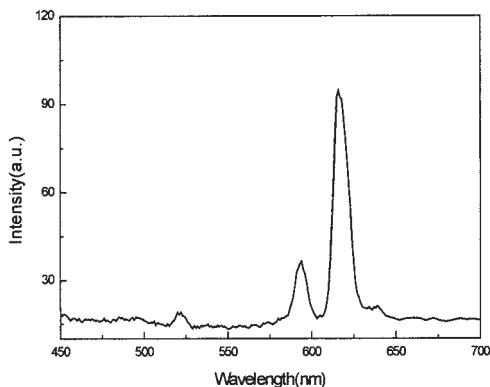


Figure 7 Fluorescence spectra of the copolymer Eu-co-PS.

the introduction of Phen groups increased the fluorescence emission of Eu^{3+} because of the conjugated π bond and rigid plane present in Phen. The triplet-state energy level of Phen at $22,940 \text{ cm}^{-1}$ was higher than the $^5\text{D}_0$ energy level ($17,250 \text{ cm}^{-1}$) and the $^5\text{D}_0$ energy level ($19,020 \text{ cm}^{-1}$) of Eu^{3+} ions; UV, absorbed by ligands, could be effectively passed to the excitation state of RE ions through S_1 and T_1 states via bond resonance, and Eu-co-PS discharged fluorescence typical of centric RE ions.^{8,9} Furthermore, the typical fluorescence of Eu^{3+} , emitted by Eu-co-PS at 617 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition), was sharp and had better monochrome properties. Accordingly, prepared by the copolymerization of an intense luminescent RE complex monomer with styrene, these materials possess fluorescence and better monochrome properties and could become a new type of photoluminescence material.

CONCLUSIONS

Highly fluorescent Eu-containing polymers were synthesized through the copolymerization of a complex with styrene. In comparison with the approaches reported previously, this work provides a simple way of obtaining a fluorescent polymer by the synthesis of a mixed ligand complex monomer. A number of low-molecular-weight ligands are available, and mild reaction conditions can be established via the proper choice of the ligands. Eu-co-PS synthesized by this approach exhibited typical Eu^{3+} fluorescence even at a low Eu content. Furthermore, the polymer lumino-phores could be cast into clear, thin films with improved thermal and moisture stable properties, which are important in optical applications.

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