

Preparation and Characterization of Novel Transparent Eu(AA)₃-Polyurethane Acrylate Copolymeric Materials

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ABSTRACT: The rare earth (RE) salts Eu(AA)₃ (AA: acrylic acid group) and the macromonomers of polyurethane acrylate (MPUA) containing vinyl groups at the end of the chain are prepared for achieving a novel transparent Eu(AA)₃-polyurethane acrylate (Eu-PUA) materials by copolymerization. The structure and properties of the Eu(AA)₃ and the Eu-PUA have been systematically characterized by infrared spectroscopy (FTIR), proton and carbon nuclear magnetic resonance (¹H-NMR, ¹³C-NMR), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and fluorescence spectrophotometer. It is proved that the Eu(AA)₃ have been successfully bonded onto the molecular chains of the polyurethane acrylate

and the glass transition temperature (*T*_g) of the polyurethane acrylate increases at the presence of Eu(AA)₃. In addition, the Eu-PUA materials show favorable thermal stability and transparency. Typically, the fluorescence spectra show that the strongest fluorescence emission peak of the Eu-PUA material appears at 614 nm at the excitation wavelength of 395 nm. This demonstrates that such material can be applied to functional optical materials in the future. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 690–696, 2012

Key words: rare earth salt; polyurethanes; macromonomers; photoluminescence; transparency

INTRODUCTION

Rare earth (RE) elements are entitled “the mines of the functional materials” due to their unique photic, electrical, magnetic properties, and so forth. In recent years, the rational design and synthesis of RE polymer material combining the characteristics of RE ion with polymer is an active area of research for the potential applications in fluorescence, laser and optics systems.^{1–7} In general, there are two kinds of methods to prepare RE polymers: one is RE compounds that act as doping agents uniformly dispersed in the polymer matrixes by physical blending (doping-type)⁸; the other is RE compounds that be bonded onto the polymer molecular chains directly by coordinating,^{2–5} grafting,^{9,10} polymerization (bonding-type).¹¹ For two

methods aforementioned, the interfacial interaction between RE compounds and the polymer matrix is the primary factor determining the properties of RE polymers. Therefore, how to improve the compatibility or increase the reaction activity between RE compounds and polymer matrix will be the pivotal technics to prepare RE polymers.

Among RE elements, Europium is one of the most important elements due to its very strong luminescence efficiency. Large numbers of Eu (III) complexes containing different ligands were synthesized to prepare RE polymers in the last few decades, such as β-diketone, aromatic carboxylic acid, and heterocyclic ligands.^{1–5,12–16} The previous work showed that Eu (III) complexes and polymers presented very narrow and sharp emission bands for the ⁵D₀–⁷F_{*j*} (*j* = 1, 2, 3, 4) transitions of the 4f orbital electrons in Eu³⁺ ions. The studies of Eu(AA)₃ containing acrylic acid and its RE polymers were also investigated.^{17–21} Nevertheless, utilizing the reaction activity of C=C– in Eu(AA)₃ to prepare bonding-type RE polymers by copolymerization of Eu(AA)₃ with polymeric matrix was seldom studied.^{10,20,21} The salts of Eu(AA)₃ that behave the characteristic emission spectra of the Eu³⁺ ions can be used as the luminescent source in the polymer matrixes. Especially, the Eu(AA)₃ salts can act as monomers for the

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C=C— of acrylic acid and polymerize with other monomers to obtain a series of bonding-type RE polymers.

The macromonomers of polyurethane acrylate made up of C=C— terminal groups of acrylate and polyurethane segments are functionality polymerizable intermediates and have attracted significant interest in basic research and application.^{22–25} It will be a new approach to prepare novel RE polymers utilizing the polymerization activity of macromonomers of polyurethane acrylate and Eu(AA)₃ salts. Recently, RE functional materials obtained by adding RE compounds to the polyurethane matrixes have been reported.^{26–29} However, most of the previous works have mainly focused on polyurethane doped with RE compounds so far. Little attention has been paid to utilize the polymerization activity of macromonomers of polyurethane acrylate and RE compounds, even though this method is easy to prepare bonding-type RE polymers. Especially, the transparent plastic boards or sheets of RE polymers have seldom been investigated in the previous studies. In comparison with the films of RE polymers,^{6,30,31} it is difficult to prepare transparent, fluorescent and applied boards or sheets of RE polymers by a general method, for the compatibility between RE compounds and polymer matrix.

In this contribution, we obtained a family of new RE bonding-type polymers Eu(AA)₃-polyurethane acrylate copolymers (Eu-PUA), which was synthesized through copolymerization of Eu(AA)₃ salts with the macromonomers of polyurethane acrylate by *in-situ* polymerization. The synthesized Eu-PUA copolymers can be cast into transparent plastic boards or sheets which exhibit excellent fluorescence and thermal stability. We herein reported the synthesis and the relevant properties of Eu-PUA copolymers.

EXPERIMENTAL

Materials

Eu₂O₃ (99.9%) was purchased from Shanghai Yue-Long Non-Ferrous Metals. The macromonomers of polyurethane acrylate were self-prepared by isophorone diisocyanate (IPDI, Shanghai Hersbit Chemical, Shanghai, China), hydroxyethyl-methylacrylate (HEMA, Tianjin Kermel Chemical Reagent, Tianjin, China), and polyethyleneglycol 600 (PEG 600, Tianjin Kermel Chemical Reagent, Tianjin, China). Acrylic acid (HAA), azobisisobutyronitrile (AIBN), dibutyltin laurate (DBTL), and other reagents and solvents were commercial products and used as received without further purification.

Characterization techniques

Fourier transform infrared (FTIR) spectra were measured on a Tensor 27 FTIR (Bruker) spectrometer

in the range of 4000–400 cm⁻¹. ¹H-NMR and ¹³C-NMR spectra were recorded with a DPX-400 (400 MHz) (Bruker), using D₂O as the solvent and tetramethylsilane as an internal reference. Fluorescence excitation and emission spectra were obtained on a F-7000 (Hitachi) fluorescence spectrophotometer with excitation slit width 5 nm. Thermogravimetric analyses (TGA) were carried out using a Diamond TG/DTA (PerkinElmer) with N₂ atmosphere and heating rate of 10°C min⁻¹. Dynamic mechanical analyses (DMA) were recorded on a TA Q800 apparatus with heating rate of 3°C min⁻¹ and in the range of 30–150°C.

Preparation of Europium (III) acrylic acid salt (Eu(AA)₃)

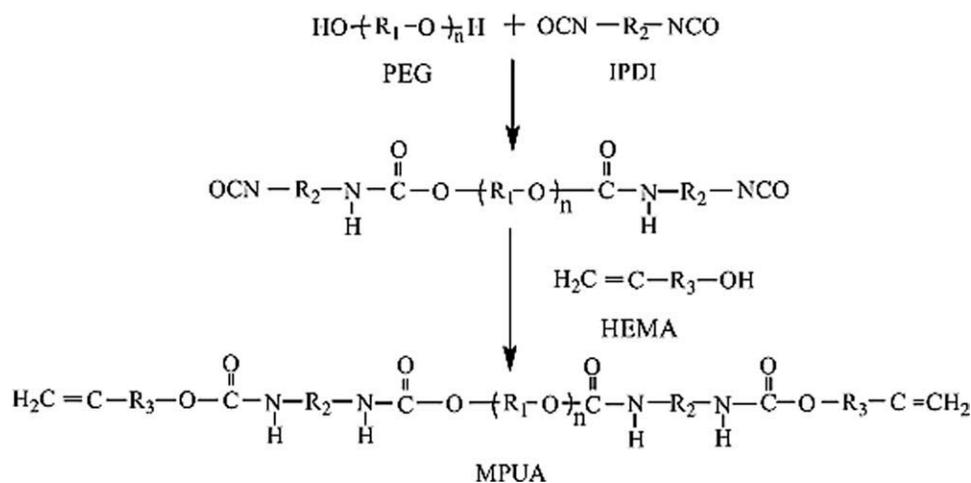
Totally, 0.10 mol Eu₂O₃ and 0.60 mol acrylic acid were added to a 250-mL flask with a little distilled water. The reaction mixture was heated and stirred at 90°C for 2 h, and then the mixture was filtrated. The solvent was removed from the filtrate in a rotary evaporator. The white product was separated out, and washed with anhydrous ethanol several times before being dried under vacuum.

Synthesis of macromonomer of polyurethane acrylate

The appropriate amount of 0.50 mol (111.15 g) IPDI and 0.25 mol (150.00 g) PEG 600 were placed in a 250-mL round-bottomed flask under a dry nitrogen atmosphere. Then the temperature was held at 30°C for 10 min. Then a predetermined amounts of 0.50 mol (111.15 g) HEMA and 0.20 mmol (0.13 g) DBTL were added to the system, and the temperature of the mixed reaction system was controlled under 35°C with vigorous stirring for 60 min. The macromonomers of polyurethane acrylate were synthesized, marked as macromonomer of polyurethane acrylate (MPUA). The synthesis of macromonomers is shown schematically as Scheme 1.

Synthesis of Eu-polyurethane acrylate (Eu-PUA)

Eu-PUA was prepared by mixing 100 g of macromonomers of polyurethane acrylate, 1 g of Eu(AA)₃ salt, and 0.38 g AIBN in a clean flask at 30°C with vigorous stirring for 60 min. The resultant compound was cast into the self-prepared glass molds and cured in an oven at the temperature of 40–70°C for 8–10 h. Then the transparent board of Eu-PUA copolymer was formed. The other relevant Eu-PUA copolymers with different amounts of Eu(AA)₃ salts were prepared according to the same procedure. The possible reaction is shown in Scheme 2 and the



Scheme 1 The reaction scheme for the synthesis of MPUA.

photographs of Eu-PUA copolymers with different amounts of $\text{Eu}(\text{AA})_3$ salts are shown in Figure 1.

RESULTS AND DISCUSSION

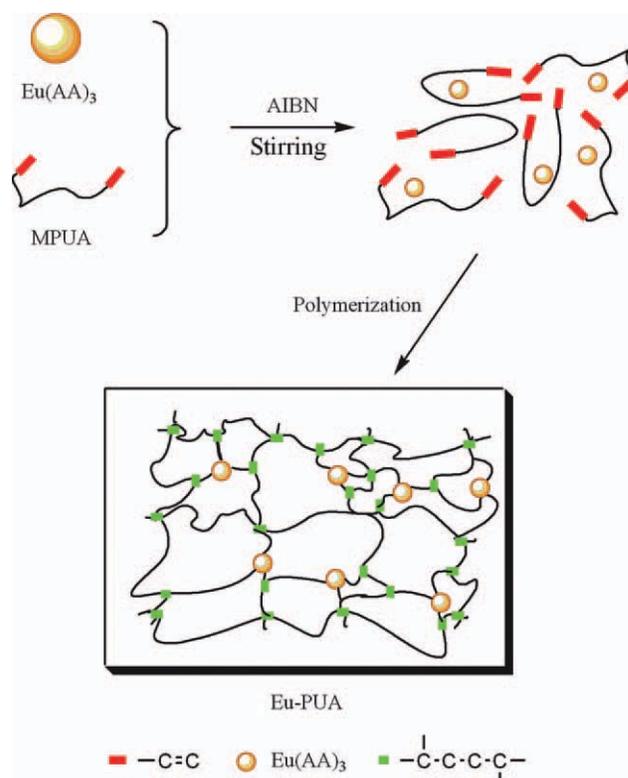
The structure and properties of $\text{Eu}(\text{AA})_3$ salts and Eu-PUA copolymer were investigated by the FTIR, TGA, DMA, and fluorescence spectrophotometer. Interestingly, we have gained the photograph of the red fluorescence of the Eu-PUA irradiated by ultraviolet radiation. All of the characterizations are followed.

Structural characterization of $\text{Eu}(\text{AA})_3$

FTIR spectra of acrylic acid, $\text{Eu}(\text{AA})_3$ salts and Eu-PUA copolymer containing 2.00 wt % $\text{Eu}(\text{AA})_3$ salts are illustrated in Figure 2. Comparing with the acrylic acid (curve a in Fig. 2), the $\text{C}=\text{O}$ characteristic band of free acrylic acid at 1718 cm^{-1} is essentially absent in the $\text{Eu}(\text{AA})_3$ (curve b in Fig. 2). There are strong bands at 1544 and 1368 cm^{-1} corresponding to the asymmetrical stretching vibration (ν_{as}) and symmetrical stretching vibration (ν_{s}) of $-\text{COO}^-$ respectively, and $\Delta\nu = \nu_{\text{as}}(-\text{COO}^-) - \nu_{\text{s}}(-\text{COO}^-) = 176\text{ cm}^{-1}$. The facts suggest that the $-\text{COOH}$ of the acrylic acid has successfully chelated onto the Eu ion in bidentate complex forms. The band at 1638 cm^{-1} is assigned to the $\text{C}=\text{C}$ double bond in $\text{Eu}(\text{AA})_3$. While the $\text{C}=\text{C}$ at 1638 cm^{-1} disappeared in the Eu-PUA (curve c in Fig. 2), this demonstrates that the $\text{Eu}(\text{AA})_3$ and macromonomers of polyurethane acrylate have polymerized and formed the copolymer of Eu-PUA through free radical polymerization.

Figure 3(A) shows $^1\text{H-NMR}$ spectrum of $\text{Eu}(\text{AA})_3$. The chemical shift of protons in the D_2O (solvent) appear at $\delta = 4.70$ ppm. The chemical shift of the proton ($\text{CH}_2=\text{CH}-$) of AA presents at $\delta = 4.00-4.20$

ppm. The peaks appear at $4.83-4.93$ ppm is assigned to the protons in terminal groups of vinyl ($\text{CH}_2=\text{CH}-$). Furthermore, the proton of carboxyl disappeared, which indicates that the $-\text{COOH}$ of the acrylic acid has also chelated onto the Eu ion. Figure 3(B) shows $^{13}\text{C-NMR}$ spectrum of $\text{Eu}(\text{AA})_3$. The chemical shifts at 127.76 ppm and 86.40 ppm are associated with the carbons in terminal groups of vinyl ($\text{CH}_2=\text{CH}-$) and ($\text{CH}_2=\text{CH}-$), respectively. The chemical shift of the carbonyl carbon is 231.55



Scheme 2 The possible reaction of preparing Eu-PUA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

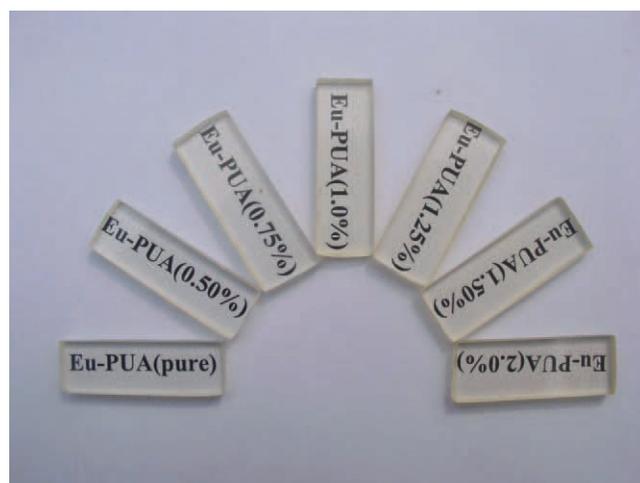


Figure 1 The photograph of Eu-PUA copolymers with different amounts of $\text{Eu}(\text{AA})_3$ salts. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ppm. So the structure of $\text{Eu}(\text{AA})_3$ prepared above has been confirmed by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra.

Photoluminescence of $\text{Eu}(\text{AA})_3$

The excitation and emission spectra of $\text{Eu}(\text{AA})_3$ are shown in Figure 4. A strong excitation band at 395 nm was observed (curve a in Fig. 4), which is attributed to the $^7\text{F}_0 \rightarrow ^5\text{L}_6$ transition of Eu^{3+} . Other excitation bands are corresponding to $^7\text{F}_0 \rightarrow ^5\text{D}_4$ (362 nm), $^7\text{F}_0 \rightarrow ^5\text{G}_1$ (382 nm), $^7\text{F}_0 \rightarrow ^5\text{D}_2$ (416 nm) transitions respectively.³² At the excitation wavelength of 395 nm, the $\text{Eu}(\text{AA})_3$ exhibits characteristic fluores-

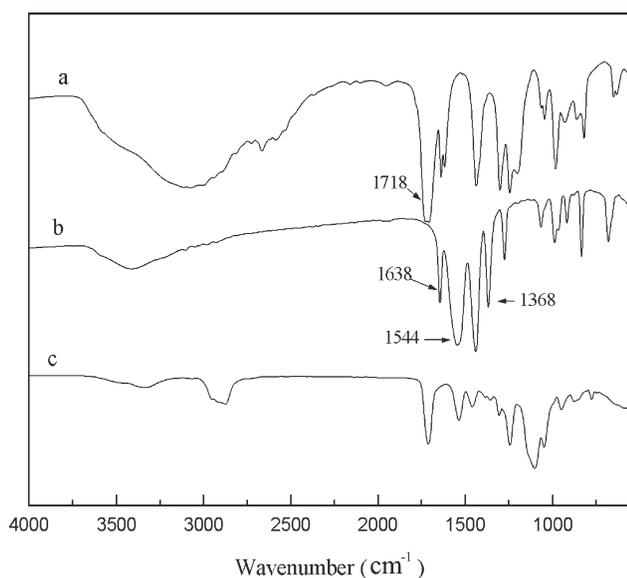


Figure 2 FTIR spectra of acrylic acid (a), $\text{Eu}(\text{AA})_3$ salts (b), and Eu-PUA copolymer (c, containing 2.00 wt % $\text{Eu}(\text{AA})_3$ salts).

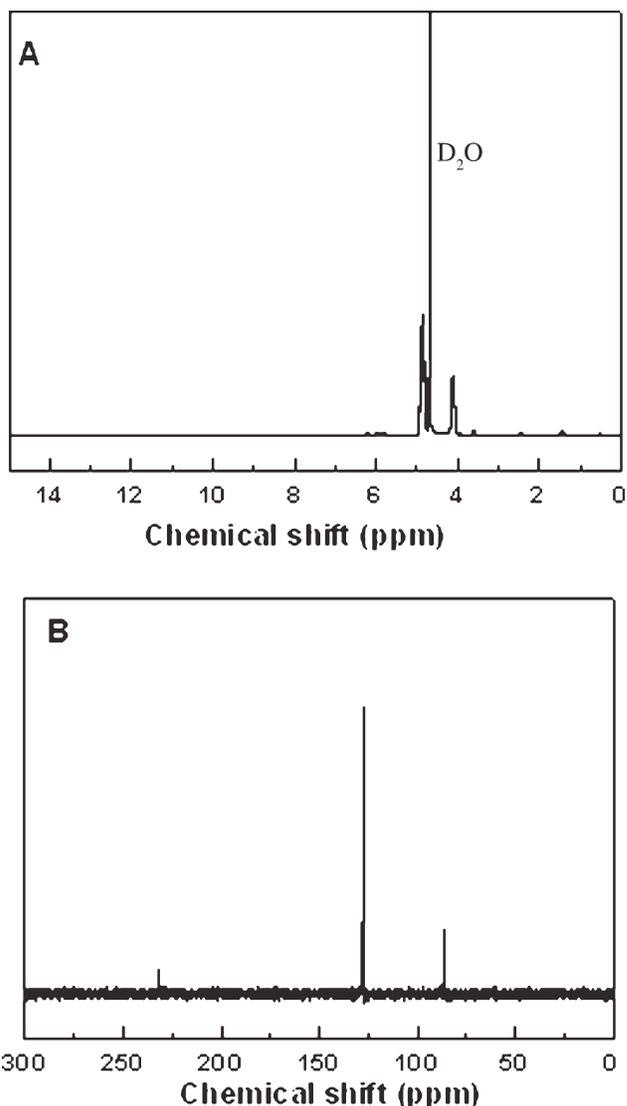


Figure 3 $^1\text{H-NMR}$ (A) and $^{13}\text{C-NMR}$ (B) spectra of $\text{Eu}(\text{AA})_3$.

cence emission bands of Eu^{3+} in Figure 4 (curve b), which is assigned to the $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($j = 0, 1, 2, 3, 4$) transitions of the 4f orbital electrons of Eu^{3+} ions. The emission bands at 579, 590, 614, 648, and 693 nm are attributed to the $^5\text{D}_0 \rightarrow ^7\text{F}_0$, $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^7\text{F}_2$, $^7\text{F}_3$, $^7\text{F}_4$ transitions, respectively. The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (614 nm) transition presents the largest relative intensity, which emits typical red fluorescence of Eu^{3+} . On the other hand, $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition belongs to electric dipole transition and is hypersensitive to the ligand field strength. Whereas, the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is magnetic dipole transition and is not sensitive to the ligand field strength. The relative intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition indicates the degree of covalence and asymmetry in the local environment of the Eu^{3+} ions. Therefore, the strong intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition indicates an asymmetric environment of the Eu^{3+} ions with a strong Eu-O bond formation.³²⁻³⁴ In addition, the narrow, sharp

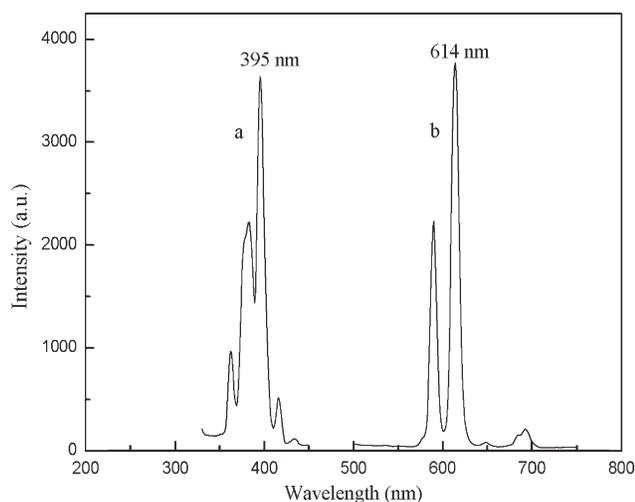


Figure 4 Solid-state excitation (a) and emission (b) spectra of $\text{Eu}(\text{AA})_3$ at room temperature.

and strong emission peaks can be observed in Figure 4 (curve b), so this shows that the lowest triplet state energy level of the acrylic acid ligand has better matching with the vibrancy energy level of the Eu^{3+} .

Photoluminescence, thermogravimetric, dynamic mechanical properties of Eu-PUA

The photoluminescence of Eu-PUA copolymer containing different amounts of $\text{Eu}(\text{AA})_3$ salts was then studied as shown in Figure 5. The spectra of Eu-PUA is similar to that of $\text{Eu}(\text{AA})_3$ salts (Fig. 4). The characteristic emission peaks correspond to the $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($j = 0, 1, 2, 3, 4$) transitions of the Eu^{3+} ions respectively. As mentioned above, the intensity form $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (614 nm) is the strongest one.

It can be observed that the fluorescence intensity of Eu-PUA increases with increasing amount of

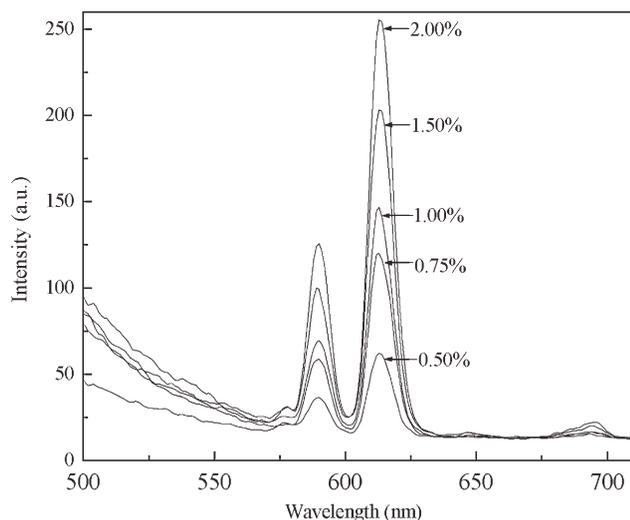


Figure 5 Emission spectra of Eu-PUA containing different amounts of $\text{Eu}(\text{AA})_3$ salts ($\lambda_{\text{ex}} = 395 \text{ nm}$).

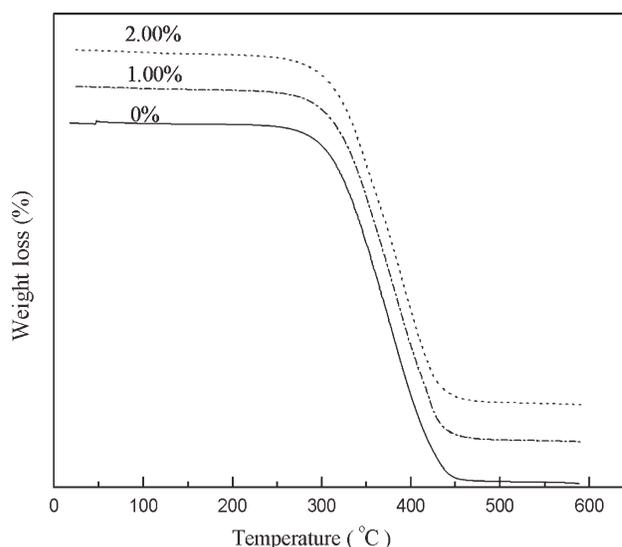


Figure 6 TGA curves of Eu-PUA containing different amounts of $\text{Eu}(\text{AA})_3$ salts (0, 1.00, and 2.00 wt %). For clarity, the curves are vertically shifted with respect to each other.

$\text{Eu}(\text{AA})_3$ salts and no fluorescence concentration quenching within the range of $\text{Eu}(\text{AA})_3$ contents from 0 to 2.00 wt %. This phenomenon can be explained in two possible reasons: (a) the amount of $\text{Eu}(\text{AA})_3$ is too little to induce the fluorescence concentration quenching; (b) the $\text{Eu}(\text{AA})_3$ salts have been polymerized with the macromonomers of polyurethane acrylate and the Eu^{3+} ions are uniformly distributed in the PUA matrix. Moreover, the increase of relative intensity ratio between $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition as increasing amount of $\text{Eu}(\text{AA})_3$ salts confirms that the polymerization of the $\text{Eu}(\text{AA})_3$ and macromonomers has altered the local environment of the Eu^{3+} , which increases the degree of asymmetry of the local environment.

The TGA curves of Eu-PUA containing different amounts of $\text{Eu}(\text{AA})_3$ salts are presented in Figure 6. It can be seen that the thermal decomposition profiles of the Eu-PUA containing 1 wt % and 2 wt % $\text{Eu}(\text{AA})_3$ salts are similar to that of the pure PUA (containing 0 wt % $\text{Eu}(\text{AA})_3$ salts). The onset degradation temperatures of Eu-PUA are 302°C, 304°C corresponding to containing 1.00 and 2.00 wt % $\text{Eu}(\text{AA})_3$ respectively, and it is slightly higher than that of pure PUA which is about 296°C. This can be contributed that the $\text{Eu}(\text{AA})_3$ salts bonded onto the molecular chains of MPUA through copolymerization and dispersed uniformly in the PUA matrix, which can prevent the heat to expand quickly and obstruct the gaseous degradation of the Eu-PUA materials.

The loss factors ($\tan \delta$) of Eu-PUA with different $\text{Eu}(\text{AA})_3$ salts contents are shown in Figure 7. It is well known that the $\tan \delta$ peak of the loss factors

corresponds to the glass transition temperature (T_g) of the polymer systems. As seen in Figure 7, the $\tan \delta$ peaks at 56.47, 56.61, 57.37, 57.94, 58.06, and 60.11°C correspond to the T_g of Eu-PUA containing 0.00, 0.50, 0.75, 1.00, 1.50, and 2.00 wt % $\text{Eu}(\text{AA})_3$ salts, respectively. This indicates that T_g of the Eu-PUA increases as the amount of $\text{Eu}(\text{AA})_3$ salts increases. The possible reason is that the $\text{Eu}(\text{AA})_3$ salts possess large spatial steric hindrance and the resistance of chain segment motion enhances as the amount of $\text{Eu}(\text{AA})_3$ salts increases. In other words, the more containing amount of $\text{Eu}(\text{AA})_3$ salts in the Eu-PUA, the more energy (or higher temperature) that the molecular chain segment demanded to overcome the internal friction of the chain segment to achieve free motion.

The chemiluminescence imaging system was used to validate the luminescence of the Eu-PUA copolymer, Figure 8 shows the photograph of Eu-PUA copolymer with different $\text{Eu}(\text{AA})_3$ salts contents irradiating by ultraviolet radiation ($\lambda = 380 \text{ nm}$) taken by using a light filter to filter ultraviolet radiation. The red fluorescence is observed in the Eu-PUA copolymer samples except the left sample (pure PUA, without $\text{Eu}(\text{AA})_3$ salts). Notwithstanding, limited the condition of the chemiluminescence imaging system, the wavelength of the irradiating ultraviolet radiation ($\lambda = 380 \text{ nm}$) is not the optimal excitation wavelength ($\lambda_{\text{ex}} = 395 \text{ nm}$) mentioned above, but the result primarily validated that it is the $\text{Eu}(\text{AA})_3$ salts that proffer the photoluminescence of the Eu-PUA copolymer. Comparing the middle sample (containing 1.00 wt % of $\text{Eu}(\text{AA})_3$ salts) with the right one (containing 2.00 wt % of $\text{Eu}(\text{AA})_3$ salts), it

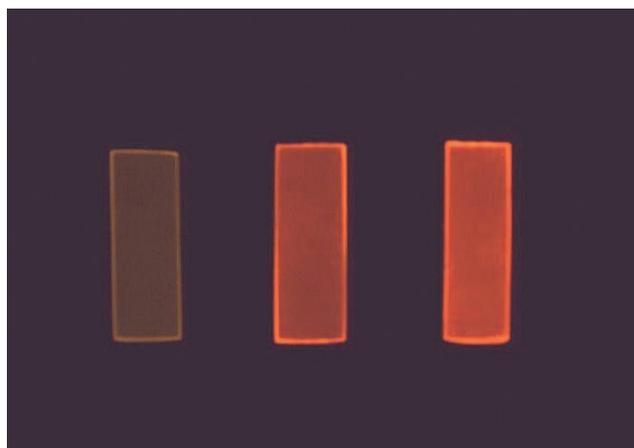


Figure 8 Photograph of Eu-PUA with different $\text{Eu}(\text{AA})_3$ salts contents (0, 1.00 and 2.00 wt %, from left to right) irradiating by 100W-Xe lamp. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

can be seen that the intensity of red fluorescence improves as the amount of $\text{Eu}(\text{AA})_3$ salts increases in the Eu-PUA, just as Figure 5 shown. Moreover, from Figure 8, it also can be observed that the Eu-PUA copolymer emits uniform red fluorescence. This testifies indirectly that the $\text{Eu}(\text{AA})_3$ salts is well dispersed in the PUA matrix. Further, this also demonstrates that the Eu-PUA copolymer can be applied to functional optical materials in the future.

The relevant results demonstrate that the Eu-PUA copolymer have excellent transparence, thermal stability and photoluminescence, so this copolymer can be used as functional or structural materials in especial optical domains, such as spaceflight, aviation and so on. We believe these results are important, because they indicate that the method of copolymerization of the macromonomers of polyurethane acrylate and the active rare earth salt (or complex) should be a feasible way to obtain a novel RE bonding-type polymer with good transparence and photoluminescence properties.

CONCLUSIONS

Novel bonding-type RE polymer materials were prepared by copolymerization of the macromonomers of polyurethane acrylate with various amounts of $\text{Eu}(\text{AA})_3$ salts. The obtained novel Eu-PUA materials combine transparence and thermal stability, emit red luminescence under ultraviolet, and show interesting potential workability. The characterization of the Eu-PUA material showed that the fluorescence intensity, thermal degradation temperature, glass transition temperature of the Eu-PUA material improved as the amount of $\text{Eu}(\text{AA})_3$ salts increased, while the transparency of the material hardly changed. Especially, the transparent copolymer plastic boards

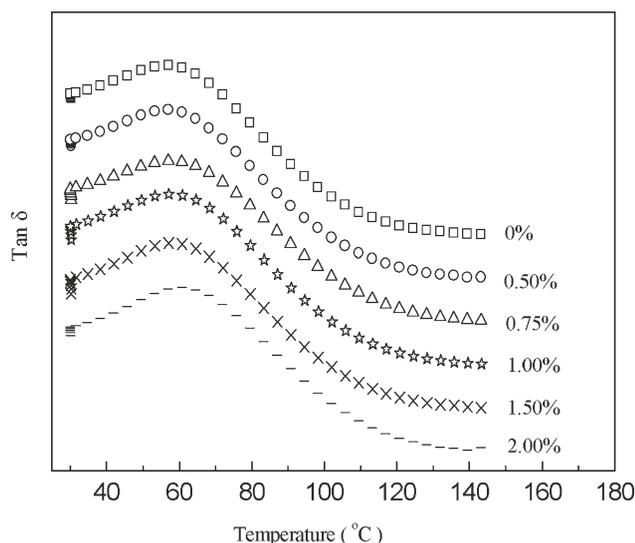


Figure 7 $\tan \delta$ vs. temperature for Eu-PUA with different $\text{Eu}(\text{AA})_3$ salts contents (0, 0.50, 0.75, 1.00, 1.50, and 2.00 wt %). For clarity, the curves are vertically shifted with respect to each other.

emitted favorable red fluorescence under ultraviolet. It can be expected, therefore, that such the Eu-PUA copolymer could be applied to functional optical materials.

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