Preparation and Characterization of a Series of Novel Eu^{III}-Complex-Polyurethane Acrylate Materials Based on Mixed 6-Hydroxy-1-naphthoate and 1,10-Phenanthroline Ligands

**Shao-Ming Fang, Cong Wang, Min Hu, Pei-Yuan Wang, Li-Ming Zhou,
Li-Jun Gao, Chun-Sen Liu**

*Henan Provincial Key Laboratory of Surface and Interface Science, Zhengzhou University of Light Industry,
Zhengzhou, Henan 450002, China*

Received 24 February 2011; accepted 27 November 2011
DOI 10.1002/app.36608

ABSTRACT: Hydroxyl groups in the coordination complex $\{[Eu(\mathbf{L})_3(phen)]\cdot H_2O\}_2$ ($\mathbf{L}$ = 6-hydroxy-1-naphthoate and phen = 1,10-phenanthroline) were used to react with —NCO functional groups of isophorone diisocyanate in the presence of dibutyltin dilaurate. A series of new luminescent Eu^{III}-complex-polyurethane acrylate materials, poly(Eu^{III}-complex-polyurethane methacrylate (PUA complex)), were prepared through *in situ* polymerization of polyurethane acrylate macromonomers and the resulting material was characterized by X-ray diffraction, IR spectra, thermogravimetry analysis, dynamic mechanical analysis, and fluorescence spectroscopy. The result indicates that both Eu^{III} complex and PUA complex can emit characteristic fluorescence of Eu^{III} ion. Moreover, the emission intensity was enhanced under the same experiment condition when the content of Eu^{III} complex in the PUA complex was increased. In addition, we have not found the fluorescence quenching in this work even the content of Eu^{III} complex was increased to 5 wt %. Such rare-earth complex-polyurethane acrylate hybrid materials are suitable for the photoluminescent applications. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 3404–3409, 2012

Key words: Eu^{III} complex; crystal structure; polyurethane acrylate; copolymerization; luminescence

INTRODUCTION

Efficiently luminescent complexes of rare earths are not only spectacular visually but also of interest in numerous photophysical applications, ranging from sensors over light emitting devices (LEDs, OLEDs) to luminescent immunoassays.[1–6] Unfortunately, the rare earth complexes obtained usually have inherently poor physicochemical stability and poor machining properties.[7,8] Practically, it is frequently desirable to incorporate them into matrix to render them applicable, or even appropriately functional in corresponding devices. Rare earth (RE) complex/polymer composites, 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.[9,10] Many reports have focused on polymer systems doped or blended with RE complexes.[11–15] However, blending may cause poor dispersion and compatibility of the rare earth complexes in a polymer matrix, and may thus induce concentration quenching, low luminescence intensity, and reduced luminescence lifetime. Although the study of luminescence materials prepared by direct reaction of RE ions with coordination groups of polymer main chains has recently been receiving growing attention, there are problems associated with this approach. The reaction system usually has ionic aggregation and the coordination microscopic environment is very complicated, which results in weak fluorescence of polymer luminophores and makes the elucidation of the fluorescent properties difficult.[16–19] A more effective approach for addressing this problem is to prepare RE organic polymers through the copolymerization of RE complex monomers with conventional monomers.[20,21] The use of a prefunctionalized ligand has led to excellent homogeneous fluorescent polymer materials. For examples, Pan group have synthesized highly fluorescent Eu-containing polymers through the copolymerization of a quaternary complex with styrene, in which the

---

Correspondence to: S.-M. Fang (smfang@zzuli.edu.cn) or C.-S. Liu (chunsenliu@zzuli.edu.cn).

Contract grant sponsor: National Natural Science Funds of China; contract grant numbers: 20801049, 20771095.

Contract grant sponsor: Natural Science Fund of the Education Department of Henan Province; contract grant number: 2011A150032.

Contract grant sponsor: Backbones of Young College Teachers in Higher Educations of Henan Province.

Journal of Applied Polymer Science, Vol. 125, 3404–3409 (2012)

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).[20] Xu and Li have reported that a series of novel highly luminescent Eu-containing copolymers were synthesized by radical copolymerization of Eu-complex monomer featuring thenoyltrifluoroacetone and 5-acryloxyethoxymethyl-8-hydroxyquinoline with MMA.[21]

In our previous work, we have designed and synthesized a series of macromonomers of polyurethane acrylate. A novel thermosetting polymer was obtained by free radical polymerization.[22] A RE polymer containing one-dimensional (1D) coordination Eu^{III} complex has been reported by us.[23] As for the 1D coordination complex, the large conjugated π-systems and the steric hindrance of —OH groups probably affect its reactivity. Considering these points above, in this article, we first selected a novel functional ligand, 6-hydroxy-1-naphthoic acid (HL), a new discrete dinuclear coordination complex {[Eu(**L**)$_3$(phen)]·H_2O}$_2$ with six exposed —OH functional groups was synthesized and used to react with —NCO functional groups of isophorone diisocyanate in the presence of dibutyltin dilaurate (DBTL), and a series of luminescence Eu^{III}-complex-polyurethane acrylate material, poly(Eu^{III}-complex-polyurethane methacrylate (PUA complex)), were further prepared through *in situ* copolymerization of polyurethane acrylate macromonomers. The modified PUA complex was well characterized to establish the structure–property correlations of the RE polymers.

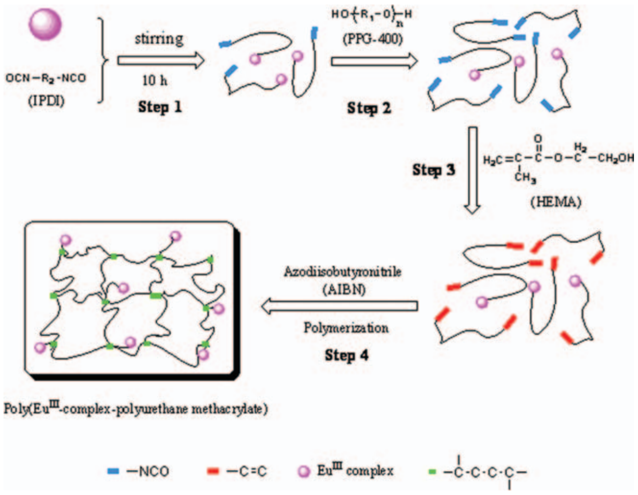
EXPERIMENTAL

Materials

Eu_2O_3 (99.99 wt %) was purchased from Tianjin Kermel Chemical Reagent Co. and used without further purification. H**L** was obtained from Tokyo Chemical Industry Development Co. 2-Hydroxyethyl methacrylate (HEMA), poly(propylene glycol)-400 (PPG-400), isophorone diisocyanate (IPDI), and azodiisobutyronitrile (AIBN) were purified before use. Other chemicals were analytical grade reagents.

Preparation of the complex {[Eu(L)$_3$(phen)]·H_2O}$_2$

The complex {[Eu(**L**)$_3$(phen)]·H_2O}$_2$ was prepared according to our reported method.[24] A mixture of Eu_2O_3, H**L**, and 1,10-phenanthroline at a molar ratio of 3 : 1 : 1 was added to the deionized water and sealed in a 25-mL Teflon-lined stainless steel autoclave. After heating at 140°C for 3 days, the system was cooled to room temperature at 10°C h^{-1}. Yellow quadrate crystals were manually collected in ca. 40% yield based on H**L**. Anal. calcd for $C_{90}H_{62}Eu_2N_4O_{20}$: C 59.28, H 3.43, N 3.07%. Found: C 59.52, H 3.49, N 3.22%. IR (KBr pellet, cm^{-1}): 3389m (br), 1625m, 1606s, 1578s, 1520s, 1463m, 1413m, 1378vs, 1282w, 1238m, 1147m, 1104w, 953w, 778w, 758w, 726m, 661m.



Scheme 1 The preparation procedure of PUA complex material. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Preparation of PUA complex

The crystal samples used in the preparation procedure for PUA complex materials was dried in vacuum at 150°C for 2 h to remove the crystal water in the complex {[Eu(**L**)$_3$(phen)]H_2O}$_2$ (Scheme 1). A mixture of the complex {[Eu(**L**)$_3$(phen)]}$_2$ and IPDI was stirred in a round-bottomed flask for 10 h and DBTL as a catalyst was added to the above mixture dropwisely with stirring. PPG-400 was added at the controlled temperature of 22°C. After stirring for 30 min, a colorless clear solution was obtained. Then HEMA was added into the solution. After the reaction mixture became transparency, the initiator AIBN was dispersed into the system and stirred for 30 min. A high vacuum was applied to remove the bubbles. The mixture was molded into the glass mold. After heating from room temperature to 80°C step by step within 24 h, the groups of —C=C in the macromonomer molecular chains polymerized. A series of novel photoluminescent materials with different Eu^{III} complex (0.1, 0.2, 0.5, 0.8, 1.0, 2.0, and 5.0 wt %) were obtained, marked as PUA complex.

Measurements and characterization

IR spectra were measured on a TENSOR 27 (Bruker) FTIR spectrometer with KBr pellets in the range of 4000–400 cm^{-1}. Elemental analyses of C, H, and N

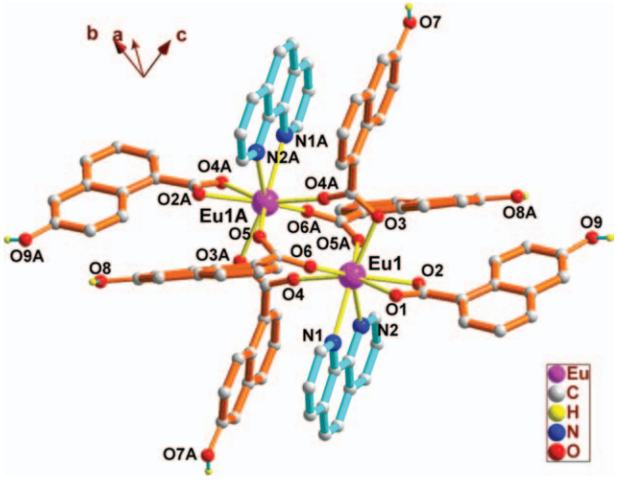


Figure 1 The dinuclear structure in Eu^{III} complex showing a local coordination environment of Eu^{III} ion. The symmetry-related atoms labeled with the suffixes A is generated by the symmetry operation ($-x + 1$, $-y + 1$, $-z + 1$). For clarity, all H atoms except hydroxyls of **L** ligands were omitted. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

were performed on a Vario EL III elemental analyzer. The crystal determination was performed on a Bruker SMART APEX II CCD diffractometer equipped with graphite–monochromatized MoKα radiation (λ = 0.71073 Å). The X-ray powder diffraction (XRPD) was recorded on a Rigaku D/Max–2500 diffractometer at 40 kV, 30 mA for a Cu-target tube and a graphite monochromator. Thermogravimetric analysis (TGA) experiments were carried out on a Perkin-Elmer Diamond SII thermal analyzer from room temperature to 900°C under nitrogen atmosphere at a heating rate of 10°C/min. Dynamic mechanical thermal analysis (DMA) was carried out in a single cantilever bending mode using a TA Q800 DMA instrument (USA), at 1 Hz and a 3.0°C/min temperature ramp over a scanning range from 25 to 170°C, the specimen of about 30 × 3.5 × 5 mm^3 was mounted on the fixture. The emission/excitation spectra were recorded on an F-7000 (HITACHI) spectrophotometer at room temperature (Scan speed: 1200 nm/min, Ex Slit: 5.0 nm, Em Slit: 5.0 nm, voltage: 700 V).

RESULTS AND DISCUSSION

Crystal structure of the complex $\{[Eu(\mathbf{L})_3(phen)]\cdot H_2O\}_2$

The X-ray crystal structure of $\{[Eu(\mathbf{L})_3(phen)]\cdot H_2O\}_2$ was previously reported.[24] The structure consists of a centrosymmetric dinuclear unit $[Eu_2(\mathbf{L})_6(phen)_2]$ with central Eu^{III} ions eight coordinated by two N-atom donors from one chelating 1,10-phenanthroline ligand and six O atoms from five distinct **L** ligands (Fig. 1). For **L**, two types of coordination modes are found for its carboxylate group, namely, μ_1-η^1 : η^1-chelating mode and μ_2-η^1 : η^1-bridging mode. In other words, four **L** ligands use its eight O atoms from four different carboxylate groups to connect two Eu^{III} atoms and form a dinuclear motif with a non-bonding Eu1…Eu1A separation of 4.159(2) Å ($A = -x + 1$, $-y + 1$, $-z + 1$). It is worth to be mentioned that hydroxyl groups are free and exposed to the outside of the Eu^{III} complex, which can be reactive centers for the attachment of complexes to polymeric backbones, isocyanates, and polyurethanes in particular.

XRPD results

XRPD experiment has been carried out for the phase purities of the Eu^{III} complex samples to confirm whether the crystal structures are truly representative of the bulk materials for the further measurements. The XRPD experimental and computer-simulated patterns of the corresponding complex are shown in Figure 2. Although the experimental patterns have a few unindexed diffraction lines and some are slightly broadened in comparison with those simulated from the single crystal modes, it still can be considered favorably that the bulk synthesized materials was identical to that obtained in the single crystals.

FTIR spectra analysis

The FTIR characterizations have been done for pure PUA and all the PUA complex. Here, we only show the FTIR spectra of pure PUA and 5.0 wt % PUA complex, which are presented in Figure 3(a,b),

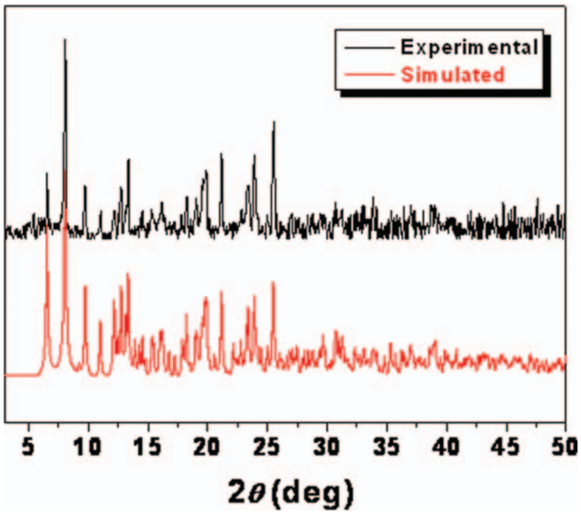


Figure 2 XRPD pattern of the Eu^{III} complex. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

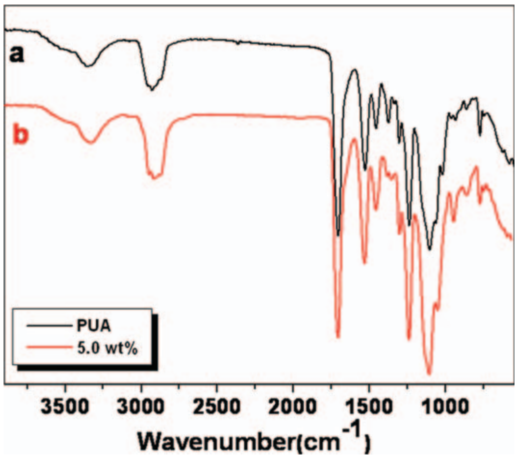


Figure 3 FTIR spectra of (a) the pure PUA and (b) PUA complex materials with 5.0 wt % content of Eu^{III} complex. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

respectively. The vibrational bands observed for PUA complex are explained on the basis of the normal modes of pure PUA. The band at 1531 cm^{-1} verified the formation of —O—CO—NH groups. The disappearance of band at 2267 cm^{-1} indicated that isocyano group entirely reacted with —OH groups. The absorption of double bond (—C=C) at 1644 cm^{-1} nearly disappears. Thus, the double bonds of the macromonomer polymerized.

Thermogravimetric analysis

TGA experiments of complex $\{[\text{Eu}(\mathbf{L})_3(\text{phen})]\cdot\text{H}_2\text{O}\}_2$ and PUA complex were performed under a nitrogen atmosphere by heating the corresponding complexes from room temperature to 900°C with a heating rate of 10°C min^{-1} (Fig. 4). With regard to the complex [Fig. 4(a)], lattice water molecules are released before 145°C (peaking at 133°C), as revealed by a total weight loss of 2.15% (calcd: 1.98%). Then the mass remained largely unchanged until the decomposition onsets the temperature of 290°C. With that, the decomposition of the residuary components occurs with several consecutive steps of weight loss (peaking at 328, 424, 536, and 707°C), which does not stop until heating to 900°C. The TGA curves of PUA and PUA complex with different complex contents are presented in Table I, and the degradation rates of PUA complex are almost the same compared with that of pure PUA, and the onset degradation is about at 250°C. The results obtained indicate that in

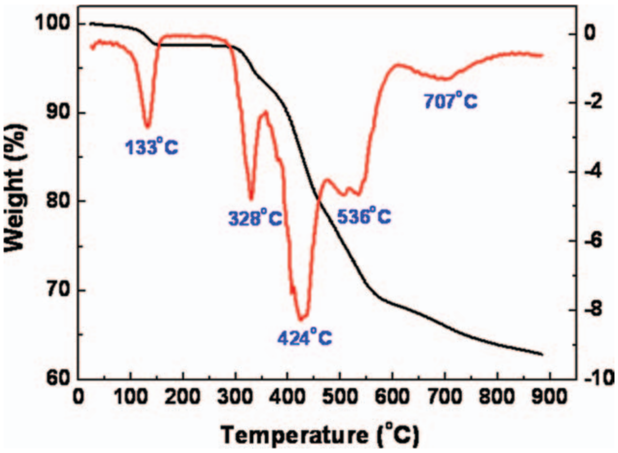


Figure 4 TGA curves of the Eu^{III} complex (the content of Eu in the complex is 16.67% theoretically). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Temperature of Onset of Mass Loss (T_{onset}) of the PUA Complex Materials with Different Content of Eu^{III} Complex

Species	PUA	1.0 wt %	2.0 wt %	5.0 wt %
T_{onset} (°C)	247.4	249.6	251.1	254.0

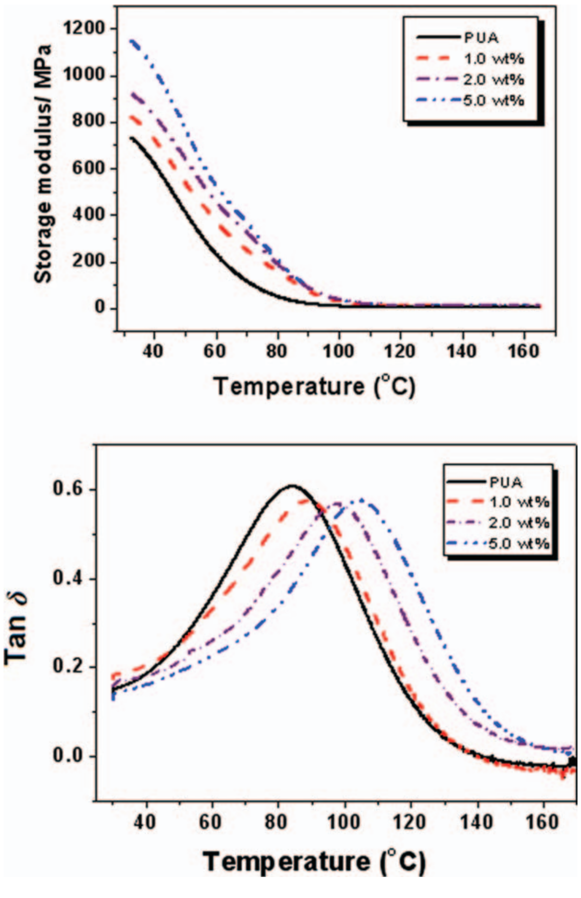


Figure 5 DMA curves for the PUA complex materials with different content of Eu^{III} complex. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

a certain range, the introduction of the complex had almost no effect on the thermal stability of the base material PUA.

Dynamic mechanical properties of PUA complex

The temperature dependence of storage modulus and tan δ for PUA complex with different content of complex is given in Figure 5. In each case in Figure 5(a), the storage modulus decreases with increasing temperature and increases with increasing content of Eu^{III} complex in PUA complex materials. As for tan δ in Figure 5(b), the PUA has a tan δ peak at 84.4°C, corresponding to its glass transition temperature (T_g), which is lower than that of the PUA complex (1.0 wt %) (89.7°C), (2.0 wt %) (97.5°C), and (5.0 wt %) (104.1°C). In other words, the addition of Eu^{III} complex increased the T_g of PUA matrix, and the higher of the Eu^{III} complex contents, the higher of the T_g of PUA complex. They may be explained that the introduction of Eu^{III} complex into PUA matrix increased the movemental resistance of macromonomer segments and crosslinking structures formed by polymerization of PUA were enhanced in a certain extent or the crosslinking density increased by the addition of complex.[25]

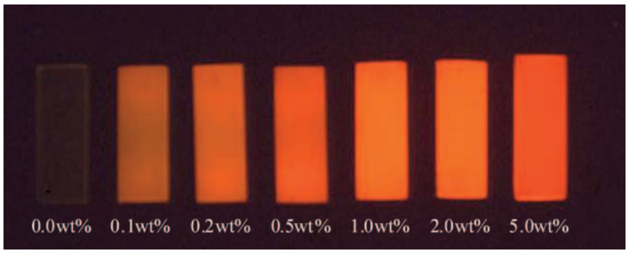


Figure 7 The photoluminescent image of the PUA complex materials with different content of Eu^{III} complex under UV light. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

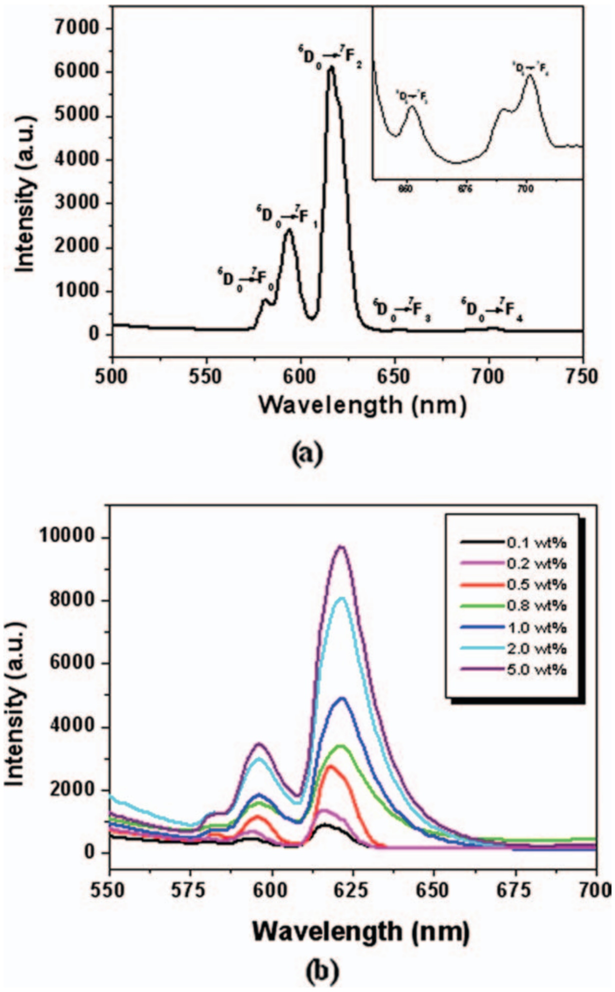


Figure 6 Emission spectra of (a) the Eu^{III} complex and (b) the PUA complex materials with different content of Eu^{III} complex. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Photoluminescent properties

When the as-synthesized Eu^{III} complex is excited at 370 nm at room temperature, characteristic luminescent bands appear at 581, 593, 616, 652, and 691 nm, which correspond to the transitions from the $^5D_0$ state to the ^7F_J (J = 0–4) levels, respectively[26–28] [Fig. 6(a)]. The spectral data do not exhibit the broad band from the ligand in the range of 370–580 nm, related to triplet state, showing an efficient energy transfer from the ligand states to the emitting $^5D_0$ level of the europium ion.[13] Among these transitions, the $^5D_0 \rightarrow {}^7F_2$ transition, which is an electric dipole transition and is extremely sensitive to chemical bonds in the vicinity of Eu^{III} ion, is the strongest one, leading to bright red luminescence.

Figure 6(b) presents the emission spectra of the PUA complex with Eu^{III} complex in the ratio 0.1, 0.2, 0.5, 0.8, 1.0, 2.0, and 5.0 wt %, recorded at room temperature (excitation at 370 nm). The emission spectra exhibit the characteristic lines of the Eu^{III} ion and they emitted the strongest emission spectra at 594 nm. As a result, a novel RE polymer material, emitting red fluorescence under UV light was created (Fig. 7). The $^5D_0 \rightarrow {}^7F_2$ transition is hypersensitive to the ligand field strength because this transition has an electric dipole nature, whereas the intensity of the magnetic dipolar $^5D_0 \rightarrow {}^7F_1$ transition is not sensitive to the ligand field strength and is generally taken as a reference.[13] Comparing the profiles of emission spectra in the range of 550 up to 700 nm, the luminescent intensity enhanced with the increase of the Eu^{III} concentration. The relationship between fluorescence intensity and content of complex indicates that the PUA complex without displaying typical fluorescence concentration quenching behavior, which is different from the results of the literature.[29] The reason may be related with the environment of Eu^{III} ion. The dinuclear units were dispersed into the polymer matrices, and the steric hindrance effects as well as the coordination segment block the congregation of Eu^{III} ion. Under this condition, rare earth emission quenching in solid complexes is not easy to produce.[23]

CONCLUSIONS

A RE complex $\{[\mathrm{Eu}(\mathbf{L})_3(\mathrm{phen})]\cdot \mathrm{H_2O}\}_2$ with favorable fluorescence and heat stability was directly bonded onto the macromolecule chain through the reaction of —OH groups in the complex and —NCO groups in isophorone diisocyanate. As a result, a series of novel photoluminescence materials, emitting red fluorescence under UV light and containing favorable workability, were constructed through in-situ polymerization of polyurethane acrylate macromonomers. Moreover, under the same experiment condition, the emission intensity enhanced with the content of Eu^{III} complex in PUA complex increasing, and the fluorescence quenching did not show up even the content of Eu^{III} complex increased to 5 wt %. The materials possess desirable fluorescence intensity, color purity, and facile preparation. Thus, they have great potential as a photoluminescence display material.

References

1. Armelao, L.; Quici, S.; Barigelletti, F.; Accorsi, G.; Bottaro, G.; Cavazzini, M.; Tondello, E. Coord Chem Rev 2010, 254, 487.
2. Tanner, P. A.; Duan, C.-K. Coord Chem Rev 2010, 254, 3026.
3. Chandler, B. D.; Cramb, D. T.; Shimizu, G. K. H. J Am Chem Soc 2006, 128, 10403.
4. Li, X.; Sun, H.-L.; Wu, X.-S.; Qiu, X.; Du, M. Inorg Chem 2010, 49, 1865.
5. Ritchie, C.; Moor, E. G.; Speldrich, M.; Kögerler, P.; Boskovic, C. Angew Chem Int Ed 2010, 49, 7702.
6. Fiedler, T.; Hilder, M.; Junk, P. C.; Kynast, U. H.; Lezhnina, M. M.; Warzala, M. Eur J Inorg Chem 2007, 2, 291.
7. Liu, L.; Lu, Y.-L.; He, L.; Zhang, W.; Yang, C.; Liu, Y.-D., Zhang, L.-Q.; Jin, R.-G. Adv Funct Mater 2005, 15, 309.
8. Pan, Y.; Zheng, A.; Xiao, H.; Hu, F. J Appl Polym Sci 2006, 102, 1547.
9. Liu, D.; Yu, H.; Wang, Z.; Nie, Q. Polym Int 2010, 59, 937.
10. Wolff, N. E.; Pressley, R. J Appl Phys Lett 1963, 2, 152.
11. Cai, Y.; Chen, M. Q.; Ji, H. N. Acta Polym Sin 2003, 4, 599.
12. Li, X. H.; Lv, P. Z.; Yuan, X. Y. Chin Rare Earths 1998, 19, 9.
13. Parra, D. F.; Mucciolo, A.; Duarte, D. G.; Brito, H. F.; Lugão, A. B. J Appl Polym Sci 2006, 100, 406.
14. Yang, C.; Liu, L.; Lu, Y.; He, L.; Zhang, W.; Zhang, L. J Appl Polym Sci 2005, 96, 20.
15. Parra, D. F.; Mucciolo, A.; Brito, H. F. J Appl Polym Sci 2004, 94, 865.
16. Dong, N.; Chen, B.; Yin, M.; Ning, L. X.; Zhang, Q. J.; Xia, S. D. J Rare Earths 2004, 22, 31.
17. Zhang, M.; Chen, X. S.; Zhou, L. X.; Chen, H. Y.; Yan, C. H.; Qiu, G. M. J Rare Earths 2004, 22, 245.
18. Wang, Y. P.; Lei, Z. Q.; Feng, H. Y.; Bao, J. T.; Wang, Y. B. J Appl Polym Sci 1992, 45, 1641.
19. Feng, H.-Y.; Jian, S.-H.; Wang, W.-P.; Lei, Z.-Q.; Wang, R.-M. J Appl Polym Sci 1998, 68, 1605.
20. Pan, Y.; Zheng, A.; Hu, F.; Xiao, H. J Appl Polym Sci 2006, 100, 1506.
21. Xu, C.-J.; Li, B.-G. Macromol Chem Phys 2010, 211, 1733.
22. Fang, S.; Gao, L.; Zhou, L.; Zheng, Z.; Guo, B.; Zhang, C. J Appl Polym Sci 2009, 111, 724.
23. Fang, S.; Ma, S.; Guo, L.; Zhang, Q.; Hu, M.; Gao, L.; Zhou, L. J Chine Rare Earth Soc 2010, 28, 154.
24. Liu, C.-S.; Hu, M.; Zhang, Q. Acta Crystallogr Sect E: Struct Rep Online 2009, 65, m1572.
25. Lin, Y.; Zhang, A.; Wang, L. J Appl Polym Sci 2008, 108, 1393.
26. Zhou, T.-H.; Yi, F.-Y.; Li, P.-X.; Mao, J.-G. Inorg Chem 2010, 49, 905.
27. Feng, X.; Zhao, J.; Liu, B.; Wang, L.; Ng, S.; Zhang, G.; Wang, J.; Shi, X.; Liu, Y. Cryst Growth Des 2009, 9, 3423.
28. Ramya, A. R.; Reddy, M. L. P.; Cowley, A. H.; Vasudevan, K. V. Inorg Chem 2010, 49, 2407.
29. Du, C.; Ma, L.; Xu, Y.; Li, W. J Appl Polym Sci 1997, 66, 1405.