

# Synthesis and luminescent properties of a novel Eu-containing nanoparticle

Chang Ik Lee, Jin Soo Lim, Song Ho Kim, Dong Hack Suh\*

*Department of Chemical Engineering, Hanyang University, Haengdang-1-Dong, Seongdong-Ku, Seoul 133-791, South Korea*

Received 1 February 2006; received in revised form 21 May 2006; accepted 26 May 2006

## Abstract

We synthesized Eu-containing nanoparticles using the ultra-dilute solution method and characterized by FT-IR, NMR, GPC, DSC, and UV–visible absorption/photoluminescence spectra. The size of Eu-containing nanoparticles was 30–150 nm and the nanoparticles were soluble in common organic solvents. A study of the dependence of emission intensities of the Eu-containing nanoparticles on the Eu content showed that the emission intensities increased nearly linearly with increasing Eu content. In addition, no significant emission concentration quenching phenomenon was observed at the Eu content of 0–9.5 mol%.

© 2006 Elsevier Ltd. All rights reserved.

*Keywords:* Nanoparticle; Europium complex; Luminescence

## 1. Introduction

Recently, rare earth metal complexes have attracted interest for applications in optical devices (electroluminescent devices, lasers, optic amplifier, and so on) due to their inherently sharp emission bands and potentially high quantum efficiency. However, there are also a few problems in using rare earth metal complexes. The first is that rare earth metal complexes are unstable in organic solutions and tend to dissociate into forms of lower complexity. The second is that most rare earth metal complexes usually contain inner-coordinated water molecules, leading to low luminescence quantum efficiency. Lastly, most rare earth metal complexes show serious emission concentration quenching in organic or inorganic materials by ionic aggregates even at low contents [1–6].

Up to now rare earth metal-containing polymers have been prepared by copolymerization of the monomer of transparent polymers and rare earth metal complexes containing the ligand of vinyl groups. However, emission intensities of polymeric Eu-complexes on the Eu content and uniform dispersion of Eu-ions on the polymer matrix are influenced by ionic aggregates. Ionic aggregates cause serious emission concentration quenching by inter- or intra-molecular non-radiative energy transfer [2].

In this paper, to overcome the limits for doped Eu-complex contents and poor dispersion of Eu-ions on the polymer matrix, we presented the nanoparticles containing highly luminescent Eu-complexes. The first luminescent Eu-complexes were designed and synthesized through the reaction of  $\text{EuCl}_3$  with 2-naphthoic acid, acrylic acid, and 1,10-phenanthroline. Then the Eu-containing copolymer was prepared by the atom transfer radical polymerization (ATRP) of the Eu-complex monomer with MMA and HEMA. The Eu-containing copolymer reacted with methacryloyl chloride, and the Eu-containing nanoparticle were prepared by the polymerization using a radical initiator in an ultra-dilute solution.

## 2. Experimental

### 2.1. Materials

All reagents were purchased from Aldrich, Across, and TCI. Before the reaction, all reagents were purified by standard procedures.

### 2.2. Measurements

FT-IR and  $^1\text{H}$  NMR were used to characterize the structure of monomers and complexes.  $^1\text{H}$  NMR spectra of monomers and complexes were obtained on a Varian VXR-300 instrument operating at frequencies of 300 MHz, respectively, using standard acquisition parameters. FT-IR spectra of the monomers and the complexes were obtained on a Nicolet Avatar 360 FT-IR ESP instrument using KBr pellets. The thermal stability

\* Corresponding author. Tel.: +82 2 2290 0523; fax: +82 2 2282 0523.  
E-mail address: [dhsuh@hanyang.ac.kr](mailto:dhsuh@hanyang.ac.kr) (D.H. Suh).

of the complex and the glass transition temperature of the polymer were measured with a Perkin–Elmer TGA-7 thermogravimetric analyzer with a heating rate of 10 °C/min. Gel permeation chromatography (GPC) was carried out using a Waters GPC system (600S controller, 616 pump, 717 Plus auto-sampler and 410 differential refractometer), Ultrastaygel columns in series (Styragel HR-4, HR-3, HR-1, and HR-5E) and tetrahydrofuran (THF) as the eluent. Film thickness of the copolymer and the nanoparticle was measured with a Tencor Alpha-Step 500 Surface Profiler.

The absorption spectra were obtained on a JASCO V-570 UV–visible/NIR Spectrophotometer instrument. The photoluminescence spectra were obtained on a Varian Cary Eclipse FP-6500 Fluorescence Spectrophotometer. The spectra of the complex and the polymer were measured at room temperature.

## 2.3. Synthesis

### 2.3.1. Synthesis of monomer

#### 2.3.1.1. Synthesis of *Eu(III)-bis(2-naphthoic acid)-mono(acrylic acid)-1,10-phenanthroline complex*. (*Eu(Nap)<sub>2</sub>(AA)Phen*) [**I**].

(1)  $\text{EuCl}_3$  (2.59 g, 10 mmol) was dissolved in 20 ml of anhydrous 2-propanol and benzene (1/1 v/v) by heating in a 150 ml flask under  $\text{N}_2$ . To this stirred solution was added a solution of sodium isopropoxide (2.46 g, 30 mmol) in 10 ml of 2-propanol. The mixture was refluxed for 4 h and then a solution of 2-naphthoic acid (3.44 g, 20 mmol) in 10 ml of THF was added. The mixture was refluxed for 2.5 h, a solution of acrylic acid (0.72 g, 10 mmol) in 10 ml of THF was added. The mixture was refluxed for 3.5 h and then a solution of 1,10-phenanthroline (2.70 g, 15 mmol) in 10 ml of THF was added. The reactive mixture was refluxed for 2 h and cooled. The result product was redissolved in benzene after the solvent evaporation. The mixture was filtered. The filtrate was concentrated with evaporation. The viscous solution was precipitated in hexane three times and dried under vacuum at 40 °C for 24 h to give the pale brown product [2] (56% of yield).

(2) Acrylic acid (0.72 g, 10 mmol), 2-naphthoic acid (3.44 g, 20 mmol), 1,10-phenanthroline (2.70 g, 15 mmol) and NaOH (1.2 g, 30 mmol) were dissolved in 100 ml of 70% EtOH aqueous solution. Then 50 ml of a  $\text{EuCl}_3$  (2.59 g, 10 mmol) aqueous solution was slowly dropped in the mixture under constant stirring. The flocculent precipitate initially formed was stirred continuously for half an hour, then filtered, washed repeatedly with a 20% EtOH aqueous solution and dried under vacuum at 40 °C for 24 h [7] (68% of yield).

FT-IR (KBr pellet  $\text{cm}^{-1}$ ) 1585, 1422 (carboxylate,  $\text{COO}^-$ ), 1520 (phen,  $\text{C}=\text{C}$ ), 1600 (coordinated  $\text{C}=\text{O}$ ), 410 (Eu-O),  $^1\text{H}$  NMR (DMSO, ppm)  $\delta=9.1, 8.5, 8, 7.8$  (8H, phen CH),  $\delta=7.5,$

7.3, 7.1 (14H, aromatic CH of Nap),  $\delta=5.9\text{--}6.4$  (3H, broad,  $\text{CH}=\text{CH}_2$ ).

### 2.3.2. Synthesis of copolymer

2.3.2.1. *MMA-co-Eu(Nap)<sub>2</sub>(AA)Phen-co-HEMA* [**II**]. The Eu-containing monomer [**I**] (1–12 equiv.), MMA (89–78 equiv.), HEMA (10 equiv.), Ethyl-2-bromoisobutylate (0.1 equiv.), CuBr (0.1 equiv.), CuBr<sub>2</sub> (0.01 equiv.), 2,2'-dipyridyl (0.2 equiv.) and solvents (MEK/1-propanol 7/3 v/v) were mixed into a glass polymerization tube. The mixture was degassed and sealed under vacuum. The polymerization was carried out by heating the sealed tube at 65 °C for 20 h. The result solution was passed over alumina to remove the Cu complex prior to remove the solvent. The polymer was precipitated in EtOH. The product polymer filtered and dried under vacuum at 40 °C for 24 h.

FT-IR (KBr pellet  $\text{cm}^{-1}$ ) 3600–3200 (HEMA O–H), 1730 (MMA  $\text{C}=\text{O}$ ), 1600 (coordinated  $\text{C}=\text{O}$ ), 1580, 1422 (carboxylate,  $\text{COO}^-$ ), 1520 (phen,  $\text{C}=\text{C}$ ), 410 (Eu-O),  $^1\text{H}$  NMR (DMSO, ppm)  $\delta=9.1, 8.5, 8, 7.8$  (8H, phen CH),  $\delta=7.5, 7.3, 7.1$  (14H, aromatic CH of Nap),  $\delta=4.8$  (1H, OH),  $\delta=3.9$  (2H,  $\text{CH}_2$  of HEMA),  $\delta=3.5\text{--}3.8$  (26H,  $\text{CH}_2$  of HEMA and  $\text{OCH}_3$  of MMA),  $\delta=1.6\text{--}2.1$  (18H,  $\text{CH}_2$  of main chain), 0.5–1.2 (28H,  $\text{CH}_3$  of MMA and HEMA).

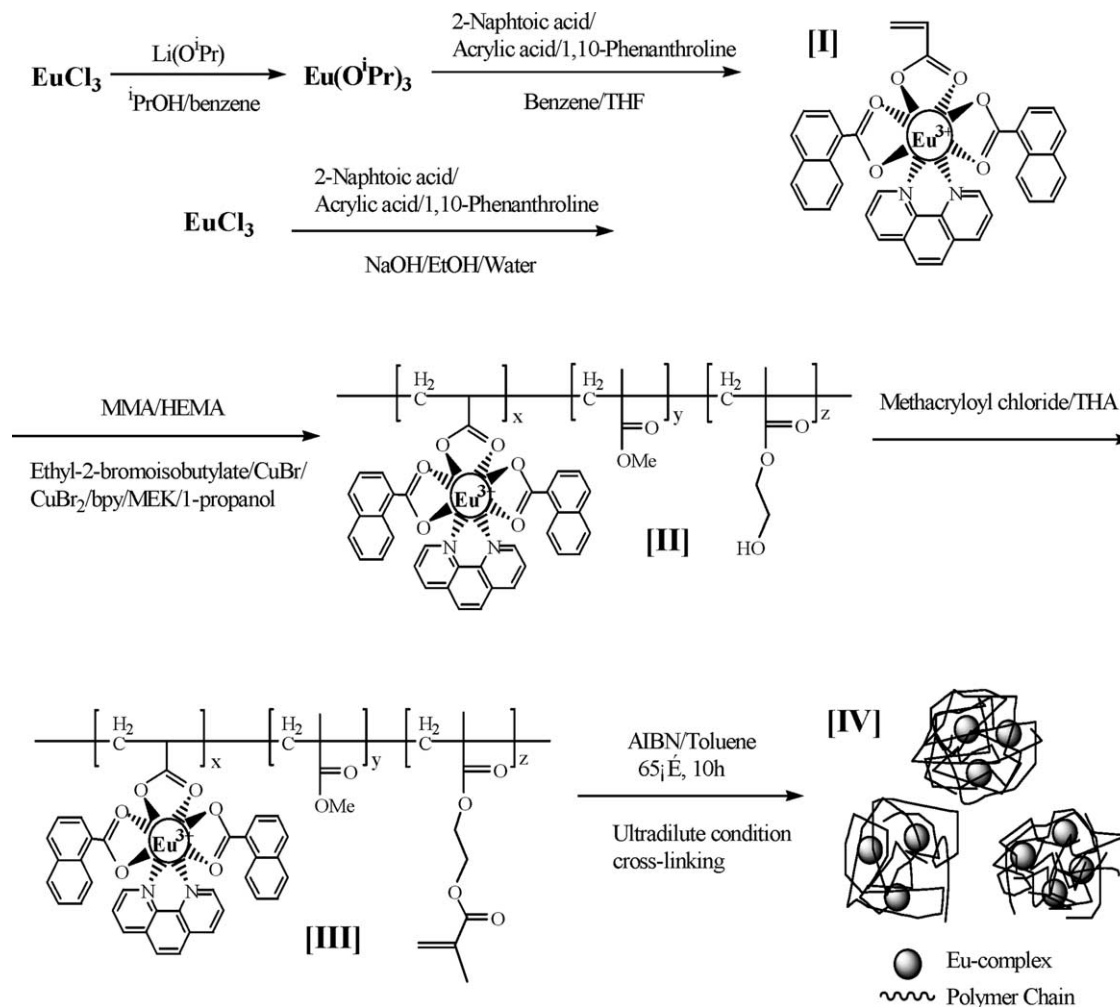
2.3.2.2. *Reaction of methacryloyl chloride with copolymer MMA-co-Eu(Nap)<sub>2</sub>(AA)Phen-co-HEMA* [**III**]. The copolymer [**II**] (1.73 g, 1 mmol of a hydroxy group) and triethylamine (TEA) (0.25 g, 2.5 mmol) were dissolved in 30 ml of dried THF. To this mixture methacryloyl chloride in THF was added dropwise at room temperature. After dropping for 24 h, the mixture was filtered and the clear solution was precipitated in hexane. The product was filtered and dried under vacuum at 40 °C for 24 h [8].

FT-IR (KBr pellet  $\text{cm}^{-1}$ ) 1730 (MMA  $\text{C}=\text{O}$ ), 1600 (coordinated  $\text{C}=\text{O}$ ), 1586, 1429 (carboxylate,  $\text{COO}^-$ ), 1526 (phen,  $\text{C}=\text{C}$ ), 410 (Eu-O),  $^1\text{H}$  NMR (DMSO, ppm)  $\delta=9.1, 8.5, 8, 7.8$  (8H, phen CH),  $\delta=7.5, 7.3, 7.1$  (14H, aromatic CH of Nap),  $\delta=6.1, 5.8$  (2H,  $\text{C}=\text{CH}_2$  of MACl)  $\delta=4.1, 4.3$  (4H,  $\text{CH}_2\text{CH}_2$  of HEMA),  $\delta=3.5\text{--}3.8$  (26H,  $\text{CH}_2$  of HEMA and  $\text{OCH}_3$  of MMA),  $\delta=1.6\text{--}2.1$  (18H,  $\text{CH}_2$  of main chain), 0.5–1.2 (31H,  $\text{CH}_3$  of MMA and HEMA).

### 2.3.3. Preparation of intramolecular cross-linked nanoparticles [**IV**]

A mixture of the copolymer [**III**] (1.8 g, 1 mmol of methacryloxy) and AIBN (0.008 g, 0.05 mmol) was dissolved in 1000 ml toluene. The mixture was degassed by bubbling  $\text{N}_2$  for 30 min and heated for 15 h at 65 °C. After the reaction, the solvent was evaporated and the polymer was dissolved in THF and precipitated in excess hexane [8].

FT-IR (KBr pellet  $\text{cm}^{-1}$ ) 1730 (MMA  $\text{C}=\text{O}$ ), 1600 (coordinated  $\text{C}=\text{O}$ ), 1586, 1422 (carboxylate,  $\text{COO}^-$ ), 1520 (phen,  $\text{C}=\text{C}$ ), 410 (Eu-O),  $^1\text{H}$  NMR (DMSO, ppm)  $\delta=9.1, 8.5, 8, 7.8$  (8H, phen CH),  $\delta=7.5, 7.3, 7.1$  (14H, aromatic CH of Nap),  $\delta=4.1, 4.3$  (4H,  $\text{CH}_2\text{CH}_2$  of HEMA),  $\delta=3.5\text{--}3.8$  (26H,



Scheme 1. The synthesis of the Eu-containing nanoparticle.

OCH<sub>3</sub> of MMA),  $\delta = 1.6\text{--}2.1$  (20H, CH<sub>2</sub> of main chain), 0.5–1.2 (31H, CH<sub>3</sub> of MMA and HEMA).

### 3. Results and discussion

As shown in Scheme 1, the Eu-complex [I] as a monomer was synthesized by two methods. The copolymer [II] was prepared by the atom transfer radical polymerization (ATRP) of [I] with MMA and HEMA. The preparation of the copolymer [III] involved the reaction of methacryloyl chloride and TEA with the copolymer [II]. The Eu-containing nanoparticle [IV] was prepared by intramolecular cross-linking of the copolymer [III] in an ultra-dilute solution using a radical initiator such as AIBN in toluene for 65 °C for 15 h.

In Fig. 1, the infrared spectrum of copolymer [II] showed that the C=O stretching vibrations of acrylic acid at 1700 cm<sup>-1</sup> and the free naphthoic acid at 1678 cm<sup>-1</sup> were essentially absent. Typical absorption of the hydroxy group of HEMA appears at 3200–3500 cm<sup>-1</sup>. After the next reaction, the OH absorption at 3200–3500 cm<sup>-1</sup> was undetectable. The hydroxy group of HEMA reacts methacryloyl chloride, completely. The typical antisymmetric and symmetric stretching vibrations of the

carboxylate ion at 1582 and 1430 cm<sup>-1</sup> and ring vibration of phenanthroline at 1520 cm<sup>-1</sup> were identified.

The copolymerization ratio of copolymers [II] and [III], the introduction of the cross-linker (methacryloyloxy group) and the extent (over 95%) of the cross-linking reaction were confirmed by <sup>1</sup>H NMR spectroscopy by monitoring the disappearance of the vinyl signals associated with a methacrylate pendant group.

In Fig. 2(a), the proton absorption bands of an OH group appear at 4.8 ppm. After next reaction, the proton of OH is undetectable and the protons of C=CH<sub>2</sub> of a methacryloyl group at the copolymer [III] appear at 5.8 and 6.1 ppm in Fig. 2(b), and the protons of CH<sub>2</sub>–CH<sub>2</sub> of HEMA are shifted from 3.8 to 4.3 and 4.1 ppm, separately. Lastly, the proton absorption bands of C=CH<sub>2</sub> of a methacryloyl group at 5.8 and 6.1 ppm decrease the integral ratio in Fig. 2(b) and (c).

The formation of the cross-linked nanoparticles is based on a favorable competition between the intramolecular reaction (involving acrylic units of a single chain) and the intermolecular reaction (between acrylic units of different chains). Since the reactivity in intra- and inter-reactions is the same, the fraction of intra- versus inter-reaction will only depend on the relative probability of encountering another

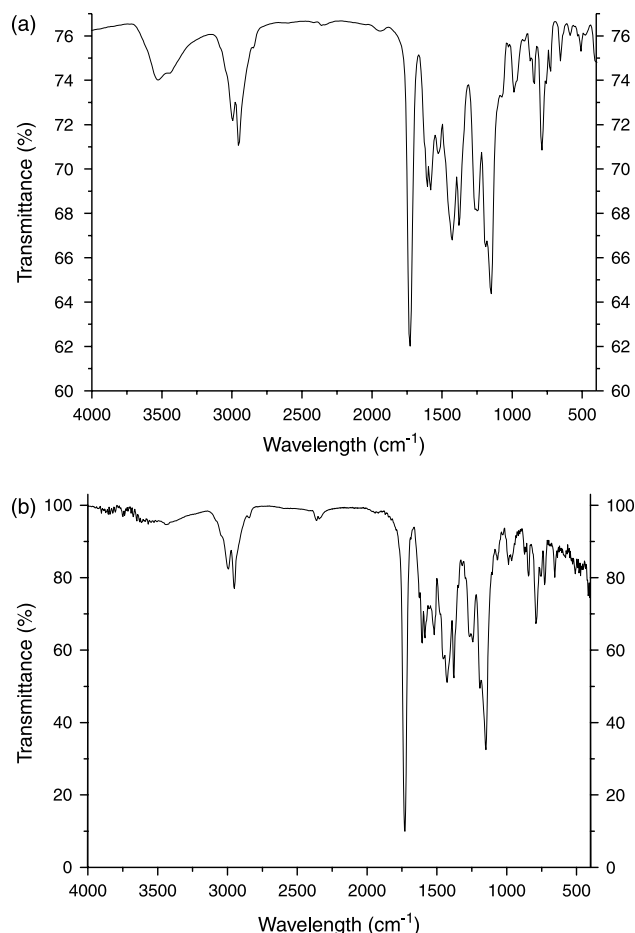


Fig. 1. The FT-IR spectrum of the copolymer [II] (a) and nanoparticle [IV] (b).

internal acrylate relative to that associated with the intermolecular reaction. This will depend exclusively on the polymer–solvent relationship. In a highly concentrated solution, the intermolecular reaction is faster than in a dilute solution, while the intramolecular reaction is more favorable.

The number-average molecular weight ( $M_n$ ), the weight-average molecular weight ( $M_w$ ) and polydispersity indexes (PDI) of the copolymer [II], the precursor copolymer [III], and the nanoparticle [IV] were in the range of 13,000–18,000, 20,000–33,000 and 1.4–1.6, respectively.  $M_n$  and  $M_w$  of copolymer [III] increased more than copolymer [II], because of attaching methacroyloxy group in polymer chain. But  $M_n$  and  $M_w$  of the nanoparticle [IV] were more decreased than the precursor polymer [III], because of occurring intramolecular cross-linking. (Fig. 3, Table 1).

The glass transition temperature ( $T_g$ ) of the Eu-copolymer was evaluated by means of differential scanning calorimeter (DSC) under  $N_2$ .  $T_g$  of the precursor polymer [III] and the cross-linked nanoparticles [IV] were each 114 °C and 118 °C (Table 2). In Fig. 4,  $T_g$  of the nanoparticle [IV] increased with increasing the Eu mol% of the nanoparticle [IV].  $T_g$  of Eu-containing polymers is higher about 10–14 °C than that of PMMA. This result indicates that  $T_g$  of the copolymers can be increased through introducing Eu-complex moieties into

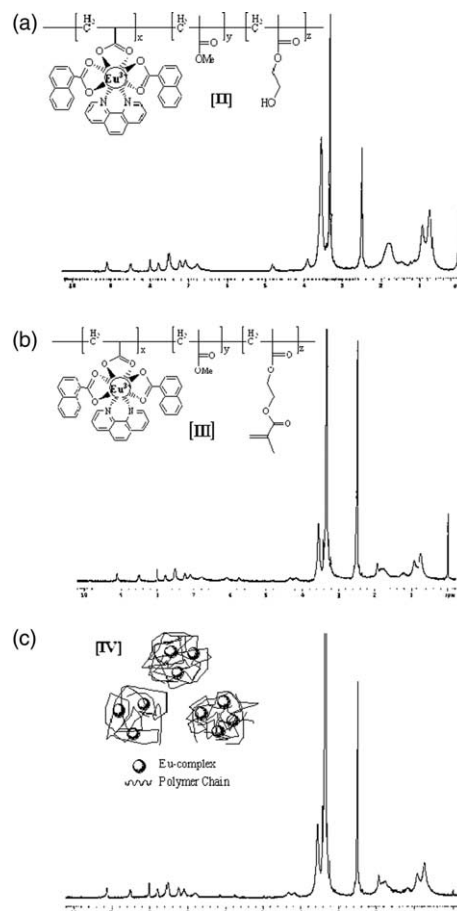


Fig. 2. The  $^1H$  NMR spectrum of the copolymer [II] (a), the copolymer [III] (b) and nanoparticle [IV] (c).

the polymer chain. Since Eu-ion is large, it can attract more than eight oxygen or nitrogen atoms, the effectively cross-linking the chains through intra- and intermolecular coordination with an oxygen atom of a carbonyl group of the MMA and the HEMA unit [2]. And the intermolecular cross-linking decreases segmental chain mobility.

As shown in Fig. 5, estimated by FE-SEM spectra, the size of the nanoparticle appeared about 30–150 nm.

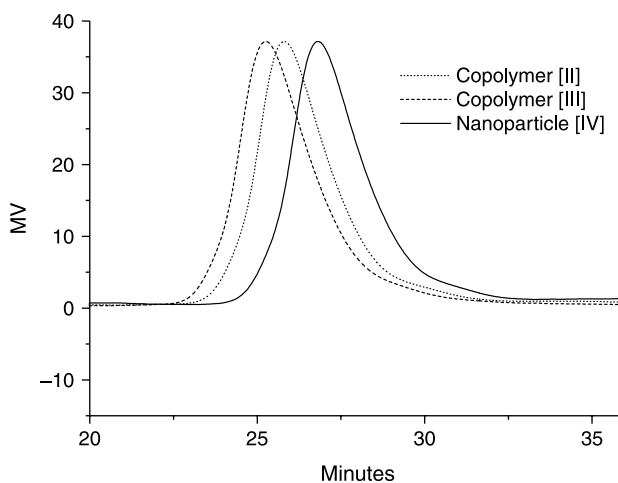


Fig. 3. GPC curves of copolymers [III], [II] and nanoparticle [IV].

Table 1  
GPC data of the copolymer [III], [III] and the cross-linked nanoparticles [IV]

Eu-copolymer	$M_n$	$M_w$	PDI
The copolymer [II]	16,783	24,056	1.43
The copolymer [III]	17,920	25,409	1.41
The cross-linked nanoparticle	15,835	22,890	1.44

Table 2  
DSC data of the precursor polymer [III] and the cross-linked nanoparticles [IV]

Eu-copolymer	$T_g$ (°C)
The precursor polymer	114
The cross-linked nanoparticle	118

The Eu-complexes, the copolymer and the cross-linked nanoparticles showed red emission with the photoluminescence maximum at 612 and 613 nm (Fig. 6). These also showed the absorption maximum at 346 and 354 nm, respectively, (Fig. 7). As shown in Fig. 8, The Eu ion contents of maximum emission intensity were 5 mol% in

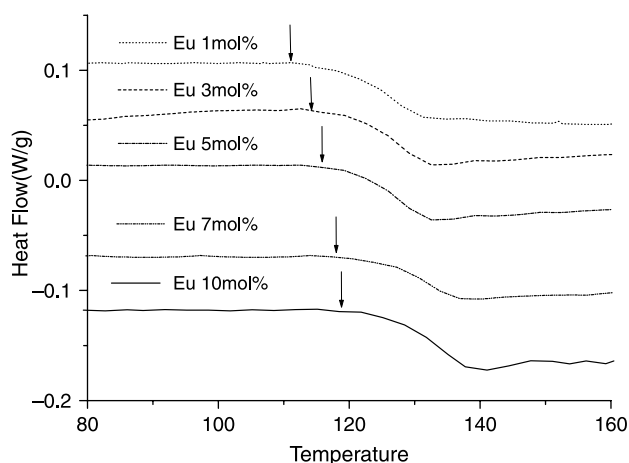


Fig. 4. DSC curves of the nanoparticle [IV].

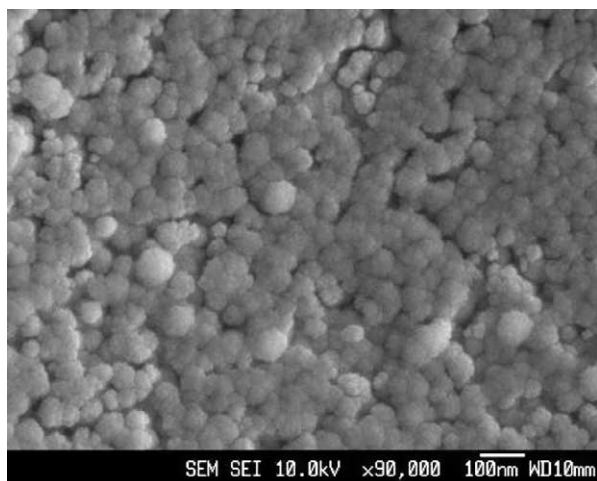


Fig. 5. FE-SEM image of Eu-containing nanoparticle [IV].

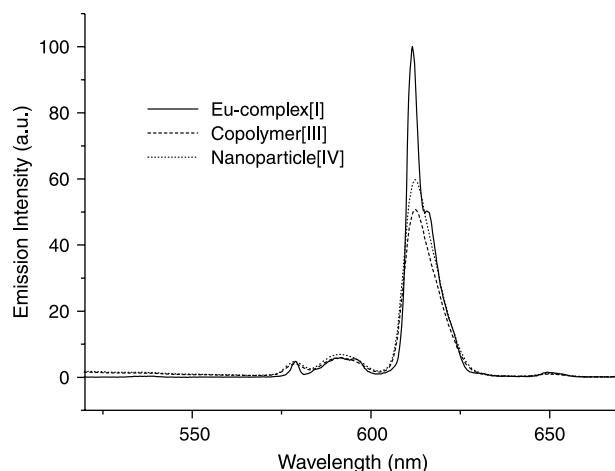


Fig. 6. The fluorescence spectrum of the Eu-complex [I], the copolymer [III] and the nanoparticle [IV].

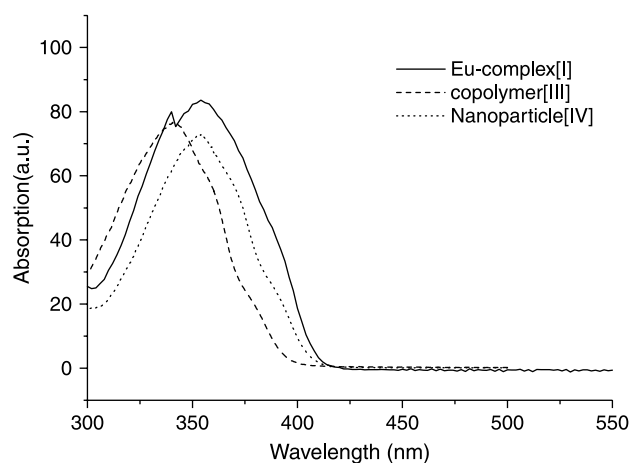


Fig. 7. The UV-vis spectrum of the Eu-complex [I], the copolymer [III] and the nanoparticle [IV].

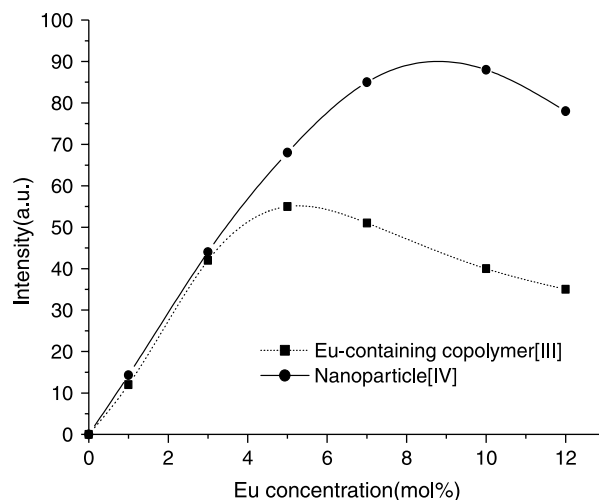


Fig. 8. Comparison to the emission intensities of the copolymer [III] film and the nanoparticle [IV] film at 613 nm (pumping at 354 nm).

the copolymer [III] film, but about 8.5 mol% in the nanoparticle film (film thickness is in range of 380–410 nm). This result shows that the nanoparticle forms more effective dispersion of Eu-complexes in the polymer than the copolymer because the dispersed Eu-complexes by the nanoparticle prevent the ionic aggregates and emission concentration quenching.

#### 4. Conclusions

The Eu-containing nanoparticles [IV] are subsequently prepared by the intramolecular cross-linking of the copolymer [III] in an ultra-dilute solution. The nanoparticles containing luminescent Eu-complex units have a great advantage that the Eu-complex units are uniformly bonded to the polymer chain and are surrounded by the polymer chain as shown in Scheme 1 [IV]. Compared with simple polymeric rare earth metal complexes, the nanoparticles formed by the above method show that there is no concentration quenching in higher rare earth metal ion contents (about 8.5 mol%). Therefore, the synthesis of the nanoparticles is an effective method that increases emission intensities. The nanoparticles containing rare earth metal complexes can be used for many applications

for optical devices such as electroluminescent devices, lasers, and optic amplifiers.

#### Acknowledgements

The authors are grateful to international outbound visiting professor program 2005 (grant no. 2005-D00019) supported by the Korea Research Foundation (KRF) for financial support.

#### References

- [1] Kuriki K, Koike Y, Okamoto Y. *Chem Rev* 2002;102:2347.
- [2] Wang LH, Wang W, Zhang WG, Kang ET, Huang W. *Chem Mater* 2000; 12:2212.
- [3] Okamoto Y, Ueba Y, Dzhanibekov NF, Banks E. *Macromolecules* 1981; 14:17.
- [4] Okamoto Y, Kwei TK, Vyprachticky D. *Macromolecules* 1998;31:9201.
- [5] Slooff LH, van Blaaderen A, Polman A, Hebbink GA, Klink SI, Van Veggel FCJM, et al. *J Appl Phys* 2002;91:3955.
- [6] Aspinall HC. *Chem Rev* 2002;102:1807.
- [7] Du C, Ma L, Xu Y, Li W. *J Appl Polym Sci* 1997;66:1405.
- [8] Mecerreyes D, Lee V, Hawker CJ, Hedrick JL, Wursch A, Volksen W, et al. *Adv Mater* 2001;13:204.