

# Graft Copolymer–Lanthanide Complexes Obtained by Radiation Grafting on Polyethylene Film

Seong-Ho Choi,<sup>1</sup> Kwang-Pill Lee,<sup>1</sup> Sang-Ho Sohn<sup>2</sup>

<sup>1</sup>Department of Chemistry Graduate School, Kyungpook National University, Taegu 702-701, South Korea

<sup>2</sup>Department of Physics, Kyungpook National University, Taegu 702-701, South Korea

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**ABSTRACT:** Radiation-induced grafting of acrylic acid (AAc) onto polyethylene (PE) film was investigated. The grafted films rapidly adsorbed Eu, Gd, Tb, and Dy ions at high efficiency. The carboxylic acid groups on the AAc-grafted PE film acted as a chelating site for the selected lanthanide ions. Complex formation of lanthanide ions and the carboxylic acid group on PE film was investigated by IR, FT–Raman, and X-ray photoelectron spectroscopy (XPS).

Photoluminescence (PL) spectra and the thermal properties of the graft copolymer–lanthanide complexes onto PE film were also investigated. The application of such prepared graft copolymer–lanthanide complexes in the field of fluorescence emission displays (FEDs) may be interest. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 328–336, 2003

**Key words:** thermal properties; graft copolymer; radiation

## INTRODUCTION

Radiation-induced graft polymerization (RIGP) is a beneficial method for the introduction of functional groups into different polymer materials using specially selected monomers. There have been several reports on radiation graft polymerization of polar monomers onto polymer film to obtain hydrophilic properties for versatile application.<sup>1–5</sup>

A polymer–metal complex<sup>6</sup> is typified by a remarkably specific structure in which central metal ions are surrounded by a bulky polymer chain. By virtue of this conformational arrangement of polymeric ligands, the polymer–metal complex shows interesting and important characteristics, for example, different catalytic activities from those of corresponding ordinary metal complexes with low molecular weight.

In a previous study,<sup>7</sup> we prepared a graft copolymer–metal complex of copper, cadmium, thorium, and uranium. The structure of the graft copolymer–metal complex was investigated by IR, UV/VIS, and X-ray photoelectron spectroscopy (XPS). Furthermore, the application of such prepared graft copolymer–

metal complexes in the field of semiconductors was examined. However, the preparation and application of the graft copolymer–lanthanide complex has not yet been studied to our knowledge.

The aim of this work was to prepare some graft copolymer–lanthanide complexes for the possible use as fluorescence emission material. In this study, graft copolymer–lanthanide complexes were prepared by RIGP and by its subsequent complexation of lanthanide ions such as Eu, Gd, Tb, and Dy. Complex formation of lanthanide ions and the carboxylic acid group on acrylic acid (AAc)-grafted polyethylene (PE) film was determined by IR, Fourier transform (FT)–Raman, and XPS. Furthermore, photoluminescence (PL) spectra and the thermal properties of PE membranes with carboxylic acid–lanthanide complexes were investigated.

## EXPERIMENTAL

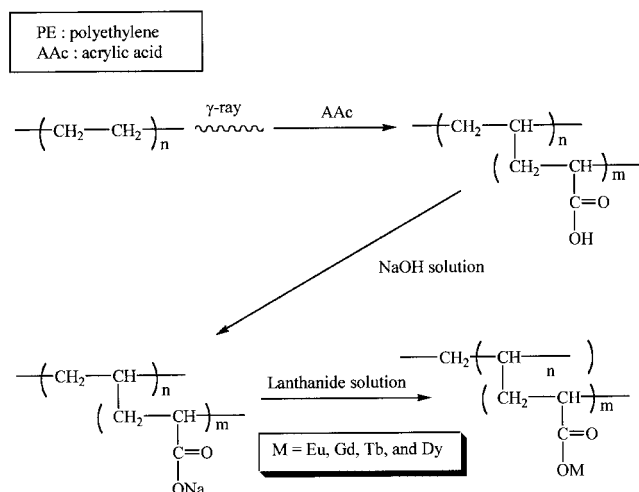
### Materials

PE film of thickness 0.03 mm (Tae-Syeng Chemistry Co., Daegu, South Korea) was washed with methanol and dried in a vacuum oven at 50°C for 8 h. Reagent-grade AAc (Junsei, Seoul, South Korea; 99%), an Eu<sub>2</sub>NO<sub>3</sub> solution (Aldrich), a Gd<sub>2</sub>NO<sub>3</sub> solution (Aldrich), Tb<sub>2</sub>NO<sub>3</sub> (Aldrich), and Dy<sub>2</sub>NO<sub>3</sub> (Aldrich) were used. All other chemicals were also reagent grade and used without further purification.

Correspondence to: K.-P. Lee (kplee@kyungpook.ac.kr).

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**Scheme 1** Preparation of the graft copolymer-lanthanide complex by RIGP method.

### Grafting procedure and preparation of graft copolymer-lanthanide ion complexes

Scheme 1 shows the preparation procedure of the graft copolymer-lanthanide complex using the radiation graft copolymerization method. The PE film was used as the base polymer for grafting polymerization. The PE film of size  $4 \times 5$  cm was irradiated by  $\gamma$ -ray of a Co-60 source (Co-60 Gamma-ray Irradiator IR-79) under atmospheric pressure and ambient temperatures and then immediately reacted with the monomer. The unreacted monomer and homopolymer after grafting of AAc were removed with hot water and subsequently with MeOH. The grafted PE film was dried in a vacuum oven at  $50^\circ\text{C}$  for 14 h. For the studies of the effects of various parameters on the grafting polymerization, the degree of grafting can be defined as

$$\text{Degree of grafting (\%)} = [(W_g - W_0)/W_0] \times 100 \quad (1)$$

where  $W_g$  and  $W_0$  denote the weights of the grafted and the ungrafted PE film, respectively.

Graft copolymer-lanthanide complexes were prepared as follows: The AAc-grafted PE film was placed in a 1.0 wt % NaOH solution at room temperature for 7 h and then the PE film with Na was inserted into the lanthanide solution ( $\sim 1000 \mu\text{g/mL}$ ) at  $50^\circ\text{C}$  for 12 h (see Scheme 1). The prepared graft copolymer-lanthanide complexes were then dried in a vacuum oven at  $50^\circ\text{C}$  for 12 h.

### IR and FT-Raman spectrophotometer measurements

IR spectra were recorded using a Nicolet Model 205 FTIR spectrometer. The NIR FT-Raman spectra were recorded with a Bruker FT-106 Raman module, equipped with a Ge detector cooled by liquid nitrogen, connected to a Bruker FTIR 66 interferometer. To excite the Raman spectra, a continuous wave diode-pumped Nd:YAG laser with radiation of wavelength 1064 nm ( $9398.4 \text{ cm}^{-1}$ ) was used. In all cases, the laser power was 300 mW, and the spectral resolution,  $2 \text{ cm}^{-1}$ .

### XPS measurements

The XPS of the samples was obtained using an ESCALab 220i (VG Scientific) equipped with a full  $180^\circ$  hemispherical electrostatic analyzer to examine the chemical state of the constituent elements. As a phonon source, Al  $K\alpha$  radiation (1486.6 eV) was used. The half-width at half-maximum of the  $4f_{7/2}$  line in the XPS spectrum of gold obtained with our XPS spectrometer was smaller than 1.0 eV. The energy scale of the spectrometer was calibrated using the lowest binding energy component of the C 1s peak (285.0 eV). The C 1s spectra were deconvoluted using a Gaussian-Lorentzian model to obtain the best binding-energy values.

**TABLE I**  
Effects of Monomer and Sulfuric Acid Concentration on the Grafting of AAc onto PE Film

| AAc concentration | Degree of grafting (%) |  |  |  |  |
|-------------------|------------------------|--|--|--|--|
|                   | No additives           | $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ( $2.5 \times 10^{-3} \text{ M}$ ) |  |  |  |
|                   |                        | No $\text{H}_2\text{SO}_4$   | $2.5 \times 10^{-3} \text{ M}$ $\text{H}_2\text{SO}_4$ | $2.5 \times 10^{-2} \text{ M}$ $\text{H}_2\text{SO}_4$ | $2.5 \times 10^{-1} \text{ M}$ $\text{H}_2\text{SO}_4$ |
| Neat              | Gel                    | —  | —  | —  | —  |
| 12.0M             | 120.0                  | 143.0  | 200.0  | 245.0  | 280.0  |
| 10.0M             | 79.0                   | 85.0   | 120.0  | 145.0  | 240.0  |
| 8.0M              | 57.0                   | 68.0   | 106.0  | 126.0  | 220.0  |
| 6.0M              | 43.0                   | 57.0   | 98.0   | 100.0  | 150.0  |
| 4.0M              | 12.0                   | 14.0   | 40.0   | 42.0   | 110.0  |

Irradiation dose, 30 kGy; thickness of PE film, 0.03 mm; reaction time, 30 min; reaction temperature,  $70^\circ\text{C}$ ; solvent,  $\text{H}_2\text{O}$ .

**TABLE II**  
Effects of Monomer Concentration and Solvent on the Grafting of AAc onto PE Film

| AAc concentration | Degree of grafting (%) |                                       |      |
|-------------------|------------------------|---------------------------------------|------|
|                   | H <sub>2</sub> O       | H <sub>2</sub> O/MeOH<br>(1/1, vol %) | MeOH |
| Neat              | Gel                    | —                                     | —    |
| 12.0M             | 143.0                  | 104.0                                 | 62.0 |
| 10.0M             | 85.0                   | 65.0                                  | 40.0 |
| 8.0M              | 68.0                   | 48.0                                  | 16.0 |
| 6.0M              | 57.0                   | 27.0                                  | 7.6  |
| 4.0M              | 14.0                   | 8.0                                   | 3.0  |

Irradiation dose, 30 kGy; thickness of PE film, 0.03 mm; reaction time, 30 min; reaction temperature, 70°C; FeSO<sub>4</sub> 7H<sub>2</sub>O = 2.5 × 10<sup>-3</sup> M.

### PL spectra measurement

The PL spectra were recorded using a Shimadzu Model RF-5301PC spectrofluorometer.

### Thermal properties

Thermogravimetric analyses (TGAs) of the polymer and polymer-lanthanide complexes were made on a TA instrument (TGA 2950 Model, DuPont Co.) with a heating rate of 10°C min<sup>-1</sup> in the temperature range of 50–700°C. Differential scanning calorimetry (DSC) of the GS-PNF was performed using a DSC-7 (Perkin-Elmer, USA) at a heating rate of 10°C min<sup>-1</sup> in the temperature range of 50–200°C.

**TABLE III**  
Effects of Monomer Concentration and Reaction Temperature on the Grafting of AAc onto PE Film

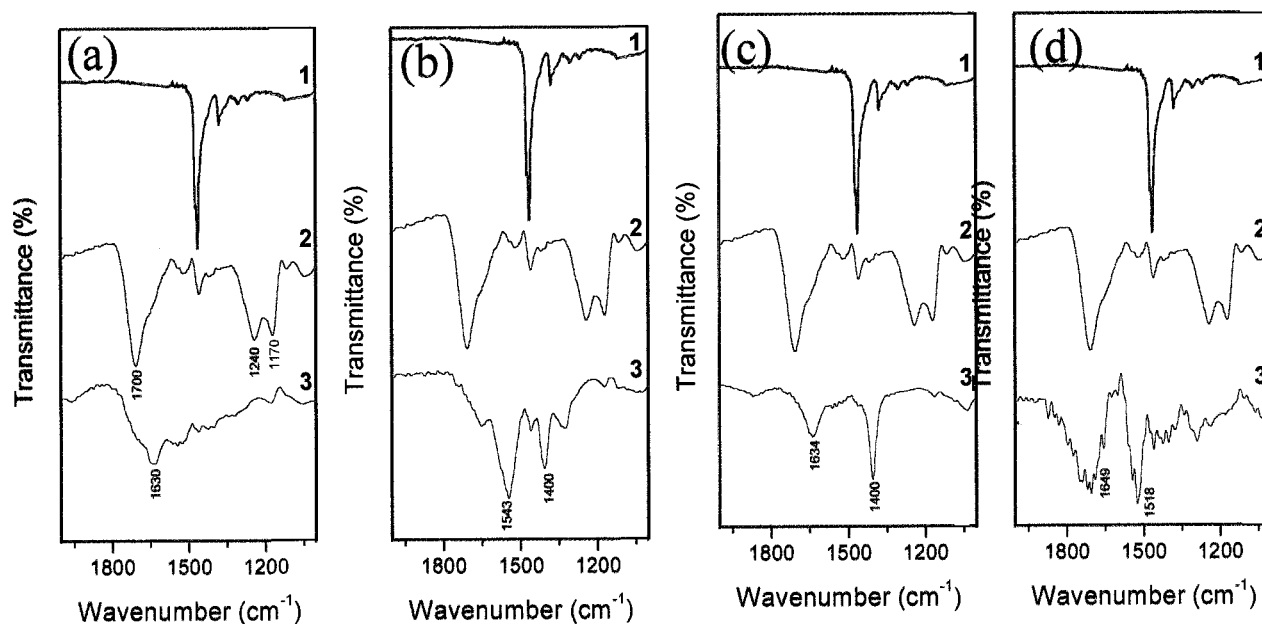
| AAc concentration | Degree of grafting (%) |       |       |
|-------------------|------------------------|-------|-------|
|                   | 30°C                   | 50°C  | 70°C  |
| Neat              | ~0                     | Gel   | Gel   |
| 12.0M             | ~0                     | 110.0 | 143.0 |
| 10.0M             | ~0                     | 65.0  | 85.0  |
| 8.0M              | ~0                     | 42.0  | 68.0  |
| 6.0M              | ~0                     | 22.0  | 57.0  |
| 4.0M              | ~0                     | 5.0   | 14.0  |

Irradiation dose, 30 kGy; thickness of PE film, 0.03 mm; reaction time, 30 min; solvent, H<sub>2</sub>O; FeSO<sub>4</sub> 7H<sub>2</sub>O = 2.5 × 10<sup>-3</sup> M.

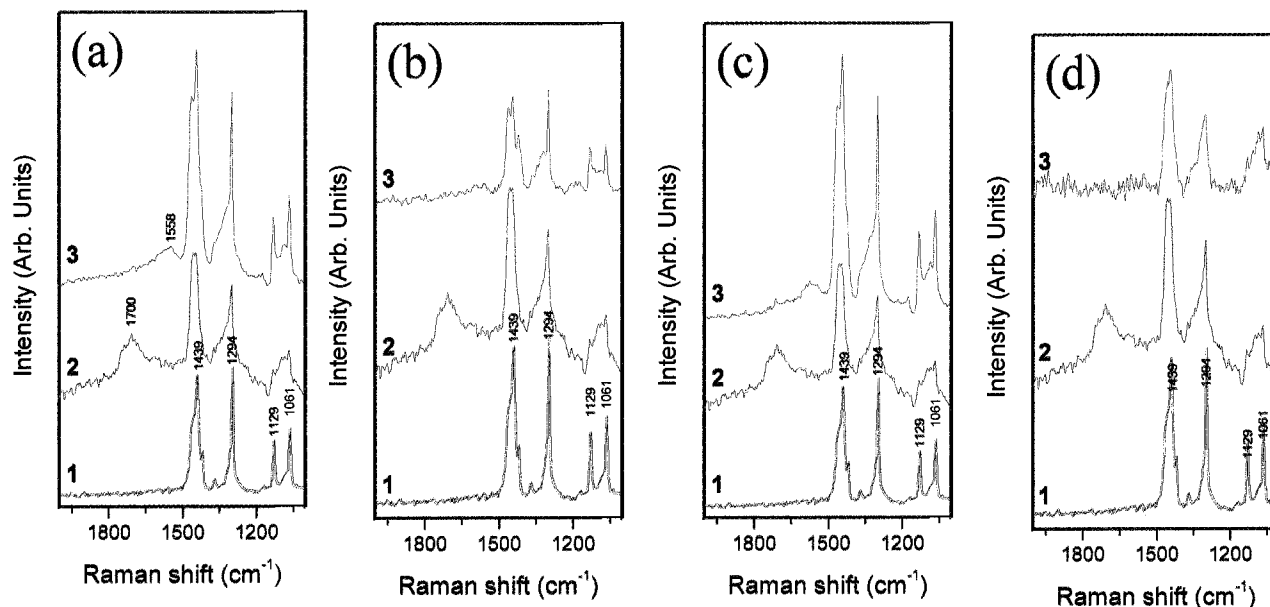
## RESULTS AND DISCUSSION

### Grafting of AAc onto PE film by RIGP

Table I shows the effects of the AAc and H<sub>2</sub>SO<sub>4</sub> concentration on the grafting of AAc onto PE film in the presence of ferrous sulfate (FeSO<sub>4</sub>). The grafting yield was much enhanced with the addition of sulfuric acid and FeSO<sub>4</sub>. FeSO<sub>4</sub> and Mohr's salt [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> · FeSO<sub>4</sub>] are two among the most commonly used compounds for inhibiting the homopolymerization of a vinyl monomer during grafting polymerization.<sup>8,9</sup> As indicated by Garnett et al.,<sup>10</sup> ferrous ion (Fe<sup>2+</sup>) in a reaction solution has a high reaction rate constant with the hydroxyl radical, and, thus, it effectively sweeps up these radicals during the grafting reaction. In a previ-



**Figure 1** FTIR-ATR spectra of the (a) Eu complex, (b) Gd complex, (c) Tb complex, and (d) Dy complex. (1) Original PE film; (2) 85% AAc-g-PE film; (3) lanthanide ion complex.



**Figure 2** FT-Raman spectra of the (a) Eu complex, (b) Gd complex, (c) Tb complex, and (d) Dy complex. (1) Original PE film; (2) 85% AAc-g-PE film; (3) lanthanide ion complex.

ous study,<sup>11,12</sup> the influence of an inhibitor on the degree of grafting was examined using  $\text{FeSO}_4$ . It was found that the addition of  $\text{FeSO}_4$  to an acrylonitrile solution inhibited effectively the homopolymer formation. Both the addition of sulfuric acid and salt ( $\text{Fe}^{2+}$ ) resulted in increase of the grafting yield of acrylonitrile onto polypropylene film in methanol at almost all monomer concentrations examined.

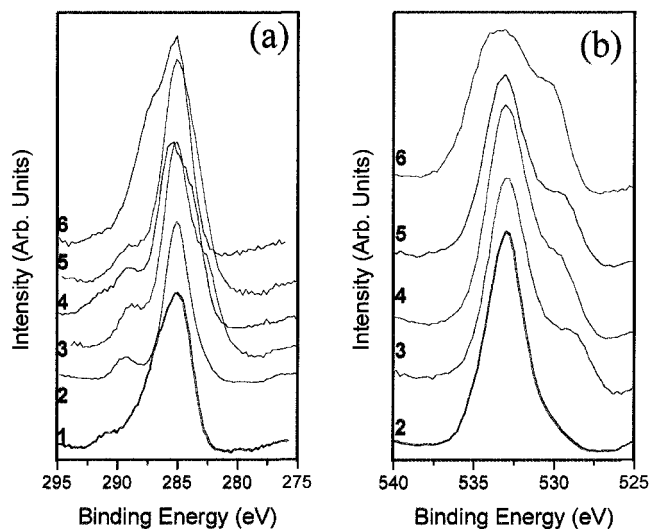
Table II shows the relationship between the solvents (water, methanol, and a water/methanol mixture) and

the monomer concentration. The degree of grafting increased with increasing AAc concentration. A large grafting yield was obtained in  $\text{H}_2\text{O}$ . This can be explained by the fact that AAc is more soluble in water than in methanol and the water/methanol mixture. On the other hand, the backbone radical ( $\text{POO} \cdot \text{O}$ ) may undergo swelling in water, which facilitates accessibility of the monomer to the active sites inside.

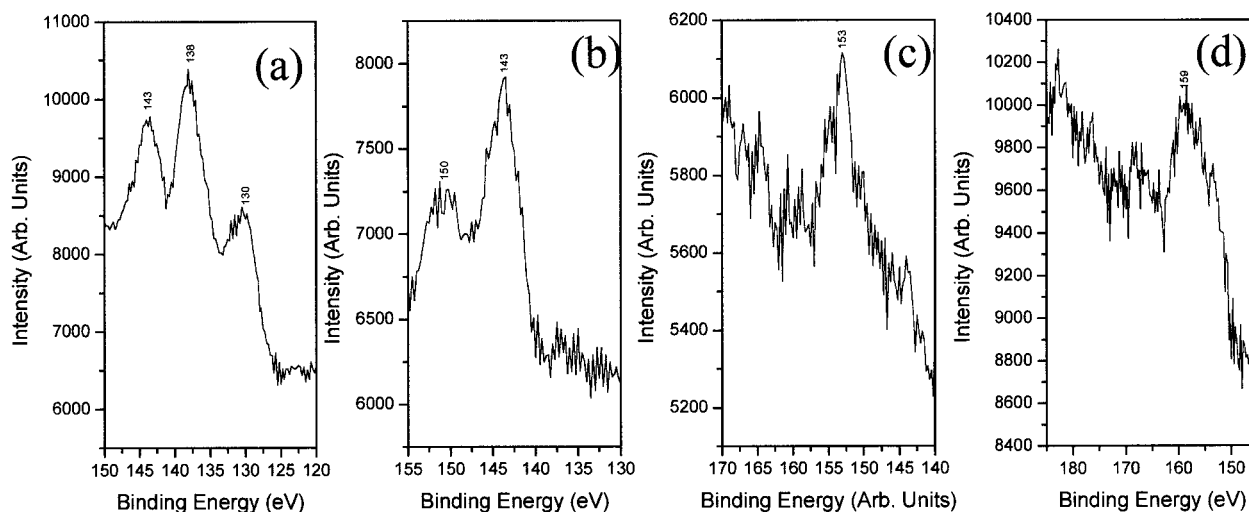
Table III shows the effects of the monomer concentration and reaction temperature on the grafting of AAc onto PE film at reaction temperatures of 30, 50, and 70°C in water. The grafting at 70°C was higher than that at 50°C. In the case of 30°C, grafting did not occur due to radicals formed when the peroxide formed during irradiation in air was decomposed at 70°C. Therefore, a relatively higher temperature is required to obtain a high grafting yield, indicating that it is an important factor for controlling the grafting yield.

### Structure of graft copolymer-lanthanide complex

Figure 1 shows FTIR-ATR spectra of the (a) Eu complex, (b) Gd complex, (c) Tb complex, and (d) Dy complex: (1) original PE film, (2) 85% AAc-grafted PE film, and (3) lanthanide ion complex of 85% AAc-grafted PE. In the IR spectrum of (2) AAc-grafted PE film, a C=O and C—O stretch of poly(AAc) was observed at 1700 and 1240  $\text{cm}^{-1}$ , respectively. No such peak was observed in the IR spectrum of (1) the original PE film. In (3) of Figure 1(a), a broad band at 1630



**Figure 3** XPS spectra of the (a) C 1s and (b) O 2p of the (1) original PE, (2) 85% AAc-g-PE, (3) Eu complex, (4) Gd complex, (5) TB complex, and (6) Dy complex.



**Figure 4** XPS spectra of the (a) Eu 4*d* of the Eu complex, (b) Gd 4*d* of the Gd complex, (c) Tb 4*d* of the Tb complex, and (d) Dy 4*d* of the Dy complex.

$\text{cm}^{-1}$  was observed due to Eu ions in the graft copolymer–lanthanide complex. On the other hand, in (3) of Figure 1(b), sharp bands at 1543 and 1400  $\text{cm}^{-1}$  appeared due to  $\text{—COO—Gd}$  ions. In (3) of Figure 1(c), sharp bands at 1643 and 1400  $\text{cm}^{-1}$  due to Tb ions in the graft copolymer–lanthanide complex were recorded. In (3) of Figure 1(d), sharp bands at 1649 and 1518  $\text{cm}^{-1}$  due to Dy (III) ions in the graft copolymer–lanthanide complex were also observed. From the results, the lanthanide ion was successfully introduced into AAC-grafted PE film.

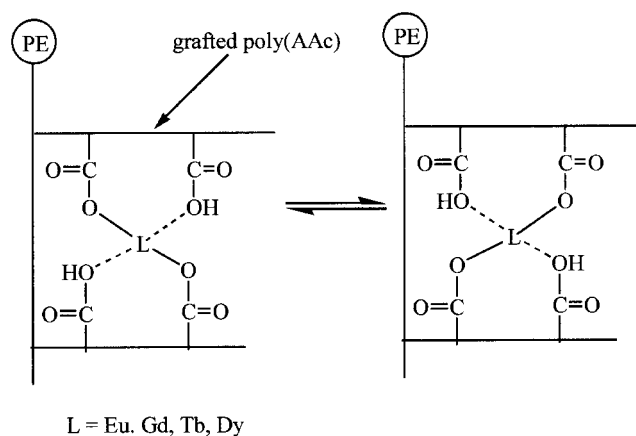
Figure 2 shows the FT-Raman spectra of the (a) Eu complex, (b) Gd complex, (c) Tb complex, and (d) Dy complex: (1) original PE film, (2) 85% AAC-grafted PE film, and (3) lanthanide ion complex of 85% AAC-grafted PE. In (1) of Figure 2 (a–c), sharp bands at 1409 and 1294  $\text{cm}^{-1}$  due to  $\text{—CH}_2$  deformation and  $\text{—CH}_2$  wag were recorded. On the other hand, bands at 1129 and 1061  $\text{cm}^{-1}$  due to C–C skeletal stretching were observed.<sup>13</sup> In (2) of Figure 2(a–d), a broad peak at 1700  $\text{cm}^{-1}$  due to the carbonyl group was observed. These results indicated that carboxylic acid was successfully grafted onto the PE film. In (3) of Figure 2 (a–c), a characteristic band at 1560  $\text{cm}^{-1}$  due to lanthanide chelate was recorded. From the results, the lanthanide ion was successfully introduced into the carboxylic acid group of the grafted PE film.

Figure 3 shows XPS spectra of (a) C 1*s* and (b) O 2*p*: (1) original PE, (2) 85% AAC-grafted PE, (3) Eu complex, (4) Gd complex, (5) Th complex, and (6) Dy complex with the same degree of grafting. The core-level binding energy of C 1*s* of the PE film was calculated to be 285.1 eV. In Figure 3(a), (2) the AAC-grafted PE film and (3–6) the graft copolymer–lanthanide complex were observed. The additional peaks at

288.7–289.5 eV was due to the carboxylic group at the polymer chains. In Figure 3(b), the binding of the O 2*p* of the carboxylic acid group [ $\text{>C(=O)—OH}$ ] of the AAC-grafted PE film was observed at 533.0 eV. On the other hand, the additional binding energy around 528 eV was shown in the graft copolymer–lanthanide complex. These results clearly indicated that the carboxylic acid group was introduced onto the PE film.

Figure 4 shows the XPS spectra of the Eu 4*d* of the (a) Eu complex, (b) Gd 4*d* of the Gd complex, (c) Tb 4*d* of the Tb complex, and (d) Dy 4*d* of the Dy complex. The core-level binding energies of Eu 4*d*<sub>5/2</sub>, Gd 4*d*<sub>5/2</sub>, Tb 4*d*<sub>5/2</sub>, and Dy 4*d*<sub>5/2</sub> in the Eu-, Gd-, Tb-, and Dy-polymer complexes were calculated to be 143, 150, 153, and 159 eV, respectively, indicating the existence of the trivalent ion.

Figure 5 shows the complex structure of lanthanide



**Figure 5** Structure of complex by lanthanide-ion bridge in polymer matrix.

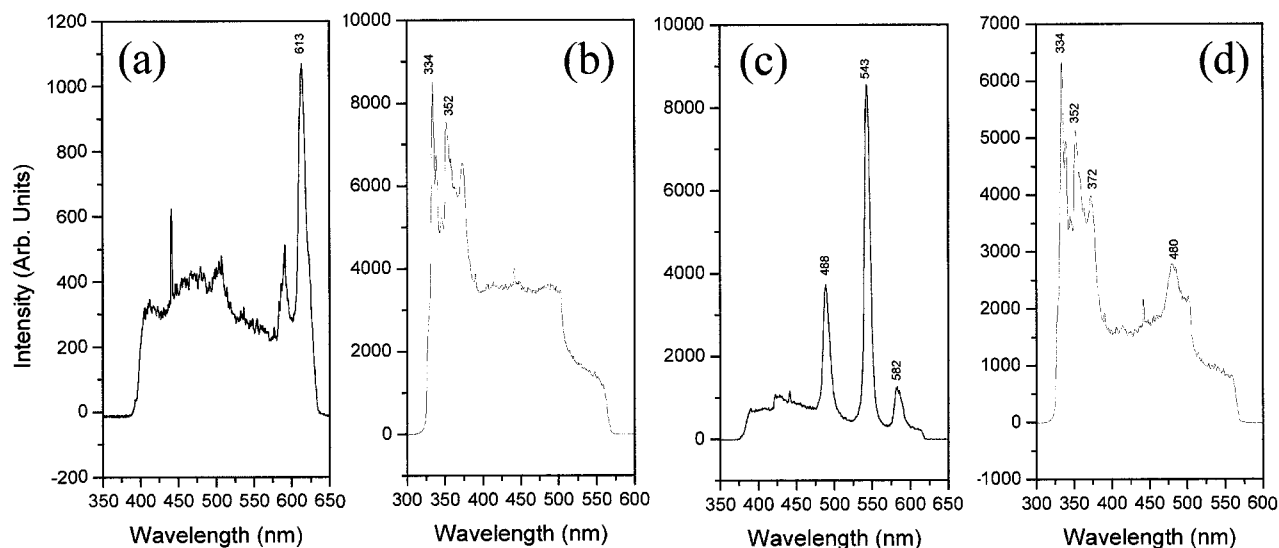


Figure 6 PL spectra of the (a) Eu complex, (b) Gd complex, (c) Tb complex, and (d) Dy complex.

ions and the carboxylic acid group on the AAc-grafted PE film. The carboxylic acid group on the AAc-grafted PE film acted as a chelating site for selected lanthanide ions. The structure of the complex by inter and/or intramolecular bridging in the polymer matrix is proposed as shown in Figure 5.

#### Fluorescence and thermal properties of the grafted copolymer-metal complex

Figure 6 shows the PL spectra of the (a) Eu complex, (b) Gd complex, (c) Tb complex, and (d) Dy complex. In Figure 6(a), the sharp peak at 613 nm due to the  ${}^5D_0 \rightarrow {}^7F_2$  transition was detected. These results may not have indicated the transition peaks of the Eu element but the transition peak of carboxylic acid group-Eu complex. The carboxylic acid group-Eu complex was reported earlier.<sup>14</sup> However, the grafted polymer-Eu complex has not been reported yet to our knowledge. In Figure 6(b), peaks at 334 and 352 nm were obtained. In Figure 6(c), strong peaks at 543 nm due to the  ${}^5D_4 \rightarrow {}^7F_5$  transition were detected. In Figure 6(d), a broad peak at 400 nm was detected.

Figure 7 shows TGA curves of the (a) ungrafted PE, (b) 85% AAc-grafted PE, (c) Eu complex, (d) GD complex, (e) Tb complex, and (f) Dy complex. A considerable change in the thermal behavior of the PE film occurred upon grafting. In Figure 7(b), weight loss was observed at four different temperature regions. The first weight loss at 120°C can be interpreted as the loss of moisture on the surface; the second weight loss at 234°C, as the dehydration of grafted poly(AAc); and the third weight loss at 310°C, as an decarboxylation of grafted poly(AAc) onto the polymer backbone. The weight loss at 470°C may be considered as the loss of

PE film. In Figure 7(c-f), weight loss was also observed in different temperature regions. These results clearly suggested that the dehydration was somewhat difficult due to the complex formation of the lanthanide and the carboxylic acid group.

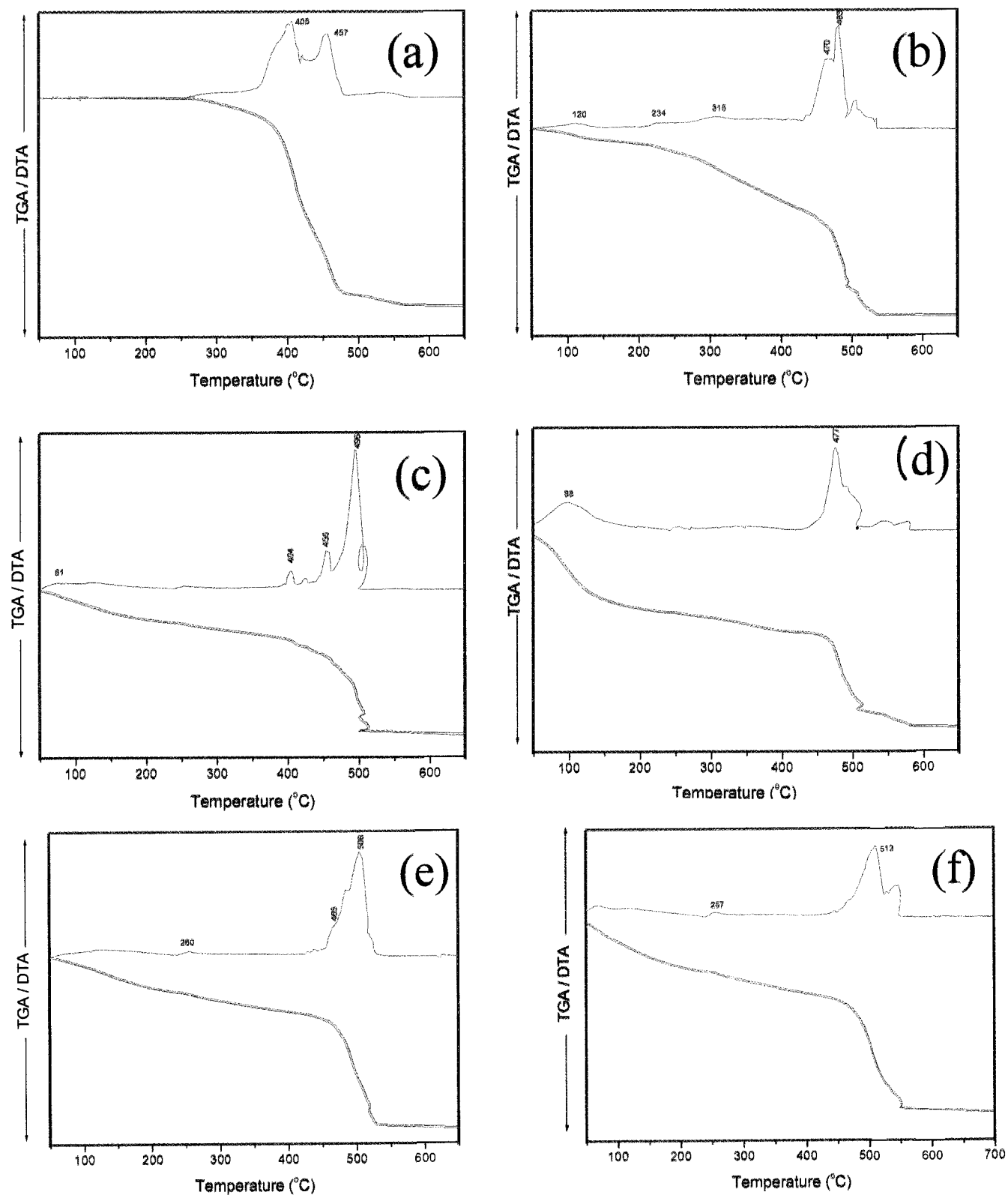
Figure 8 shows DSC curves of the (a) ungrafted PE, (b) 85% AAc-grafted PE, (c) Eu complex, (d) GD complex, (e) Tb complex, and (f) Dy complex. In Figure 8(a), the melting temperature at 108°C was due to PE. In Figure 8(b), the three melting temperatures at 106, 198, and 250°C of the AAc-grafted PE film may be interpreted as the PE, graft polymer, and graft polymer melting temperatures, respectively. These results indicated that the lanthanide ions were introduced successfully onto the AAc-grafted PE film.

#### CONCLUSIONS

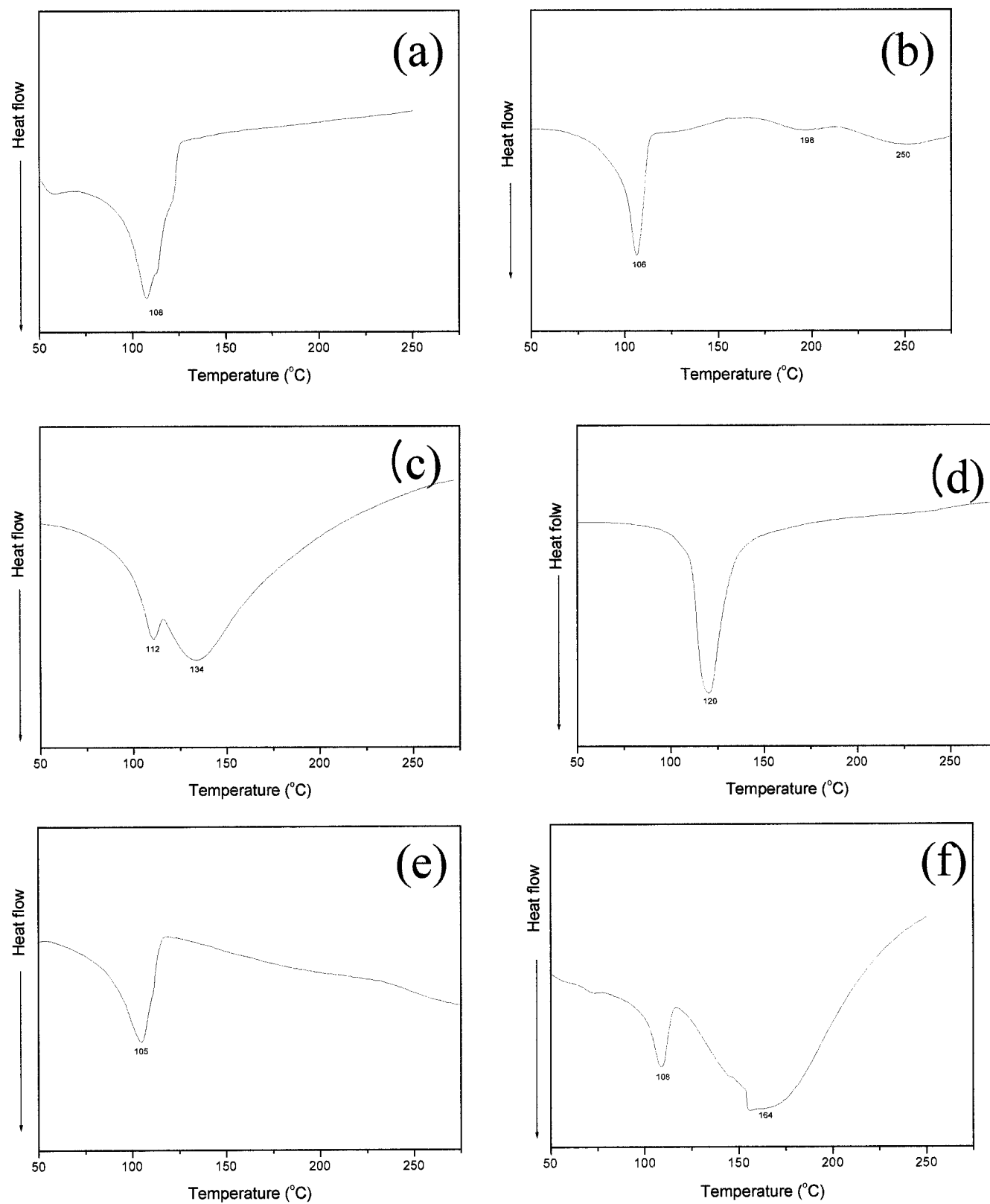
Graft copolymer-lanthanide complexes were prepared by radiation-induced grafting of AAc onto PE film and subsequently by its complexation of Eu, Gd, Tb, and Dy ions:

1. The grafted films rapidly adsorbed Eu, Gd, Tb, and Dy in high efficiency.
2. The carboxylic acid group on the AAc-grafted PE film acted as a chelating site for selected lanthanide ions.
3. The application of such prepared graft copolymer-lanthanide complexes in the field of fluorescence emission displays (FEDs) may be of interest.

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**Figure 7** TGA curves of (a) original PE, (b) 85% AAc-g-PE, (c) Eu complex, (d) Gd complex, (e) Tb complex, and (f) Dy complex.



**Figure 8** DSC curves of (a) original PE, (b) 85% AAc-g-PE, (c) Eu complex, (d) Gd complex, (e) Tb complex, and (f) Dy complex.



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