

# Study on Macromolecular Lanthanide Complexes (V): Synthesis, Characterization, and Fluorescence Properties of Lanthanide Complexes with the Copolymers of Styrene and Acrylic Acid

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**ABSTRACT:** In this study, the luminescent macromolecular lanthanide complexes Ln-PSt/AA (Ln = Eu and Tb; St = styrene; AA = acrylic acid) have been synthesized, and an extensive characterization has been carried out by means of elemental analysis, FTIR, thermal analysis, and fluorescence determination. The results showed that the carboxylic groups on the chain of the polymers acted as bidentate ligands coordinated to lanthanide ions; and the coordination degree of  $-\text{COO}^-/\text{Ln}^{3+}$  in the macromolecular complexes was closely dependent on both the pH value of the solution and the molar ratio of St to AA in the polymeric ligands. Thermal analysis manifested that

these Ln-PSt/AA (Ln = Eu and Tb) complexes had high thermal stability and solvent resistance, and these macromolecular complexes were highly crosslinked. The fluorescence determination indicated that Ln-PSt/AA complexes could emit characteristic fluorescence with comparatively high brightness and good monochromaticity, and the fluorescence intensity changed with increasing lanthanide ions content. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1064–1069, 2009

**Key words:** lanthanide complexes; luminescence; synthesis; characterization; fluorescence; coordination degree

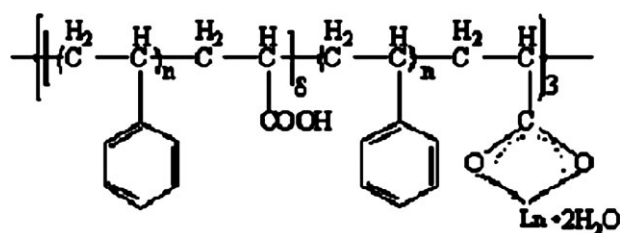
## INTRODUCTION

Macromolecular metal complexes have attracted increasing interest to researchers because of their excellent properties of both polymeric and inorganic materials.<sup>1–7</sup> Compounds possessing considerable compatibility with polymeric materials of similar structure, overcoming the defect of low-molecular-weight complexes such as low thermal stability and poor mechanical properties, have been widely applied in material technology and engineering.<sup>6,7</sup> Recently, macromolecular lanthanide complexes (MLnC) are of increasing interest in supermolecular chemistry, biology, and functional materials.<sup>8,9</sup> They are excellent photoluminescent materials with high brightness and good monochromaticity, which have been extensively studied as potential molecular and supermolecular devices,<sup>10</sup> fluorescent probes and luminescent labels in chemical, biological systems, and medical diagnostics.<sup>11–13</sup>

As a part of our continuing studies on the macromolecular metal complexes,<sup>14–17</sup> we synthesized the

luminescent Ln-PSt/AA (Ln = Eu and Tb; St = styrene; AA = acrylic acid) complexes, and a detailed research on the structure and characterization for both the copolymers and the Ln-PSt/AA complexes had been performed. The results suggested that these polymer ligands were random; and these Ln-PSt/AA belonged to bonding-type lanthanide polymers having higher thermal stability when compared with the general doping-type lanthanide polymers. The chemical analysis showed the predominating carboxylic groups in the copolymers PSt/AA combined with lanthanide ions, thus the nonstoichiometric macromolecular complexes were formed. The fluorescence determination demonstrated that the complexes exhibited characteristic fluorescence with comparatively high brightness and good monochromaticity,<sup>18,19</sup> which indicated an effective energy transfer between the lowest excited triplet state energy level of ligand and the excited state energy level of the corresponding lanthanide ions. The results also manifested that fluorescence intensity of Ln-PSt/AA (Ln = Eu and Tb) complexes increased with the increasing lanthanide ions content under certain value, but a typical fluorescence concentration quenching behavior occurred while the content of lanthanide ions was above this value.

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Scheme 1 The structure units of Ln-PSt/AA complexes.

## EXPERIMENTAL SECTION

### Materials and instruments

AA was redistilled under reduced pressure before polymerization. St was washed with 10% aqueous sodium hydroxide to remove the inhibitor, and this was followed by washing with water until it was neutral. Hydrated lanthanide nitrates  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  were prepared by dissolving weighed 2–3 g of corresponding oxides in concentrated nitrate acid, and then the solution was heated to evaporate the excess acid.<sup>20</sup> Other chemicals of analytical reagent grade were used without further purification. The average molecular weight of PSt/AA was estimated by a SN-01A gel permeation chromatography (GPC) with THF as eluent. The content of C and H in Ln-PSt/AA complexes was determined on an Elemental Vario-EL elemental analyzer, and the metal content was determined by volumetric titration with EDTA using xylenol orange as indicator. Thermal analysis (TG-DTA) was carried out on a PCT-2A thermal balance. Vibration spectra from 4000 to 400  $\text{cm}^{-1}$  were recorded on a Nicolet 170 XET-IR spectrometer (KBr discs). Fluorescence spectra were measured on an F-4500 fluorescence spectrophotometer with a 150 W xenon lamp as excitation source at room temperature.

### Copolymerization of styrene with acrylic acid

Copolymerization of St/AA was carried out in toluene at 75°C in the presence of BPO. The mixed solution of St and AA (the mole ratio of St to AA was 1 : 9, 1 : 3, and 3 : 1, respectively) was placed in a three-necked flask equipped with a condenser, mechanically stirred with a magnetic bar at the reflux temperature. A solution of BPO (1 mol % of total monomer) in toluene was added dropwise into the reaction mixture (the toluene volume approximately quadrupled the volume of total monomer). After 12 h, the solvent was removed by distilling under reduced pressure. The product was washed with toluene to further remove the unpolymerized monomer and any other impurities, and finally dried under vacuum at 40°C for 24 h. The resulting copolymer was a white amorphous solid, and the final

yield was up to 90%. The average molecular weight of the copolymer was evaluated by GPC method.

### Synthesis of Ln-PSt/AA (Ln = Eu and Tb) complexes

The weighed copolymer was dissolved in methanol and the solution obtained was adjusted to be slightly acidic with the methanol solution of KOH. Then, a methanol solution of calculated lanthanide nitrate was added dropwise into the solution under stirring. The mixture was stirred for 24 h and the resulting precipitate was filtered, washed with absolute methanol, and dried under vacuum at 40°C for 24 h. The final Ln-PSt/AA (Ln = Eu and Tb) complexes were pale yellow and insoluble in most organic solvents.<sup>21</sup>

## RESULTS AND DISCUSSION

### Chemical analysis of the complexes

According to the results of chemical analysis, the structure units of Ln-PSt/AA complexes can be shown in Scheme 1. The elemental analysis data of the copolymers PSt/AA and their lanthanide complexes are listed in Tables I and II, respectively.

From Tables I and II it can be seen that  $\delta$  is the number of uncoordinated carboxylic groups ( $\text{COO}^-$ ) in the structure units of Ln-PSt/AA complexes, and  $n$  is the molar ratio of St to AA in the copolymers. Each lanthanide ion is bonded to three carboxylic groups in the chains of the polymers (not necessarily in the same chain), forming stable and repeatable structure units.

The design procedure of  $n$  is as follows:

$$n = \frac{m_1 m_2 / 12.01 - 300CV}{800CV}$$

where  $m_1$  is the mass of the copolymer;  $C$  is the concentration of an aqueous solution of potassium hydroxide, which is used to determine the content of the carboxylic groups in the copolymers;  $V$  is the volume of the used aqueous solution of potassium hydroxide; and  $m_2\%$  is the mass fraction of carbon in copolymers, which is determined by elemental analysis.

TABLE I  
Elemental Analysis Data of Ligands PSt/AA

Feed (St/AA) <sup>a</sup>	C (Cal) (%)	H (Cal) (%)	$n$ in the copolymer
0.11 (L <sub>1</sub> )	64.87 (65.45)	6.55 (6.34)	0.40
0.33 (L <sub>2</sub> )	70.22 (70.34)	6.69 (6.58)	0.64
3.00 (L <sub>3</sub> )	84.88 (85.03)	7.42 (7.32)	3.33

<sup>a</sup> Mole ratio.

TABLE II  
Elemental Analysis Data of Ln-PSt/AA Complexes

Complexes	C (Cal) (%)	H (Cal) (%)	Ln (Cal) (%)	$\delta$
Eu-L <sub>1</sub>	44.47 (44.62)	4.54 (4.49)	26.20 (26.19)	0.16
Tb-L <sub>1</sub>	44.23 (44.09)	4.50 (4.44)	27.15 (27.06)	0.16
Eu-L <sub>2</sub>	51.52 (51.30)	4.98 (4.95)	22.43 (22.22)	0.20
Tb-L <sub>2</sub>	50.19 (49.98)	4.78 (4.90)	23.18 (23.01)	0.20
Eu-L <sub>3</sub>	76.33 (76.37)	6.32 (6.14)	8.10 (8.37)	0.30
Tb-L <sub>3</sub>	75.87 (76.08)	6.29 (6.11)	8.65 (8.72)	0.30

The design procedure of  $\delta$  is as follows:

$$\delta = \frac{m_3M/12.01m_4 - 3(8n + 3)}{8n + 3}$$

where  $m_3\%$  is the mass fraction of carbon in Ln-PSt/AA complex;  $M$  is the atomic weight of rare earth metal;  $m_4\%$  is the metal content in complex, which is determined by volumetric titration with EDTA using xylenol orange as indicator; and  $n$  is known by the above formula.

It has been found that the value of  $\delta$  in the structure units of Ln-PSt/AA complexes is closely dependent both on the pH value and the molar ratio of St/AA in the copolymers. The effect of different pH value on the composition of the complexes was investigated. At low pH value, some free carboxylic groups present in the structure units of Ln-PSt/AA complexes, owing to the fact that the polymeric ligands PSt/AA are weak polyacid,  $\text{Ln}^{3+}$ , cannot replace the proton of the carboxylic groups of PSt/

AA at higher acidity because partial carboxylic groups have not participated in the coordination. Figure 1 shows the changes of  $\delta$  with pH value of the solution.

A further study confirmed that the composition and structure units of Ln-PSt/AA complexes varied with the changing molar ratio of St to AA in the copolymers. As shown in Tables I and II, from L<sub>1</sub>, L<sub>2</sub> to L<sub>3</sub>, with the increasing molar ratio of St to AA in the copolymers, the value  $\delta$  in Ln-PSt/AA complexes increased. This phenomenon might be resulted from the hindrance of polymeric chains, that is, the more rigidity phenyl rings in PSt/AA chain, the more difficult to make the carboxylic groups combine with  $\text{Ln}^{3+}$  thoroughly. Because of the synergetic effect of the two factors mentioned earlier, the formed Ln-PSt/AA complexes are nonstoichiometric complexes; this is different from our previous studies for macromolecular Ln-PAA complexes.<sup>17</sup>

### IR analysis

A detailed study on the IR spectra of Ln-PSt/AA complexes and the ligands PSt/AA has been performed. The IR spectra of the complexes resemble each other, but obviously different from that of the ligands PSt/AA. The IR spectra data of the ligands PSt/AA and Ln-PSt/AA complexes are listed in Table III. The results indicated that all Ln-PSt/AA complexes had a weaker absorption band at 1702–1708  $\text{cm}^{-1}$  ascribed to  $\nu_{\text{C=O}}$  of carboxylic groups; the absorption intensity was apparently lower than that

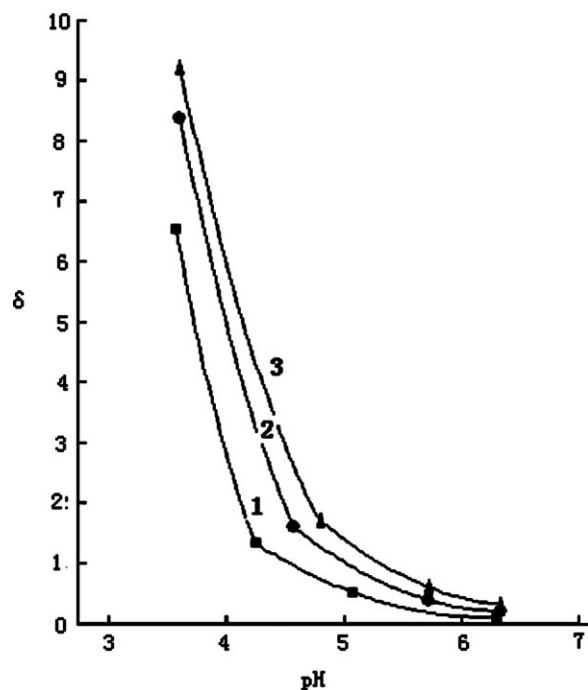
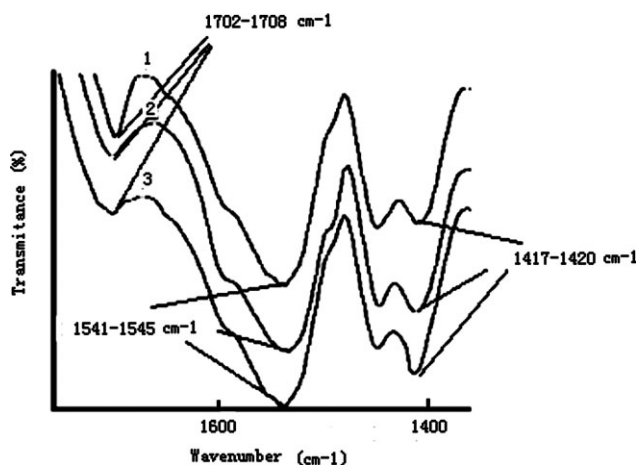


Figure 1 Number of free carboxylic groups versus pH value of the solution (1: EuL<sub>1</sub>; 2: EuL<sub>2</sub>; 3: EuL<sub>3</sub>).

TABLE III  
IR Spectra Data of Ligands PSt/AA and Ln-PSt/AA Complexes ( $\text{cm}^{-1}$ )

Complexes	$\nu_{\text{O-H}}$	$\nu_{\text{C=O}}$	$\nu_{\text{as, COO}^-}$	$\nu_{\text{s, COO}^-}$	$\Delta\nu_{\text{as-s}}$	$\nu_{\text{Ln-O}}$
PSt/AA	2930	1704				
K-L <sub>i</sub>	2931	1693	1563	1404	159	
Eu-L <sub>1</sub>	2929	1708	1543	1419	124	416
Tb-L <sub>1</sub>	2930	1702	1542	1420	122	417
Eu-L <sub>2</sub>	2927	1703	1542	1416	126	416
Tb-L <sub>2</sub>	2925	1703	1544	1419	125	415
Eu-L <sub>3</sub>	2924	1704	1545	1417	128	415
Tb-L <sub>3</sub>	2926	1705	1541	1417	124	416

L<sub>i</sub>: L<sub>1</sub> and L<sub>2</sub>.



**Figure 2** The comparative IR spectra of Eu-PSt/AA complexes (1: EuL<sub>1</sub>; 2: EuL<sub>2</sub>; 3: EuL<sub>3</sub>).

of free ligands PSt/AA and dependent on the  $n$  value in the coordination units. Two strong absorption bands at  $1417\text{--}1420\text{ cm}^{-1}$  and  $1541\text{--}1545\text{ cm}^{-1}$  were observed in Ln-PSt/AA complexes, which were assigned to the symmetric vibration absorption ( $\nu_s, \text{COO}^-$ ) and asymmetric vibration absorption ( $\nu_{as, \text{COO}^-}$ ) of the carboxylic groups, respectively. Figure 2 shows the comparison of IR spectra of Ln-PSt/AA complexes, from which we can see that the intensity of  $\nu_{\text{C}=\text{O}}$  decreased with the descending  $\delta$  in the complexes, but the intensity of  $\nu_{as, \text{COO}^-}$  and  $\nu_s, \text{COO}^-$  increased on the contrary. It is concluded that, differing from the doping-type metal complexes containing polymers, the carboxylic groups in Ln-PSt/AA complexes are bonded to central Ln<sup>3+</sup> ions.

The  $\nu_{\text{C}=\text{O}}$  absorption band at ca.  $1700\text{ cm}^{-1}$  in Ln-PSt/AA complexes cannot disappear completely. This phenomena is due to a higher hindrance caused by polystyrene moiety in the chains of PSt/AA polymer, which makes Ln-PSt/AA complexes appear in nonstoichiometric form.

The determined  $\Delta\nu$  [ $\Delta\nu = \nu_{as, \text{COO}^-}(\text{A}) - \nu_s, \text{COO}^- (\text{A})$ ] for Ln-PSt/AA complexes is far smaller than that of K-PSt/AA ( $159\text{ cm}^{-1}$ ) complexes, which shows that the symmetry of the carboxylic groups in the complexes is C<sub>2v</sub>, the same as the free ions. This clearly states that the carboxylic groups act as a bidentate chelate coordinated to the lanthanide ions in the complexes.<sup>22–24</sup> In addition, the weaker absorption bands at  $415\text{--}417\text{ cm}^{-1}$  can be attributed to the vibration of Ln–O bond in the macromolecular Ln-PSt/AA complexes.

### TG-DTA analysis

Thermal behavior of Ln-PSt/AA complexes has been studied. Samples of about 10 mg were placed in a crucible, and heated up to  $900^\circ\text{C}$  at the rate of  $10^\circ\text{C min}^{-1}$  under an air atmosphere at ambient pressure,

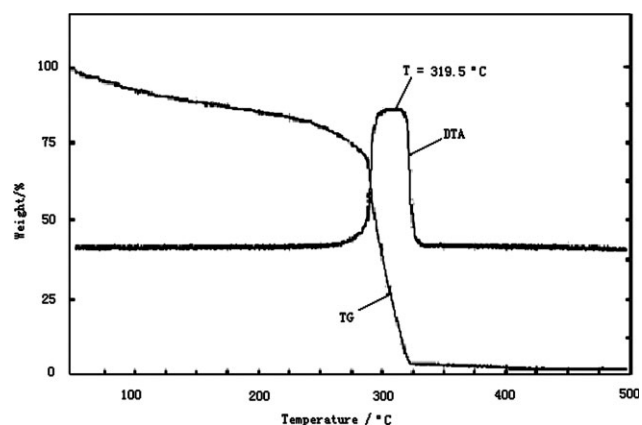
**TABLE IV**  
The Data of TG-DTA Analysis of Ln-PSt/AA Complexes

Complexes	Weight loss in first stage (%)		Remnant (%)	
	Determined	Calculated (water %)	Determined	Calculated (oxide %)
Eu-L <sub>1</sub>	6.47	6.20	30.58	30.32
Tb-L <sub>1</sub>	6.39	6.13	31.97	31.86
Eu-L <sub>2</sub>	5.54	5.26	25.56	25.75
Tb-L <sub>2</sub>	5.48	5.21	27.17	27.16
Eu-L <sub>3</sub>	2.15	1.98	12.88	12.74
Tb-L <sub>3</sub>	2.14	1.97	10.51	10.33

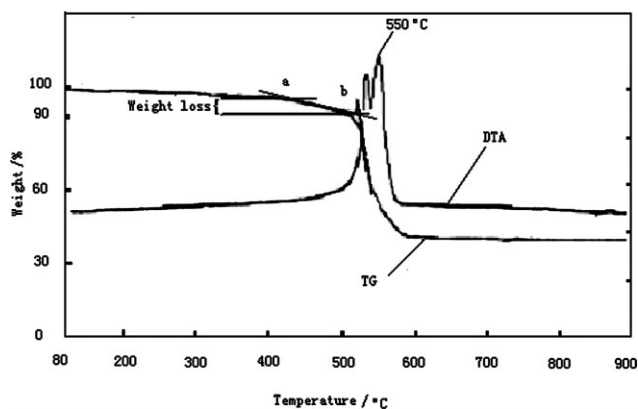
The final decomposition product of Tb-PSt/AA is Tb<sub>4</sub>O<sub>7</sub>.

using  $\alpha\text{-Al}_2\text{O}_3$  as reference material. The data of TG-DTA analysis of the Ln-PSt/AA (Ln = Eu and Tb) complexes are demonstrated in Table IV.

The thermal behavior of Ln-PSt/AA (Ln = Eu and Tb) complexes is resemble of each other, which suggests that the decomposition of these complexes is in the same way, but it is quite different from that of the ligands PSt/AA (as shown in Fig. 3). The decomposition of the ligand PSt/AA (L<sub>1</sub>) begins with a progressive weight loss ascribed to the form of anhydride from the carboxylic acid on the polymer chain,<sup>14</sup> the following step is primarily a combustion process at low temperatures, and there is no residue. All the Ln-PSt/AA complexes show good thermal stability and are decomposed in two steps. The TG-DTA curve of Ln-PSt/AA (Ln = Eu and Tb; PStAA = L<sub>1</sub>, L<sub>2</sub>, and L<sub>3</sub>) complexes were all investigated, herein we only depict the TG-DTA curve of Tb-PSt/AA (Tb-L<sub>1</sub>) complexes in Figure 4 to illustrate the decomposition process. It is shown that the first decomposition stage in the temperature range of  $160\text{--}300^\circ\text{C}$  is losing water, but the determined weight loss in TG curves is somewhat larger than the content of calculated water in Ln-PSt/AA



**Figure 3** A typical TG-DTA curve of PSt/AA (L<sub>1</sub>) complexes ( $\beta = 10^\circ\text{C/min}$ ).



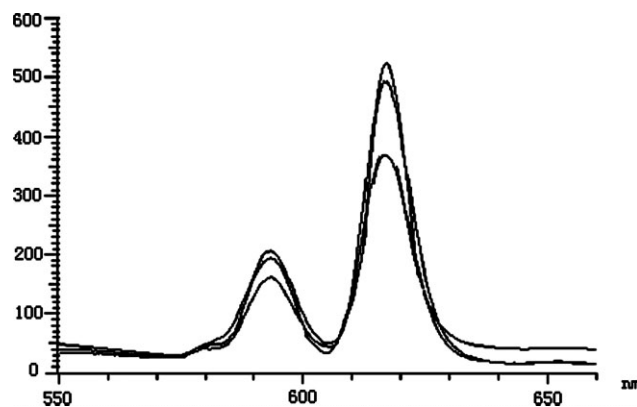
**Figure 4** A typical TG-DTA curve of Tb-PSt/AA (Tb-L<sub>1</sub>) complexes ( $\beta = 10^\circ\text{C}/\text{min}$ ).

complexes. An examination using IR spectra for Ln-PSt/AA complexes sample heated under the temperature of  $300^\circ\text{C}$ , shows that, besides the absorption bands of coordinated water in the range of  $3400\text{ cm}^{-1}$  and  $550\text{--}600\text{ cm}^{-1}$ , the characteristic absorption bands of uncoordinated carboxylic groups in  $1705\text{ cm}^{-1}$  also disappear. So, the larger weight loss of Ln-PSt/AA complexes in the first decomposition stage (from the temperature range a to b shown in Fig. 4) than the content of calculated water is due to the elimination of uncoordinated carboxylic groups in the structure units of Ln-PSt/AA complexes<sup>14</sup>; this phenomenon is similar to that of the ligands PSt/AA. The second decomposition stage of Ln-PSt/AA complexes is a continuous oxidation decomposition process, demonstrated by a series of stronger exothermic peaks on DTA curves up to  $550^\circ\text{C}$ . The final residue coincides with the general formula of oxides, which was later confirmed by chemical analysis for the lanthanide ions content in them. The relatively higher temperature for losing water confirms that the water is coordinated to  $\text{Ln}^{3+}$  in inner sphere, which is consistent with the result that 8 is the coordination number found most commonly in lanthanide carboxylates.<sup>25</sup>

**TABLE V**  
Fluorescence Spectra Data of the Solid Ln-PSt/AA Complexes

Complexes	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{em}}$ (nm)	$I^*$	Transition
Eu-L <sub>1</sub>	396	593/617	191/522	$^5\text{D}_0 \rightarrow ^7\text{F}_1 / ^5\text{D}_0 \rightarrow ^7\text{F}_2$
Tb-L <sub>1</sub>	282	492/548	190/340	$^5\text{D}_4 \rightarrow ^7\text{F}_6 / ^5\text{D}_4 \rightarrow ^7\text{F}_5$
Eu-L <sub>2</sub>	396	593/617	206/494	$^5\text{D}_0 \rightarrow ^7\text{F}_1 / ^5\text{D}_0 \rightarrow ^7\text{F}_2$
Tb-L <sub>2</sub>	282	492/548	169/291	$^5\text{D}_4 \rightarrow ^7\text{F}_6 / ^5\text{D}_4 \rightarrow ^7\text{F}_5$
Eu-L <sub>3</sub>	396	593/617	162/369	$^5\text{D}_0 \rightarrow ^7\text{F}_1 / ^5\text{D}_0 \rightarrow ^7\text{F}_2$
Tb-L <sub>3</sub>	282	491/546	130/287	$^5\text{D}_4 \rightarrow ^7\text{F}_6 / ^5\text{D}_4 \rightarrow ^7\text{F}_5$

$I^*$  relative intensity; slit ex/em = 1.0/1.0 (nm).

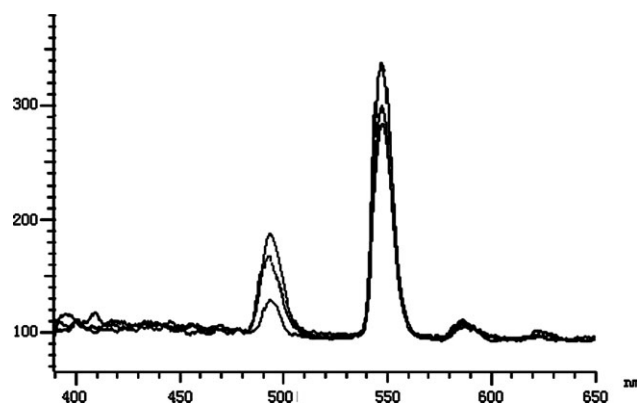


**Figure 5** Typical emission spectra of the solid Eu-PSt/AA complexes of different europium content,  $\lambda_{\text{ex}} = 396\text{ nm}$ ; slit ex/em = 1.0/1.0 (nm).

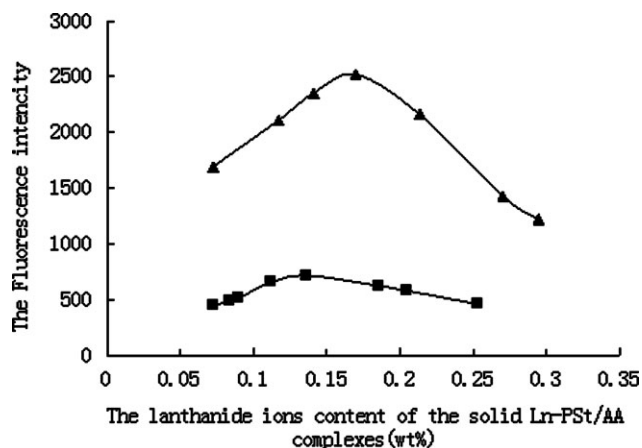
### Fluorescent properties

The fluorescence determination of Ln-PSt/AA (Ln = Eu and Tb) complexes showed that these complexes could emit intense fluorescence in the visible area. The fluorescence spectra data of the solid complexes are listed in Table V, and the emission spectra of the solid complexes are demonstrated in Figures 5 and 6.

The solid Ln-PSt/AA (Ln = Eu and Tb) complexes emit characteristic fluorescence of lanthanide ions on excitation with UV light. The bright red emission lines of  $\text{Eu}^{3+}$  centered at 617 nm are assigned to transition from the  $^5\text{D}_0$  levels to all the multiple levels of  $^7\text{F}$ . These emission spectra were obtained on excitation at 396 nm, corresponding to the  $^5\text{L}_7$  level of the  $\text{Eu}^{3+}$  ion. Similar fluorescence spectra of the Tb-PSt/AA complexes were obtained on excitation at 282 nm. Both complexes exhibit enhancing fluorescence intensity with increasing lanthanide ions content up to certain value without typical fluorescence concentration quenching behavior. The effect of lanthanide ions content on fluorescence intensity is shown in Figure 7. The molar ratio of St/AA in



**Figure 6** Typical emission spectra of the solid Tb-PSt/AA complexes of different terbium content,  $\lambda_{\text{ex}} = 282\text{ nm}$ ; slit ex/em = 1.0/1.0 (nm).



**Figure 7** Fluorescence intensity of the solid Tb-PSt/AA and Eu-PSt/AA complexes versus different lanthanide ions content ( $\blacktriangle$ : Tb-PSt/AA;  $\blacksquare$ : Eu-PSt/AA); slit ex/em = 2.5/2.5 (nm).

the copolymer PSt/AA in Figure 7 was different from that of the aforementioned three polymers ( $L_1$ ;  $L_2$ ;  $L_3$ ). The results also suggest that lanthanide ions in the macromolecular complexes are homogeneously dispersed and do not contain ion aggregates throughout the polymer matrix, which are very important in optical applications. Thus, the luminescent Ln-PSt/AA complexes would be used as potential photoluminescence materials.<sup>26</sup>

It is evident that photophysical properties of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions markedly depend on their environment. To get an efficient cation emission, the chromophoric ligands should first absorb light strongly in the UV region and transfer it to the lanthanide ions efficiently, and secondly protect it from solvent molecules that can quench the central ions emission.

As we depicted earlier, Ln-PSt/AA (Ln = Eu and Tb) complexes possess strong fluorescence intensity, showing that there is an efficient intramolecular energy transfer from polymer matrix to lanthanide ions. The lowest excited triplet state energy level of PSt/AA matches well with the excited state energy level of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions.

## CONCLUSIONS

Luminescent Ln-PSt/AA (Ln = Eu and Tb) complexes have been synthesized and well characterized by means of elemental analysis, FTIR, thermal analysis, and fluorescence determination. The results indicated that the complexes had three-dimensional crosslinked structures, in which the predominating carboxylic groups coordinated with lanthanide ions

and acted to be bidentate. TG-DTA showed that Ln-PSt/AA (Ln = Eu and Tb) complexes had good thermal stability. In visible area, the complexes could emit intense fluorescence and had good monochromaticity. Over a suitable range, the fluorescence intensity of Ln-PSt/AA (Ln = Eu and Tb) complexes enhanced with increasing lanthanide ions content, but the fluorescence concentration quenching behavior occurred while lanthanide ions content was out of the range.

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