Synthesis, Characterization, and Fluorescence Properties of Lanthanide Complexes with the Copolymers of 2-Butenedioic Acid (z)-Mono-Ethyl Ester and Styrene

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ABSTRACT: In this study, the luminescent macromolecular lanthanide complexes with the copolymers of styrene (St) and 2-butenedioic acid (z)-mono-ethyl ester (BAME) 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 -COO$^-$/Ln^{3+} in the macromolecular complexes was closely dependent on both the pH value of the solution and the molar ratio of St to BAME in the polymeric ligands. Thermal analysis manifested that the macromolecular complexes Ln-PSt/BAME (Ln = Y, Sm, Dy, Eu, and Tb) were highly crosslinked and had high thermal stability and solvent resistance. The fluorescence determination indicated that Ln-PSt/BAME complexes could emit characteristic fluorescence with comparatively high brightness and good monochromaticity, and the fluorescence intensity increased with an increasing of lanthanide content. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 472–478, 2012

Key words: lanthanide complexes; reactivity ratio; luminescence; synthesis; characterization

INTRODUCTION

Macromolecular metal complexes have attracted much interest to researchers because of their excellent properties of both polymeric and inorganic materials,[1–7] this kind of compounds possessing considerable compatibility with polymeric materials of similar structure, overcoming some defects of low-molecular-weight complexes, such as low thermal stability and poor mechanical properties, have been widely applied in material technology and engineering.[6,7] Recently, macromolecular lanthanide complexes (MLnC) are of increasing interest in supermolecular chemistry, biology, and functional materials.[8,9] They are excellent photoluminescent materials being extensively studied as potential molecular and supermolecular devices,[10] fluorescent probes and luminescent labels in chemical, biological systems, and medical diagnostics.[11,12]

As a part of our continuing studies on the macromolecular metal complexes,[13–17] we synthesized the luminescent Ln-PSt/BAME (Ln = Y, Sm, Dy, Eu and Tb; St = styrene; BAME = 2-butenedioic acid (z)-mono-ethyl ester) complexes, and a detailed research on the structure and characterization for both the copolymers and the Ln-PSt/BAME complexes had been performed. The results suggested that these polymer ligands were random; and the Ln-PSt/BAME complexes were crosslinked bonding-type lanthanide polymers having higher thermal stability than the general doping-type lanthanide polymers, in which each metal ion was bonded to three carboxylic groups in the chain of PSt/BAME. When the metal contents were in the range of relatively low degree, these macromolecular lanthanide complexes possess film-forming ability to insurance these luminescent materials can be utilized both in solid state and membrane materials. The fluorescence determination demonstrated that the complexes exhibited characteristic fluorescence with comparatively high brightness and good monochromaticity,[18,19] 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/BAME (Ln = Y, Sm, Dy, Eu, and Tb) complexes increased with the increasing lanthanide content.

EXPERIMENTAL

Materials and instruments

Maleic anhydride, dissolved in chloroform and filtered, was recrystallized to eliminate maleic acid. Styrene was washed with 10% aqueous sodium hydroxide to remove the inhibitor, and this was followed by washing with water until it was neutral, then dried with anhydrous magnesium sulfate. Hydrated lanthanide nitrates $Ln(NO_3)_3 6H_2O$ were prepared by dissolving weighed 2–3 g corresponding oxides in concentrated nitrated acid, then the solutions were heated to nearly dry to decompose the excess acid. Other chemicals of analytical reagent grade were used without further purification. The contents of C, H in the ligands and complexes were determined on an Elemental Vario-EL elemental analyzer. The metal content of complexes were determined by volumetric titration with EDTA using xylenol orange as indicator. Fluorescence spectra were measured with a F-4500 fluorescence spectrophotometer with a 150W xenon lamp as the excitation source at room temperature. Thermal analysis (TC-DTA) was carried out on a PCT-2A thermal balance. Vibration spectra from 4000 to 400 cm^{-1} were recorded on a Nicolet 170 XET-IR spectrometer (KBr discs).

Synthesis of ligands

Mixed maleic anhydride (4900 mg, 50 mmol) and 3.5 mL (58 mmol) ethanol absolute in a round bottom flask with a condenser and stirred for two days at room temperature. The system was pumped to remove the excess ethanol absolute. It could get the pure 2-butenedioic acid (z)-mono-ethyl ester (BAME). Styrene (2438 mg, 23.44 mmol) and BAME (5620 mg, 3.90 mmol) (mol/mol = 6:1) were dissolved in 4.5 mL acetone. 0.15g BPO was added into the solution as the initiator. The resulting mixture was stirred and heated to 95–100°C for 2.5 h. Then, the reaction system was cooled to room temperature. By transferring it slowly to quantities of petrol ether, it appears to be white deposition immediately. Filtrating and washing deposition several times with

TABLE I
Elemental Analysis of the Ligands ($n_1:n_2$ = Molar Ratio of Styrene: BAME in Feed)

Ligands	%C	%H	n value
HL^1 ($n_1:n_2 = 6:1$)	81.72	7.33	4.15
HL^2 ($n_1:n_2 = 3:1$)	75.2	6.85	2.04
HL^3 ($n_1:n_2 = 1.9:1$)	69.35	6.64	1.17
HL^4 ($n_1:n_2 = 1:1$)	67.98	6.24	1.02
HL^5 ($n_1:n_2 = 1:3$)	65.19	5.81	0.78

water, drying it in vacuum drying oven for three days at about 60°C, product was obtained in above 70% yield. It was signed L^1.

In the same way, the polymeric ligands of styrene with BAME in feed ration of 3:1, 2:1, 1:1, 1:3 were prepared. They were signed L^2, L^3, L^4, L^5, respectively.

Synthesis of complexes

Totally, 0.45 g HL^5 was dissolved in the 40 mL solution of water and ethanol (V: V = 1:1). NaOH water solution(C = 0.1 mol/L) was added into the system to adjust pH value to be about 7. 0.3 g $Eu(NO_3)_3 \cdot 6H_2O$ was dissolved in 10 mL H_2O and added into the system dropwise. The mixture was stirred for two days and white precipitate formed. The precipitate was collected and washed three times with distilled water. Further drying in a vacuum afforded a powder-like complex $EuL^5_3 \cdot 3H_2O$. In the same way, complexes $SmL^5_3 \cdot 3H_2O$, $TbL^5_3 \cdot 3H_2O$, $DyL^5_3 \cdot 3H_2O$, $YL^5_3 \cdot 3H_2O$ were prepared.

RESULTS AND DISCUSSION

Chemical analysis of the ligands and complexes

The data listed in Table I showed the elemental contents in polymeric ligands, in which n is the mole ratio of St/BAME and the n is calculated by titration. The data listed in Table II and Table III shows the elemental composition of complexes. The structure units of complexes can be shown in Scheme 1. δ is the number of uncoordinated carboxylic groups and is calculated by elemental analysis and titration. Each lanthanide metal ion is bonded to three

TABLE II
Elemental Analysis of the Complexes ($n_1:n_2$ = Original Feed Molar of Styrene:BAME)

Complexes	%C Found(Calcd)	%H Found (Calcd)	Metal contents (%) Found (Calcd)	n value	δ value
$YL^5_3 \cdot 3H_2O$	54.75 (54.90)	5.81 (5.89)	10.72 (10.67)	0.78	0.10
$TbL^5_3 \cdot 3H_2O$	50.64 (50.86)	5.32 (5.46)	16.41 (16.69)	0.78	0.10
$DyL^5_3 \cdot 3H_2O$	49.98 (50.78)	5.29 (5.44)	17.36 (16.98)	0.78	0.10
$SmL^5_3 \cdot 3H_2O$	51.37 (51.33)	5.46 (5.54)	15.43 (15.92)	0.78	0.10
$EuL^5_3 \cdot 3H_2O$	50.79 (51.24)	5.34 (5.50)	16.22 (16.07)	0.78	0.10

Elemental Analysis of the Complexes (n_1:n_2 = Original Feed Molar of Styrene:BAME)

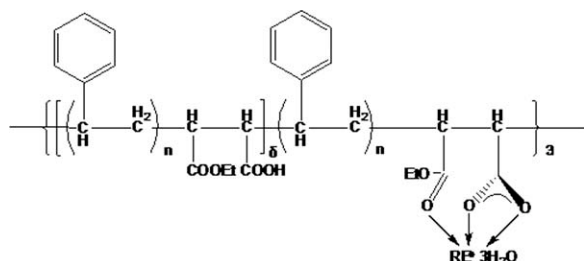| Complexes	%C Found (Calcd)	%H Found (Calcd)	Metal contents (%) Found (Calcd)	n value	δ value
$EuL^1_3 \bullet 3H_2O$	74.16 (74.27)	7.22 (7.30)	6.40 (6.41)	4.15	0.28
$EuL^2_3 \bullet 3H_2O$	67.85 (67.98)	6.52 (6.45)	11.52 (10.67)	2.04	0.15
$EuL^3_3 \bullet 3H_2O$	55.02 (54.81)	6.48 (6.57)	14.21 (14.26)	1.17	0.13
$EuL^4_3 \bullet 3H_2O$	52.81 (52.74)	6.50 (6.46)	15.23 (15.11)	1.02	0.12
$EuL^5_3 \bullet 3H_2O$	50.79 (51.24)	5.34 (5.50)	16.22 (16.07)	0.78	0.10

carboxylic groups in the chain of copolymer, forming stable and repeatable units.

It has been found that the value of δ in th0e structure units of Ln-PSt/BAME complexes is closely dependent both on the pH value and the molar ratio of St/BAME 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/BAME complexes, owing to the fact that the polymeric ligands PSt/BAME are weak polyacid, Ln^{3+}, cannot replace the proton of the carboxylic groups of PSt/BAME at higher acidity because partial carboxlic groups have not participated in the coordination. Figure 1 shows the changes of δ with pH value of the solution.

A further study confirmed that the composition and structure units of Ln-PSt/BAME complexes varied with the changing molar ratio of St to BAME in the copolymers. As shown in Tables I and III, from L^1, L^2, L^3, L^4, to L^5, with the increasing molar ratio of St to BAME in the copolymers, the value δ 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/BAME chain, the more difficult to make the carboxylic groups combine with Ln^{3+} thoroughly.

Reactivity ratio determination

By Kelen-Tudos,[20] the monomer reactivity ratio of copolymerization of styrene with BAME at 95–100°C was calculated as 0.38 (styrene) and 0.40 (BAME), respectively.

By composition equation:

$$\frac{d\,[M_1]}{d\,[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1\,[M_1] + [M_2]}{r_2\,[M_2] + [M_1]}$$

M_1 stands for the monomer St and M_2 stands for the monomer BAME. r_1 is the reactivity ratio of St and r_2 is the reactivity ratio of BAME. If $f = d[M_1]/d[M_2]$, $F = [M_1]/[M_2]$, changing the equation above, we can get the linear equation : $F\text{-}F/f = F^2/f\, r_1 - r_2$.

We can observe the analyzed results of St/BAME polymerization in Figure 2. By normalization, the function of reactivity ratio was following: $F\text{-}F/f = 0.6075F^2/f\text{-}0.8857$. Thus, the monomer reactivity ratios of St and BAME are 0.45 and 1.15, respectively.

IR analysis

The IR spectra of ligands PSt/BAME resemble each other beside of the intensity of the carboxyl group, indicating they have similar structure, but quite different from that of the lanthanide complexes.

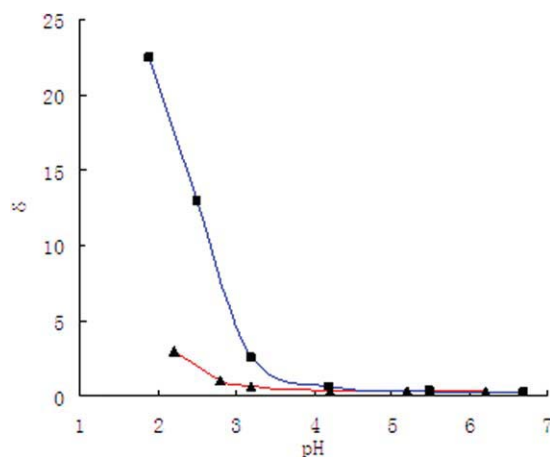A detailed study on the IR of free ligands and complexes has been performed. We can see the

Figure 1 Relationship between pH and the δ value for $EuL^3_3 \bullet 3H_2O$ and $TbL^4_3 \bullet 3H_2O$. (▲: $EuL^3_3 \bullet 3H_2O$; ■: $TbL^4_3 \bullet 3H_2O$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

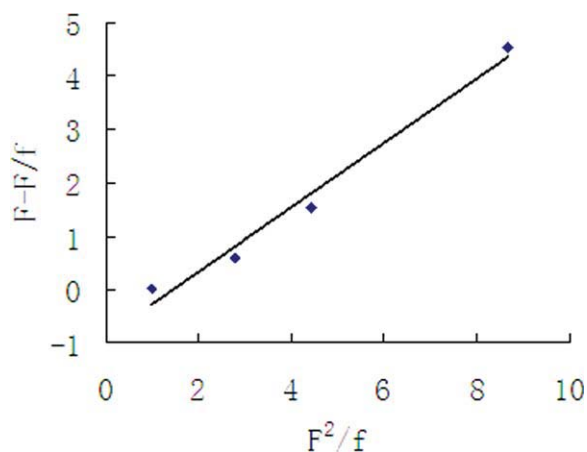**Scheme 1** The structure of complexes-$REL^n_3 \cdot 3H_2O$.

Figure 2 The (F-F/f)~ F^2/f copolymerization figure of 2-BAME with St. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

difference from the Figure 3. Take $EuL^3_3 \cdot 3H_2O$ as an example, the result shows that the free ligand appeared two peaks at 1704 cm^{-1} and 1731 cm^{-1}, the higher wave numbers ascribed to the $v_{c=o}$ of ester and the lower wave numbers ascribed to the $v_{c=o}$ of carboxylic group. The complex has single weaker absorption band at 1716 cm^{-1}, which was attributed to the $v_{c=o}$ vibration of ester. The red shift of ester carbonyl shows the carbonyl oxygen is coordinated to lanthanide ions. Two strong absorption bands at 1425 cm^{-1} and 1556 cm^{-1} were observed in the complex, which were assigned to the symmetric vibration absorption and asymmetric vibration absorption of the carboxylic group respectively. The determined $\Delta v (\Delta v = v_{as\text{-}coo\text{-}} - v_{s\text{-}coo\text{-}})$ (listed in Table IV) for the $REL^3_3 \cdot 3H_2O$ is far smaller than that of
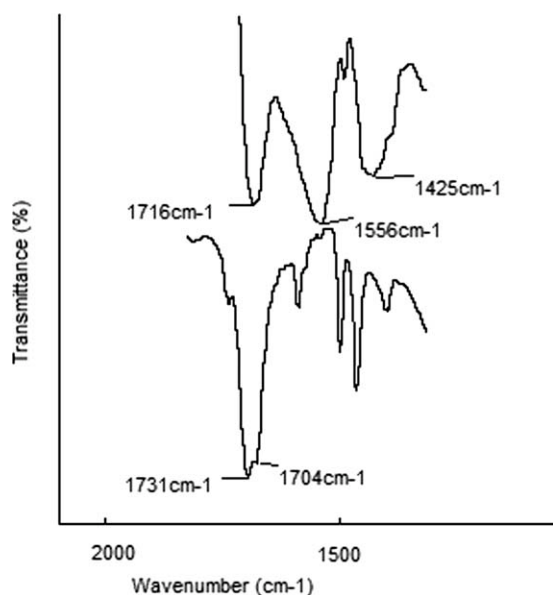

Figure 3 The comparative IR spectra of $EuL^3_3 \cdot 3H_2O$ complexes and L^3 ligand.

TABLE IV
FTIR Spectra Data of Ligand L_5 and Complexes (cm^{-1})

Complexes	v_{O-H}	$v_{C=O}$	v_{COO^-}		$\Delta v_{as\text{-}s}$
L^3	3420	1731	1704		
			$v_{as\text{-}coo\text{-}}$	$v_{s\text{-}coo\text{-}}$	
NaL^3	3447	1719	1573	1402	171
$YL^3_3 \bullet 3H_2O$	3414	1716	1557	1426	131
$TbL^3_3 \bullet 3H_2O$	3423	1721	1551	1426	125
$DyL^3_3 \bullet 3H_2O$	3424	1720	1560	1424	136
$EuL^3_3 \bullet 3H_2O$	3420	1716	1556	1425	131
$SmL^3_3 \bullet 3H_2O$	3423	1722	1548	1429	119

NaL^3 (171 cm^{-1}), which shows that the symmetry of the carboxylic group in the complexes is C_{2v}, the same as free ion. This indicated that the carboxylic group acted as a bidentate chelate coordinated to the lanthanide ions in the complexes.[21]

Fluorescent properties

The excitation and emission spectra, as well as the fluorescence intensity, were measured on dried and finely powered samples at room temperature. The solid state complexes of Eu^{3+} and Tb^{3+} showed
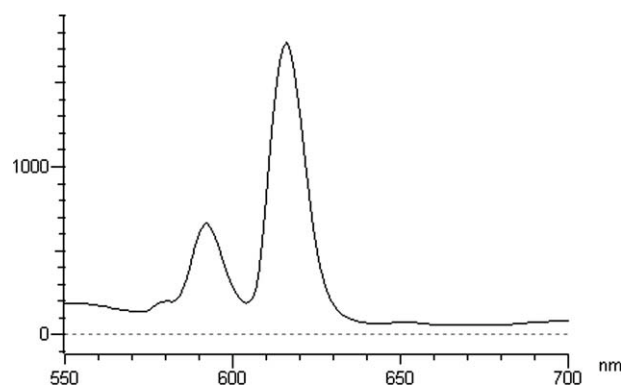

Figure 4 Typical emission spectra of the solid $EuL^5_3 \cdot 3H_2O$ complex.

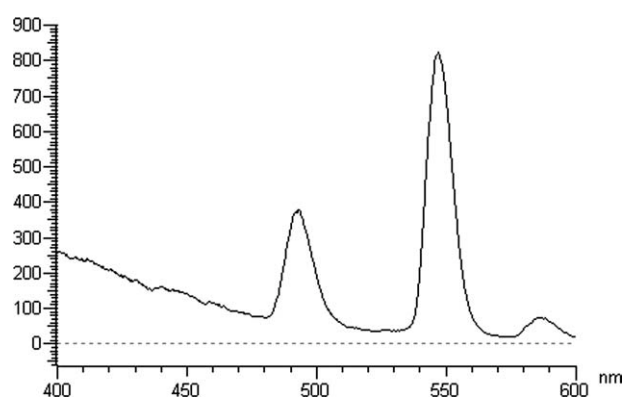**Figure 5** Typical emission spectra of the solid $TbL^5_3 \cdot 3H_2O$ complex.
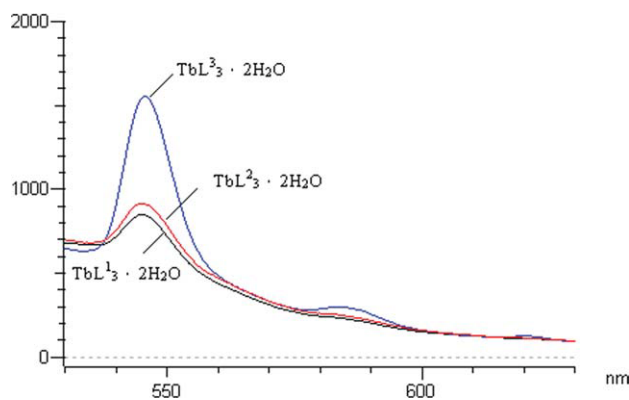
Figure 6 The fluorescence overlay of different Tb complexes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7 Relationship between the fluorescence intensity and the metal content for $TbL^4_3 \bullet 3H_2O$ and $EuL^3_3 \bullet 3H_2O$. (▲: $TbL^4_3 \bullet 3H_2O$; ■: $EuL^3_3 \bullet 3H_2O$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

characteristic fluorescence on excitation with UV light. Under an excitation of 397 nm, (listed in Fig. 4) compound $EuL^5_3 \cdot 3H_2O$ displays an emission band at 592 nm($^5D_0 \rightarrow {}^7F_1$), where intensity is 665 a.u.; a strong emission band at 616 nm($^5D_0 \rightarrow {}^7F_2$), where intensity is 1741 a.u. Between the two transitions, $^5D_0 \rightarrow {}^7F_2$ is the preferred transition containing luminescent material, which was the electro-dipole transition and sensitive to the crystalline field. $^5D_0 \rightarrow {}^7F_1$ was magnetic dipole transition and insensitive to the crystalline field.[22,23]

Under an excitation of 319 nm, compound $TbL^5_3 \cdot 3H_2O$ (listed in Fig. 5) displays an emission band at 493 nm ($^5D_4 \rightarrow {}^7F_6$), where intensity is 381 a.u.; an strong emission band at 547 nm ($^5D_4 \rightarrow {}^7F_5$), where intensity is 824 a.u.; an weak emission band at 585 nm ($^5D_4 \rightarrow {}^7F_4$), where intensity is 75 a.u. Theoretically, there is another transition ($^5D_4 \rightarrow {}^7F_3$) at about 680 nm. Because it is very weak and located in multiple frequencies, we can not observe it in Tb complexes with PSt/BAME. Among these peaks, the $^5D_4 \rightarrow {}^7F_5$ transition is the best monochromatic emission. The Figure 6 shows the fluorescence overlay of different Tb complexes. We can see the fluorescence intensity associates with the n value.

Under an excitation of 292 nm, the fluorescence of compound $SmL^5_3 \cdot 3H_2O$ can not be observed. Maybe there is an energy level $^6F_{1/2}$ between exciting transi-

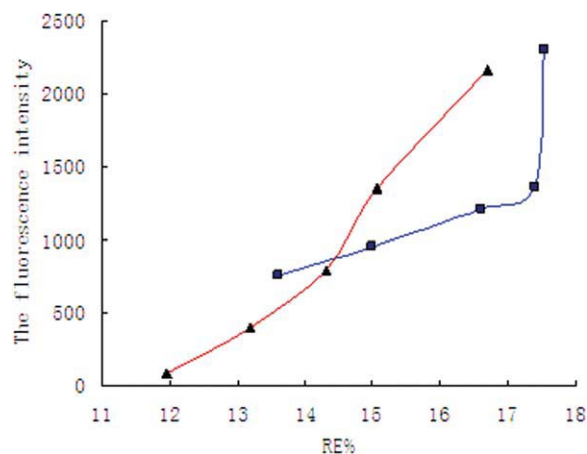tion $^4G_{5/2}$ and ground state, which is easy to arise nonradiant transition to quench the fluorescence.

In our experiments, the fluorescence intensity of the Eu^{3+} and Tb^{3+} macromolecular complexes with PSt/BAME increases with the increase of the metal content (listed in Fig. 7).

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°C at the rate of 10°C min^{-1} under an air atmosphere at ambient pressure, using α-Al_2O_3 as reference material. The data of TG-DTA analysis of the Ln-PSt/BAME (Ln = Y, Sm, Dy, Eu, and Tb; PSt/BAME = L^5) complexes are demonstrated in Table V. The thermal behavior of Ln-PSt/BAME (Ln = Y, Sm, Dy, Eu, and Tb) complexes is resemble of each other, which suggests that the decomposition of these complexes is in the same way. All the Ln-PSt/BAME complexes show good thermal stability and are decomposed in two steps. The TG-DTA curve of Ln-PSt/BAME (Ln = Y, Sm, Dy, Eu, and Tb; PStBAME = L^5) complexes were all investigated, herein we only depict the TG-DTA

TABLE V
The Date of TG-DTA of the Complexes

| Complexes | Endothermic peak | | Exothermal peak temp range/°C | | | Total remnant/% | RE_2O_3 Calcd remnant |
	Temp range/°C	Mass loss/%	1	2	3		
$YL^5_3 \bullet 3H_2O$	<274°C	8.98	333–380	380–475	479–512	12.8	12.78
$SmL^5_3 \bullet 3H_2O$	<266°C	8.23	329–375	375–479	484–529	18.18	18.42
$EuL^5_3 \bullet 3H_2O$	<259°C	8.75	307–335	335–448	455–485	18.72	18.46
$TbL^5_3 \bullet 3H_2O$	<237°C	8.67	335–381	381–453	465–479	19.47	19.71
$DyL^5_3 \bullet 3H_2O$	<284°C	8.49	337–379	379–468	479–521	20.91	19.76
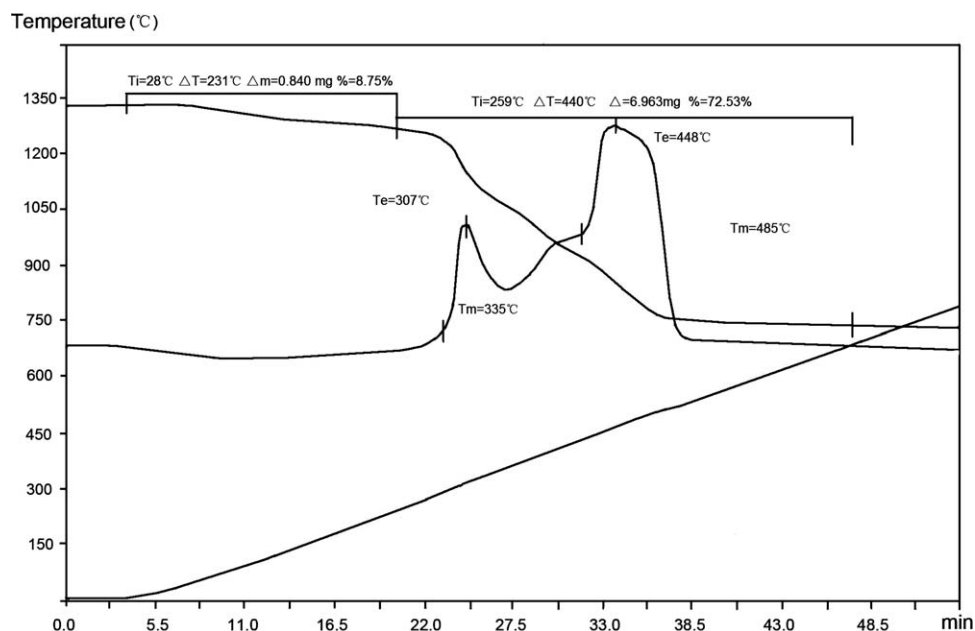
Figure 8 A typical TG-DTA curve of the compound $EuL^5_3{\bullet}3H_2O$.

curve of Eu-PSt/BAME ($EuL^5_3{\bullet}3H_2O$) complexes in Figure 8 to illustrate the decomposition process. It is shown that the first decomposition stage below the temperature 237°C is losing water, but the determined weight loss in TG curves is somewhat larger than the content of calculated water in Ln-PSt/BAME complexes. An examination using IR spectra for Ln-PSt/AA complexes sample heated under the temperature of 300°C shows that besides the absorption bands of coordinated water in the range of 3400 cm^{-1} and 550–600 cm^{-1}, the weak absorption bands of uncoordinated carboxylic groups in 1720 cm^{-1} also disappear. So, the great weight loss of Ln-PSt/BAME complexes in the first decomposition stage is both due to losing water and elimination of uncoordinated carboxylic groups in the structure units of Ln-PSt/AA complexes.[13] The second decomposition stage of Ln-PSt/BAME complexes is a continuous oxidation decomposition process, demonstrated by a series of stronger exothermic peaks on DTA curves up to 448°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 Ln^{3+} in inner sphere, which is consistent with the result that the coordination number of Ln^{3+} is 12, shown in Scheme 1, which is found most commonly in lanthanide carboxylates.[24]

CONCLUSIONS

A new series of copolymers (PSt/BAME) through different ratio of styrene (St) and 2-butenedioic acid (z)-mono-ethyl ester (BAME) and their macromolecular lanthanide complexes have been synthesized and well characterized by means of elemental analysis, FT-IR, TG-DTA and thermal analysis. The monomer's reactivity ratios and stoichiometry of copolymer were obtained by elements analysis. The results indicated that the complexes have similar formula. Carboxylic groups in the chain of polymers were partially coordinated with lanthanide ions and acted to be bidentate. TG-DTA showed complexes had good thermal stability. In the visible area, the Eu^{3+} and Tb^{3+} complexes could emit intense fluorescence and have good monochromaticity.

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