# Synthesis, Characterization of the Luminescent Lanthanide Complexes with Copolymer of (Z)-4-oxo-4-phenyloxyl-2-butenoic Acid and Styrene

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**ABSTRACT:** The copolymers of (Z)-4-oxo-4-phenoxyl-2-butenoic acid with styrene (PSt/OPBA) and their macro-molecular luminous lanthanide complexes (Ln-PSt/OPBA) have been synthesized and characterized by means of GPC, elemental analysis, FTIR, X-ray powder diffraction, spectral analysis, and thermal analysis. The IR studies showed that the carboxylic groups on the side chain of the polymer were coordinated to lanthanide ions by bidentate manner. However, the ethereal oxygen, instead of carbonyl, also bonded to the central lanthanide ions, which was an intriguing phenomenon for ester-coordinated complexes. X-ray diffraction experiments revealed that these PSt/OPBA copolymers were amorphous, but Ln-PSt/OPBA were crystalline, in which the complex Eu-L$^c$ belonged to a high symmetric structure of orthorhombic quadratic system, with $a = 10.59 \pm 0.02$ Å, $c = 8.02 \pm 0.01$ Å; $c/a = 0.763$. In addition, the value $\delta$ (the number of free carboxylic groups) in Ln-PSt/OPBA complexes increased with the decreasing mole ratio of styrene in the copolymers, while it decreased with increasing pH values of the solution. Eu$^{3+}$ and Tb$^{3+}$ complexes exhibited characteristic fluorescence with comparatively high brightness and good monochromaticity, and the fluorescence intensity was enhanced with increasing the content of lanthanide up to around 18 wt % without typical fluorescence concentration quenching behavior in the solid state. So using polymers as a matrix, Ln-PSt/OPBA are likely to provide new materials that possess specific properties and desired features. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2540–2547, 2012

**Key words:** (Z)-4-oxo-4-phenoxyl-2-butenoic acid with styrene; Ln-PSt/OPBA; characterization; structure

## INTRODUCTION

Macromolecular metal complexes (MMC) have been an increasingly attractive subject to research, because of their excellent properties of both polymeric and inorganic materials. Such compounds, having considerable compatibility and miscibility with polymeric materials of similar structure, have been applied widely in material technology and engineering[1] for the reason of overcoming some limitations of low molecular weight complexes in terms of thermal stability and mechanical properties.

Lanthanide(III) ions have widespread applications in an impressive number of fields.[2–5] Owing to the interesting magnetic and fluorescence properties, many efforts have been devoted to design, synthesis and application of macromolecular lanthanide complexes (Ln-PSt/OPBA) in recent years.[6–8] These complexes are of increasing interests in supramolecular chemistry, biology and medicine. Especially luminescent Eu$^{3+}$ and Tb$^{3+}$ complexes, which are excellent photoluminescence materials with high brightness and good monochromaticity, have been extensively studied as potential molecular and supramolecular devices,[9] and they have been applied in the fields of microscopy,[10] bioassay,[11] and sensor development.[12] Eu$^{3+}$ and Tb$^{3+}$ ions have excellent luminescence properties, but their absorption bands are weak and narrow. To enhance absorption, lanthanide (III) ions are usually chelated with ligands that have broad intense absorption bands. In these systems intense ion luminescence originates from the intramolecular energy transfer through the excited state of the ligand to the emitting level of the lanthanide ion. The derivatives of 2-butenedioic acids, such as its alkyl ester, possess the conjugated structure and have been widely applied as potential catalysts, semiconductor, photoresist, and can improve the stability of polymers remarkably. Our previous study indicated that the highly conjugated polydentate ligand (Z)-4-oxo-4-phenoxyl-2-butenoic acid (OPBA) could form a chelate ring with the center metal ion in which the ethereal oxygen and carboxylic group of the ligand coordinated to a central metal ion.[13] Such systems and this type of unusual coordination

form would enhance the luminescence efficiency of lanthanide ions greatly. As a part of our continuing investigation into the preparation of macromolecular metal complexes and exploration of their application value as luminescence materials, in this article, we have synthesized the alternative copolymers of PSt/OPBA by radical polymerization, and the macromolecular lanthanide complexes of trivalent europium and terbium coordinated with a series of synthesized copolymers (Ln-PSt/OPBA) have been prepared and characterized as well. The results indicate that the OPBA units in the copolymer chains are partially coordinated to $Ln^{3+}$ in the manner similar to its small molecular complexes. We have also researched into the effect of pH values on the number of free carboxylic groups and the relationship between the fluorescence intensity and the metal content for Ln-PSt/OPBA.

## EXPERIMENTAL

### Materials

Hydrated lanthanide nitrates $Ln(NO_3)_3 \cdot 6H_2O$ were prepared by dissolving 2–3 g corresponding oxides in concentrated nitrate acid, then heated to evaporate the excess acid. The monomer (Z)-4-oxo-4-phenoxyl-2-butenoic acid (OPBA) was synthesized in our laboratory and characterized by $^1$H-NMR and $^{13}$C-NMR spectroscopy. Styrene (St) was washed with aqueous alkaline solution and water in turns, and then distilled under reduced pressure before polymerization. Benzoyl peroxide (BPO) was purified by precipitating BPO-methanol solution into chloroform and recrystallized in methanol at 0°C before using, and others were analytical grade used without further purification unless stated otherwise.

### Methods and instrumentations

#### GPC analysis

The average molecular weights of the copolymer were estimated by a SN-01A gel permeation chromatography (GPC) consisting of a Waters 1515 HPLC pump, three Styragel HT columns, and a Waters 2414 refractive index detector. Tetrahydrofuran(THF) was used as solvent with a flow rate of 1.0 mL/min, and the instrument was calibrated using PS standards (narrow standard).

#### Determination of C, H, N, and metal contents

The contents of C, H, and N in the Ln-PSt/OPBA complexes were determined with a Carlo Erba 1106 elemental analyzer, and the metal contents were determined by volumetric titration with EDTA using xylenol orange as indicator.

#### DSC analyses and TG-DTA measurements

Differential scanning calorimetry (DSC) was performed with Sapphire DSC (Perkin–Elmer instruments), calibrated with indium. About 10 mg of samples were packed into standard aluminum pans, and scanned with a heating rate of 5°C/min thermal analysis (TG-DTA) was carried out on a PCT-2A thermal balance.

#### Spectral measurements

Infrared spectra from 4000 to 400 cm$^{-1}$ were recorded on a Nicolet 170 SXET-IR spectrometer (KBr, thin film, cm$^{-1}$) by 10 times scans at a maximum resolution of 4 cm$^{-1}$. X-ray diffraction studies were carried out with a Shimadzu XRD-6000 X-ray powder diffraction spectrometer, using Ni-filtered Cu K$_\alpha$ (1.542 Å) radiation. A set of data encompassing the wide angles was obtained. Fluorescence studies were performed with a RF-5400 fluorescence spectrophotometer with a 150 W xenon lamp as the excitation source at room temperature. The bandwidth of both the excitation and emission monochromators was set at 5 nm. The powder sample was ground as fine and uniform as possible and kept dry to avoid the quenching of fluorescence by adsorbed moisture until the measurements were taken. Powder samples were placed in the solid sample holder attached to the instrument and measured the fluorescence at 90° to the exciting beam.

### Copolymerization of (Z)-4-oxo-4-phenoxyl-2-butenoic acid with styrene (PSt/OPBA)

The monomer OPBA was prepared according to the procedures we had reported previously,[13] and the copolymerization of PSt/OPBA was carried out in 2-butanone at 75°C in the presence of BPO (1 mol % of total monomer). The mixture of different molar ratio of St/OPBA and BPO were placed in a three-neck flask equipped with a condenser containing 30 mL 2-butanone, stirred with a magnetic bar at the reflux temperature for 12 h. Then the solvent was removed by distilling under reduced pressure. The product was washed with toluene and absolute ethanol in turn to remove the unpolymerized monomers, and finally dried under vacuum at 40°C for 24 h. The resulting copolymer was white, amorphous solid, and soluble in ketone. The purified copolymer was then analyzed by GPC analysis, as summarized in Table I.

### Synthesis of Ln-PSt/OPBA

The weighed copolymer was dissolved in excessive sodium hydroxide, and a solution of hydrochloric acid was added to neutralize the excessive sodium

TABLE I
Analyses of the PSt/OPBA Copolymers

| Copolymers (St/OPBA)[a] | GPC (mol wt) | |
| --- | --- | --- |
| | $M_w$ (Da) | $M_w$/Wn |
| 10:1(L[a]) | 74,790 | 1.41 |
| 3:1(L[b]) | 68,041 | 1.47 |
| 1:1(L[c]) | 71,728 | 1.95 |

[a] Mole ratio.



Figure 1  The composition of copolymer PST/OPBA.

hydroxide. Then a water solution of calculated lanthanide nitrate was added slowly to the solution. The mixture was stirred for 2 days, and the precipitate was filtered, washed with absolute ethanol, and dried under vacuum at 40°C for 24 h. The macromolecular $Eu^{3+}$ and $Tb^{3+}$ complexes Ln-PSt/OPBA were pale yellow and insoluble in most organic solvent.

## RESULTS AND DISCUSSION

### Composition analysis

The synthesized monomer (Z)-4-oxo-4-phenoxyl-2-butenoic acid possesses two attracting electron groups which make it not form a homopolymer, whereas the conjugation effect causes the C=C double bond in styrene electron enriched, so the two monomers can easily form an alternative copolymer.[14] Thus the composition of copolymer PSt/OPBA can be shown as Figure 1.

The mol ratio of carboxylic group, which equal to that of OPBA in the copolymers, is determined by neutralization titration and further confirmed by elemental analyses. The data of elemental analyses of the copolymers PSt/OPBA and their lanthanide complexes are listed in Table II. The results indicate that the composition of copolymers are slightly different from the two monomers as starting materials, and this may be caused by the different reactivity ratio of two monomers.
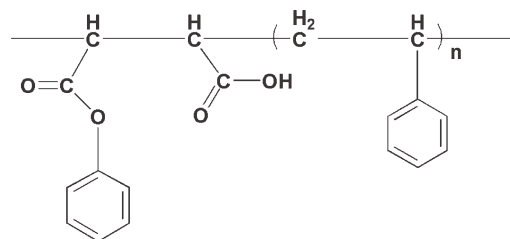
From the data listed earlier, it is confirmed that the structure unit of Ln-PSt/OPBA could be illustrated as Figure 2.

As shown in Figure 2, the δ is the number of free carboxylic groups, which represent the number of uncoordinated OPBA in the structure unit of Ln-PSt/OPBA complexes, and $n$ is the mole ratio of St/OPBA in the copolymers. Elemental analysis data reveals that each lanthanide ion is bonded to three carboxylic groups in the chain of the polymer (not necessarily in only one chain), forming stable and repeatable building blocks. In addition, as shown in Figure 3, from L[a], L[b] to L[c], with the increasing mole ratio of OPBA in the copolymers, the value δ in Ln-PSt/OPBA complexes increased. The ratio of carboxylic groups combined with lanthanide ions descended correspondingly at identical neutralization degree and this phenomenon may be resulted from the higher coordination number of lanthanide ion required, which made the carboxylic groups in polymeric chains difficult to combine with $Ln^{3+}$ thoroughly. Despite this, as shown in Table II, the metal contents in Ln-PSt/OPBA complexes are still increasing in the above order.

### IR analysis

The IR spectra of these Ln-PSt/OPBA complexes are obviously different from that of the corresponding copolymers but resemble each other.

Comparison of the IR spectra of Ln-PSt/OPBA complex with the corresponding ligand (in Fig. 4)

TABLE II
Elemental Analysis Data of the Copolymers and Their Lanthanide Complexes (Cal)

| (St/OPBA)[a] complexes | C (%) | H (%) | Ln (%) | $n$ in the copolymer | δ |
| --- | --- | --- | --- | --- | --- |
| 10:1(L[a]) | 88.23(88.01) | 7.01 (7.45) | | 11 | |
| 3:1(L[b]) | 82.35(82.20) | 6.33 (6.50) | | 3.6 | |
| 1:1(L[c]) | 76.07(75.86) | 5.66 (5.75) | | 1.5 | |
| Eu-L[a] | 84.35(84.74) | 6.94 (6.89) | 3.02 (3.40) | | 0.074 |
| Tb-L[a] | 84.19(84.60) | 7.22 (6.88) | 3.28 (3.55) | | 0.074 |
| Eu-L[b] | 74.92(75.79) | 6.51 (5.94) | 6.87 (7.09) | | 0.163 |
| Tb-L[b] | 75.13(75.54) | 6.34 (5.92) | 7.21 (7.40) | | 0.163 |
| Eu-L[c] | 67.74(68.15) | 5.58 (5.10) | 9.20 (9.25) | | 0.413 |
| Tb-L[c] | 67.08(67.86) | 5.21 (5.08) | 9.65 (9.64) | | 0.413 |

[a] Mole ratio.
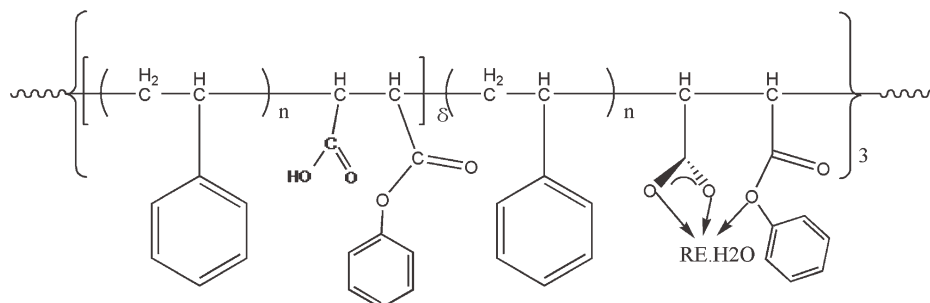
**Figure 2** The structure unit of the macromolecular lanthanide complex with copolymer of PSt/OPBA.

shows that carboxylic acid groups in the copolymer chains are fully uncoordinated, resulting in the decrease in intensity and no disappearance of the carbonyl acid absorption in 1705 cm$^{-1}$, which is consistent with the results of composition determination. The main IR absorption bands of the PSt/OPBA copolymers and their Eu$^{3+}$ and Tb$^{3+}$ complexes are listed in Table III. Two new, strong absorption bands in 1552–1556 cm$^{-1}$ and 1413–1422 cm$^{-1}$ regions for the Ln-PSt/OPBA complexes are attributed to the asymmetric vibration absorption ($v_{asCOO(A)}$) and symmetric vibration absorption ($v_{sCOO(A)}$) of carboxylic group of the complexes, respectively. The $\Delta v$ ($\Delta v = v_{asCOO(A)}$-$v_{sCOO(A)}$) is far smaller than that of Na-L(179 cm$^{-1}$), confirming that the symmetry of the carboxylic group in the complex is $C_{2v}$, the same symmetry as the free ion, so the coordinated carboxylic groups in the complexes act as a bidentate chelate bonded to the lanthanide ions.[15] It is noteworthy that, the vibration absorption bands of some ester carbonyl ($v_{CO(E)}$) have blue shifted apparently from 1745 to 1779–1782 cm$^{-1}$, and this is an evidence that the ethereal oxygen has coordinated to the central metal ions,[16,17] which coincides with the result in small M-OPBA coordination compounds we had studied before.[18] Additionally, the distinct absorption bands of coordinated water

were observed both in the range of 3424–3444 cm$^{-1}$ and 550–600 cm$^{-1}$, respectively.

## Thermal analysis

Shown in Figure 5 are that differential scanning calorimetry (DSC) provides evidence that for the series of copolymers of PSt/OPBA, only L$^a$ with the least functional group has a low melting temperature and weak endothermic peak at around 97°C. The thermal behavior of L$^b$ and L$^c$, both containing relatively higher contents of carboxylic acid as side groups on the polymer chains, have high melting temperature and endothermic peaks on DSC curves and accompany anhydride formation reaction at temperature of 194°C and 165°C, respectively in the melting process, resembling to polymers containing carboxylic as side groups on the polymer chain.[19,20] This could be further confirmed by a slight weight loss observed on thermo gravimetric (TG) curve in the melting process of L$^b$ and L$^c$, respectively.

An examination using IR spectrum for the samples of Ln-PSt/OPBA complexes heated under the temperature of 200°C shows that, besides the
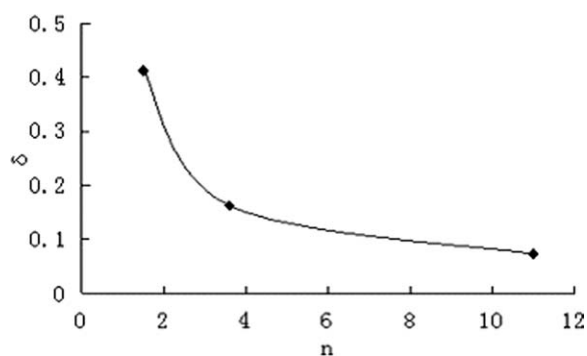


**Figure 3** Relationship between the proportion of uncoordinated OPBA ($\delta$) in the structure unit of Ln-PSt/OPBA complexes and the mole ratio of St/OPBA (n) in copolymers.
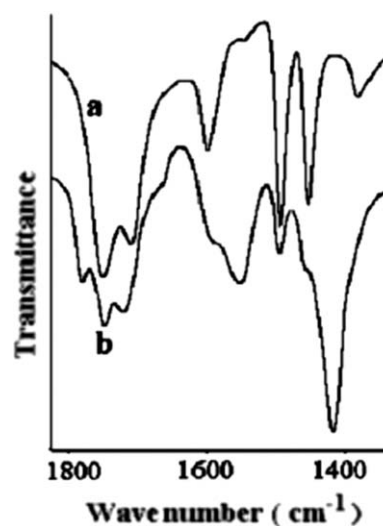


**Figure 4** The comparative FTIR spectra of copolymer PSt/OPBA (a) with the complex of Eu-PSt/OPBA (b).

**TABLE III**
**FTIR Spectra Data of the Copolymer and Ln-PSt/OPBA Complexes (cm$^{-1}$)**

| Complexes | $\nu_{O-H}$ | $\nu_{CO(E)}$ | $\nu_{as\ COO^-(A)}$ | $\nu_{s\ COO^-(A)}$ | $\Delta\nu_{as-s}$ |
|---|---|---|---|---|---|
| H-L$^c$ | 3426 | 1745 | 1708 | | |
| Na-L$^c$ | 3459 | 1721 | 1576 | 1397 | 179 |
| Eu-L$^a$ •H$_2$O | 3435 | 1782 | 1552 | 1413 | 139 |
| Tb-L$^a$ •H$_2$O | 3433 | 1780 | 1552 | 1414 | 138 |
| Eu-L$^b$ •H$_2$O | 3424 | 1781 | 1556 | 1422 | 134 |
| Tb-L$^b$ •H$_2$O | 3427 | 1780 | 1555 | 1420 | 135 |
| Eu-L$^c$ •H$_2$O | 3444 | 1782 | 1553 | 1418 | 135 |
| Tb-L$^c$ •H$_2$O | 3426 | 1779 | 1554 | 1418 | 136 |

absorption bands of coordinated water in the range of 3424–3444 cm$^{-1}$ and 550–600 cm$^{-1}$, the characteristic band of uncoordinated acid carbonyl absorption in 1705 cm$^{-1}$ also disappeared (in Fig. 6). The thermal behaviors of the macromolecular lanthanide complexes are very similar but quite different from that of the free copolymer ligands, suggesting that the decomposition of the complexes in the same way. All the Ln-PSt/OPBA complexes show good thermally stability and decompose in three procedures. A typical TG-DTA curve of the Ln-PSt/OPBA complexes is shown in Figure 7, and the data of TG-DTA analysis for Ln-PSt/OPBA complexes are listed in Table IV. The first decomposition stage in the temperature range of 150–280°C is losing water, and the determined weight loss in TG curves is somewhat larger than the calculated water content in the macromolecular complexes. The larger weight loss of the Ln-PSt/OPBA complexes in first decomposition stage (in the temperature range of a-b shown in Fig. 7) than the contents of water is duo to the elimination of uncoordinated carboxylic group in Ln-PSt/OPBA structure units.[21] The second and third decomposition stages of the Ln-PSt/OPBA complexes were continuous oxidation decompositions, demonstrated by a series of stronger exothermic peaks on DTA curves up to 700°C. The final residues coincide with the general formula of Ln(CO$_3$)(O)$_{0.5}$

rather than oxides, and later confirmed by chemical analysis for the metal and carbonate content in them.[22]

Based on the results, the macromolecular lanthanides complex Ln-PSt/OPBA shows a higher thermal stability. Considering the result of elemental analyses and IR spectra, it is obvious that the coordination number of both Eu$^{3+}$ and Tb$^{3+}$ in Ln-PSt/OPBA complexes is 18 wt %, the same value as the corresponding low molecular weight OPBA complexes of lanthanide we reported previously.

The X-ray diffraction experiments reveal that all of the PSt/OPBA copolymers are amorphous, but their macromolecular lanthanide complexes are crystalline. The X-ray diffraction patterns of the PSt/OPBA copolymers and their Eu$^{3+}$ complexes are reported in Figure 8. An intense and broad diffuse scatter between 19.14 and 19.50 degree 2θ ($d$ = 4.63–4.55 Å) for the copolymers was observed, assigned to the diffraction pattern of the lateral packing of the nematic mesophase.[23] Despite the melting endothermic peaks were observed in the DSC curves of the copolymers, no evidence of L$^a$, L$^b$, and L$^c$ crystallinity was observed through X-ray diffraction. On the contrary, indicative of a more highly ordered phase, there were a great number of sharp wide-angle diffraction peaks for the macromolecular lanthanides complex. The patterns of macromolecular europium complexes with L$^a$ and L$^b$ were almost identical with only subtle changes in the crystallinity. The
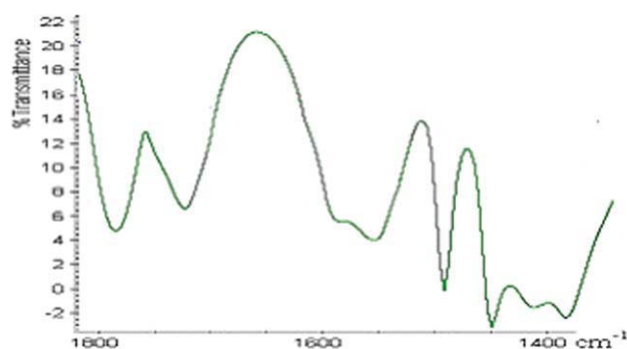


**Figure 5** DSC curves for PSt/OPBA copolymers of L$^a$ (1), L$^b$ (2), and L$^c$ (3).



**Figure 6** The typical IR spectrum of Ln-PSt/OPBA complexes heated under 200°C for 1 hour.
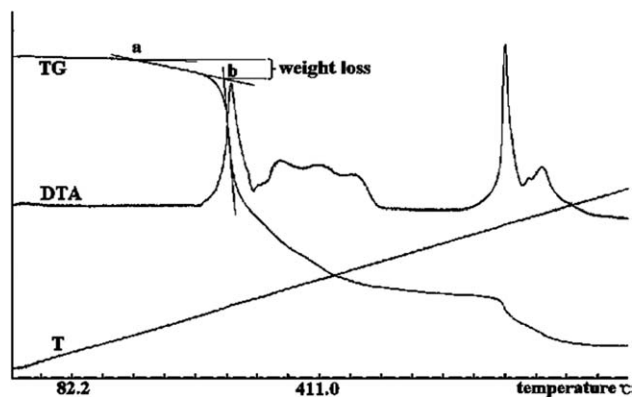
**Figure 7** A typical TG-DTA curve of the Ln-PSt/OPBA complexes.



**Figure 8** Wide-angle X-ray diffraction diagrams of the OPBA/St copolymers (1) and Eu-PSt/OPBA complexes (2).
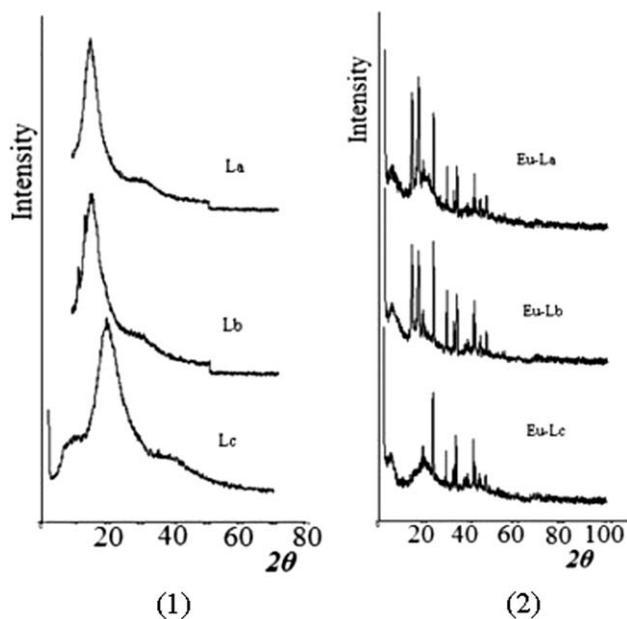
lower crystallinity of Eu-L$^a$ would be resulted from the longer polymer chains, especially when the highest fraction of polystyrene chain existed among the Ln-PSt/OPBA structure units. The lamellar spacing, $d$, obtained from the WAXS data by application of the Bragg equation to the lowest angle peak of the phase for both of the complexes Eu-L$^a$ and Eu-L$^b$ was 5.250 Å. For the complex Eu-L$^c$, in which the copolymer ligand contains the highest mole ratio of carboxylic group, exhibiting a nearly identical X-ray diffraction pattern with a known inorganic compound CsYb[Fe(CN)$_6$]•4H$_2$O in both $d$ values and intensities.[24] This is an evidence that the two compounds are isostructure, belonging to a high symmetric structure of orthorhombic quadratic system, with $a = 10.59 \pm 0.02$ Å, $c = 8.02 \pm 0.01$ Å; $c/a = 0.763$.[25] Compared with Eu-L$^b$, the complex Eu-L$^c$ has a relatively lower crystallinity, which may be caused by the largest amount of uncoordinated OPBA in the structure unit of Eu-L$^c$ complex as discussed previously.[26]

The decreasing $\delta$ values from Eu-L$^a$, Eu-L$^b$ to Eu-L$^c$ is in agreement with the increasing of carboxylic content in the copolymer ligands, indicating that the central lanthanides ion tend to form a more compact structure with higher carboxylic group content in the ligand.

## Effect of pH values on the number of free carboxylic groups

The chelating of Ln$^{3+}$ ions with the polymer ligand is highly dependent on the pH values and the molar ratio of St to (Z)-4-oxo-4-phenoxyl-2-butenoic acid with styrene in PSt/OPBA copolymer.[27,28] The effect of pH values on the composition of Ln-PSt/OPBA complexes is illustrated in Figure 9, which shows that the $\delta$ (the number of uncoordinated carboxylic groups) in the structure unit of Ln-PSt/OPBA complexes decreases with increasing pH values of the solution. The reason may be that at lower pH values, some free carboxylic groups present in the structure
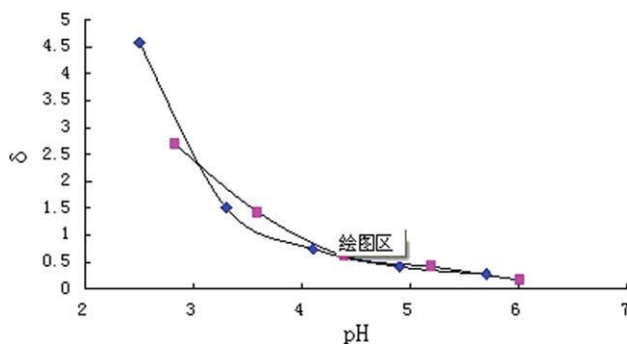
**TABLE IV**
**The Data of TG-DTA Analysis for Ln-PSt/OPBA Complexes**

| | Weight loss in first stage (%) | | Total weight loss (%) | |
| | Determined | Water content | Determined | Calculated |
| Complexes | | | | |
|---|---|---|---|---|
| Eu-L$^a$ | 0.51 | 0.40 | 93.92 | 94.89 |
| Tb-L$^a$ | 1.07 | 0.85 | 88.78 | 89.36 |
| Eu-L$^b$ | 1.70 | 1.10 | 85.34 | 86.11 |
| Tb-L$^b$ | 0.53 | 0.40 | 93.69 | 94.75 |
| Eu-L$^c$ | 1.06 | 0.84 | 88.31 | 89.07 |
| Tb-L$^c$ | 1.72 | 1.09 | 85.54 | 85.75 |



**Figure 9** Relationship between pH and the $\delta$ value for EuL$^c_3$•H$_2$O and TbL$^c_3$•H$_2$O. (◆: EuL$^c_3$•H$_2$O; ■: TbL$^c_3$•H$_2$O). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE V
Fluorescence Spectral Data of the Solid Complexes of
Eu(III) and Tb(III)

| Complexes | $\lambda_{ex}$ (nm) | $\lambda_{em}$ (nm) | I (relative intensity) | Transition |
|---|---|---|---|---|
| Eu-L[a] | 396 | 617/593 | 369/162 | $^5D_0\to{}^7F_2/^5D_0\to{}^7F_1$ |
| Tb-L[a] | 282 | 548/492 | 302/168 | $^5D_4\to{}^7F_5/^5D_4\to{}^7F_6$ |
| Eu-L[b] | 396 | 617/593 | 389/230 | $^5D_0\to{}^7F_2/^5D_0\to{}^7F_1$ |
| Tb-L[b] | 282 | 548/492 | 339/184 | $^5D_4\to{}^7F_5/^5D_4\to{}^7F_6$ |
| Eu-L[c] | 396 | 617/593 | 494/207 | $^5D_0\to{}^7F_2/^5D_0\to{}^7F_1$ |
| Tb-L[c] | 282 | 546/491 | 354/192 | $^5D_4\to{}^7F_5/^5D_4\to{}^7F_6$ |

unit of Ln-PSt/OPBA complexes, owing to the fact that the polymer ligand is weak polyacid, and competition exists between protons and $Ln^{3+}$ ions for coordination sites, $Ln^{3+}$ ions cannot replace the proton of the carboxylic groups at high acidity, so the partial carboxylic groups have not participated in coordination. On the contrary, at higher pH values, the tendency of $Ln^{3+}$ ions to form coordinated anion with carboxylic groups enhances, which causes δ decrease in the Ln-PSt/OPBA complexes.

## Fluorescence spectra

The fluorescence determination of the macromolecular $Eu^{3+}$ and $Tb^{3+}$ complexes shows 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 fluorescence spectra of the solid complexes of Eu-PSt/OPBA and Tb-PSt/OPBA are demonstrated in Figure 10, respectively.

The macromolecular complexes of the copolymer ligands with $Eu^{3+}$ and $Tb^{3+}$ show characteristic lanthanide ion fluorescence in the solid state on excitation with UV light.[29] As in Table V, it is possible to

distinguish changes of different Ln-PST/OPBA complexes, by analyzing the ratio of the relative intensity (I*). The complexes of Eu-PST/OPBA show two prominent emissions at 593 nm ($^5D_0\to{}^7F_1$) and 617 nm ($^5D_0\to{}^7F_2$) which are responsible for the red color. This emission spectrum is obtained under excitation at 396 nm, corresponding to the $^5L_7$ level of the $Eu^{3+}$ ion. Similar fluorescence spectra of the $Tb^{3+}$ Complexes are obtained on excitation at 282 nm.[30] The complexes of Tb-PST/OPBA emission bands are assigned to transitions from $^5D_4$ to the $^7F_5$ and $^7F_6$ levels at 492 and 548 nm, respectively.

We have also found that both of complexes exhibit enhanced fluorescence intensity with increasing lanthanide ion content up to around 18 wt % without typical fluorescence concentration quenching behavior. As shown in Figure 11, the fluorescence intensity of $Eu^{3+}$ complexes are much stronger than $Tb^{3+}$ Complexes when the lanthanide ions content is the same. The fluorescence quantum yield (Φ) of the Eu(III) and Tb(III) complexes in the solid state were measured and found to be 4.62% and 3.23% using an integrating sphere, respectively. The emission intensity and fluorescence quantum yield of the Eu(III) complex are more stronger between these complexes under the same conditions.

The results also suggest that lanthanide ions in the macromolecular complexes are homogeneously dispersed throughout the polymer matrix, which are very important in optical applications.[31] On the basis of these measurements, it is concluded that the Ln-PSt/OPBA complexes of PSt/OPBA do not contain ion aggregates up to 18 mol % (molar ratio: $n_{europium}/n_{carboxylate}$). Comparison between Ln-PSt/OPBA complexes and small Ln-St/OPBA complexes shows that the latter display relatively low fluorescence intensity. It is evident that, photophysical properties of $Eu^{3+}$ and $Tb^{3+}$ ion markedly depend on their
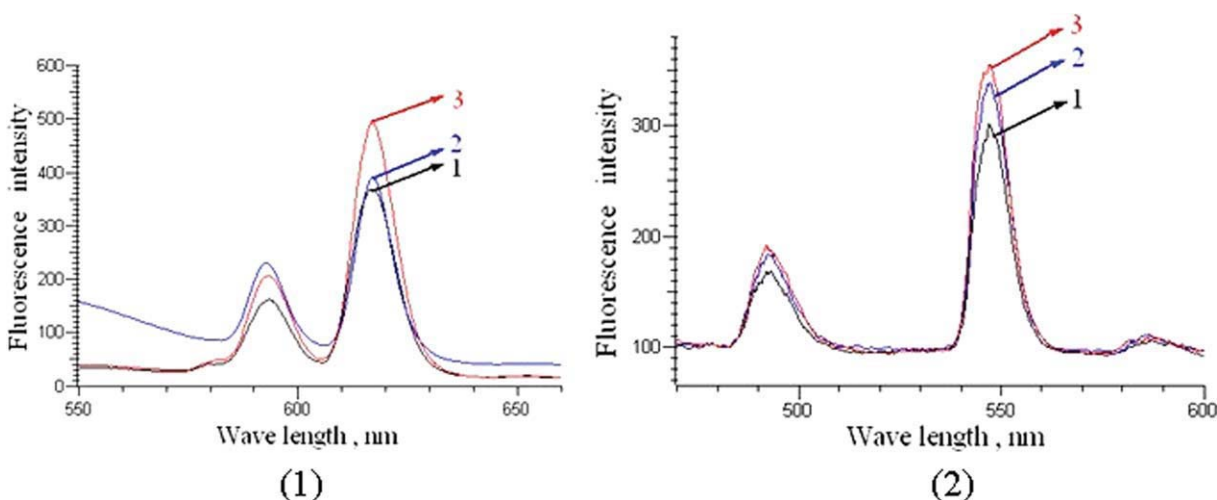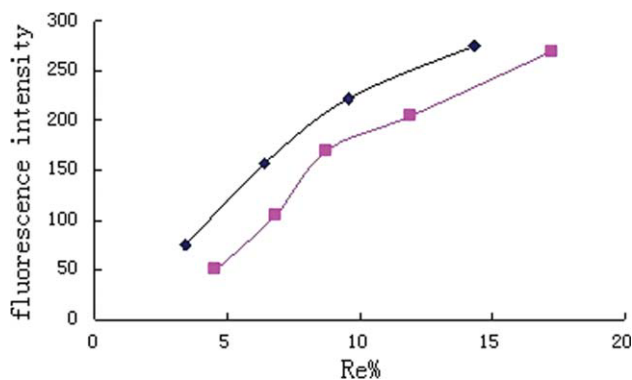


**Figure 10** Fluorescence spectrum of the solid Ln-PSt/OPBA complexes [For (1), **1**, Eu-L[a]; **2**, Eu-L[b]; **3**, Eu-L[c] and for (2), **1**, Tb-L[a]; **2**, Tb-L[b]; **3**, Tb-L[c]]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Figure 11** Relationship between the fluorescence intensity and the metal content for $TbL^c_3 \cdot H_2O$ and $EuL^c_3 \cdot H_2O$. (■: $TbL^c_3 \cdot H_2O$;◆: $EuL^c_3 \cdot H_2O$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

environment.[32,33] To get an efficient cation emission, the chromophoric ligand should firstly absorb light strongly in the UV region and transfer it to the lanthanide ion efficiently, and secondly protect it from solvent molecules which could quench the central metal emission.[34] The intense luminescence indicated there had an effective energy transfer from the copolymer ligand to $Ln^{3+}$ ion.

## CONCLUSIONS

A series of functional copolymers of (Z)-4-oxo-4-phenoxyl-2-butenoic acid with styrene (PSt/OPBA) were synthesized by free radical polymerization, which possesses excellent and unique coordination ability to metal ions. The macromolecular lanthanide complexes Ln-PSt/OPBA (Ln = $Eu^{3+}$ and $Tb^{3+}$) with the ligands of PSt/OPBA were prepared, and a detailed study on the structural and property characterization for both the copolymers and Ln-PSt/OPBA complexes had been performed. IR analysis proved that the carboxylate in these copolymers could bond to the central $Ln^{3+}$ ions in the form of bidentate; An interesting result was that the ethereal oxygen, instead of carbonyl in copolymer chain, also bonded to the central lanthanide ions to form a chelate ring in structure unit of Ln-PSt/OPBA. X-ray diffraction experiments showed that although the PSt/OPBA copolymers were amorphous, but their macromolecular lanthanide complexes Ln-PSt/OPBA were crystalline. It was suggested that the value δ in Ln-PSt/OPBA complexes increased with the decreasing mole ratio of styrene in the copolymers, while it decreased with increasing pH values of the solution. The fluorescence determination indicated that macromolecular $Eu^{3+}$ and $Tb^{3+}$ complexes could emit characteristic fluorescence with comparatively high brightness and good monochromatic, and the fluorescence intensity was enhanced with increasing the

content of lanthanide up to around 18% without typical fluorescence concentration quenching behavior in the solid state on excitation with UV light, which meant there exhibited an effective intramolecular energy transfer from PSt/OPBA chains to $Ln^{3+}$ ions. Thus, the luminescent lanthanide complexes Ln-PSt/OPBA would be used as potential photoluminescence materials.

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