

Synthesis, Characterization, and Fluorescence Properties of Lanthanide Complexes with Poly(styrene-*co*-methacrylic acid)

Tonghuan Liu, Ying Yang, Guojian Duan, Yaping Gao, Zhengzhi Zeng

College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China

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ABSTRACT: A series of new complexes of poly(styrene-*co*-methacrylic acid) with Ln(III) (Ln = La, Eu, Tb) were synthesized and well characterized by means of elemental analysis, FTIR, differential scanning calorimetric (DSC) analysis, TG-DTA analysis, X-ray diffraction (XRD), and fluorescence determination. The elemental analysis and FTIR studies showed that a large part of carboxylic groups on the side chain of the copolymer are coordinated with Ln(III) ions. The TG-DTA and DSC analysis results indicated that

the complexes have good thermal stability. XRD experiments showed that copolymers and the complexes are amorphous. Among these complexes, Eu(III) complexes and Tb(III) complexes exhibit characteristic fluorescence with comparatively high brightness and good monochromaticity. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3388–3394, 2009

Key words: lanthanide complexes; poly(styrene-*co*-methacrylic acid); fluorescence properties; synthesis

INTRODUCTION

Macromolecular metal complexes have been an increasingly attractive subject of research because of their excellent properties of both polymeric and inorganic materials.^{1,2} These complexes possess both the properties of inorganic metal ions and conjugation polymers and have many advantages when compared with inorganic and organic small molecules complexes, such as good thermal stability, process ability, and easy film forming. The complexes play an important role in light-emitting materials,^{3–5} which have good electronic transfer functions due to the intramolecular charge transfer transitions from ligand-to-ligand (LLCT) and ligand-to-metal (LMCT). Such compounds have been widely applied in material technology and engineering for the reason of overcoming some limitations of low-molecular-weight complexes in terms of thermal stability and mechanical properties. Beginning with the preparation of polymer materials containing rare earth metal studied by Okamoto and coworkers,^{6–8} considerable efforts have been devoted to the design, synthesis, and application of macromolecular rare earth complexes during the last two decades. It is well known that the excited europium(III) and terbium(III) complexes have strong fluorescence emission, large Stokes shifts, narrow emission profiles, and long fluorescence life-

time,⁹ and they have been widely used in many aspects such as fluorescence mark, fluorescence analysis, environmental sciences, and cell biology.^{10–13} Their use has opened up a lot of opportunities in growing fields of large social and economical impact.¹⁴ Up to now, all main-chain polymeric metal complexes are coordinated with common metal ions, however, the reports on those complexes that coordinated with rare earth metal ions are few. To combine the advantages of macromolecular compound and rare earth, in this article, a series of styrene-*co*-methacrylic acid (STMAA) copolymers and Ln(III) complexes have been synthesized, and their composition, FTIR spectra, thermal properties, and fluorescent spectra have been studied. At the same time, the coordination ability of STMAA to Ln(III) ions at different pH values and the cause which affects the fluorescence intensity of Ln(III) complexes have also been studied.

EXPERIMENTAL

Materials and Methods

Styrene (ST) (96%, chemical reagent, Shanghai Heyi Chemical Co., Ltd., Shanghai, China) was washed several times with aqueous alkaline solution and water. Methacrylic acid (MAA) (96%, chemical reagent, Tianjin Plant, Tianjin, China) was distilled under reduced pressure before polymerization. Benzoyl peroxide (BPO) (99%, analytical reagent grade, Shanghai Heyi Chemical Co., Ltd., Shanghai, China) was purified by precipitating BPO-methanol solution into chloroform and recrystallized in methanol at

Correspondence to: Y. Yang (yangying@lzu.edu.cn).

0°C before using. Hydrated lanthanide nitrates $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were prepared in our laboratory,¹⁵ and other chemicals were of analytical reagent grade used without further purification. The average molecular weight of copolymers were estimated by a SN-01A gel permeation chromatography (GPC), and THF was used as the eluting solvent. The contents of C and H in the complexes were determined on a Vario-EL elemental analyzer, and the metal ions contents were determined by EDTA titration using xylene orange as an indicator. Differential scanning calorimetric (DSC) curves were taken on a Sapphire DSC (Perkin Elmer Instruments) to eliminate the heat history, and each sample was heated from room temperature to 250°C and cooled to 10°C and then heated to 250°C for recording with a heating rate of 10°C/min in air. TG-DTA analysis was carried out on a PCT-2A thermal balance. IR spectra were recorded on a Nicolet Avatar 360 FTIR spectrometer (KBr discs) in the 4000 to 400 cm^{-1} region. Fluorescence measurements were made on a Hitachi F-4500 spectrophotometer and a Shimadzu RF-540 spectrofluorophotometer equipped with quartz cuvettes of 1-cm path length. The excitation and emission spectra and the relative fluorescence intensity were measured on dried and finely powdered samples at room temperature. The excitation and emission slit widths were 2.5 nm. The structure of copolymer and complex were examined by a X-ray diffraction (XRD)-6000 spectrometer with Cu $K\alpha_1$ radiation of wavelength $\lambda = 1.542 \text{ \AA}$.

Synthesis of STMAA and Ln(III) complexes

Random copolymerizations were carried out in a 250-mL three-necked flask equipped with a condenser. As a typical procedure, 100 mL butanone was added into the flask, which was kept at 80°C in an oil bath, and the mixture of ST and MAA (1 : 5 mol ratio) and the initiating agent of BPO (1 mol % of total monomer) was added with 15 min stirring, and then the mixture was reacted continuously for 10 h. Then the solvent was removed by distillation under reduced pressure. The product was washed with toluene and absolute ethanol in turn to remove

TABLE I
Elemental Analysis of the Copolymers
(calculated values in parentheses)

Feed (ST/MAA)	C%	H%	x^a
0.2 (L_1)	62.76 (63.07)	6.956 (7.278)	0.28
1.0 (L_2)	72.96 (72.81)	7.083 (7.416)	0.85
5.0 (L_3)	84.35 (84.46)	7.271 (7.580)	3.39

^a x is the mol ratio of ST/MAA in the copolymers.

TABLE II
Elemental Analysis of the Ln(III) Complexes
(calculated values in parentheses)

Complexes	C%	H%	Ln%	y^a
LaL_1	43.85 (44.71)	5.365 (5.414)	23.12 (22.87)	0.63
LaL_2	55.52 (56.17)	5.895 (5.929)	18.36 (17.91)	0.36
LaL_3	74.12 (74.94)	6.567 (6.836)	9.02 (8.77)	0.18
EuL_1	43.05 (43.78)	4.872 (5.031)	24.79 (24.48)	0.63
EuL_2	54.49 (55.19)	5.512 (5.831)	19.95 (19.26)	0.36
EuL_3	73.68 (74.33)	6.445 (6.780)	10.86 (9.52)	0.18
TbL_1	42.47 (43.29)	5.019 (5.241)	25.95 (25.32)	0.63
TbL_2	54.13 (54.71)	5.443 (5.780)	20.33 (19.98)	0.36
TbL_3	73.25 (74.01)	6.462 (6.751)	10.21 (9.91)	0.18

^a y is the number of free acid, which represent the number of uncoordinated MAA in the structural unit of the complexes.

the unpolymerized monomers, and then dried under vacuum at 40°C for 2 days. The resulting copolymers are all white amorphous solid and soluble in common organic solvents. The average molecular weights of the copolymers are all in the range of 4800–5300. In this report, three copolymers of the mol ratio of ST to MAA is 1 : 5, 1 : 1, and 5 : 1 were synthesized, denoted as L_1 , L_2 , and L_3 , respectively. The acid content of the obtained polymer was determined by titration in 1 : 1 (v/v) methanol–water solvent with standardized sodium methoxide, using phenolphthalein as an indicator.¹⁶

The weighted copolymer was dissolved in methanol, and the solution was kept with the methanol solution of NaOH to neutralize 95 mol % (80 or 50 mol %) of the acid (Solution **a**). A mol ratio 3 : 1 of acid to Ln(III) ions was used, and then weighted lanthanide nitrate was dissolved in 5 mL methanol (Solution **b**). Then **b** was added dropwise to **a** with stirring, after the solution was stirred 2 days, the precipitate was isolated from the solution by centrifugation, it was washed with water and methanol several times and dried under vacuum for 2 days at 50°C. Other operations were similar to the typical procedure. The complexes are white powders and insoluble in most organic solvents. The subscripts m and n represent the complexes that neutralized 80 and 50 mol % of the acid, respectively. XRD patterns of STMAA and Ln(III) complexes show that no diffraction peaks appear,

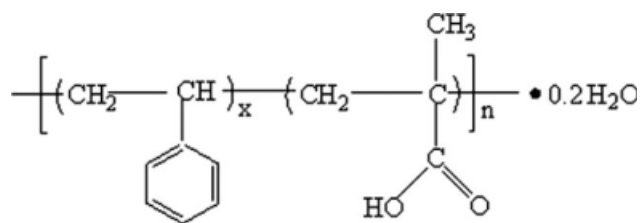


Figure 1 The structural unit of the copolymers.

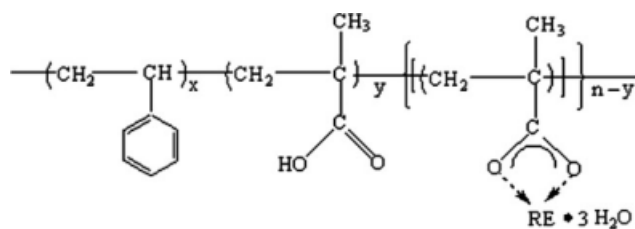


Figure 2 The structural unit of Ln(III) complexes.

indicating that the copolymers and the complexes are noncrystal compounds.

RESULTS AND DISCUSSION

Composition analysis

The elemental analytical results of the copolymers and the complexes are presented in Tables I and II.

Each Ln(III) ion is bonded to three carboxylic groups in the chain of the copolymers (not necessarily in only one chain). The structural unit of complexes was determined by the results of the composition analysis and neutralization titration, and it is illustrated in Figure 1.

From the data listed in Table II, the structural unit of the complexes is illustrated in Figure 2.

In addition, as shown in Figure 3, the mol ratio of MAA, which is uncombined with Ln(III) ions, decreases with increasing ST content. This phenomenon may be due to the requirement of higher coordination number of Ln(III) ions, and when the content of MAA is higher, the carboxylic groups that have been combined with Ln(III) ions would obstruct the other carboxylic groups to combine with Ln(III) ions, but when the content of MAA is lower, the effect becomes weaker. At the same time, the pH value of the solution would affect the coordination ability of the carboxylic groups as well; this aspect will be studied later.

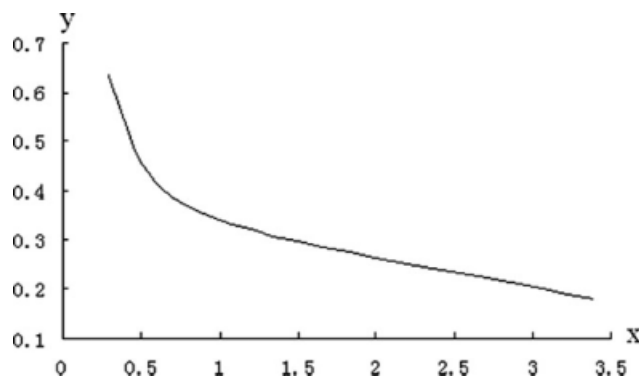


Figure 3 Relationship of x and y in the complexes.

IR analysis

The important IR data of the STMAA and Ln(III) complexes are given in Table III. The IR spectra of the complexes are similar, but different with the copolymers.

A detailed study on the IR spectra of the copolymers and the Ln(III) complexes has been performed. The strong absorption peaks at ca. 1700 cm^{-1} ascribed to $\nu_{\text{C=O}}$ of carboxylic group, which is a hydrogen-bonded cyclic dimer band.¹⁷ The absorption intensity of the carboxylic groups becomes very weak, indicating that the carboxylic groups take part in the coordination with the Ln(III) ions. The absorption bands due to the phenyl ring were observed at ca. 760 and 700 cm^{-1} , respectively, and the absorption intensities of these peaks increased with increasing the ST concentration in the copolymer. The bands lying at the ranges of $1544\text{--}1507\text{ cm}^{-1}$ and $1414\text{--}1405\text{ cm}^{-1}$ assigned to the symmetric vibration absorption ($\nu_{\text{s,COO}^-}$) and asymmetric vibration absorption ($\nu_{\text{as,COO}^-}$) of the carboxylic group. The determined $\Delta\nu$ ($\Delta\nu = \nu_{\text{as,COO}^-} - \nu_{\text{s,COO}^-}$) for the complexes are far smaller than that of Na-PMAA (184 cm^{-1}),¹⁸ which shows that the symmetry of the carboxylic group in the complexes is C_{2v} , the same as the free ion. This state clearly indicates

TABLE III
FTIR Spectra Data of the Copolymers and Ln(III) Complexes (cm^{-1})

Complexes	$\nu_{\text{O-H}}$	$\nu_{\text{C=O}}$	$\nu_{\text{as,COO}^-}$	$\nu_{\text{s,COO}^-}$	$\Delta\nu_{\text{as-s}}$	$\nu_{\text{C-H}}$	$\delta_{\text{C-C}}$
L ₁	3428	1702				760	702
L ₂	3425	1698				757	700
L ₃	3430	1698				757	698
LaL ₁	3407	1701	1543	1405	138	760	703
LaL ₂	3409	1700	1539	1406	133	757	701
LaL ₃	3416	1700	1539	1408	131	757	699
EuL ₁	3419	1702	1534	1408	126	763	704
EuL ₂	3408	1703	1543	1407	136	758	701
EuL ₃	3421	1699	1544	1412	132	757	699
TbL ₁	3411	1703	1527	1410	117	760	703
TbL ₂	3415	1701	1528	1412	116	758	701
TbL ₃	3425	1699	1528	1414	114	757	699

that the carboxylic group acting as a bidentate chelate coordinated to the Ln(III) ions in the complexes.^{19,20} At the same time, we have studied the coordination ability of the carboxylic group to Ln(III) ions at different pH values. The results indicate that with the increase of the neutralization, the coordination ability of carboxylic group is increased. Figure 4 shows the comparative IR spectra of Eu(III) complexes, from which we can see that the absorption intensity of C=O is increased with the pH values of the solution. Because of the fact that MAA is a weak organic acid, Ln(III) ions is difficult to replace the proton of the carboxylic group of MAA at higher acidity. MAA units exist in an ionized form (−COO[−]) when carboxylic group of MAA was neutralized, and it is very easy for Ln(III) ions to combine with them.

Thermal properties

The thermal property of copolymers was determined by DSC, the glass transition temperature (T_g) of the copolymers (L_1 , L_2 , and L_3) are 221.9, 191.8, and 108.2°C, respectively (Fig. 5). We could find that the T_g is changed with the mol ratio of ST to MAA. The thermal property of Eu(III) complexes (EuL_1 , EuL_2 , and EuL_3) were determined by simultaneous TG-DTA, the thermal behaviors of the three complexes are similar, suggesting that the decomposition of the complexes were in the same way. The DTA data of Eu(III) complexes are shown in Figure 6. For the

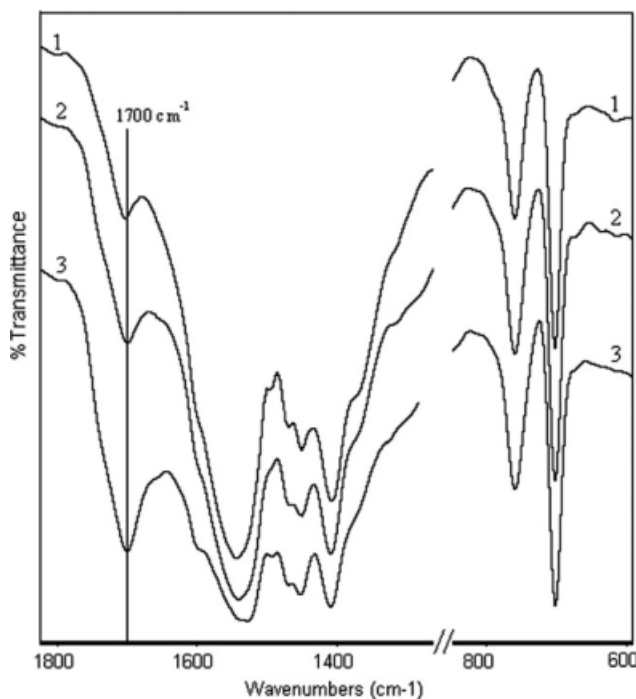


Figure 4 The comparative FTIR spectra of Eu(III) complexes (1: EuL_2 , 2: EuL_{2m} , 3: EuL_{2n}).

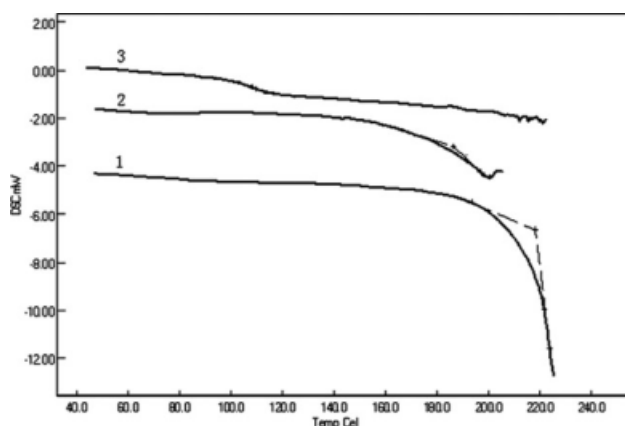


Figure 5 The DSC curves of copolymers (1: L_1 , 2: L_2 , 3: L_3).

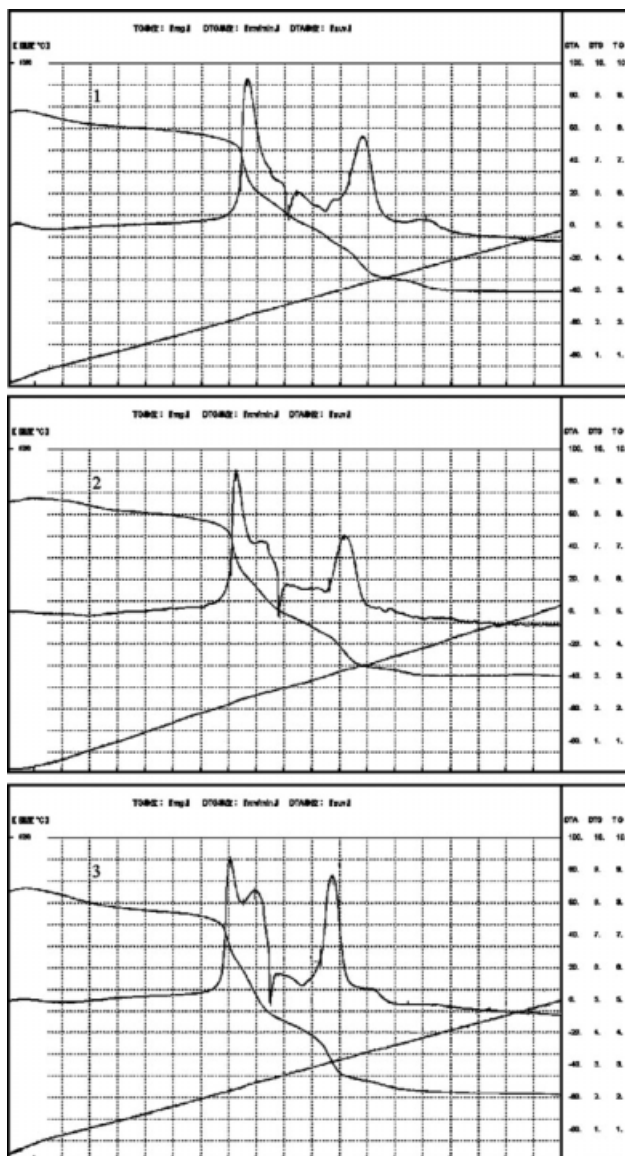


Figure 6 The DTA spectra of Eu(III) complexes (1: EuL_2 , 2: EuL_{2m} , 3: EuL_{2n}).

TABLE IV
Fluorescence Spectra Data of the
Solid Ln(III) Complexes

Complexes	λ_{ex} (nm)	λ_{em} (nm)	RFI	Transition
TbL ₁	371	491.8	1471	$^5\text{D}_4 \rightarrow ^7\text{F}_6$
		547.6	3233	$^5\text{D}_4 \rightarrow ^7\text{F}_5$
		584.8	309.5	$^5\text{D}_4 \rightarrow ^7\text{F}_4$
		623.0	192.3	$^5\text{D}_4 \rightarrow ^7\text{F}_3$
TbL ₂	371	492.4	1224	$^5\text{D}_4 \rightarrow ^7\text{F}_6$
		548.0	2785	$^5\text{D}_4 \rightarrow ^7\text{F}_5$
		584.4	291.7	$^5\text{D}_4 \rightarrow ^7\text{F}_4$
		622.0	189.6	$^5\text{D}_4 \rightarrow ^7\text{F}_3$
TbL ₃	371	492.0	699.1	$^5\text{D}_4 \rightarrow ^7\text{F}_6$
		546.8	1758	$^5\text{D}_4 \rightarrow ^7\text{F}_5$
		585.2	127.1	$^5\text{D}_4 \rightarrow ^7\text{F}_4$
		621.4	56.42	$^5\text{D}_4 \rightarrow ^7\text{F}_3$
EuL ₁	395	590.2	243.6	$^5\text{D}_0 \rightarrow ^7\text{F}_1$
		613.2	946.7	$^5\text{D}_0 \rightarrow ^7\text{F}_2$
EuL _{1m}	395	590.4	195.0	$^5\text{D}_0 \rightarrow ^7\text{F}_1$
		614.0	737.1	$^5\text{D}_0 \rightarrow ^7\text{F}_2$
EuL _{1n}	395	590.6	92.29	$^5\text{D}_0 \rightarrow ^7\text{F}_1$
		614.4	310.6	$^5\text{D}_0 \rightarrow ^7\text{F}_2$
EuL ₂	395	591.2	193.2	$^5\text{D}_0 \rightarrow ^7\text{F}_1$
		613.2	719.7	$^5\text{D}_0 \rightarrow ^7\text{F}_2$
EuL _{2m}	395	592.4	168.9	$^5\text{D}_0 \rightarrow ^7\text{F}_1$
		616.0	529.5	$^5\text{D}_0 \rightarrow ^7\text{F}_2$
EuL _{2n}	395	592.8	99.1	$^5\text{D}_0 \rightarrow ^7\text{F}_1$
		615.8	283.4	$^5\text{D}_0 \rightarrow ^7\text{F}_2$
EuL ₃	395	590.6	117.7	$^5\text{D}_0 \rightarrow ^7\text{F}_1$
		613.6	396.3	$^5\text{D}_0 \rightarrow ^7\text{F}_2$

RFI, relative fluorescence intensity.

Eu(III) complexes, three strong exothermic peaks on DTA curves could be observed in the range of 300–550°C. Although the discontinuous changes on TG curves indicate that the decomposition have taken place in steps, the changes are so nearly to deduce the detailed decomposition processes.

Fluorescence properties

The major fluorescence spectral of the solid-state macromolecular complexes of the Eu(III) complexes and Tb(III) complexes results and excitation wavelength are listed in Table IV. The emission spectra of Eu(III) complexes and Tb(III) complexes are shown in Figure 7.

As shown in Figure 7, four characteristic emission peaks were observed in Tb(III) complexes. These peaks were corresponding to the $^5\text{D}_4 \rightarrow ^7\text{F}_j$ transition. Among them, the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition (547 nm) shows high brightness and good monochromatic emission. The two bright red emission lines of Eu(III) complexes centered at ca. 591 and 614 nm were observed and assigned to $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition, respectively. Between the two transitions, $^5\text{D}_0 \rightarrow ^7\text{F}_2$ is the electro-dipole transition and sensitive to the crystalline field, and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ is the magnetic dipole transition and insensitive to the crystalline field.^{21–23} The determined intensity ratio $I(^5\text{D}_0 \rightarrow ^7\text{F}_2)/I(^5\text{D}_0 \rightarrow ^7\text{F}_1)$ is about 3, and these results indicate that Eu(III) is located at an asymmetric center in Eu(III) complexes.²⁴

In addition, we have done some further studies. First, as shown in Figure 8(a,b), the fluorescence intensity of these peaks increased by increasing the Eu(III) concentration in the complexes. The relationship between fluorescence intensity and lanthanide content of STMAA complexes indicated that the complexes without displayed typical fluorescence concentration quenching behavior; this is different with the results of the literature.^{2,25}

Second, it was observed that the fluorescence intensity depends on the ST content as well. When the Eu(III) content is close, the fluorescence intensities parabolically increases by increasing the ST content [Fig. 7(c,d)]. The Eu(III) content of EuL_{2m} and EuL_{1n}

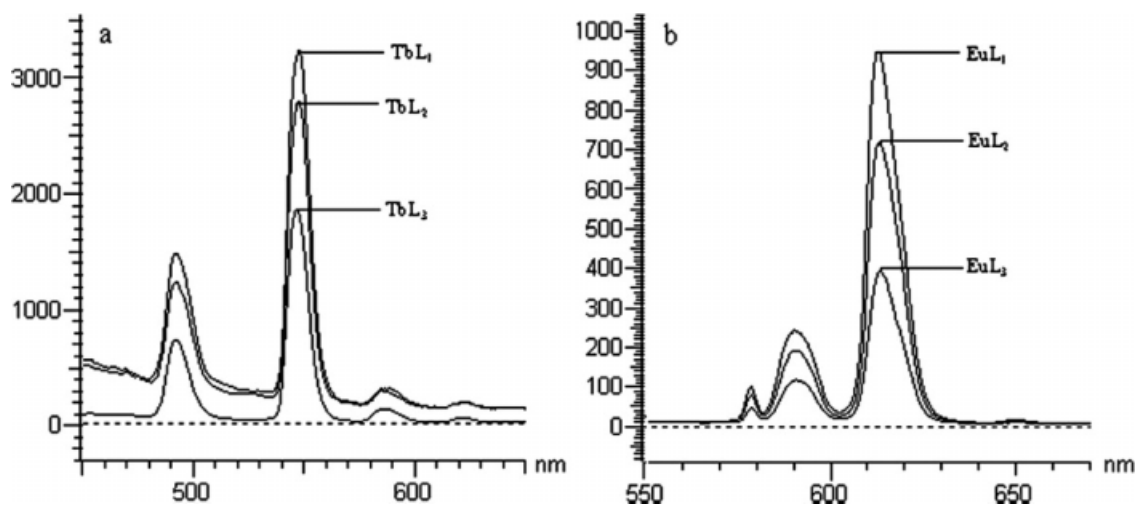


Figure 7 The fluorescence spectra of Tb(III) and Eu(III) complexes.

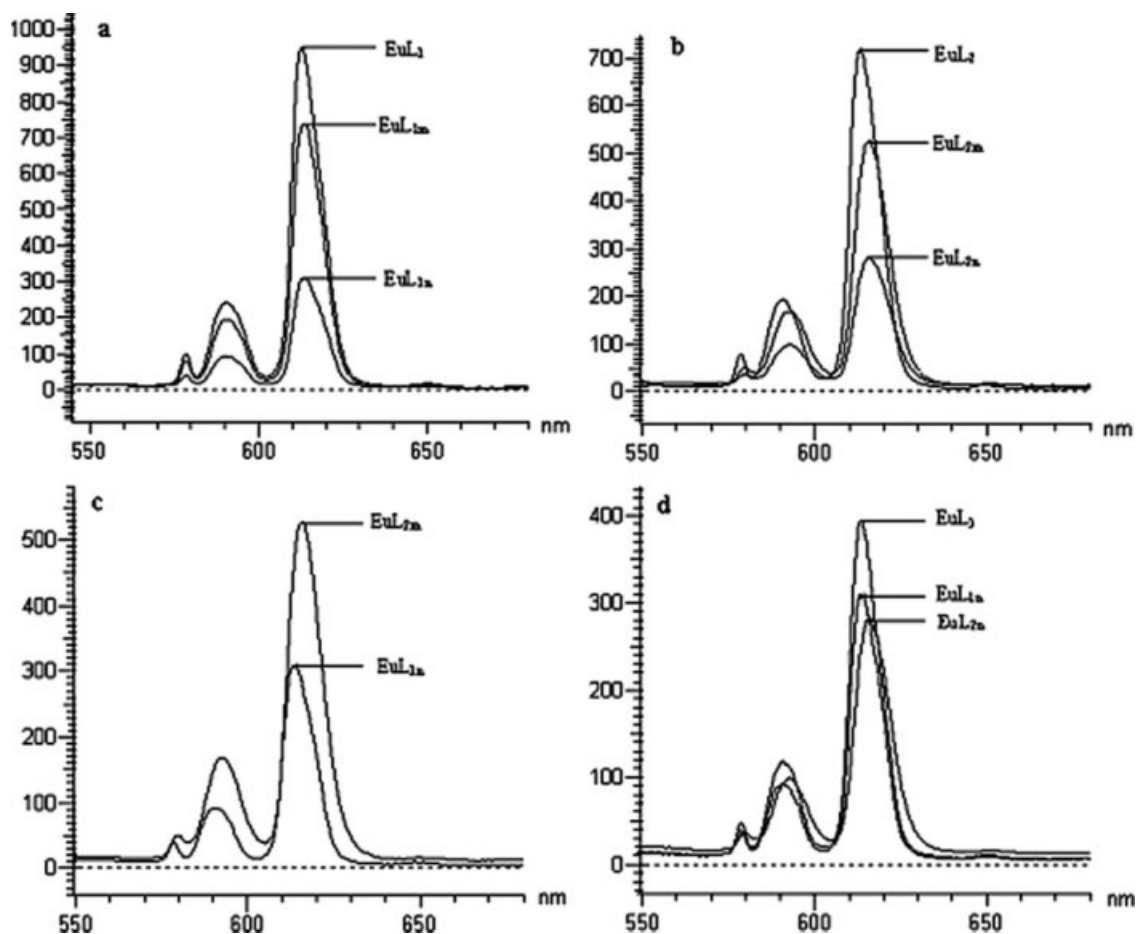


Figure 8 The comparative fluorescence spectra of different Eu(III) complexes.

is 19.96% and 19.47%, respectively, but the fluorescence intensity of EuL_{2m} is higher than EuL_{1n} in evidence. The Eu(III) content of EuL_{1n} , EuL_{2n} , and EuL_3 is 19.47, 15.96, and 10.92%, but the fluorescence intensity of EuL_3 is the strongest, and the fluorescence intensity of EuL_{1n} and EuL_{2n} is adjacent. This phenomenon may be resulted from the conjugative effect enhanced with the ST content, so more energy could transfer from copolymer to Ln(III) ions.

Third, the fluorescence intensity of Tb(III) complexes is stronger than the corresponding Eu(III) complexes, which means a more effective intramolecular energy transfer from STMAA chain to Tb(III) ions.

CONCLUSIONS

A series of functional copolymers of STMAA were synthesized by free radical polymerization, the macromolecular lanthanide complexes were prepared and well characterized. According to the results of composition analysis and IR spectra, we knew that the coordination ability of carboxylic groups to the Ln(III) ions is affected by the mole ratio of ST to MAA and pH value of the solution. The results of

DSC and TG-DTA analysis indicate that the copolymers and complexes have good thermal stability. According to the study on the fluorescence spectra, we could find that the fluorescence intensity depends on the content of ST and Ln(III) ions.

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