

Synthesis and Fluorescence Properties of Terbium–Polybis(benzylsulfinyl) Ethane Complexes

ZIQIANG LEI, YUNPU WANG

Department of Chemistry, Northwest Normal University, Lanzhou 730070, China

Received 11 March 1996; accepted 23 October 1996

ABSTRACT: A functional polymer polybis(benzylsulfinyl) ethane (PBBSE) and Tb³⁺–PBBSE–L (where L is low-molecular-weight organic ligands) ternary complexes were synthesized. The structures of the polymer complexes were investigated by elementary analysis and by comparison of infrared (IR) and fluorescence spectra between the polymer complexes and the corresponding low-molecular-weight complexes. Emission bands of *f* → *f* transition of Tb³⁺ in the polymer complexes were characterized. There are 4–7 emission peaks in the fluorescence spectra of the polymer complexes at excitation of ultraviolet light at room temperature. Of particular interest is the strong fluorescence intensity of the polymer ternary complex Tb–PBBSE–Phen. The fluorescence intensity of the complexes was increased in the following order: Tb–PBBSE (27.0) < Tb–PBBSE–TTA (82.3) < Tb–PBBSE–Phen (172.2). The maximum excitation energy and the apparent Stokes shift were increased just as this order in the Tb–PBBSE–low-molecular-weight ligand system complexes. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1575–1583, 1997

Key words: rare-earth-containing polymers; fluorescence; terbium complexes

INTRODUCTION

Metal complexes play an important role in the preparation of fluorescence active materials. Chelating compounds containing rare earth ions coordinating to β -diketone were widely studied.^{1–3} Certain lanthanide ions possess sharp emission lines in the visible and infrared (IR) regions. The emission coming from the hypersensitivity transition of the lanthanide ions in complexes makes the use of *f*–*f* fluorescence particularly attractive as a probe of lanthanide–ligand interaction and as fluorescence materials. But the *f*–*f* fluorescence is of limited utility because of the very weak emission in common complexes. Some of these emissions are too weak to be detected at room temperature due to the lack of efficiently energy transfer between ligands and lanthanide ions and short of sensitization of these ions in usual complexes. The possibil-

ity of transferring energy efficiently to these ions by way of strongly absorbing transitions characteristic of organic ligands has stimulated research interest of many workers to investigate lanthanide chelates as potential laser materials.^{4,5} Polymeric systems in which rare earth metal ions are directly bonded to the polymer have been investigated by Okamoto, Banks, and Ueba.^{6–8} The most widely studied of these polymer chelates has been those having β -diketone moiety as the ligand and europium (III) as the central ion. Polymers containing rare earth metal have interesting fluorescence characterizations. In a previous work, we reported the synthesis and fluorescence properties of rare earth metal ion–polymer ligand–low-molecular-weight ligand ternary complexes.^{9,10} The fluorescence intensity of polymer ternary complexes were many times stronger than that of the corresponding polymer binary complexes. The polymer ternary system complexes are very convenient to prepare by employing different kinds of low molecular weight ligands or by changing synthetic reaction conditions.

Correspondence to: Z. Lei.

© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/081575-09

In the present work, we report the synthesis and fluorescence characterization of a functional polymer polybis(benzylsulfinyl) ethane (PBBSE) as well as the Tb^{3+} -PBBSE-low-molecular-weight ligand complexes. Polymer disulfoxide appears to be an efficient energy transferring organic bidentate ligand. The polymer ternary complexes containing bisulfinyl as ligand and terbium ion as the central ion emit very strong fluorescence. The formation of polymer ternary complexes leads to a large enhancement of terbium ion luminescence, which is attributed to the sensitization of Tb^{3+} emission. The fluorescence intensity of Tb -PBBSE-Phen complex was six times stronger than that of the analogous polymer binary complex, even stronger than that of the europium- β -diketone complexes, such as Eu^{3+} -TTA complex. There are 4–7 emission peaks in the fluorescence spectra of the polymer complexes at room temperature, which correspond to the $f \rightarrow f$ transition of Tb^{3+} in the polymer complexes and may be very useful in analytical chemistry for the study of the characterization of $f \rightarrow f$ transition and for the monitoring of chemical change of the lanthanide ion in complexes, or may be used as a probe for analysis of sulfur-containing proteins.

EXPERIMENTAL

Materials

Terbium oxide was used as obtained from Johnson Matthey Chemicals Limited. All low-molecular-weight ligands were analytically pure.

Poly(benzylchloride styrene) (PBCS), purchased from Nankai University, (crosslink density 6%, chloride content 17.6 wt %) was ground to fine powder (200 mesh) before reaction.

High-melting bis(benzylsulfinyl) ethane (BBSE) was prepared by the method described in the literature [mp 181–183°C, ^1H NMR (60 MHz, CDCl_3), δ (ppm): 2.93 (m.4H), 8.29 (m.5H), and 4.10 (m.2H)].¹¹ IR and elementary analysis results were listed in Table I.

Bisethylene disulfhydrate ($\text{HSCH}_2\text{CH}_2\text{SH}$) was obtained as the intermediate product from the preparation of BBSE.

Polybis(benzylsulfinyl) Ethane

In an argon atmosphere, 7.4 g of potassium hydroxide (85% pure, 0.11 mmol) was dissolved in 25 mL of absolute ethanol. 5 g of ethylene disulfhydrate (0.05 mmol) was added to the solution dropwise with stirring, then 10 g of finely pow-

dered (200 mesh) poly(benzylchloride styrene) (PBCS, Cl 0.05 mmol) was added to the mixture in portions. After refluxed for 4 h, 6.5 g of benzylchloride (0.05 mmol) was added, and the reaction mixture was refluxed for 2 h. The product was washed with 5% KOH solution, deionized water, and ethanol, respectively; filtered under reduced pressure; and dried under vacuum at room temperature over phosphorus pentoxide for 48 h to afford polybis(benzylthio) ethane (PBBTE). 4 mL of nitric acid solution (concentrated nitric acid, 3 mL; water, 1 mL) was added dropwise to 25 mL of dry benzene containing 5 g of PBBTE at 10–15°C and stirred for 5 h; then the mixture was allowed to stand overnight at room temperature; filtered; washed thoroughly with 5% Na_2CO_3 solution, deionized water, ethanol, and chloroform; and dried under vacuum at room temperature over phosphorus pentoxide for 48 h to give light yellow PBBSE. IR and elementary analysis results were shown in Table I and Figure 1.

Tb^{3+} -PBBSE-Low-Molecular-Weight Ligand Ternary Complexes

A 7 mL solution of TbCl_3 (Tb^{3+} 0.4 mmol) in ethanol, PBBSE, and low-molecular-weight ligand (weighted according to the following molar ratio of Tb^{3+} : polymer functional group : low-molecular-weight ligand = 1 : 1 : 2) were added to 30 mL of mixed solvent of 25 mL of absolute ethanol and 5 mL of triethyl orthoformate. The mixture was stirred and refluxed for 7–15 h; allowed to stand overnight at room temperature; filtered under reduced pressure; washed with chloroform, absolute ethanol, and ether, respectively; and dried under vacuum at room temperature over phosphorus pentoxide for 48 h to afford light pink Tb^{3+} -PBBSE-Phen (phen = phenanthroline), Tb -PBBSE-TTA (TTA = thenoyltrifluoroacetone) and Tb -PBBSE-bipy (bipy = 2,2'-bipyridine). IR and elementary analysis results were shown in Tables I–II and Figures 1–2.

Tb^{3+} -PBBSE Binary Complexes

A solution of TbCl_3 (Tb^{3+} 0.3 mmol) in ethanol and 0.42 g of PBBSE (functional group 0.8 mmol) were added to 25 mL of ethanol containing 5 mL of triethyl orthoformate. The mixture was stirred and refluxed for 9 h, and filtered, washed, and dried in the same way as that for the preparation of Tb^{3+} -PBBSE-low-molecular-weight ternary complexes described above. IR and elementary analysis results were shown in Tables I–II and Figure 2.

Table I Element Analytical Results

Compound	C (%)	H (%)	N (%)	S (%)	Tb (%)	Mol Ratio of Tb/L
BBSE	62.83 (62.71)	5.96 (5.92)	—	—	—	—
PBBSE	66.24	5.80	—	12.60	—	—
Tb ³⁺ -PBBSE	—	—	—	—	12.60	—
Tb(BBSE)(Phen)Cl ₃ · $\frac{3}{2}$ H ₂ O	43.01 (43.17)	3.70 (3.75)	3.67 (3.60)	—	20.11 (20.40)	1.04
Tb ³⁺ -PBBSE-Phen	58.82	5.10	1.87	—	10.37	1.02
Tb-PBBSE-TTA	—	—	—	—	5.37	—

Calculated values in parentheses.

Tb(BBSE)(Phen)Cl₃· $\frac{3}{2}$ H₂O

Tb(BBSE)(Phen)Cl₃· $\frac{3}{2}$ H₂O was prepared according to the method described in the literature.¹² IR and elementary analysis results were listed in Table II and Figure 1.

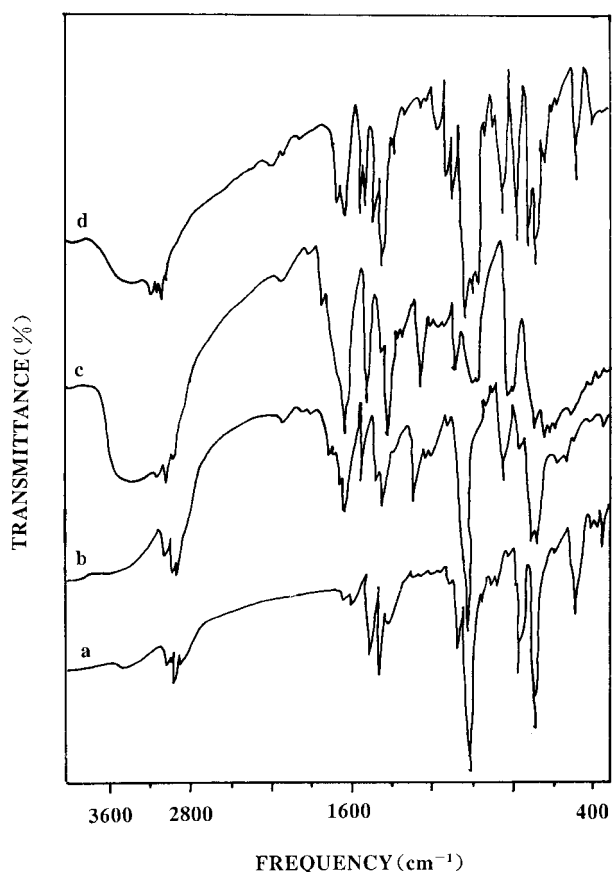
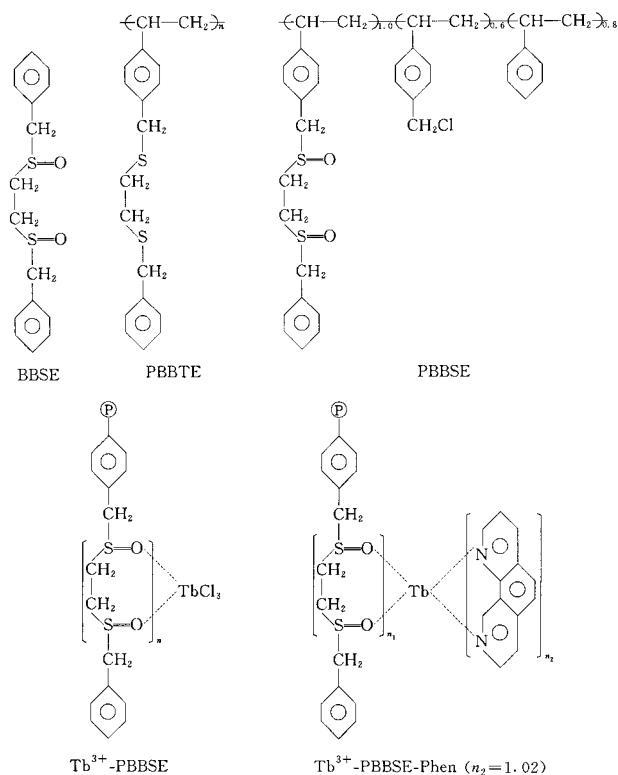


Figure 1 Infrared spectra of (a) BBSE, (b) PBBSE, (c) the Tb³⁺-PBBSE-Phen complex, and (d) Tb(BBSE)(Phen)Cl₃· $\frac{3}{2}$ H₂O.

Elementary Analysis of Polymer Complexes

C, H, and N content in the polymer complexes was determined by routine analysis using a Carlo-Erba 1106 model elementary analyzer. The amount of Tb in the polymer complexes was determined by ICP-AES analysis on an Australia LAB-TAM 8410 plasmascan. The complexes were decomposed using concentrated nitric acid.



Fluorescence Measurement

Fluorescence spectra measurements were carried out at room temperature using a Shimadzu RF-540 spectrofluorophotometer. Finely powdered (200 mesh) samples were prepared for the mea-

Table II IR Spectral Data of Ligand and Complexes

Compound	$\nu_{s=0}$ (cm^{-1}) ^a	$\nu_{s=0}$ (cm^{-1}) ^b	$\nu_{s=0}$ (cm^{-1}) ^c	$\Delta\nu_1$ (cm^{-1}) ($\nu_{s=0} - \nu_{s=0}$) ^{a,b}	$\Delta\nu_2$ (cm^{-1}) ($\nu_{s=0} - \nu_{s=0}$) ^{a,c}	$\nu_{c=0}$ (cm^{-1})
HTTA	—	—	—	—	—	1662, 1664
BBSE	1020	—	—	—	—	—
PBBSE	1019	—	—	—	—	—
Tb ³⁺ -PBBSE	1018	997	1034	-21	16	—
Tb(BBSE)(Phen)Cl ₃ · $\frac{3}{2}$ H ₂ O	—	992	—	-28	—	—
Tb ³⁺ -PBBSE-Phen	1018	992	1039	-26	21	—
Tb ³⁺ -PBBSE-TTA	1017	1001	1042	-16	25	1610

^a Uncoordinated sulfinyl stretching frequency.

^b Oxygen atom coordinated sulfinyl stretching frequency.

^c Sulfur atom coordinated sulfinyl stretching frequency.

surement. The results were shown in Tables III–IV and Figures 3–6.

RESULTS AND DISCUSSION

The IR Characterization and the Composition of the Polymer Complexes

In a previous work, the structures of the functional polymers and their Eu³⁺-containing ter-

nary complexes were investigated by elementary analysis and IR spectra.¹⁰ In the present work, the comparison of IR characterization of Tb³⁺-PBBSE-low-molecular-weight ligand ternary complexes with corresponding low-molecular-weight ternary complexes was made to indicate the structures of the polymer complexes. The results were list in Tables I–IV and Figures 2–3.

The structural similarity of the products Tb³⁺-PBBSE-Phen and Tb(BBSE)(Phen)Cl₃· $\frac{3}{2}$ H₂O was showed by the elementary analysis result and by comparison of the sulfinyl region in the IR spectra. The double bond in the sulfinyl group is consist of the σ bond and $O \rightarrow S p_x \rightarrow d_x$ back-donation bond. When the sulfinyl group coordinated to the Tb ion with oxygen atoms, the charge on the oxygen atom is decreased, and the $p_x \rightarrow d_x$ back-donation bond is weakened, sulfinyl stretching frequencies in the IR spectra of the complexes will consequently shift to a lower frequency region. When the sulfinyl group coordinated to the Tb ion with sulfur atoms, the $p_x \rightarrow d_x$ back-donation bond will be strengthened, and the sulfinyl stretching frequency will therefore shift to higher frequency region. The IR spectra of the polymer PBBSE and polymer complexes showed the characteristic absorption frequency of the free sulfinyl group at 1019 cm^{-1} , of the oxygen bonded sulfinyl group at 992–997 cm^{-1} , and the sulfur atom bonded sulfinyl group at 1032–1040 cm^{-1} (Fig. 2). The results indicate that there were free, oxygen bonded and sulfur bonded sulfinyl groups in the polymer complexes. The shift (16–27 cm^{-1}) assigned to the bonded sulfinyl group from 1019 cm^{-1} to low frequency in the IR spectra of the polymer complexes was particularly diagnostic of oxygen coordinate.

Due to the steric hindrance and the decrease of the freedom of the bond rotation of the crosslinked

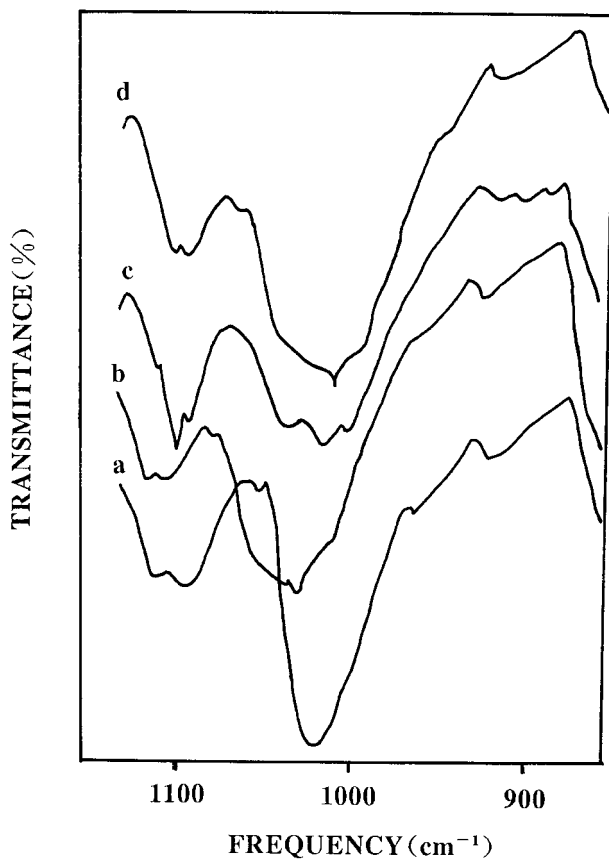


Figure 2 Infrared spectra of (a) PBBSE, (b) Tb³⁺-PBBSE-TTA, (c) Tb³⁺-PBBSE-Phen, and (d) Tb³⁺-PBBSE.

Table III Excitation, Emission Wavelength, and Fluorescence Intensity of the Complexes

Complex	E_x^{\max} (nm)	E_m^{\max} (nm)	Rel. I
Tb ³⁺ -PBBSE	358.5	546.8	27.0
Eu ³⁺ -PBMAS ^b	400.4	612.2	<0.1
Tb ³⁺ -PBBSE-TTA	357.0	547.4	82.3
Eu ³⁺ -PBMAS-TTA ^b	374.1	613.4	61.0
Eu ³⁺ -PBAAS-TTA ^b	369.9	613.0	42.0
Tb ³⁺ -PBBSE-Phen	334.3	547.4	172.2
Eu ³⁺ -PBMAS-Phen ^b	396.7	519.3	2.6
Tb(BBSE)(Phen)Cl ₃ · $\frac{3}{2}$ H ₂ O	354.8	548.1	423.6

Sensitivity low; slit ex/em = 10/10 (nm); ordinate scale $\times 1$; finely powdered samples at room temperature. From Wang and Lei.¹⁰

polymer complexes, the formation of multiple coordination bond between Tb³⁺ and the polymer sulfinyl group may be restricted. Compared with the corresponding low-molecular-weight ligand ternary complex (model compound), the composition of polymer ternary complexes is more complicated. The dominant composition of the polymer complexes Tb³⁺-PBBSE-Phen and Tb³⁺-PBBSE are shown above. The coordinated number of phenanthroline was determined by the N content in the complexes.

Fluorescence Characterization

The excitation, emission, and the fluorescence intensity of the polymer complexes are presented in Figures 3–6 and Tables III–IV. The fluorescent spectra of the polymer complexes show the terbium (III) ion $^5D_4 \rightarrow ^7F_J$ ($J = 1, 2, \dots, 6$) emission bands. The emission spectra of Tb³⁺-PBBSE and Tb³⁺-PBBSE-TTA complexes were obtained by exciting into the coordinated sulfinyl moiety absorption band ca. 358 nm. The spectrum of Tb³⁺-PBBSE-Phen complex was obtained either by excitation of coordinated phenanthroline absorption band ca. 343 nm or by exciting into the coordinated sulfinyl moiety absorption band ca. 358 nm. The sensitization of terbium (III) ion emission of the polymer complexes occurs by (1) radiative coordinated sulfinyl group or phenanthroline excitation, (2) nonradiative transfer of energy to the terbium (III) ion, and (3) emission of terbium (III) ion.^{13,14}

The fluorescence intensity is relevant to the structure, the stability of the polymer complexes, and the efficiency of energy transfer from the ligand triplet to the terbium (III) ion.

The strong fluorescence intensity of the Tb³⁺-PBBSE system complexes indicates that the bis-sulfinyl group is a efficient energy transferring

ligand in the polymer complexes. The fluorescence intensity of polysulfinyl-group-coordinated terbium complexes is even stronger than that of europium-TTA system complexes; for example, the fluorescence intensity of Tb³⁺-PBBSE-Phen complex is nine times stronger than that of Eu³⁺-Poly(benzylacetone styrene)-Phen complex and four times stronger than that of the Eu³⁺-poly(benzylacetone styrene)-TTA complex.¹⁰

The similarity of fluorescent spectra of the Tb³⁺-PBBSE-Phen complex and Tb(BBSE)(Phen)Cl₃· $\frac{3}{2}$ H₂O indicated that there are similar components in the two complexes. The $^5D_4 \rightarrow ^7F_3$, $^5D_4 \rightarrow ^7F_4$, $^5D_4 \rightarrow ^7F_5$, and $^5D_4 \rightarrow ^7F_6$ transition of the Tb³⁺ in the Tb³⁺-PBBSE-Phen complex give rise to the emission of light at the band of 621.9, 587.1, 547.4, and 492.4 nm, respectively. The maximum emission band at 547.4 nm is assigned to the $^5D_4 \rightarrow ^7F_5$ transition. Similarly, the corresponding transition of the Tb³⁺ in the model compound Tb(BBSE)(Phen)Cl₃· $\frac{3}{2}$ H₂O exhibits the fluorescence at the wavelength of 618.9, 589.4, 548.1, and 492.5 nm, respectively. The maximum emission band is at 548.1 nm, also assigned to the $^5D_4 \rightarrow ^7F_5$ transition. There are five emission bands in the fluorescence spectrum of the Tb³⁺-PBBSE-Phen complex. The emission intensity is in the order of 172.2 (547.4 nm, $^5D_4 \rightarrow ^7F_5$) > 107.1 (492.4 nm, $^5D_4 \rightarrow ^7F_6$) > 13.8 (587.1 nm, $^5D_4 \rightarrow ^7F_4$) > 2.1 (621.9 nm, $^5D_4 \rightarrow ^7F_3$) > 2.0 (414.0 nm). The model compound Tb(BBSE)(Phen)Cl₃· $\frac{3}{2}$ H₂O also has five emission bands. The intensity of these emissions is in the order of 423.6 (548.1 nm, $^5D_4 \rightarrow ^7F_5$) > 136.2 (492.5 nm, $^5D_4 \rightarrow ^7F_6$) > 11.7 (589.4 nm, $^5D_4 \rightarrow ^7F_4$) > 4.2 (618.6 nm, $^5D_4 \rightarrow ^7F_3$) > 0.6 (467.4 nm). The differentiation among fluorescence spectra of the two complexes reveals the discrepancy of the structures in the two complexes. These spectroscopic properties

Table IV Emission Band and the Corresponding $f \rightarrow f$ Transition of Tb^{3+} in Polymer Complexes

Sample	E_x^{max} (nm)	Emission (nm) and ${}^5D_4 \rightarrow {}^7F_j$ Transition ($j = 1, 2, 3, 4, 5, 6, \dots$)								
					${}^5D_4 \rightarrow {}^7F_6$	${}^5D_4 \rightarrow {}^7F_5$	${}^5D_4 \rightarrow {}^7F_4$	${}^5D_4 \rightarrow {}^7F_3$	${}^5D_4 \rightarrow {}^7F_2$	${}^5D_4 \rightarrow {}^7F_1$
$\text{Tb}^{3+13,14}$	—	—	—	—	492.3	547.0	586.4	616.3	647.4	658.4
Tb^{3+} -PBBSE	385.5	414.0	442.0	—	492.3	546.8	586.4	616.3	647.4	658.4
$\text{Tb}(\text{BBSE})_4\text{Cl}_3 \cdot 3\text{H}_2\text{O}$	358.6	—	—	467.9	492.6	548.1	589.5	619.0	—	—
Tb^{3+} -PBBSE-Phen	334.3	414.0	—	—	492.4	547.4	587.1	621.9	—	—
$\text{Tb}(\text{BBSE})(\text{Phen})\text{Cl}_3 \cdot \frac{3}{2}\text{H}_2\text{O}$	354.8	—	—	467.4	492.5	548.1	589.4	618.6	—	—
Tb^{3+} -PBBSE-TTA	357.0	—	—	—	492.4	547.4	585.9	619.5	—	—

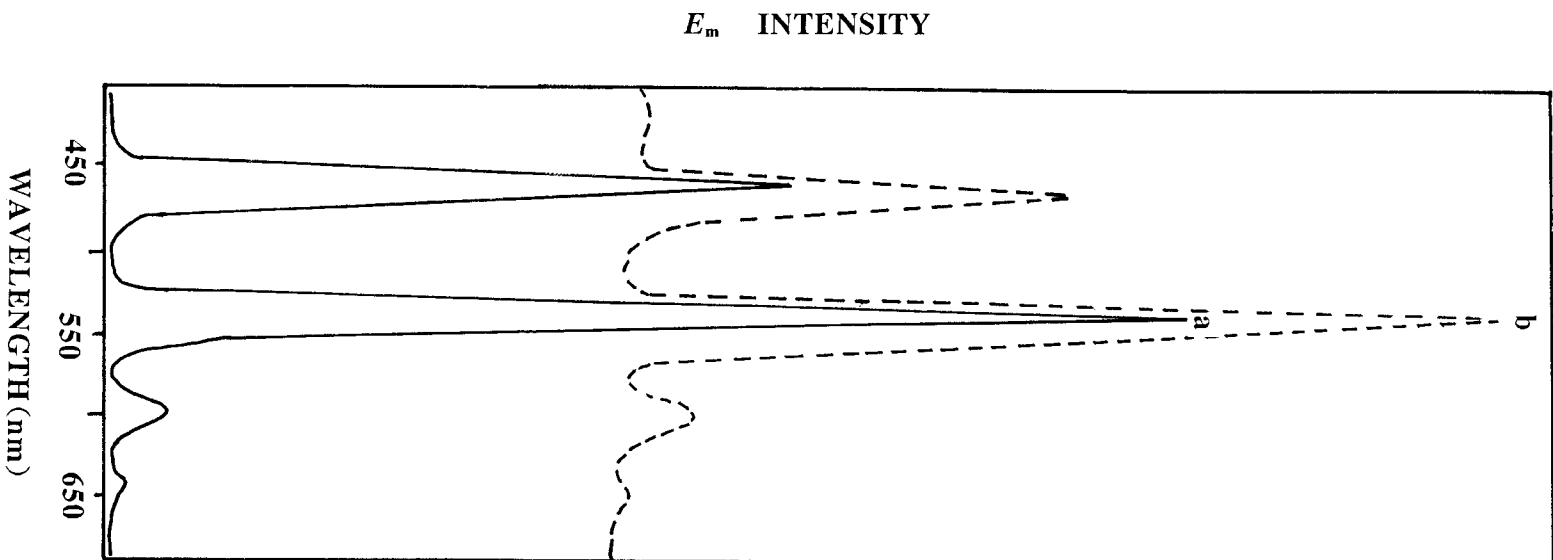


Figure 3 Emission spectra of (a) the model compound $\text{Tb}(\text{BBSE})(\text{Phen})\text{Cl}_3 \cdot \frac{3}{2}\text{H}_2\text{O}$ ($\lambda_{\text{ex}} = 354.8$ nm) and (b) the Tb^{3+} -PBBSE-Phen ($\lambda_{\text{ex}} = 334.3$ nm) complex.

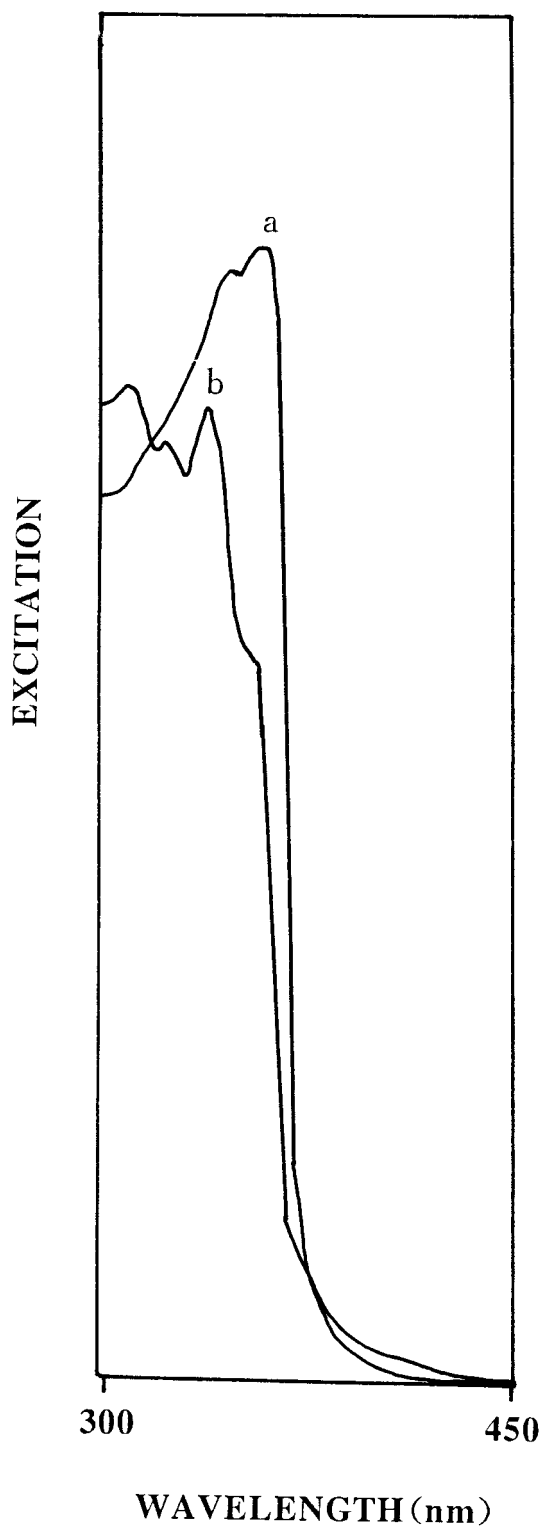


Figure 4 Excitation spectra of (a) the model compound $\text{Tb}(\text{BBSE})(\text{Phen})\text{Cl}_3 \cdot \frac{3}{2}\text{H}_2\text{O}$ ($\lambda_{\text{em}} = 548.1 \text{ nm}$) and (b) the Tb^{3+} -PBBSE-Phen complex ($\lambda_{\text{em}} = 547.4 \text{ nm}$).

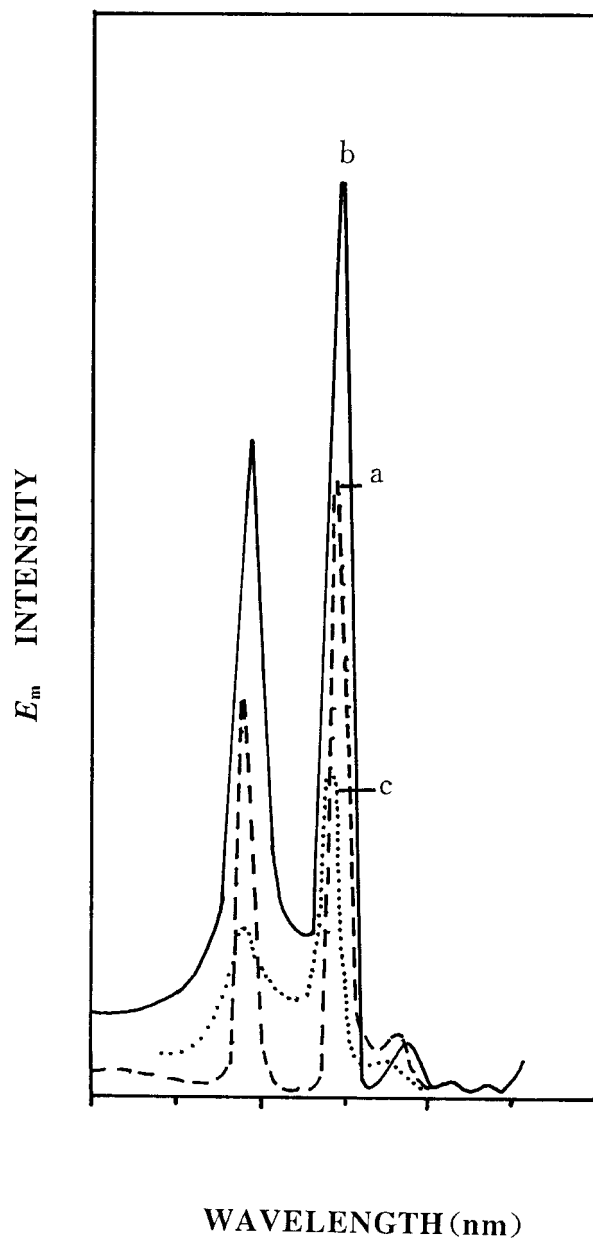


Figure 5 Emission spectra of (a) Tb^{3+} -PBBSE ($\lambda_{\text{ex}} = 358.5 \text{ nm}$; slit ex/em = 10/10 nm), (b) Tb^{3+} -PBBSE-TTA ($\lambda_{\text{ex}} = 357.0 \text{ nm}$; slit ex/em = 10/10 nm), and (c) Tb^{3+} -PBBSE-Phen ($\lambda_{\text{ex}} = 334.3 \text{ nm}$; slit ex/em = 10/5 nm).

may be used as probe to the structures and the symmetries of the complexes and some proteins.

Compared with corresponding Tb^{3+} -PBBSE polymer binary complex, the Tb^{3+} -PBBSE second ligand polymer ternary complexes are different in the characterization of the excitation bands, the emission peaks, and the fluorescence intensity. The excitation wavelength of the Tb^{3+} -PBBSE, Tb^{3+} -PBBSE-Phen, and Tb^{3+} -PBBSE-

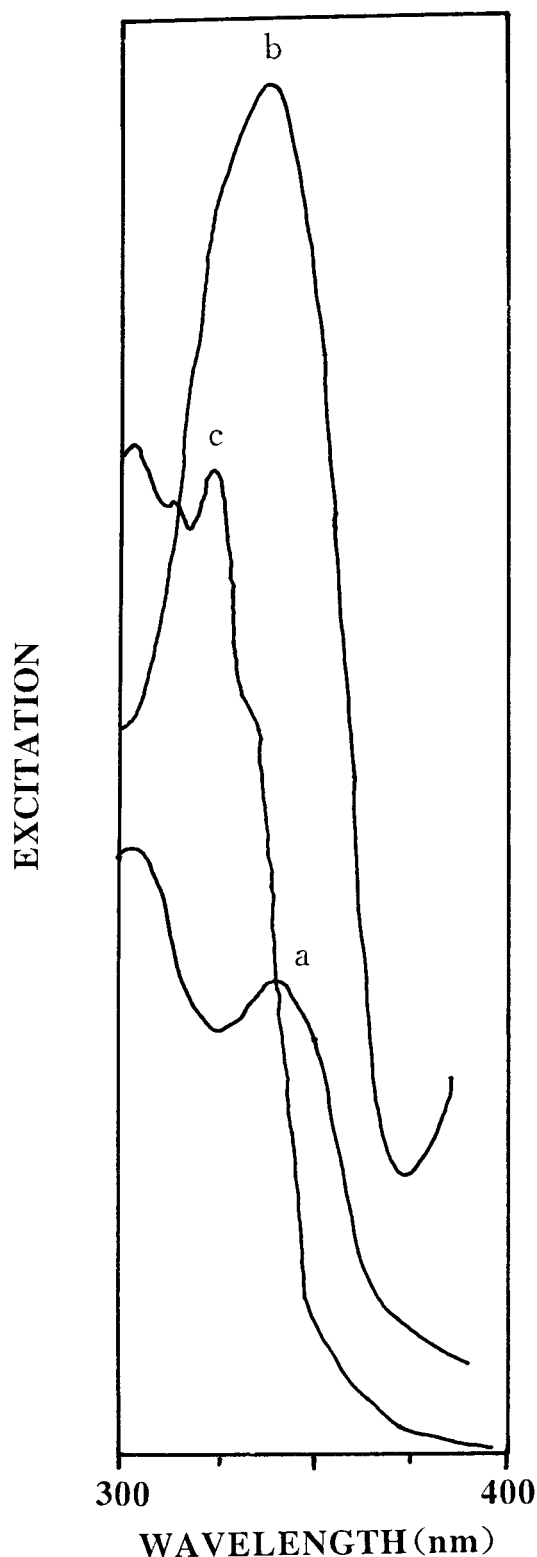


Figure 6 Excitation spectra of (a) Tb^{3+} -PBBSE ($\lambda_{\text{em}} = 546.8 \text{ nm}$), (b) Tb^{3+} -PBBSE-TTA ($\lambda_{\text{em}} = 547.4 \text{ nm}$), and (c) Tb^{3+} -PBBSE-Phen ($\lambda_{\text{em}} = 547.4 \text{ nm}$).

TTA complexes were 358.5, 343.3, and 357.0 nm, respectively, shows that there are different excited ligands in the different complexes. The excited ligand of the Tb^{3+} -PBBSE and Tb^{3+} -PBBSE-TTA complexes may be the coordinated bisulfanyl group, and that of the Tb^{3+} -PBBSE-Phen complex may be the coordinated phenanthroline group. The emission bands of the Tb^{3+} -PBBSE, Tb^{3+} -PBBSE-Phen, and Tb^{3+} -PBBSE-TTA complexes of 8, 5, and 4, respectively, present that there is a discrepancy in the coordination numbers and in the symmetries of the three polymer complexes. The fluorescence intensity of the Tb^{3+} -PBBSE-Phen ternary complex is 6.4 times stronger than that of the Tb^{3+} -PBBSE binary complex indicates that the rigid structure, and the stability of the two complexes are different.

CONCLUSIONS

Polybis(benzylsulfanyl) and its binary and ternary complexes with terbium (III) ion were synthesized. The IR and fluorescence measurements performed in this study were designed to investigate the formation and structure of the functional polymer PBBSE and the complexes. Comparison of the spectroscopic characterization between the Tb^{3+} -PBBSE binary complex and the Tb^{3+} -PBBSE second ligand ternary complex, as well as between the Tb^{3+} -PBBSE-Phen ternary complex and the model compound $\text{Tb}(\text{BBSE})(\text{Phen})\cdot\frac{3}{2}\text{H}_2\text{O}$ was made to characterize the coordination properties. The formation of polymer ternary complexes leads to a large enhancement of terbium (III) ion luminescence. This enhancement is attributed to the sensitization of terbium (III) ion emission. The fluorescence intensity of the Tb^{3+} -PBBSE-Phen ternary complex is 6.4 times stronger than that of the corresponding Tb^{3+} -PBBSE binary complex. The fluorescence intensity of terbium (III) ion-polybissulfanyl complexes even stronger than that of the strong luminescent europium (III) ion- β -diketone complexes.

REFERENCES

1. H. Samelson, A. Lempicki, V. A. Brophy, and C. Brecher, *J. Chem. Phys.*, **40**, 2547 (1964).
2. G. A. Crosby, R. E. Whan, and R. M. Alire, *J. Chem. Phys.*, **34**, 743 (1961).
3. E. P. Riedel and R. G. Charles, *J. Chem. Phys.*, **45**, 1908 (1966).
4. E. H. Huffman, *Nature*, **200**, 158 (1963).

5. E. J. Schimitscheck, *Appl. Phys. Lett.*, **3**, 1107 (1963).
6. E. Bank, Y. Okamoto, and Y. Ueba, *J. Appl. Polym. Sci.*, **25**, 359 (1980).
7. Y. Ueba, E. Bank, and Y. Okamoto, *J. Appl. Polym. Sci.*, **25**, 2007 (1980).
8. Y. Okamoto, *J. Macromol. Sci., Chem.*, **A24**, 455 (1987).
9. Z. Q. Lei and Y. P. Wang, *Chinese Chem. Lett.*, **2**, 881 (1991).
10. Y. P. Wang and Z. Q. Lei, *J. Appl. Polym. Sci.*, **45**, 1641 (1992).
11. X. P. Shao, M. D. Gui, and J. T. Chen, *Chem. Reagent (Chinese)*, **5**, 39 (1983).
12. R. H. Zhang and Q. S. Xue, *Chem. J. Chinese University (Chinese)*, **8**, 204 (1987).
13. S. Salama and F. S. Richardson, *J. Phys. Chem.*, **84**, 512 (1980).
14. S. Salama and F. S. Richardson, *Inorg. Chem.*, **19**, 635 (1980).