

Synthesis and Fluorescence Properties of Rare Earth Metal Ion–Polymer Ligand–Low Molecular Weight Ligand Ternary Complexes

YUNPU WANG, ZIQIANG LEI,* HANYU FENG, JIUNTANG BAO, and YAOBIN WANG

Department of Chemistry, Northwest Normal University, Lanzhou (730070), People's Republic of China

SYNOPSIS

Eu³⁺-containing polymer ternary complexes were synthesized using different kinds of functional polymers such as poly(benzylmalonic acid styrene) (PBMAS), poly(benzylacetone styrene) (PBAAS), and poly(benzyl-azo-*o*-hydroxybenzoic acid styrene) (PBAHBAS) as polymer ligands. The structures of the complexes were investigated by elemental analysis and IR spectroscopy. The fluorescence intensity of Eu³⁺-polymer-TTA (2-thenoyltrifluoroacetone ion) complexes was decreased in the order PBMAS(61) > PBAAS(42) > PBAHBAS(32). In system of Eu³⁺-PBMAS-low molecular weight ligand, the emission spectrum shape, the fluorescence intensity, and the wavelength of the maximum emission peak were changed when the low molecular weight ligand was varied. The fluorescence intensity of the Eu³⁺-PBMAS-TTA ternary complex was 610 times stronger than that of the Eu³⁺-PBMAS binary complex and 160 times stronger than that of Eu³⁺-PBMAS-oxine complex. The fluorescence intensity of the Eu³⁺-PBAAS-TTA complex was enhanced greatly when the proper mol ratio of HTTA/Eu³⁺ and pH in the reaction were chosen.

INTRODUCTION

There is great interest in the preparation of rare earth (RE) metal-containing polymers and this interest is stimulated by the potentially important use of these functional polymers in fluorescence and laser systems.^{1–3} Recently, we have synthesized polymeric systems in which RE metal Eu is directly bonded to the polymer chain and second ligands (low molecular weight ligands) are coordinated to Eu. There has been little study on these polymer ternary complexes. Because many low molecular ligands are at hand and mild reaction conditions are easy to adjust, it is very convenient to obtain polymer complexes that possess useful fluorescence properties or possible laser application by employing different kinds of low molecular weight ligands or by changing the synthesis reaction conditions such as pH, solvent, and ratio of reactants.

EXPERIMENTAL

Materials

Eu₂O₃ (99.99 wt %) was purchased from the Shanghai Yao Long chemical factory. All low molecular weight materials were analytically pure.

Solution of EuCl₃ in Ethanol

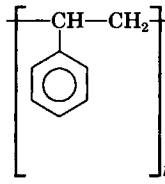
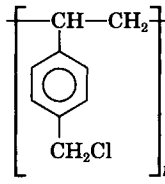
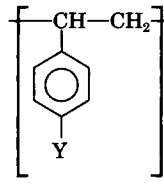
Eu₂O₃ (1.00 g) was dissolved in 7 mL concentrated hydrochloric acid and evaporated to dryness, then ethanol was added to the crystal. The concentration of the solution of EuCl₃ in ethanol was determined by EDTA titration.

Function Polymer

Poly (benzylchloride styrene) (PBCS) (Nankai University, cross-link density 6%, Cl content 17.6 wt %) was ground to fine powder (200 mesh) before reaction. Poly (benzylmalonic acid styrene) (PBMAS), poly (benzylacetone styrene) (PBAAS),

* To whom correspondence should be addressed.

Table I. Functional Section in the Polymer

Polymer	Y	n_1	n_2	n_3	Analytical Approach
PBMAS		0.90	0.80	1.00	Na 9.6 wt % (ICP)
PBAAS		8.00	15.0	1.00	IR
PBAHBAS		0.82	0.64	1.00	IR N 6.02 wt %
PBCS	$-\text{CH}_2\text{Cl}$	1.00	2.00	0	Cl 17.6 wt %

and poly(benzyl-azo-*o*-hydroxybenzoic acid styrene) (PBAHBAS) were prepared from PBCS by the method described in the literature.⁴⁻⁶ The functional group was identified by measuring IR spectra and analyzing the relevant elements in the polymer. The results are shown in Table I.

Eu³⁺-Polymer-Second Ligand Ternary Complexes

The typical preparation of the Eu³⁺-polymer-second ligand ternary complexes was as follows: A 7 mL solution of EuCl₃ (Eu³⁺ 0.4 mmol) in ethanol, polymer ligand, and second ligand (weighed according to the mol ratio of Eu³⁺ : polymer functional group : second ligand = 2 : 1 : 3) were added to a 25 mL Florence flask containing 50 mL ethanol. The pH of the solution was adjusted to neutrality (pH ~ 7) by dripping an ethanol solution of sodium hydroxide. The mixture was stirred with a magnetic stirring bar and refluxed for 7-9 h. The product was filtered, washed with ethanol, and then dried under vacuum at room temperature. The mol ratio of the Eu³⁺/second ligand in the complexes were determined by ICP and routine analysis. The results are listed in Table II.

Determination of Eu, P, N, and S in Polymer Complexes

The amount of Eu in polymer complexes was determined by ICP-AES analysis on an Australia

LABTAM 8410 plasmascan. The complexes were decomposed using concentrated nitric acid, and phosphorus-containing complexes were treated with concentrated sulfuric acid-nitric acid to change phosphorus into phosphate and then analyzed as ammonium phosphomolybdate deposit. N and S content in the complexes was determined by routine analysis using a Carlo-Erba 1106 model elementary analyzer.

Fluorescence Measurement

Fluorescence spectra measurements were carried out at room temperature using a Shimadzu RF-540 spectrofluorophotometer. Fine powder samples were prepared for the measurement.

Table II The Mol Ratio of Eu³⁺/Second Ligand of the Complexes

Complex	Eu Content (wt %)	Mol Ratio of Eu/Second Ligand
Eu ³⁺ -PBAHBAS-TTA	6.3	1/2.3
Eu ³⁺ -PBAAS-TTA	0.5	1/2.4
Eu ³⁺ -PBMAS-TTA	9.3	1/2.7
Eu ³⁺ -PBMAS-Pph ₃	6.7	1/0.4
Eu ³⁺ -PBMAS-Phen	7.2	1/1.2
Eu ³⁺ -PBMAS-oxin	7.7	1/0.2

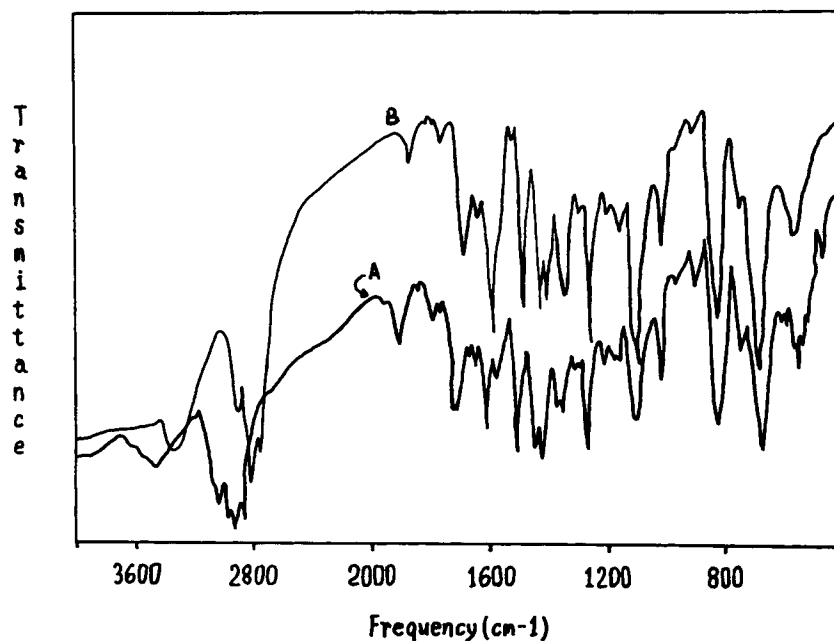


Figure 1 Infrared spectra of (B) Eu^{3+} -PBAAS-TTA complex and (A) PBAAS.

RESULTS AND DISCUSSION

The Structure of the Eu^{3+} -Polymer-Second Ligand Complexes

The structure of the functional polymers and their Eu^{3+} -containing ternary complexes were investigated by analyzing the elements and measuring the IR spectra. The results are shown in Table I and II and Figures 1 and 2. The ratio of the Eu^{3+} /second ligand (Table II) shows that there were Eu^{3+} -polymer-binary complexes and Eu^{3+} -polymer-second ligand ternary complexes attached to the polymer chain with a different coordination number in the ternary system. When the functional organic groups were incorporated into the crossed polystyrene chain, the formation of multiple coordination bonding between Eu^{3+} and the polymer may be restricted by the increasing steric hindrance and the decrease of the freedom of the bond rotation.^{1,7-8} In the ternary systems, the multiple coordination number of Eu^{3+} -polymer may be further restricted by the competing reaction between Eu^{3+} -polymer and Eu^{3+} -second ligand. The formation of the Eu^{3+} -polymer-second ligand ternary complexes will be efficient only when Eu^{3+} -polymer and Eu^{3+} -second ligand binary complexes possess the same or similar geometric configuration. The stability of the ternary complexes depend on the bond energy of the Eu^{3+} -polymer and Eu^{3+} -second ligand. The composition

of the ternary complexes are relevant to the relative concentration of the polymer ligand and second ligand in the reaction.

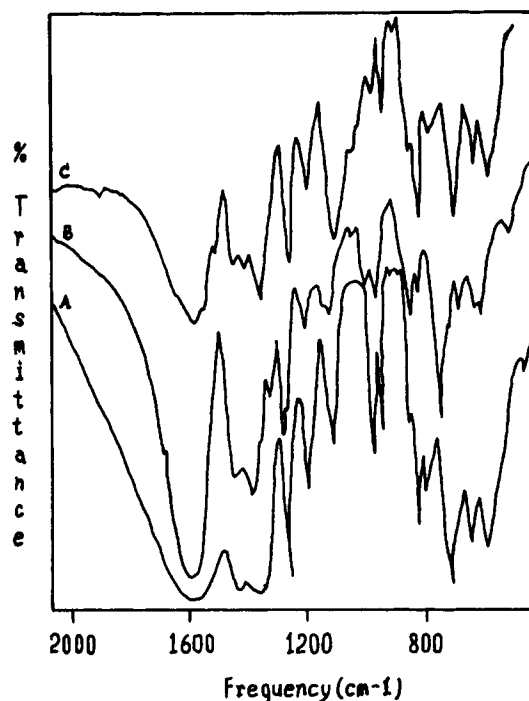
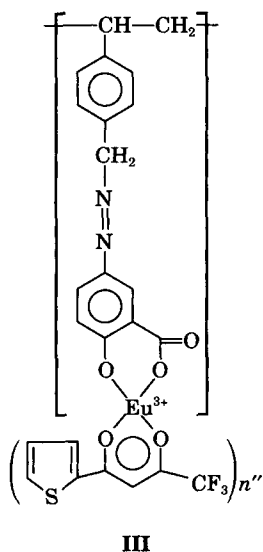
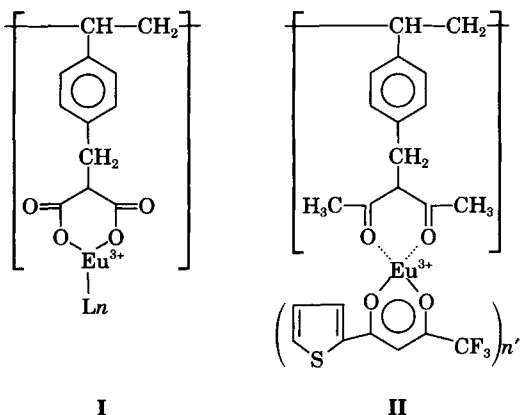


Figure 2 Infrared spectra of (A) Eu^{3+} -PBMA-S-Pph₃, (B) Eu^{3+} -PBMA-S-TTA, and (C) Eu^{3+} -PBMA-S complexes.

The dominant composition of the ternary complexes, I, II, and III, are shown below:



L	n	Eu ³⁺ /L
Pph ₃	1	0.4
Oxine	1	0.2
Phen	1	1.3
TTA	3	2.7

The IR spectra of II [Fig. 1(B)] shows that there is middle intensity absorption at 1717 cm⁻¹ due to the uncoordinated carbonyl group. The strong absorption band between 1550 and 1610 cm⁻¹ corresponds to the overlap of the coordinated carbonyl stretching frequencies of TTA and PBAAS [Fig. 1(B)] or that of carbonyl and carboxylate stretching frequencies of TTA and PBMA [Fig. 2(B)].

Fluorescence Properties

The excitation and emission, as well as the fluorescence intensity, were measured on dried and finely powdered samples at room temperature. The results are shown in Tables III and IV and Figures 3-10. The scatter of data was 5%.³ The bright brown-red fluorescence light of Eu³⁺ at around 600 nm was assigned to the transition from the ⁵D₀ level to the levels of ⁷F_j (j = 1,2). The emission peak at 589.3-592.6 nm (Figs. 3-5 and Table III) corresponds to the ⁵D₀-⁷F₁ transition of Eu³⁺ (magnetic dipole transition, insensitive to the crystalline field). The emission peak at 611.5-613.7 nm (Figs. 3-5 and Table III) corresponds to the ⁵D₀-⁷F₂ transition of Eu³⁺ (electric dipole transition, sensitive to the crystalline field).⁹⁻¹¹

In Eu³⁺-containing complexes, the coordinated ligands absorbed a photon and changed to the ex-

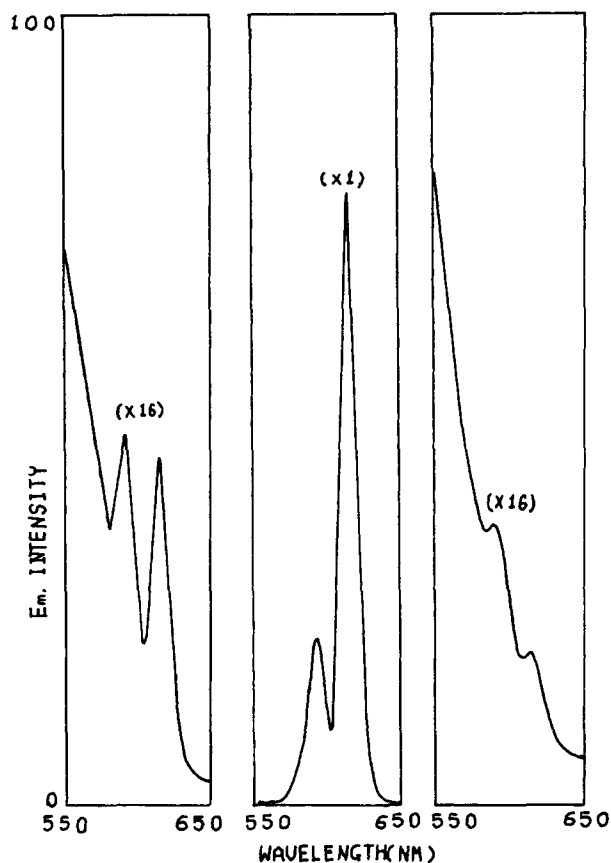


Figure 3 Emission spectrum of Eu³⁺-PBMA-Phen complex, λ_{ex} = 396.7 nm.

Figure 4 Emission spectrum of Eu³⁺-PBMA-TTA complex, λ_{ex} = 374.1 nm.

Figure 5 Emission spectrum of Eu³⁺-PBMA-Pph₃ complex, λ_{ex} = 397.3 nm.

Table III Fluorescence Intensity of Eu^{3+} -Polymer-TTA Complexes with Different Kinds of Polymer Ligands^a

Complex	Excitation (nm)	Emission (nm)	Rel. I	Eu (wt %)
Eu^{3+} -PBAHBAS-TTA	373.5	613.7	32	6.3
		592.4	6.8	
Eu^{3+} -PBAAS-TTA	369.9	613.0	42	0.5
		592.4	9.0	
Eu^{3+} -PBMA-S-TTA	374.1	613.4	61	9.3
		592.6	17	

^a Sensitivity low; slit ex/em = 10/10 (nm); ordinate scale $\times 1$; fine powder sample at room temperature.

cited state. This excited ligand nonradiatively transferred to a triplet state and then excited the Eu^{3+} by transferring the energy to the europium ion.¹²⁻¹⁴ The rigid structure, stability, and efficiency of energy transfer from the ligand triplet to the europium ion of the ternary complexes varied with the change of polymer ligand, low molecular weight ligand, and other factors such as reaction pH and mol ratio of the reactants. These variations result in the different fluorescence properties.

Binary polymer complexes were different from the corresponding ternary polymer complexes in both fluorescence intensity and emission wavelength. The Eu^{3+} -PBMA-S-TTA ternary complexes emitted strong light while the Eu^{3+} -PBMA-S binary complexes emitted very weak light. With different kinds of second ligands, the fluorescence intensity of Eu^{3+} -PBMA-S-second ligand ternary complexes was enhanced 4-610 times compared to that of the corresponding Eu^{3+} -PBMA-S binary complex (Table IV). The fluorescence intensity of the Eu^{3+} -polymer-TTA system complexes was changed with

the variation of the polymer ligands. It is decreased in the following order: PBMA-S (61) > PBAAS (42) > PBAHBAS (32) (Table III).

Table IV Fluorescence Properties of Eu^{3+} -PBMA-S-Second Ligand Complexes^a

Complex	Excitation (nm)	Emission (nm)	Rel. I
Eu^{3+} -PBMA-S	400.4	612.2	<0.1
Eu^{3+} -PBMA-S-oxin	400.1	597.6	0.4
		468.8	611.5
Eu^{3+} -PBMA-S-Pph ₃	397.3	589.3	1.9
		612.2	1.1
Eu^{3+} -PBMA-S-Phen	396.7	591.3	2.6
		613.7	2.4
Eu^{3+} -PBMA-S-TTA	374.1	592.6	17.0
		613.4	61.0

^a See footnote to Table III.

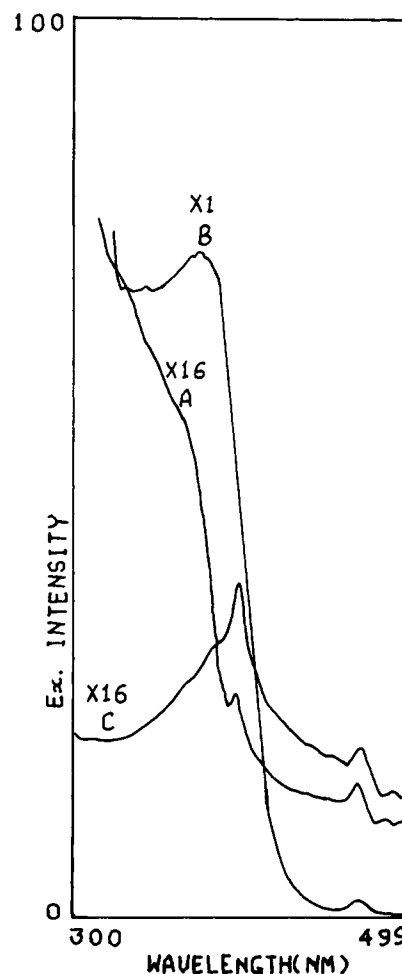


Figure 6 Excitation spectra of Eu^{3+} -PBMA-S-Phen (A, $\lambda_{em} = 591.3$ nm), Eu^{3+} -PBMA-S-TTA (B, $\lambda_{em} = 613.4$ nm), and Eu^{3+} -PBMA-S-Pph₃ (C, $\lambda_{em} = 589.3$ nm) complexes.

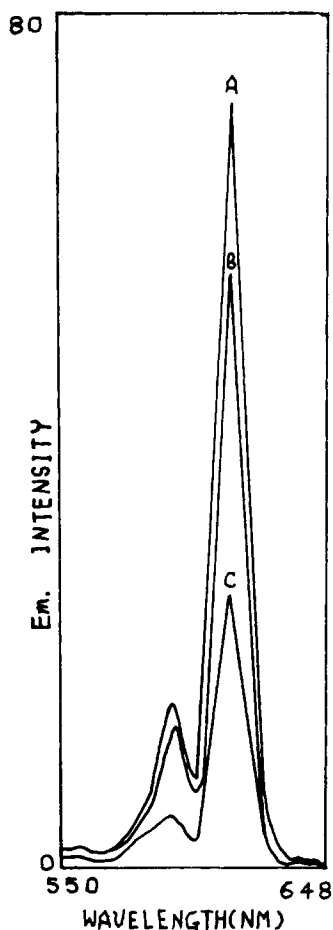


Figure 7 Emission spectra of Eu^{3+} -PBAAS-TTA complex with different pH in synthesis reaction (A, pH ~ 7 , $\lambda_{\text{ex}} = 369.9$ nm; B, pH ~ 6 , $\lambda_{\text{ex}} = 368.6$ nm; C, pH ~ 4 , $\lambda_{\text{ex}} = 354.5$ nm).

The relationship between fluorescence intensity of Eu^{3+} -PBAAS-TTA ternary complexes and the mol ratio of HTTA/ Eu^{3+} in the reaction was investigated. The results are shown in Figure 9. The fluorescence emission intensity of the Eu^{3+} -PBAAS-TTA complex reached maximum intensity when the mol ratio of HTTA/ Eu^{3+} in the reaction approached 5. The fluorescence intensity was increased with the increase of mol ratio of HTTA/ Eu^{3+} before this ratio approached 5 and decreased with the increase of that ratio after it reached 5. This phenomenon reveals that the fluorescence intensity is enhanced when the coordination number increased. In the reaction process, there is a tendency for Eu^{3+} to be coordinated with as many second ligands (HTTA) as possible. However, when the second ligand (HTTA) concentration or the mol ratio of HTTA/ Eu^{3+} in the reaction mixture is more

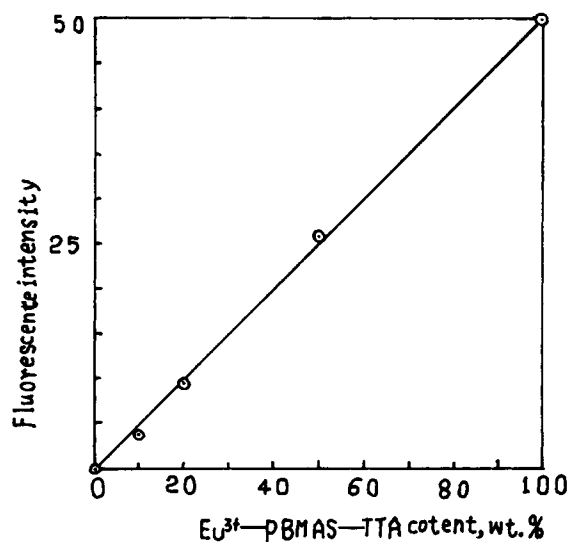


Figure 8 Fluorescence emission intensity vs. Eu^{3+} -PBMAS-TTA complex content in Eu^{3+} -PBMAS-TTA complex/PBMAS mixture. Sensitivity low; slit ex/em = 10/10 (nm); ordinate scale $\times 1$; $\lambda_{\text{ex}} = 370$ nm.

than what is needed for Eu^{3+} to be coordinated with, the excess HTTA will form soluble $\text{Eu}^{3+}(\text{TTA})_n$ ($n = 1-4$) and low molecular weight complexes and

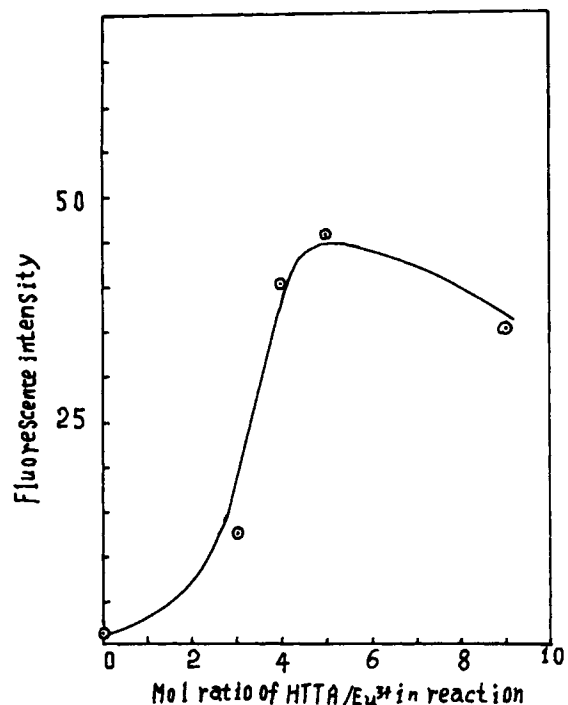


Figure 9 Relationship between fluorescence emission intensity of Eu^{3+} -PBAAS-TTA complex and mol ratio of HTTA/ Eu^{3+} in reaction. Sensitivity low; slit ex/em = 10/10 (nm); ordinate scale $\times 1$; $\lambda_{\text{ex}} = 370$ nm.

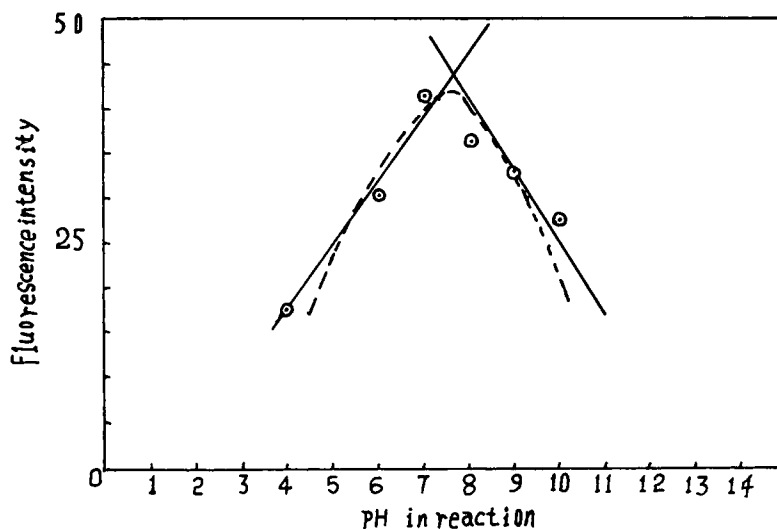
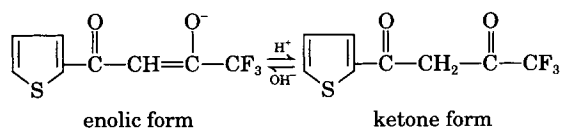


Figure 10 Relationship between fluorescence emission intensity of Eu^{3+} -PBMAAS-TTA complex and synthesis reaction pH. Sensitivity low; slit ex/em = 10/10 (nm); ordinate scale $\times 1$; $\lambda_{\text{ex}} = 370$ nm.

reduce the luminous portion in the polymer, hence, decreasing the fluorescence intensity of the Eu^{3+} -PBAAS-TTA ternary complex.

Figure 10 shows that fluorescence intensity of the Eu^{3+} -PBAAS-TTA system complexes changed with the different pH in the reaction. The fluorescence intensity was first increased with the change of the PH in the reaction (from pH ~ 4 to ~ 7.5) and then decreased with the increase of the pH in the reaction (from pH ~ 7.5 to ~ 14). This can be illuminated by the following:

When the pH in the reaction changed from 4 to 7.5, the balanced equation of HTTA was shifted to the enolic form (enolic ion) and this enolic form ion coordinated with Eu^{3+} more effectively:



The Eu—O bond distance in the Eu^{3+} -enolic form ion complexes is shorter than that in the Eu^{3+} -ketone form complexes. The shorter Eu—O bond distance in the complexes has the advantage over the longer Eu—O bond distance in transferring energy from the oxygen atom to the europium ion; as a result, the fluorescence intensity will be stronger in the Eu^{3+} -enolic form ion complexes than that in the Eu^{3+} -ketone form complexes. However, when the pH in the reaction changed from 7.5 to 14, the

formation of the $\text{Eu}(\text{OH})_3$ deposit and decomposition of HTTA will gradually occur and the formation of the luminous polymer complex is limited.

CONCLUSIONS

Rare earth metal ion-polymer ligand-low molecular weight ligand ternary complexes Eu^{3+} -polymer ligand-TTA (where polymer ligand = PBAHBAS, PBAAS, and PBMAAS) and Eu^{3+} -PBMAAS-second ligand (where second ligand = oxine, Pph_3 , phen, and TTA) were synthesized. Some of the polymer ternary complexes exhibited promising emission properties and possessed potential use in the fluorescence system. Compared with that of the corresponding polymer binary complex Eu^{3+} -PBMAAS, the fluorescence intensity of the polymer ternary complexes was enhanced 4–610 times in the Eu^{3+} -PBMAAS-second ligand system. The fluorescence intensity of Eu^{3+} -PBMAAS-TTA complex was enhanced greatly when the proper mol ratio of HTTA/ Eu^{3+} and pH in the reaction were chosen.

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