

Study on Macromolecular Metal Complexes: Synthesis, Characterization, and Fluorescence Properties of Stoichiometric Complexes for Rare Earth Coordinated with Poly(acrylic acid)

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ABSTRACT: Poly acrylic acid (PAA) and its stoichiometric complexes with trivalent rare earth (RE) have been synthesized and well characterized by means of elemental analysis, IR, TG-DTA, fluorescence spectra, etc. Chemical analysis indicated that the molar ratio of $-\text{COO}^-$ and RE^{3+} in the complex was closely dependent on the pH and the molar ratio of PAA and RE in the feed. The stoichiometric complexes in which the molar ratio of $-\text{COO}^-$ and RE^{3+} is 3:1 can be formed under the conditions of pH 6.0 and PAA:RE = 3:1 (molar ratio in the feed). Spectroscopic studies suggested that the carboxylate bonded to the central

metal ions was in the form of bidentate and these stoichiometric complexes possessed high-temperature resistance. Due to efficient energy transfer from polymer to central metal ions, the emission intensity of Eu^{3+} and Tb^{3+} complexes was stronger than that of simple compounds. Therefore, these complexes can be promising as potential fluorescent probes and photoluminous materials. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 351–357, 2007

Key words: macromolecular complex; rare earth; poly acrylic acid; synthesis; fluorescence properties

INTRODUCTION

The properties of synthesizing macromolecular containing metal have been extensively investigated in recent years.^{1–3} Among them, the design and construction of macromolecular metal complexes (MMC) have attracted much attention due to their intriguing topologies and potential applications as functional materials.^{4–7}

Rare earth (RE) complexes are of increasing interests in supramolecular chemistry, biology, and medicine. For example, luminescent Eu^{3+} and Tb^{3+} complexes with encapsulating ligands have been extensively studied as potential molecular and supramolecular devices,⁸ fluorescent probes, and luminescent labels in biological systems and medical diagnostics^{9,10}; Gd^{3+} complexes are possible contrast-enhancing agents for magnetic resonance imaging.^{11,12} Recently, RE complexes have been used as catalysts for the hydrolysis of phosphodiester and of DNA,^{13,14} and scavengers of superoxide radicals.¹⁵ Interests in macromolecular RE complexes (MREC) have been stimulated by their excellent fluorescent and laser properties,^{16–19} and furthermore, MREC have various applications such as biological and analytical probes, color screen, and RE

containing optical fibers.²⁰ Among these complexes, polymers could be applied as a matrix.^{21,22}

Due to interesting magnetic and fluorescence properties,^{23,24} MREC are likely to provide new materials that possess specific properties and desired features. As part of our continuing investigation into the preparation of macromolecular RE complexes, in this article, complexes of a series of trivalent RE ions coordinated with PAA have been synthesized and detailed studies on the complexes have been carried out as well. The results indicate that the synthesized macromolecular complexes not only overcome some limitations of low-molecular-weight complexes in terms of stability and process ability, but also have considerable compatibility with polymeric materials of similar structure, which makes it possible to develop new luminescence materials containing RE metals.

EXPERIMENTAL

Materials and instruments involved mainly

All the chemicals were of analytical reagent grade. Acrylic acid was distilled under reduced pressure before polymerization and others were used without further purification unless stated otherwise. Vibration spectra from 4000 to 400 cm^{-1} were recorded on a Thermo Nicolet Mattson 2110 spectrometer (KBr discs); thermal analysis was carried out on a PCT-2A

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thermal balance; elemental analysis was treated with on an Elemental Vario-EL elemental analyzer; fluorescence data were collected on a F-4500 fluorescence spectrophotometer; $^1\text{H-NMR}$ was conducted on a Varian FT-80A spectrophotometer with Me_4Si (TMS) as internal standard; XRD patterns of the complexes were recorded with a X'Pertpro Philips spectrometer using $\text{Cu K}\alpha_1$ radiation (wavelength 1.540 56 Å); metal contents were determined by volumetric titration with EDTA using xylenol orange as indicator; potassium contents were determined on a Hitachi 180-80 polarized Zeeman atomic absorption spectrometer.

Synthesis of PAA and RE complexes

Hydrated lanthanide nitrates $\text{RE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were prepared by dissolving weighed 2–3 g corresponding oxides in concentrated nitrate acid. The metal contents were determined by volumetric titration of EDTA using xylenol orange as indicator.

Polymerization of acrylic acid was carried out in a three-necked flask equipped with a condenser containing 100 mL distilled water. When it was heated to 90–95°C, 80 mL water solution of 50 g acrylic acid and 30 mL solution of 4 g $\text{K}_2\text{S}_2\text{O}_8$ were respectively, added dropwise to it for 1.5 h, and the mixture was stirred with a magnetic bar for 1–2 h. Then the solvent and the unconverted monomer were removed by distillation under reduced pressure and the product was dried under vacuum for several days. The resulting polymeric PAA is a white crystal and the average molecular weight determined by gel permeation chromatography (GPC) is 3000.

About 0.5 g of dried polymer PAA was weighed and put into dilute KOH solution; the mixture was stirred for 1–2 h at room temperature to dissolve it completely; and then the pH value of the obtained K-PAA solution was adjusted carefully in the range of 5–6. According to designed molar ratio of ligand PAA and RE, different concentration solutions of calculated $\text{RE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were added dropwise to the K-PAA solution respectively. The mixtures were neutralized until the pH 6.0, and then they were stirred continuously for several days. The macromolecular RE complexes were isolated from the solutions by centrifugation, then washed with distilled water to remove coprecipitated and any other impurities present, and finally washed with methanol and dried in a vacuum desiccator. The complexes cannot be dissolved in water, alcohol, and other organic solvents, but can be easily dissolved in concentrated acid with the decomposing of the complexes.

XRD patterns of the complexes (Fig. 1) shows that no diffraction peaks appear which indicates that the complexes are noncrystal compounds.

RESULTS AND DISCUSSION

IR and $^1\text{H-NMR}$ analysis of ligand PAA

IR analysis shows that no absorption band for $-\text{C}=\text{C}-$ is present in the spectrum, which indicates that the polymerization reaction of acrylic acid is finished completely. There are two kinds of peaks lying at 4.774 and 4.139 ppm in the $^1\text{H-NMR}$ spectrum of PAA (Fig. 2) respectively, which can be assigned to $-\text{CH}-$ and $-\text{CH}_2-$, and their area ratio 1 : 2 is consistent with the predicted results.

Composition analysis

The dependence of compositions on pH

The effects of different pH on the compositions of the complexes were investigated. It has been found that the molar ratio of $-\text{COO}^-$ and $\text{RE}^{3+(n)}$ in the complexes is closely dependent on the pH. At lower pH (pH < 4), elemental analysis implied that $n > 3$, which can be ascribed to the fact that partial carboxylic groups had not participated in the coordination. In the range of pH 5–6, especially at pH 6.0, no absorption band of free carboxylic group emerged from IR spectra, and the stoichiometric complexes can be formed; this can be confirmed by the results of elemental analysis also. So to prepare the stoichiometric macromolecular RE complexes, pH 6.0 was selected for further study.

The effect of different molar ratios of PAA and RE in the feed on the composition

Carboxylic content in the MREC was determined by neutralization titration and further validated by elemental analysis. The influences of different molar ratios of PAA and RE in the feed on the compositions of the complexes were investigated. A typical tendency scheme of relationship between n (the molar ratio of $-\text{COO}^-$ and RE^{3+} in the complexes) and the molar ratio of PAA and RE in the feed is shown in Figure 3. The results illuminate that n exhibits linear increase with increasing molar ratio of PAA and RE in the feed. It is obvious that the general formula for the stoichiometric MREC with PAA can be achieved as $\text{REL}_3 \cdot z\text{H}_2\text{O}$ (L is the polymerized acrylic acid unit in the polymer chain, z is in the range of 4.5–6.0). All of the RE ions can form the stoichiometric MREC with PAA at the optimum condition, that is, pH 6.0 and the molar ratio of PAA and RE in the feed is 3:1. The determined data of elemental analysis for the stoichiometric MREC are listed in Table I.

It is noteworthy that for Ce^{3+} complex, n (3.28) > 3, that is likely the formation of Ce^{4+} as a result of partial oxidation of Ce^{3+} , which increases the num-

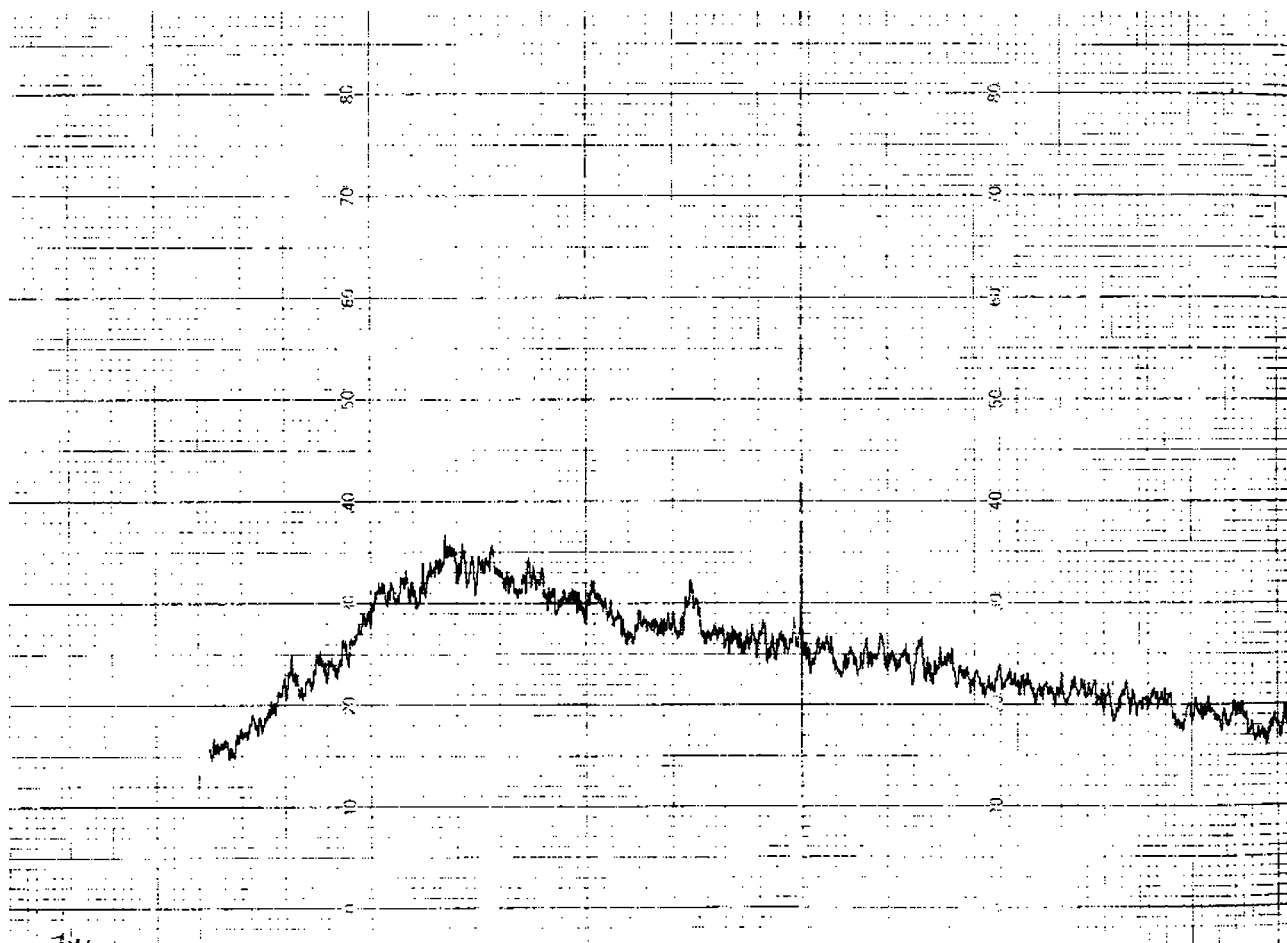


Figure 1 A typical XRD pattern of RE-PAA.

ber of carboxylic group coordinated with the metal ion, and hence, Ce complex possesses the composition of $RE_{L_{3.28}} \cdot 2H_2O$.

IR analysis

All complexes present similar IR features, which means that the complexes possess similar structure. A careful study to compare the infrared spectra of complexes with free ligand PAA has been achieved.

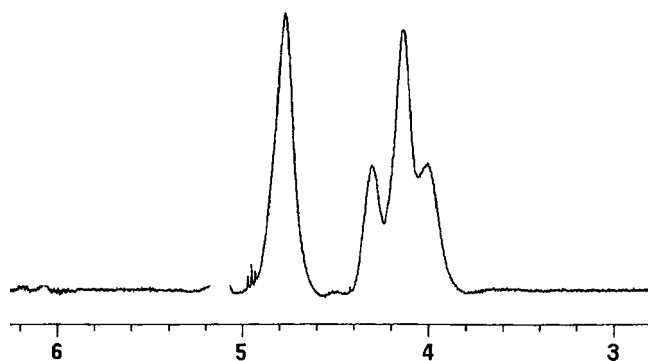


Figure 2 1H -NMR of PAA.

The results indicated that the vibration band of asymmetric vibration absorption (ν_{asCOO}) of carboxylic group in the complexes had shifted from 1708 cm^{-1} to lower wave number of $1543\text{--}1566\text{ cm}^{-1}$ (Table II), and the vibration band of symmetric vibration

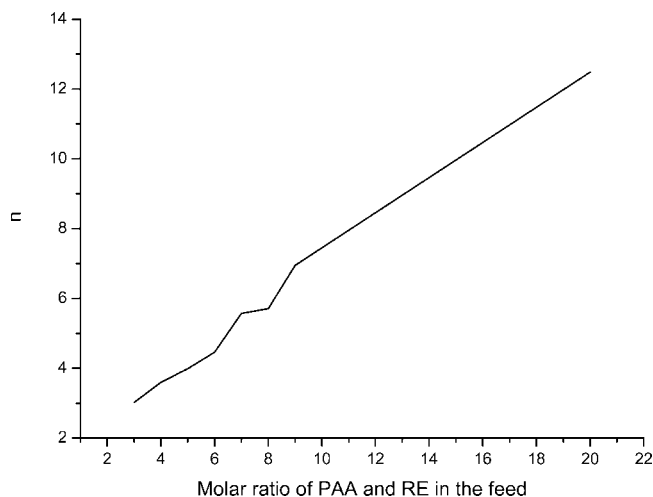


Figure 3 The tendency scheme of the effect of different molar ratios of PAA and RE in the feed on the compositions.

TABLE I
Elemental Analysis Data of $REL_3 \cdot zH_2O$

RE	%C		%H		%RE		n^a	z^b
	Found	Calcd	Found	Calcd	Found	Calcd		
La	24.83	24.93	4.78	4.16	32.09	32.06	2.98	4.5
Sm	22.99	22.90	5.20	4.45	32.05	31.88	2.99	6.0
Eu	22.87	23.26	3.65	4.31	33.30	32.74	2.90	5.5
Gd	23.03	23.45	5.51	4.13	34.56	34.14	2.91	5.0
Tb	22.22	22.49	4.23	4.37	32.62	33.09	3.00	6.0
Dy	22.60	22.74	3.62	4.21	34.49	34.22	2.93	5.5
Y	27.86	27.54	4.79	4.84	22.78	22.67	3.00	5.0

^a n represents the molar ratio of $-COO^-$ and RE^{3+} in the complexes.

^b z is the total number of water molecule in the complexes. Optimum conditions are as follows: PAA : RE = 3 : 1 (molar ratio in the feed), pH = 6.0.

absorption (ν_{sCOO}) of carboxylic group in the complexes lying $1407\text{--}1416\text{ cm}^{-1}$ was similar to that of free ligand at 1406 cm^{-1} , which was attributed to the coordination of carboxylate to RE ions. Because the formation of coordination bond of carboxylate with central metals will diminish the charge density on the carboxylate oxygen and thus decrease the force constant k of it, which produce the results mentioned above.

IR analysis also shows that the symmetry of the carboxylate group in the complex is $C2v$, whereas the $\Delta\nu$ ($\Delta\nu = \nu_{asCOO(A)} - \nu_{sCOO(A)}$) is in the range of $127\text{--}136\text{ cm}^{-1}$, which is much smaller than that of K-PAA (159 cm^{-1}). In monodentate coordination, the two C—O bonds of a carboxylate become inequivalent, the antisymmetric stretching frequency increases from its free ion value, whereas the symmetric frequency decreases. Hence, a large splitting of the CO_2 -stretching frequency is often an indication of monodentate coordination. When acting as a bidentate chelate, the carboxylate group retains $C2v$; therefore, from a symmetry viewpoint, the CO_2 -stretching frequency are not expected to be greatly different from the free ion spectrum.^{25,26} So the carboxylate group in the complexes acts as a bidentate chelate.

For stoichiometric complexes, the strong broadening bands in the range of $3378\text{--}3431\text{ cm}^{-1}$ and the absorption bands lying in $609\text{--}640\text{ cm}^{-1}$ can account for the presence of water. Compared IR spectra of complexes prepared freshly with those of complexes dried at 180°C for 2 h, it can be seen that the two absorption band trended to smaller, but not disap-

peared. This indicated that some water existed in the complexes was in the form of absorbed water and others occurred in manner of coordination water.

For the macromolecular complexes RE-PAA, the force constant k of RE-O in RE-PAA is about $k = 1.5\text{ N cm}^{-1}$, which shows that RE-O possesses mostly covalent bond. There appears an increase in the degree of covalent character of RE-O bond with the decrease in the radius of RE metal ions. However, $\Delta\nu$ values do not show a gradual variation.

TG-DTA analysis

The simultaneous TG-DTA curves of all complexes were carried out and heated to 850°C using $\alpha\text{-Al}_2\text{O}_3$ as reference material; samples of about 10 mg were placed in a crucible and heated at the rate of $10^\circ\text{C}/\text{min}$ in an air atmosphere at ambient pressure.

TG-DTA curves indicated that all complexes were thermally stable and started to decompose at around 400°C . Typical TG-DTA data of these complexes are shown in Table III. It can be seen that there is partial weight loss under 100°C ; this can be attributed to the existence of water, but the determination value of weight loss in this procedure was far smaller than that of theoretical water contents. This is accounted for the fact that besides adsorbed water, coordination water is also present in the complexes, and the calculated number of coordination water is 2–3. This conclusion is consistent with the result that 8 and 9 are the coordination numbers that are most common in RE carboxylates.²⁷

TABLE II
The Selected IR Bands of $REL_3 \cdot zH_2O$ Complexes (cm^{-1})

RE	PAA	K	La	Ce	Sm	Eu	Gd	Tb	Dy	Y
ν_{asCOO}	1708	1566	1546	1544	1545	1543	1545	1545	1544	1552
ν_sCOO	1406	1407	1414	1414	1416	1414	1414	1418	1414	1416
$\Delta\nu^a$	—	159	132	130	129	129	131	127	130	136
ν_{H_2O}	3430	3429	3428	3418	3428	3404	3425	3378	3386	3431

^a $\Delta\nu = \nu_{asCOO} - \nu_sCOO$.

TABLE III
TG-DTA Data of $RE_2O_3 \cdot zH_2O$

Complexes	Endothermal peaks T_e-T_m ($^{\circ}C$), weight loss (%) (calculated weight loss of water)	Exothermal peaks T_e-T_m ($^{\circ}C$)	Total remnant %	RE_2O_3 calculated remnant %
PAA	51.0–64.0, 6.2 (8.57)	434.0–451.0	0	–
K	40.0–77.0, 14.9 (–)	417.0–431.0	40.30	–
La	82.0–104.0, 11.14 (18.70)	346.0–354.0, 412.0–420.0	38.60	37.86
Ce	76.0–88.0, 10.77 (8.79)	453.0–468.0, 483.0–499.0	41.65	42.02 ^a
Sm	65.0–78.0, 14.36 (22.90)	451.0–464.0, 481.0–493.0	37.40	36.96
Eu	48.0–79.0, 12.17 (21.32)	397.0–417.0, 451.0–458.0	36.81	37.91
Gd	55.0–84.0, 13.01 (19.54)	455.0–463.0, 473.0–488.0	36.12	39.36
Tb	60.0–83.0, 10.12 (22.49)	451.0–464.0, 477.0–497.0	39.55	38.92 ^b
Dy	61.0–82.0, 18.87 (20.85)	405.0–412.0, 465.0–480.0	39.20	39.28
Y	75.0–93.0, 13.64 (22.95)	461.0–488.0, 549.0–570.0	29.76	28.79

^a The final decomposition product of Ce-PAA is CeO_2 .

^b The final decomposition product of Tb-PAA is Tb_4O_7 .

The final decomposition products of the complexes are RE_2O_3 except for Ce (CeO_2) and Tb (Tb_4O_7). Based on the discussions, a proposed diagram for the stoichiometric MREC is shown in Figure 4.

Fluorescent properties

The excitation and emission spectra, as well as the fluorescence intensity, were measured on dried and finely powdered samples at room temperature. The major fluorescence spectral data are summarized in Table IV and the typical excitation and emission spectra of the ligand PAA and several solid complexes are shown in Figure 5(a–e). The fluorescence spectra of MREC showed that the characteristic emission of some RE was maintained in the complexes, and the relative positions of these lines vary

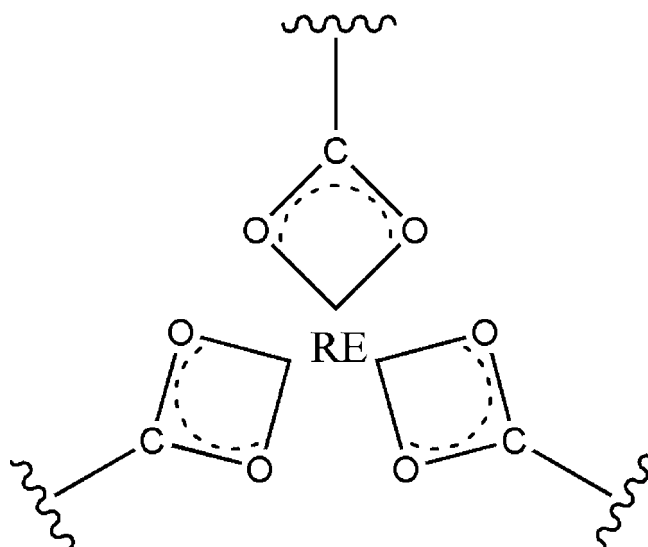


Figure 4 A proposed diagram for the stoichiometric complex (water molecules are omitted for clarity).

slightly, but the intensities change obviously with the changes in the environment.

Two characteristic emission peaks lying at 544 ($^5D_4 \rightarrow ^7F_5$ transition) and 583 nm ($^5D_4 \rightarrow ^7F_4$ transition) were observed in Tb-PAA complex [Fig. 5(b)]. The hypersensitive transition $^5D_4 \rightarrow ^7F_5$ was the dominant one which presented a sharp, stronger peak with well homochromaticity.²⁸

Two visible bright brown-red emission peaks of Eu-PAA, centered at 590 and 613 nm, were observed and assigned to $^5D_0 \rightarrow ^7F_1$ (magnetic dipole transition, insensitive to the crystalline field) and $^5D_0 \rightarrow ^7F_2$ (electrodipole transition, sensitive to the crystalline field).^{29–31} Between the two transitions, $^5D_0 \rightarrow ^7F_2$ is the preferred transition for Eu^{3+} -containing luminescent materials, and is extremely sensitive to chemical bonds in the vicinity of Eu^{3+} ion. Furthermore, it is interesting that $^5D_0 \rightarrow ^7F_2$ transition of Eu-PAA complex is much more intense than $^5D_0 \rightarrow ^7F_1$ transition, and the intensity ratio $I(^5D_0 \rightarrow ^7F_2)/I(^5D_0 \rightarrow ^7F_1)$ is 2.52. All of these indicate that Eu^{3+} is located in an asymmetric central in Eu-PAA complex.

The fluorescence of Sm-PAA cannot be observed almost and the fluorescence of Dy-PAA is rather

TABLE IV
Fluorescence Spectral Data of the Solid Complexes and PAA

Complexes	λ_{ex} (nm)	λ_{em} (nm)	Intensity	Transition
PAA-Tb	239.0	489.6	70.96	$^5D_4 - ^7F_6$
		544.0	161.2	$^5D_4 - ^7F_5$
		582.6	17.40	$^5D_4 - ^7F_4$
PAA-Eu	394.6	590.2	308.8	$^5D_0 - ^7F_1$
		613.2	779.2	$^5D_0 - ^7F_2$
PAA-Sm	273.8	314.1	115.1	–
PAA-Dy	483.6	500.6	4.770	$^4F_{9/2} - ^6H_{15/2}$
		708.6	1.514	$^4F_{9/2} - ^6H_{13/2}$
PAA	344.6	414.4	32.57	–

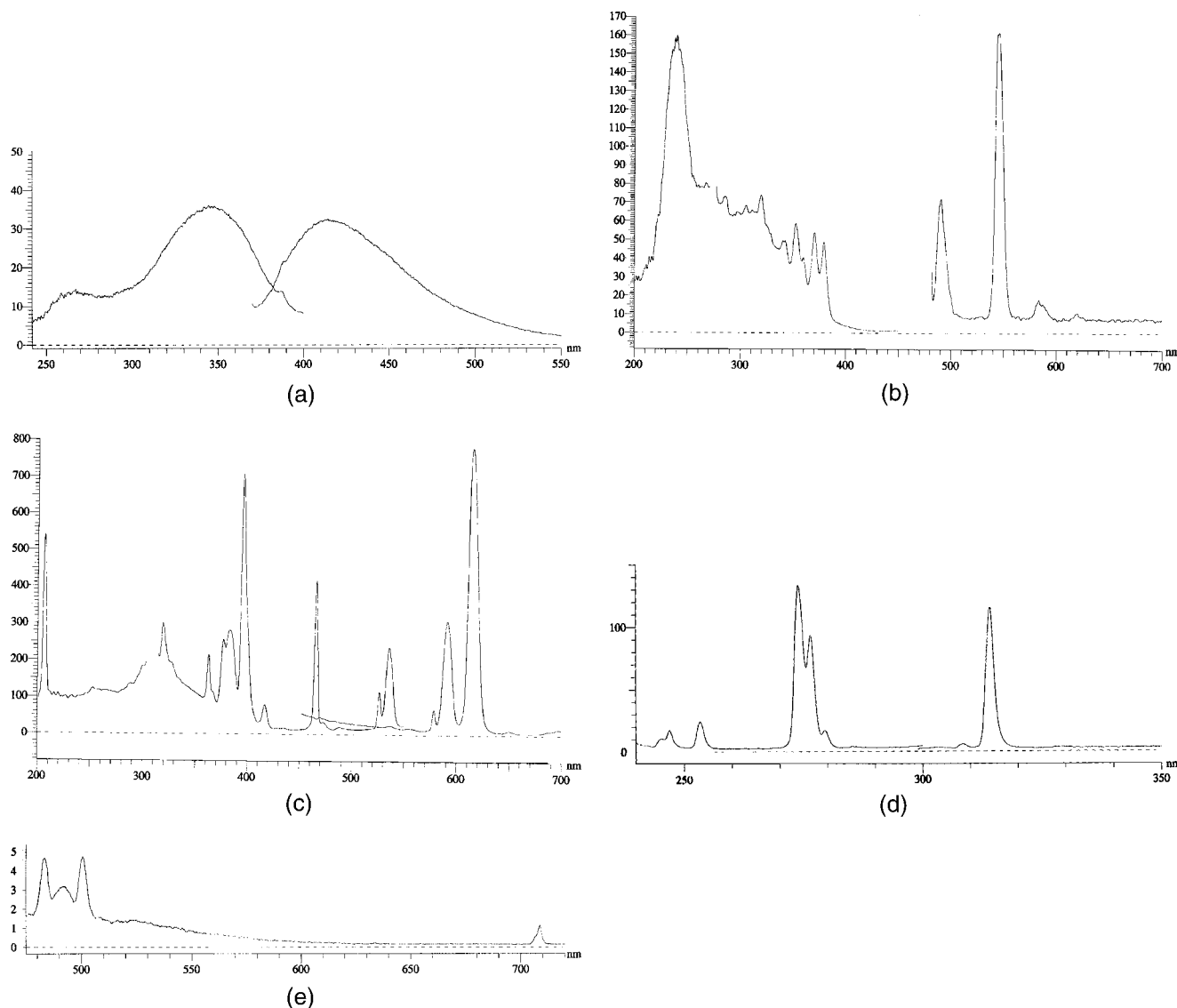


Figure 5 Fluorescence spectra of the solid-state compounds. Excitation and emission spectrum of (a) PAA; (b) Tb-PAA; (c) Eu-PAA; (d) Sm-PAA; and (e) Dy-PAA.

lower. For Sm-PAA complex, the emission peak lies at 314 nm, but the intensity is only about 115, obviously lower than that of Tb-PAA and Eu-PAA complexes lying in the visible region. This is because the excitation absorption intensity of the ligand PAA at lower wavelength is rather weaker which cannot satisfy the demand of emission of Sm-PAA. The energy transferred from ligand to Sm undergone the course of nonradiation relaxation completely and returned to the ground state. So the transferred energy from ligand to Sm cannot be converted effectively into fluorescence radiation. According to antenna effect, the luminous intensity of RE ions is affected by three factors: absorption intensity of ligand, energy transfer efficiency from ligand to RE^{3+} , and emission efficiency of RE^{3+} . The macromolecular RE complexes of PAA, especially Eu-PAA and Tb-PAA, possess

stronger fluorescence showing that the lowest excited triplet state energy level of PAA holds matches well with the excited state energy level of Eu^{3+} and Tb^{3+} , and when the ligand is excited, it can transfer energy effectively from polymer matrix to Eu^{3+} and Tb^{3+} .

CONCLUSIONS

Macromolecular complexes for RE coordinated with PAA have been synthesized and well characterized by means of elemental analysis, IR, TG-DTA, fluorescence spectra, etc. The result indicated that the formation of MREC was closely dependent on the pH and the molar ratio of PAA and RE in the feed. Stoichiometric complexes $\text{REL}_3 \cdot z\text{H}_2\text{O}$ can be formed

under controlled conditions of pH 6.0 and PAA:RE = 3:1(molar ratio in the feed). IR analysis proved that the carboxylate in these complexes was bonded to the central metal ions in the form of bidentate; TG-DTA investigation implied that these stoichiometric complexes were thermally stable up to 400°C. The emission intensity of macromolecular Eu³⁺ and Tb³⁺ complexes was stronger than that of simple compounds due to efficient energy transfer from polymer to central metal ions, this would make them to be potential as new luminescence materials.

References

1. Dimos, A.; Tsaousis, D.; Michaelides, A.; Skoulika, S.; Golhen, S.; Ouahab, L.; Didierjean, C.; Aubry, A. *Chem Mater* 2002, 14, 2616.
2. Cui, D. M.; Nishiura, M.; Hou, Z. M. *Macromolecules* 2005, 38, 4089.
3. Eisenberg, A.; King, M. *Ion-Containing Polymers*; Academic Press: New York, 1977.
4. Guo, X. D.; Zhu, G. S.; Fang, Q. R.; Xue, M.; Tian, G.; Sun, J. Y.; Li, X. T.; Qiu, S. L. *Inorg Chem* 2005, 44, 3850.
5. Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew Chem Int Ed* 1999, 38, 2638.
6. Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* 2002, 295, 469.
7. Zheng, S. L.; Yang, J. H.; Yu, X. L.; Chen, X. M.; Wong, W. T. *Inorg Chem* 2004, 43, 830.
8. Lehn, J. M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH:Weinheim, 1995; Chapter 8, p 89.
9. Pietraszkiewicz, M. *Comprehensive Supramolecular Chemistry*; Pergamon Press: Oxford, 1996.
10. Bunzli, J. C. G.; Choppin, G. R. *Lanthanide Probes in Life, Medical and Earth Sciences*; Elsevier: Amsterdam, 1989.
11. Lauffer, R. B. *Chem Rev* 1987, 87, 901.
12. Choppin, G. R.; Schaab, K. M. *Inorg Chim Acta* 1996, 252, 299.
13. Ragunathan, K. G.; Schneider, H. J. *Angew Chem Int Ed* 1996, 35, 1219.
14. Haner, R.; Hall, J.; Rihs, G. *Helv Chim Acta* 1997, 80, 487.
15. Yu, S. Y.; Wang, S. X.; Luo, Q. H.; Wang, L. F.; Peng, Z. R.; Gao, X. *Polyhedron* 1993, 12, 1093.
16. Piguet, C.; Buezli, J. C. G.; Bernardinelli, G.; Hopfgartner, G.; Williams, A. F. *J Am Chem Soc* 1993, 115, 8197.
17. Buono-Core, G. E.; Li, H.; Marciniak, B. *Coord Chem Rev* 1990, 99, 55.
18. Qian, D. J.; Yang, K. Z.; Nakahara, H.; Fukuda, K. *Langmuir* 1997, 13, 5925.
19. Galaup, C.; Picard, C.; Cathala, B.; Cazaux, L.; Tisnès, P.; Autiero, H.; Aspe, D. *Helv Chim Acta* 1999, 82, 543.
20. Zhang, Q. J.; Wang, P.; Zhai, Y. *J Appl Polym Sci* 1998, 67, 1431.
21. Banks, E.; Okamoto, Y.; Ueba, Y. *J Appl Polym Sci* 1980, 25, 359.
22. Wolff, N. E.; Pressley, R. J. *Appl Phys Lett* 1963, 2, 152.
23. Bruce, T. C.; Tsubouchi, A.; Dempcy, R. O.; Olson, L. P. *J Am Chem Soc* 1996, 118, 9867.
24. Xu, J. D.; Raymond, K. N. *Angew Chem Int Ed* 2000, 39, 2745.
25. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986.
26. Emeleus, H. J.; Sharpe, G. A. *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 20; Academic Press: London, 1977.
27. Gao, J. D.; Yang, W.; Kang, J. W. *Spectroscopic Properties of the Lanthanide Complexes in Aqueous Solution*; University of Electronic Science and Technology of China: Chengdou, 1995.
28. Richardson, F. S. *Chem Rev* 1982, 82, 541.
29. Wang, Y. P.; Lei, Z. Q.; Feng, H. Y.; Bao, J. T.; Wang, Y. B. *J Appl Polym Sci* 1992, 45, 1641.
30. Kirby, A. F.; Richardson, F. S. *J Phys Chem* 1983, 87, 2544.
31. Hu, J.; Zhao, H.; Zhang, Q. J.; He, W. D. *J Appl Polym Sci* 2003, 89, 1124.