

STUDY ON POLYMER-RARE EARTH METAL ION COMPLEXES I. FLUORESCENT PROPERTIES OF POLY(ACRYLIC ACID-CO-4-VINYLPYRIDINE)-RARE EARTH METAL COMPLEXES

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ABSTRACT

A kind of copolymer of acrylic acid and vinylpyridine was synthesized and the fluorescent properties of the complexes of the copolymer with Eu^{3+} or Tb^{3+} were studied. It was found that the fluorescence intensity of the complexes of the copolymer with Eu^{3+} was 20 times as high as that of the complexes of polyacrylic acid with Eu^{3+} and twice as high as that of the complexes of polyvinylpyridine with Eu^{3+} . The effects of the composition of the copolymer and the content of Eu^{3+} or Tb^{3+} in the complexes were studied. The fluorescence lifetime of the complexes was measured and it was found that two or more kinds of energy transfer mechanism existed.

INTRODUCTION

Fluorescent inorganic rare earth metal materials have long been studied, and have been widely used in fluorescent screens in color TV sets since 1960's. For polymeric complexes with rare earth metal ions, however, there has just been a great stimulation of interest in their fluorescent properties in connection with their uses in fluorescent and laser materials, and plastic magnets.

Okamoto et al. studied the fluorescent properties of Eu^{3+} - β -diketone ligands-containing polymer complexes^[1], Eu^{3+} -carboxylbenzoyl and carboxynaphthoyl ligand-containing polymer complexes^[2] and Eu^{3+} or Tb^{3+} bipyridyl complex-containing polymer complexes. They also found enhancement of fluorescence intensity when Tb^{3+} was bound to some polyelectrolytes or polysaccharides in aqueous solution^[3,4]. But there has been few reports about study on rare earth metal ion-different kind of functional group-containing polymer complexes. In order to investigate the effect of different kind of functional group on fluorescent properties of the polymer-rare earth metal ion complexes, copolymers of acrylic acid (AA) and vinylpyridine (VP) were synthesized and the fluorescent properties of the complexes formed from the copolymer and rare earth metal ion Eu^{3+} or Tb^{3+} were studied.

EXPERIMENTAL

Materials

(1) Synthesis of the copolymers

Copolymers of acrylic acid and vinylpyridine were polymerized by free radical initiator

$K_2S_2O_8$ in distilled water at $75^\circ C^{[5]}$. The polymers obtained were purified repeatedly by precipitation from aqueous solution with propanol. The composition of the copolymers was determined by elemental analysis and NMR spectroscopy.

(2) Formation of complexes

Aqueous solutions of the copolymer and a rare earth metal salt were mixed and the obtained mixture was refluxed for 24 h. The solvent was evaporated from the mixture. The obtained complex was ground up, and then dried in vacuum at $50^\circ C$ for 72 h.

(3) Spectral measurements

A Hitachi model MPF-4 fluorescence spectrophotometer was used for measurements of the fluorescence spectra and fluorescence intensity of the complexes. The fluorescence intensity (emission at 615 nm) was recorded with excitation at 349 nm for Eu^{3+} -containing complexes, and at 244 nm for Tb^{3+} -containing complexes emission at 545 nm.

A Varian model XL-200 NMR spectrometer was used to record ^{13}C NMR spectrum at 50.5 MHz .

A Kratos model ES-300 was used to measure the electron spectrum.

Fluorescence lifetime was determined using laser induced fluorescence spectrophotometer.

RESULTS AND DISCUSSIONS

The structure of the copolymer is as follows,

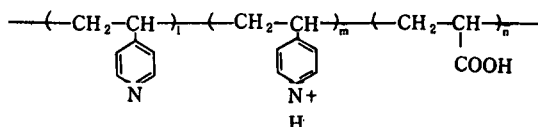


Table 1 Composition of copolymers of AA with VP

No. of sample	AA in copolymers* (unit mol.%)
1	15.9
2	32.6
3	47.4
4	78.6

* From elemental analysis

Table 1 shows the composition of the copolymers of AA with VP.

Measurement of X-ray photoelectron spectrum of the complex showed that the binding energy of Eu^{3+} or Tb^{3+} in the complex was 0.2 eV lower than that in their chlorides; the binding energy of oxygen in the copolymer was 0.2 eV higher after complexation with Eu^{3+} or Tb^{3+} ; and the binding energy of nitrogen in the copolymer was 0.5 eV or 0.8 eV higher after complexation with Eu^{3+} or Tb^{3+} . All these confirmed the formation of complexes of the copolymer with Eu^{3+} or Tb^{3+} through carboxyl group or nitrogen atom.

The fluorescence spectra of the copolymer- Tb^{3+} complex and the copolymer- Eu^{3+} complex

are shown in Fig.1 and Fig.2, respectively. In the range of wave length of the emission, PAA and PVP and the copolymers were not fluorescent.

When Eu^{3+} and Tb^{3+} were complexed with PAA, PVP and the copolymer respectively, the shapes and the wave lengths of the fluorescence spectra were not changed, but the fluorescence intensity at 615 nm or 545 nm was varied obviously as shown in Table 2.

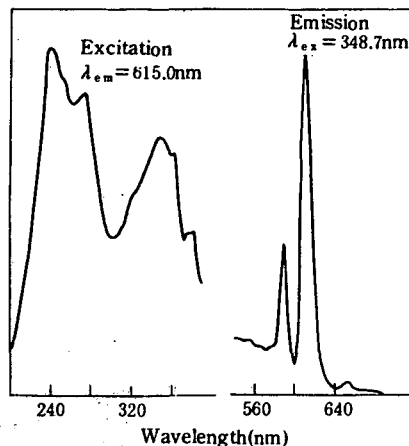
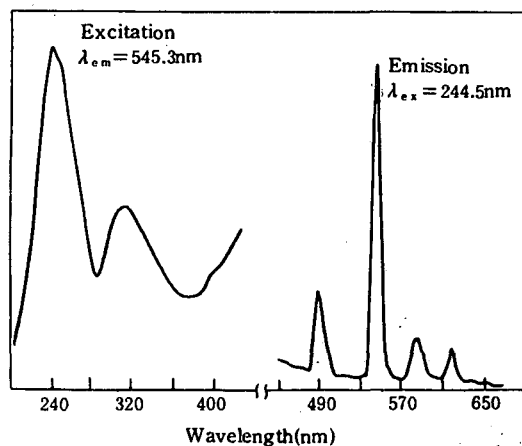


Fig. 1 Fluorescence spectra of the copolymer- Tb^{3+} Fig. 2 Fluorescence spectra of the copolymer- Eu^{3+}

Table 2 Fluorescence intensity of polymer-rare earth metal ion system*

	PVP	Poly(AA-co-VP)**	PAA
Eu^{3+} ***	103.8	244.2	12.4
Tb^{3+} ***	80.6	219.0	191.9

* All measurement was under the same condition.

** The copolymer contained 32.6% of acrylic acid unit.

*** The content of rare earth metal ion in the system was 7.2%.

As pointed before, main factors to affect the fluorescence intensity were ligands complexed with rare earth metal ions. Unlike conventional systems in which the optical pump energy is absorbed by the rare earth metal ion itself, in the complex systems the pump energy is absorbed by organic groups complexed with the rare earth metal ion on the polymers and then was efficiently transferred to the rare earth metal ion. The efficiency of the energy transfer depends on the nature and the number of the groups, and also the arrangement of the groups around the rare earth metal ion. The higher the efficiency is, the greater the fluorescence intensity. In the present example, the fluorescence intensity was the lowest for Eu^{3+} when it was complexed with PAA. This demonstrated that the carboxyl on the PAA was unable to transfer absorbed energy efficiently. However, when Eu^{3+} was complexed with PVP fluorescence intensity of the system was enhanced obviously. This demonstrated that, in contrast to PAA, the PVP could transfer absorbed energy efficiently, which may be due to the conjugate π -bond of the VP unit. On the other hand, the fluorescence intensity of the complex of the copolymer with Eu^{3+} was twice as high as that of the complex of PVP with Eu^{3+} , and 20 times as high as that of the complex of PAA with Eu^{3+} . This

was interesting because in many articles published recently the polymers used were PAA or its salts. It was supposed that there was a hybrid coordination produced by acrylic acid unit and vinylpyridine unit on the copolymer surrounding the rare earth metal ions, and that the hybrid coordination made energy transfer more efficient. In order to explain the phenomenon, the chain structure of the copolymer, especially the distribution of the AA unit and VP unit on the chain, was analysed using NMR spectroscopy. Results obtained showed that the probability for a VP unit attached to another VP unit was $X_{00} = 0.396$; and the probability for a VP unit attached to an AA unit was $X_{01} = X_{10} = 0.247$; and the probability for an AA unit attached to another AA unit was $X_{11} = 0.110$. This meant that when a carboxyl was complexed with a rare earth metal ion, the probability that the adjacent unit was a VP one was nearly 5 times as large as the probability that the adjacent was an AA unit, which provided a structural factor for the hybrid coordination.

When the rare earth metal ion was Tb^{3+} , the case was different. The fluorescence intensity was the lowest when the polymer used was PVP, and was doubled or more for PAA. This demonstrated that AA unit transferred energy more efficiently for Tb^{3+} . Like Eu^{3+} , the fluorescence intensity was the largest when the copolymer was used. This meant that the hybrid coordination also existed in this system and enhanced the efficiency of energy transfer.

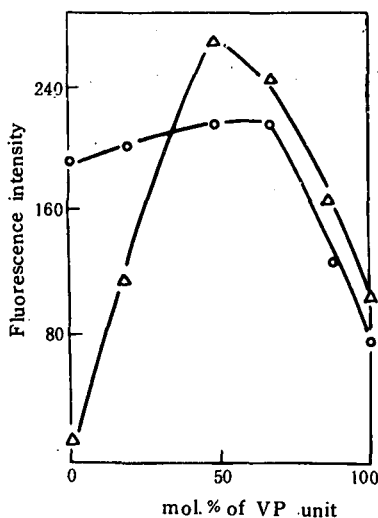


Fig.3 Relationship between the content of VP unit in the copolymer and fluorescence intensity
(Δ) copolymer- Eu^{3+} ; ($\circ$) copolymer- Tb^{3+}

Figure 3 shows the relationship between the content of VP unit in the copolymer and fluorescence intensity. It shows that the fluorescence intensity is affected by the composition of the copolymer considerably, and when the copolymer contained 47.4% of VP unit, the system had the highest fluorescence intensity. This was because the described hybrid coordination needed a certain chain structure, especially a certain distribution of the units on the copolymer chain, and when the copolymer contained about 50% of VP unit, the optimum hybrid coordination was reached.

Fluorescence intensity usually varies with the number of ligands complexed with a rare earth metal ion. Generally speaking, the more the ligands one rare earth metal ion has, the higher the

fluorescence intensity. Because the number of ligands complexed with a rare earth metal ion varied with the content of the ion in a certain system, the content is often a factor to affect the fluorescence intensity of the system. Figure 4 shows the relationship between fluorescence intensity of copolymer- Eu^{3+} or Tb^{3+} complex system and the content of Eu^{3+} or Tb^{3+} in the system. It shows that the fluorescence intensity of copolymer- Eu^{3+} complex system increased first with increasing content of Eu^{3+} , but when the content reached about 4%, the fluorescence intensity almost did not vary with the content any more. This might be due to some complexation form of Eu^{3+} with more ligands was formed which emitted stronger fluorescence. The quantity of this complexation form increased with increasing content of Eu^{3+} , and on reaching a certain content of Eu^{3+} , this kind of complexation form did not increase, and fluorescence intensity of the system hardly varied. As to copolymer- Tb^{3+} system, in the experimental range of Tb^{3+} content, fluorescence intensity of the system increased with increasing content of Tb^{3+} . This demonstrated the difference between Eu^{3+} and Tb^{3+} in the nature of formation of complexes.

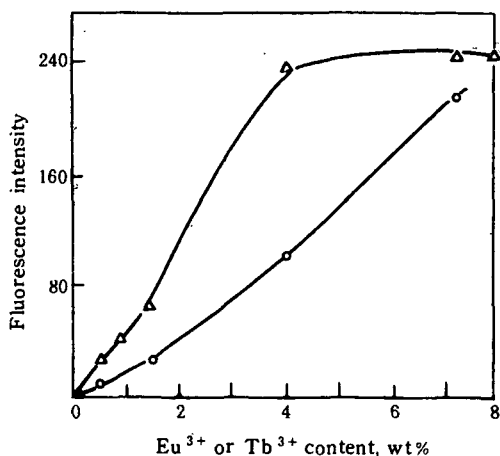


Fig. 4 Relationship between fluorescence intensity of copolymer- Eu^{3+} or Tb^{3+} complex and the content of Eu^{3+} or Tb^{3+} :

(Δ) copolymer- Eu^{3+} ; (O) copolymer- Tb^{3+}

The fluorescence lifetime of a substance usually represents the average time of the molecule remains in the excited state. Lifetime measurement is frequently necessary in fluorescence spectroscopy. These data can reveal the frequency of collisional encounters with quenching agents, the rate of energy transfer, and the rate of excited state reactions. The precise nature of the fluorescence decay can reveal details about the interactions of the fluorophore with its environment.

The observed decay is generally fitted to a sum of exponentials,

$$F(t) = \sum_i a_i e^{-t/\tau_i} \quad (1)$$

where a_i is a preexponential factor representing the fractional contribution to the time-resolved decay of the component with a lifetime τ_i ^[6].

Results of measurement of the lifetime showed that the copolymer- Eu^{3+} system did not show multiple exponential decay when the content of AA unit in the copolymer was under 15.9%, but

with increasing content of AA unit, the system had a tendency of multiple exponential decay when the content of AA unit was 32.6% and the decay of the system fitted a multiple exponential one when the content of AA unit was 78.6%. This demonstrated that at least two kinds of energy transfer mechanism existed in the system when the content of AA unit was over a certain quantity. This was consistent with the preceding results, and might be due to coexistence of interaction of AA unit and VP unit in the copolymer with the rare earth metal ion, and hybrid coordination of VP unit and AA unit with the rare earth metal ion. The interaction and hybrid coordination produced different energy transfer mechanism.

Table 3 Relationship between fluorescence intensity and fluorescence lifetime of copolymer-Eu³⁺ complex

	AA unit in the copolymer (%)			
	0	15.9	32.6	78.6
fluorescence intensity	103.8	166.2	244.2	115.0
fluorescence lifetime(ms)	1.57	1.60	1.58	0.81

Table 3 shows the relationship between fluorescence intensity and fluorescence lifetime of copolymer-Eu³⁺ complex system.

Fluorescence lifetime of a substance is given by

$$\tau = 1 / (K + K_{\text{nonrad}}), \quad (2)$$

where τ is the lifetime; K is the rate constant for the emission of photons; and K_{nonrad} is the rate constant for nonradiative deexcitation. Table 3 shows that when the content of AA unit in the copolymer increased from 0 to 32.6% the lifetime hardly varied, but the fluorescence intensity increased obviously. This demonstrated that when the content of AA unit in the copolymers increased another energy transfer mechanism with higher efficiency occurred, and this might be the mechanism in connection with the preceding hybrid coordination. It increased K , and decreased K_{nonrad} at the same time. So the fluorescence intensity increased with increasing content of AA unit while the fluorescence lifetime almost keeping constant. When the content of AA unit was 78.6%, the fluorescence lifetime was almost half decreased, and the fluorescence intensity was decreased obviously. This demonstrated that the total efficiency of energy transfer was decreased when the content of AA unit was high. As pointed out, this might be due to the decrease of the hybrid coordination and the complexation form of AA unit with the rare earth metal ion existed to some extent which had lower efficiency of energy transfer. When the content of AA unit was high, K decreased and K_{nonrad} increased, and the results was given.

Keywords: Poly(acrylic acid-co-4-Vinylpyridine); Rare Earth ion; Complex; Fluorescence

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