

# Fluorescent Properties of Polymer–Rare Earth Ion Complexes. II. Poly(acrylic Acid-co-Acrylamide)–Rare Earth Ion Complexes

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## Synopsis

Poly(acrylic acid-co-acrylamide) with uniform composition was synthesized from acrylic acid and acrylamide by azeotropic copolymerization. The fluorescent properties of the copolymer–Eu<sup>3+</sup> or –Tb<sup>3+</sup> complexes were investigated. It was found that the fluorescence intensity of the complexes is dependent on the composition of the copolymer. Fluorescence lifetime measurement indicates that Eu<sup>3+</sup> or Tb<sup>3+</sup> exists in the complexes in at least two coordination forms, and the difference of the nature or relative quantity of the coordination forms varies with the composition of the copolymer. The fluorescence lifetime of Eu<sup>3+</sup> or Tb<sup>3+</sup> in the complexes is also dependent on the composition of the copolymer. It was also found that intramacromolecular hybrid coordination of oxygen containing and nitrogen containing coordination groups makes Eu<sup>3+</sup> or Tb<sup>3+</sup> fluoresce more strongly than intermacromolecular hybrid coordination of the two types of coordination groups does.

## INTRODUCTION

In recent years, investigations on fluorescent properties of polymer–rare earth ion complexes have been stimulated because the complexes can be used as fluorescent and laser materials with good quality. Copolymers are often used in this kind of investigations. Okamoto et al. have synthesized copolymers which contain coordination groups and substituted styrene and studied the fluorescent property of the copolymer–rare earth ion complexes.<sup>1–4</sup> In our laboratory, the copolymer of vinylpyridine and acrylic acid have been synthesized and the fluorescent properties of the copolymer–rare earth ion complex have been studied.<sup>5</sup>

In the polymer–rare earth ion complexes, the microscopic environment of the rare earth ion is very complicated. Several coordination forms of the rare earth ion often exist in the complexes and make a very different contribution to the fluorescent properties of the complexes. Recently we synthesized a series of copolymers of acrylic acid and acrylamide. And the copolymer–rare earth ion complexes were prepared. The effects of the microscopic environment upon fluorescent properties was studied by changing the composition of the copolymer, and by forming intermacromolecular complexes containing rare earth ion.

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In fluorescent complexes, many radiationless processes compete with fluorescing process. The number of the processes and the effects of the processes upon the fluorescent properties of the complexes are influenced by the microscopic environment around the rare earth ion. Studying the coordination forms and the effects of the microscopic environment upon the radiationless processes in the complexes is of great use for finding proper ways to improve the fluorescent properties of the complexes. Fluorescence lifetime measurement can facilitate this kind of investigation. So in this paper, the properties of the fluorescence lifetime of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  in the poly(acrylic acid-co-acrylamide)- $\text{Eu}^{3+}$  or - $\text{Tb}^{3+}$  complexes have also been studied.

## EXPERIMENTAL

### Acrylic Acid-Acrylamide Copolymer.

Commercial acrylic acid (AA) (Beijing Chemical Plant) was purified by distillation under reduced pressure. Commercial acrylamide (AAm) (Guangzhou Chemical Plant) was purified by recrystallization from benzene twice and then dried in vacuum oven. The aqueous solution of the monomers was adjusted to the desired pH value by adding stoichiometric amount of aqueous solution of sodium hydroxide. And then a three-necked flask with the solution was placed in a water bath and copolymerization was carried out at  $60 \pm 0.1^\circ\text{C}$  with potassium persulfate as the initiator. Nitrogen was bubbled through the solution during the copolymerization. The copolymer obtained was purified by reprecipitating twice from water-acetone, and dried in a vacuum oven at  $50^\circ\text{C}$ . The composition of the copolymers was determined from their nitrogen content.

### Polyacrylamide (PAAm)

PAAm was prepared by the method described in the literature.<sup>6</sup> The resulting polymer was purified by reprecipitating twice from water-methanol. The intrinsic viscosity of PAAm was 2.5 dL/g in 1M  $\text{Na}_2\text{CO}_3$  solution at  $30^\circ\text{C}$ .

### Poly(acrylic Acid) (PAA)

PAA was prepared by the method described in the literature.<sup>7</sup> The resulting polymer was purified by reprecipitating twice from water-methanol.

### Poly(4-Vinylpyridinium Chloride) (PVPy)

Poly(4-vinylpyridine) was prepared by the method described in the literature.<sup>8</sup> The resulting polymer was purified by reprecipitating twice from alcohol-water. PVPy was prepared by neutralizing the purified poly(4-vinylpyridine) with hydrochloric acid.

### Europium Chloride and Terbium Chloride

Spectrographically standardized europium oxide and terbium oxide (Johnson Matthey Chemicals Ltd. U.K.) were dissolved in hydrochloric acid, respectively. The solvent was evaporated, and the chlorides were dried.

### Polymer-Eu<sup>3+</sup> or -Tb<sup>3+</sup> Complexes

Aqueous solutions of the copolymer and EuCl<sub>3</sub> or TbCl<sub>3</sub> were mixed and heated at 100°C for 24 h. After the solvent was evaporated, the complex was dried and ground up, and then dried in a vacuum oven at 50°C for 72 h.

### Bipolymer-Eu<sup>3+</sup> or -Tb<sup>3+</sup> Complexes

Aqueous solutions of the copolymer and EuCl<sub>3</sub> or TbCl<sub>3</sub> were mixed and heated at 100°C for 24 h. The other polymer was added into the mixture. The obtained mixture was heated at 100°C for another 24 h. After the solvent was removed, the complex was dried and ground up, and then dried in a vacuum oven at 50°C for 72 h.

### Fluorescence Measurement

A Model MPF-4 Hitachi fluorescence spectrophotometer was used to measure the fluorescence spectra of the Eu<sup>3+</sup>- or Tb<sup>3+</sup>-copolymer complexes. The measurements were carried out at room temperature just after removing the samples from a drying oven in order to avoid the quenching of fluorescence by absorbed moisture.

### Fluorescence Lifetime Measurement

Fluorescence lifetime was determined using a laser induced fluorescence spectrophotometer.

## RESULTS AND DISCUSSION

In order to study the effect of the composition of the copolymer on the fluorescent properties of the copolymer-Eu<sup>3+</sup> or -Tb<sup>3+</sup> complexes, the copolymer must have uniform composition. Azeotropic copolymerization is the best way for obtaining uniform copolymer. The condition of azeotropic copolymerization is described by the following equation:

$$\frac{[M_1]}{[M_2]} = \frac{r_2 - 1}{r_1 - 1} \quad (1)$$

where  $[M_1]$  and  $[M_2]$  are the concentration of monomer 1 and monomer 2 in azeotropic copolymerization, respectively, and  $r_1$  and  $r_2$  are the reactivity ratios of monomer 1 and monomer 2 in azeotropic copolymerization, respectively. Equation (1) shows that by adjusting  $r_1$  and  $r_2$ , a series of uniform copolymer with various composition can be synthesized. The copolymerization of acrylic acid and acrylamide is such an example. The reactivity ratios of acrylic acid ( $r_1$ ) and acrylamide ( $r_2$ ) change with changing pH value of the reaction medium, although the course of many radical reactions including copolymerizations is fairly independent of the medium in which these reactions take place.<sup>9</sup> At low pH values, acrylamide is present in its protonated form which causes its reactivity to be low whereas at high pH values the reactivity of acrylic acid is decreased owing to its dissociation. So by changing pH value of the reaction medium, a series of uniform copolymers of acrylic

TABLE I  
Composition and Intrinsic Viscosity of the Copolymer Obtained from AA and AAm  
at Various pH Values and Feed Ratios

pH Value of the medium	Composition of the feed (AAm%)	Composition of the <sup>a</sup> copolymer (AAm unit%)	Intrinsic <sup>b</sup> viscosity (dL/g)
3.10	16.7	19.0	4.8
3.45	37.5	38.8	6.0
3.77	50.0	47.6	5.9
4.25	62.5	61.6	3.2
4.60	83.3	88.6	3.2

<sup>a</sup>From elementary analysis.

<sup>b</sup>In 1M Na<sub>2</sub>CO<sub>3</sub> aqueous solution at 30°C.

acid and acrylamide can be obtained by azeotropic copolymerization. Table I shows the composition of the obtained copolymers at various pH values and feed ratios, and the intrinsic viscosity of the copolymers.

The fluorescence spectra of the copolymer-Eu<sup>3+</sup> and the copolymer-Tb<sup>3+</sup> complexes are shown in Figures 1 and 2, respectively.

Figure 3 shows the relationship between fluorescence intensity of the copolymer-Eu<sup>3+</sup> complex and the composition of the copolymer. It can be noticed that the fluorescence intensity is affected greatly by the composition of the copolymer. The fluorescence intensity reaches a maximum when the molar ratio of carboxyl to amido in the copolymer is 1, and decreases with further increasing or decreasing carboxyl content in the copolymer. As the copolymer of AA and AAm has two kinds of coordination groups, Eu<sup>3+</sup> can coordinate with only carboxyl or amido, or with carboxyl and amido simultaneously. The relative quantity of the three coordination forms is affected by

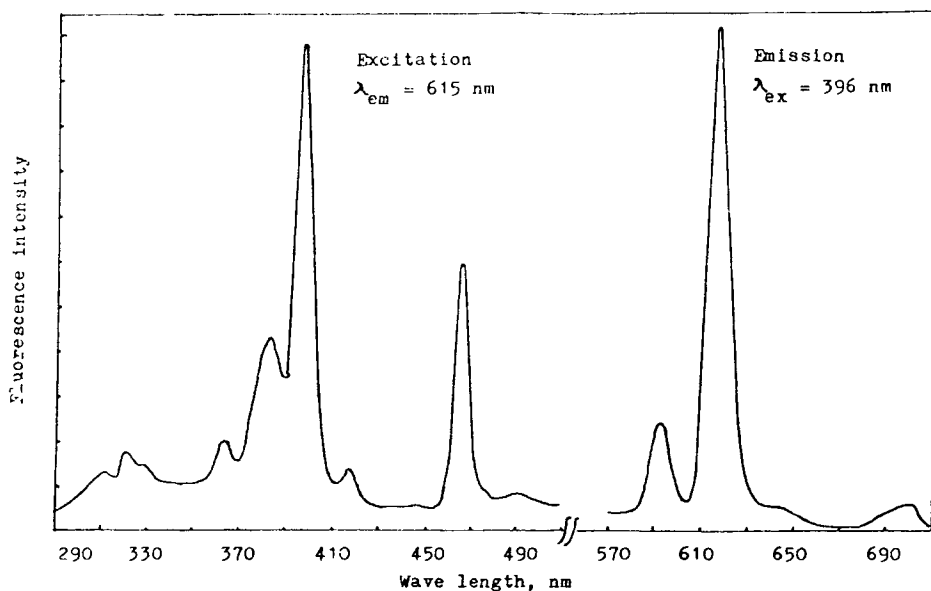


Fig. 1. Fluorescence spectra of the copolymer-Eu<sup>3+</sup> (Eu<sup>3+</sup>, 7.2 wt %) complex.

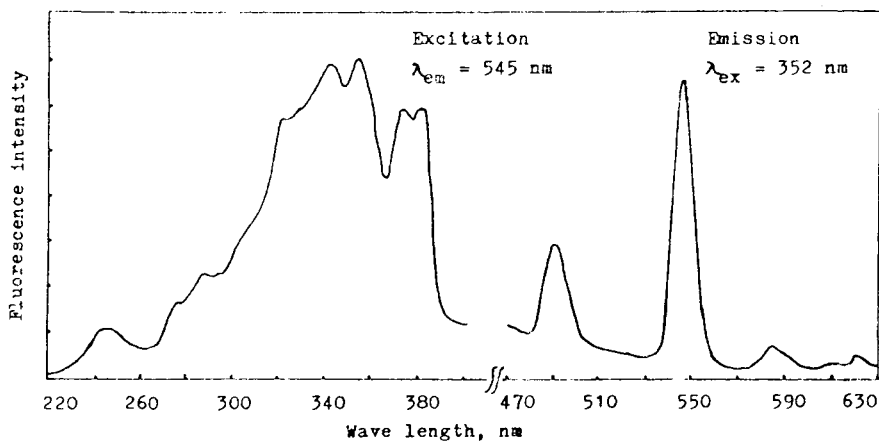


Fig. 2. Fluorescence spectra of the copolymer- $\text{Tb}^{3+}$  ( $\text{Tb}^{3+}$ , 7.2 wt %) complex.

the composition of the copolymer. When the molar ratio of carboxyl to amido is 1, the probability of the hybrid coordination of carboxyl and amido to  $\text{Eu}^{3+}$  is the greatest, with carboxyl content in the copolymer further increasing or decreasing, the probability of the hybrid coordination of carboxyl and amido to  $\text{Eu}^{3+}$  decreases. So Figure 3 demonstrates that the hybrid coordination of carboxyl and amido to  $\text{Eu}^{3+}$  enhances the fluorescence intensity more greatly than coordination of only carboxyl or amido.

The copolymer- $\text{Tb}^{3+}$  complex shows the similar changing tendency of the fluorescence intensity with the composition of the copolymer to the copolymer- $\text{Eu}^{3+}$  complex (see Fig. 4). The fluorescence intensity also reaches a

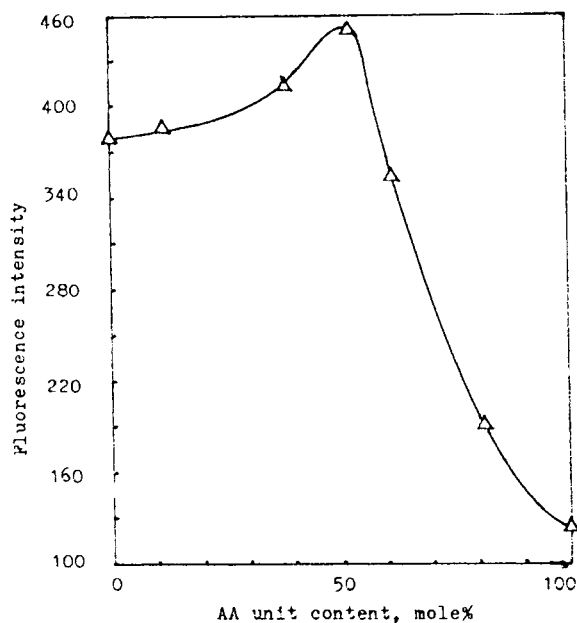


Fig. 3. Relationship between fluorescence intensity of the copolymer- $\text{Eu}^{3+}$  ( $\text{Eu}^{3+}$ , 7.2 wt %) complex and the composition of the copolymer.

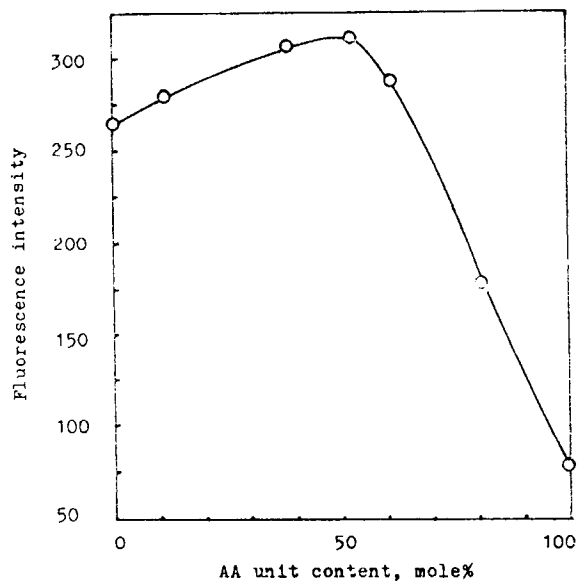


Fig. 4. Relationship between fluorescence intensity of the copolymer-Tb<sup>3+</sup> (Tb<sup>3+</sup>, 7.2 wt %) complex and the composition of the copolymer.

maximum when the molar ratio of carboxyl to amido is 1. This again indicates that the hybrid coordination of carboxyl and amido enhances the fluorescence intensity more greatly.

The fluorescence lifetime of a substance usually represents the average period of time during which the molecule remains in the excited state. Lifetime measurement is frequently necessary in study on fluorescent properties of fluorescent materials. The precise nature of the fluorescence decay can reveal details about the interaction nature of the fluorophore with its environment.

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

$$F(t) = \sum a_i e^{-t/\tau_i} \quad (2)$$

where  $a_i$  is a preexponential factor representing the fractional contribution to the time-resolved decay of the component with a lifetime  $\tau_i$ .

Figure 5 shows the relationship between  $\ln F(t)$  and the decay time for the copolymer-Eu<sup>3+</sup> complex. It can be noticed that the complex shows a multiple exponential decay. This demonstrates that at least two coordination forms of Eu<sup>3+</sup> exist in the complex apparently. When decay time is short, all coordination forms contribute to  $F(t)$ ; with decay time increasing, the contribution of the coordination form with short lifetime decreases, and, at last, most of the contribution to  $F(t)$  is made by the coordination form with a long lifetime. And the relationship between  $\ln F(t)$  and decay time becomes a linear one.

The tendency of multiple exponential decay for the copolymer-Tb<sup>3+</sup> complex is much less than that for the copolymer-Eu<sup>3+</sup> complex (see Fig. 6). The copolymer used in both Figures 5 and 6 contains 47.62% of the AAm unit.

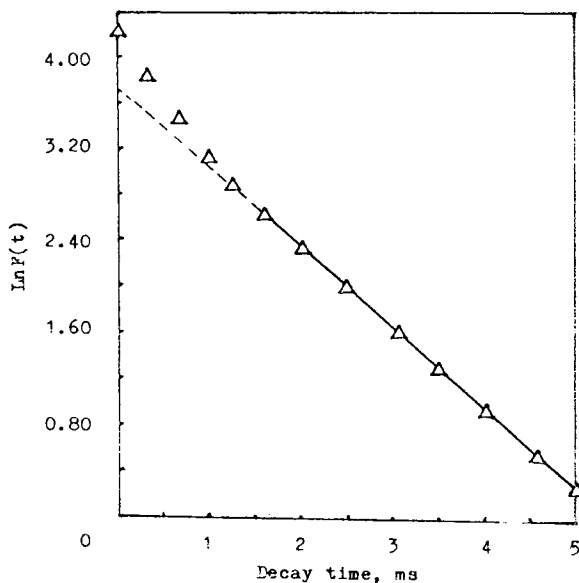


Fig. 5.  $\ln F(t)$  vs. decay time for the copolymer- $\text{Eu}^{3+}$  ( $\text{Eu}^{3+}$ , 7.2 wt %) complex.

In a polymer-rare earth ion complex with more than one coordination forms of rare earth ion, the complex often shows a linear relationship between  $\ln F(t)$  and decay time when decay time is long; but when decay time is short, some deviation from the linear relationship is often observed. The deviation represents the difference of the nature or the relative quantity of the coordination forms of the rare earth ion. The greater the deviation, the greater is the difference of the nature or the relative quantity of the coordination forms of the rare earth ion. The results of the fluorescence lifetime measurement of

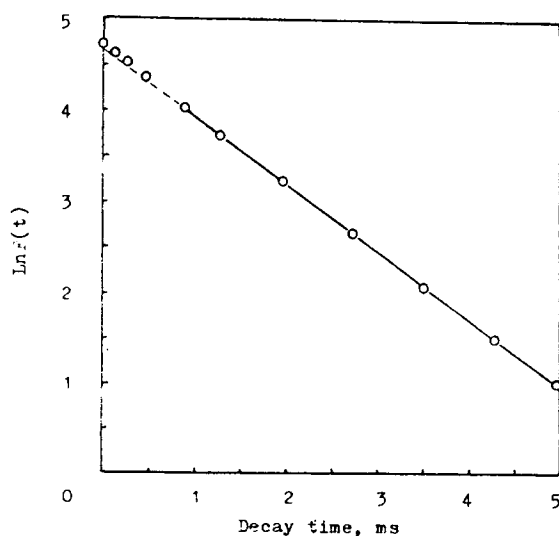


Fig. 6.  $\ln F(t)$  vs. decay time for the copolymer- $\text{Tb}^{3+}$  ( $\text{Tb}^{3+}$ , 7.2 wt %) complex.

the copolymer-Eu<sup>3+</sup> or -Tb<sup>3+</sup> complexes show that the deviation from the linear relationship depends on the composition of the copolymer in the complexes. The deviation increases with increasing AA unit content in the copolymer, reaches a maximum when the copolymer contains about 50% AA unit, and decreases with further increasing AA unit content in the copolymer.

The fluorescence lifetime of a fluorescent material is given by

$$\tau = \frac{1}{K_f + \sum K_d} \quad (3)$$

where  $K_f$  is the molecular probability that the excited molecule will fluoresce (rate constant for fluorescence) and  $\sum K_d$  is the sum of the rate constants for deactivation of the lowest excited singlet state by all competitive radiationless processes. Because of the radiationless processes, of a given number of molecules in the lowest vibrational level of their lowest excited singlet state at any instant of time, not all will return to the ground state by fluorescence. The fraction of excited molecules that do fluoresce is called the quantum yield of fluorescence ( $\phi$ ), or fluorescence efficiency, and under given conditions of temperature and environment is a physical constant of the excited molecular species. The greater  $\phi_f$ , the stronger will be fluorescence intensity. In terms of fluorescence lifetime,  $\phi_f$  is given by

$$\phi_f = K_f \cdot \tau = \frac{K_f}{K_f + \sum K_d} \quad (4)$$

The relationship between fluorescence lifetime of Eu<sup>3+</sup> in the copolymer-Eu<sup>3+</sup> complex and the composition of the copolymer is shown in Figure 7. It

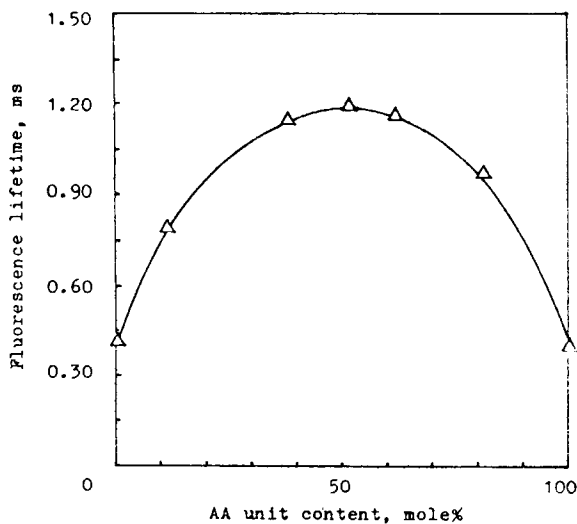


Fig. 7. Relationship between fluorescence lifetime of Eu<sup>3+</sup> in the copolymer-Eu<sup>3+</sup> (Eu<sup>3+</sup>, 7.2 wt %) complex and the composition of the copolymer.



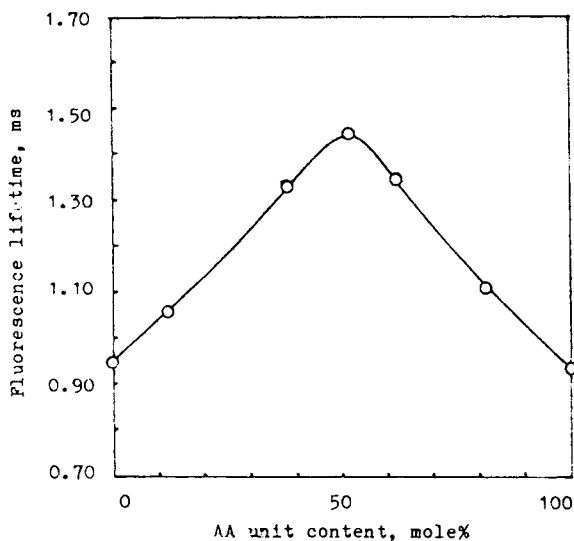


Fig. 8. Relationship between fluorescence lifetime of  $Tb^{3+}$  in the copolymer- $Tb^{3+}$  ( $Tb^{3+}$ , 7.2 wt %) complex and the composition of the copolymer.

can be noticed that the relationship is similar to that between fluorescence intensity and the composition of the copolymer. When the copolymer contains about 50% of AAm unit, the lifetime reaches a maximum like  $\phi_f$ . This demonstrates that the value of  $\Sigma K_d$  depends upon the composition of the copolymer and becomes the smallest when the copolymer contains about 50% of AAm unit. It can be deduced from this result that the decrease in  $\Sigma K_d$  is

TABLE II  
Fluorescence Intensity and Fluorescence Lifetime of Bipolymer- $Eu^{3+}$  or  $Tb^{3+}$  Complexes

Composition	Fluorescence intensity	Fluorescence lifetime (ms)
Copolymer (47.6%)– $Eu^{3+}$	100.0	1.192
Copolymer (19.0%)–PVPy– $Eu^{3+}$	43.6	0.613
Copolymer (19.0%)–PAAm– $Eu^{3+}$	49.0	0.704
Copolymer (38.8%)–PVPy– $Eu^{3+}$	56.7	0.837
Copolymer (38.8%)–PAAm– $Eu^{3+}$	73.9	0.901
Copolymer (61.6%)–PAA– $Eu^{3+}$	71.3	0.875
Copolymer (88.6%)–PAA– $Eu^{3+}$	60.3	0.781
Copolymer (47.6%)– $Tb^{3+}$	100.0	1.443
Copolymer (19.0%)–PVPy– $Tb^{3+}$	47.4	1.207
Copolymer (19.0%)–PAAm– $Tb^{3+}$	82.9	1.220
Copolymer (38.8%)–PVPy– $Tb^{3+}$	68.6	1.316
Copolymer (38.8%)–PAAm– $Tb^{3+}$	94.3	1.231
Copolymer (61.6%)–PAA– $Tb^{3+}$	86.6	1.293
Copolymer (88.6%)–PAA– $Tb^{3+}$	76.1	1.255

\* <sup>a</sup>All the complexes contain 47.6 mol % of AAm unit or nitrogen-containing unit, and 7.2 wt % of rare earth ion.

<sup>b</sup>The figures in the brackets are the AAm content in mol % in the copolymers.

<sup>c</sup>The fluorescence intensity of the copolymer (47.6%)– $Eu^{3+}$  and the copolymer (47.6%)– $Tb^{3+}$  complexes is taken as 100.0.

the reason that the hybrid coordination of carboxyl and amido to  $\text{Eu}^{3+}$  makes the fluorescence intensity of  $\text{Eu}^{3+}$  stronger than homogenous coordination of amido or carboxyl to  $\text{Eu}^{3+}$  does.

The dependence of fluorescence lifetime upon the composition of the copolymer for the copolymer- $\text{Tb}^{3+}$  complex is similar to that for the copolymer- $\text{Eu}^{3+}$  complex (see Fig. 8).

Table II shows the relationship between the composition of the complexes, fluorescence intensity, and fluorescence lifetime for the copolymer- $\text{Eu}^{3+}$  or - $\text{Tb}^{3+}$  and bipolymer- $\text{Eu}^{3+}$  or - $\text{Tb}^{3+}$  complexes. It can be noticed that for either  $\text{Eu}^{3+}$ - or  $\text{Tb}^{3+}$ -containing complexes, all the bipolymer-rare earth ion complexes fluoresce more weakly than the copolymer-rare earth ion complex does when the molar ratio of amido or nitrogen-containing group to carboxyl in the complexes is the same. This demonstrates that, although hybrid coordination of carboxyl and amido or nitrogen-containing group to  $\text{Eu}^{3+}$  or  $\text{Tb}^{3+}$  can take place in the two types of complexes, intramacromolecular hybrid coordination makes  $\text{Eu}^{3+}$  or  $\text{Tb}^{3+}$  fluoresce more strongly than intermacromolecular hybrid coordination does.

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