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### Synthesis, Characterization, and Applications of Polymers Containing Lanthanide Metals

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# **SYNTHESIS, CHARACTERIZATION, AND APPLICATIONS OF POLYMERS CONTAINING LANTHANIDE METALS**

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## **ABSTRACT**

This paper reviews the author's work on polymers containing lanthanide metals. The discussion focuses on the use of lanthanide-metal-ion probes to investigate the structures of ionomers and the ion-binding properties of polyelectrolytes. Preliminary fluorescence results of europium and terbium in chelating polymers are also discussed.

## **INTRODUCTION**

Recently, in our laboratory, investigations have been initiated on the preparation, characterization, and applications of polymers containing lanthanide-metal ions. Our primary objectives are 1) to utilize lanthanide-metal ion probes to elucidate the structures of ionomers, 2) to utilize lanthanide-metal ion probes to study the ion binding properties of polyelectrolytes, and 3) to study detailed fluorescence properties of lanthanide-metal-containing synthetic polymers and to explore the possible laser application. This paper reviews these studies to the present date.

## DISCUSSION AND RESULTS

### I. Use of Lanthanide-Metal Probes to Elucidate the Structure of Ionomers

The properties of synthetic polymers containing metal ions have been extensively investigated in recent years [1, 2]. An important class of these polymers consists of the ethylene-carboxylic acid copolymers which have been either partially or wholly neutralized with Group I and II cations. This kind of polymer has been named "ionomer." On neutralization of the carboxylic acid, it is found that properties such as optical clarity, tensile strength, impact resistance, and melt viscosity are dramatically enhanced.

Low molecular weight organic complexes of lanthanide metals have unique and interesting properties. Interest in lanthanide complexes has been stimulated by their fluorescent and laser properties [3]. Polymers have been utilized as a matrix for these complexes, and their fluorescent and laser properties have been investigated [4, 5]. However, polymeric systems in which lanthanide metals are directly bonded to the chain have been studied only slightly. Recently, we have synthesized lanthanide ( $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ , etc) salts of polymers such as poly(acrylic acid) (PAA), poly(methacrylic acid) (PMA), partially sulfonated or carboxylated styrene, styrene-acrylic acid copolymers (PSAA), and methyl methacrylate-methacrylic acid copolymers (PMM/MA).

The fluorescence intensity was measured on dried and finely powdered samples or their films. The scatter of data was found to be 5%. Typical excitation and emission spectra of the  $\text{Eu}^{3+}$ -polymer complex are shown in Fig. 1. The bright transitions from the  ${}^5D_0$  levels to all the  ${}^7F$  multiplet levels can be seen. This emission spectrum was obtained under excitation at 396 nm, corresponding to the  $\text{Eu}^{3+} {}^5L_7$  level.

We have also prepared samples in which  $\text{Eu}^{3+}$  acetate is uniformly dispersed in polymer matrices such as polystyrene and poly(methyl methacrylate). Both in  $\text{Eu}^{3+}$ -polymer salts and in  $\text{Eu}^{3+}$  acetate,  $\text{Eu}^{3+}$  was coordinated with carboxylate. As shown in Fig. 2 for the europium acetate system, the fluorescence intensity was found to increase linearly with Eu content. However, in the polymer- $\text{Eu}^{3+}$  complex system, the fluorescence intensity reached a maximum at Eu as low as 4-5 wt% and subsequently decreased with increasing Eu content (Fig. 3). The observed dependence of fluorescence intensity on increasing  $\text{Eu}^{3+}$  content is a typical fluorescence-quenching pattern [6] and the result provides supporting evidence that the PSAA copolymers have ionic aggregates in which metal ions are close together. In other words, the local concentration of  $\text{Eu}^{3+}$  ions in these regions is much higher than the overall average concentration. A similar trend in  $\text{Tb}^{3+}$  polymer salts was also observed (Fig. 3) [7, 8].

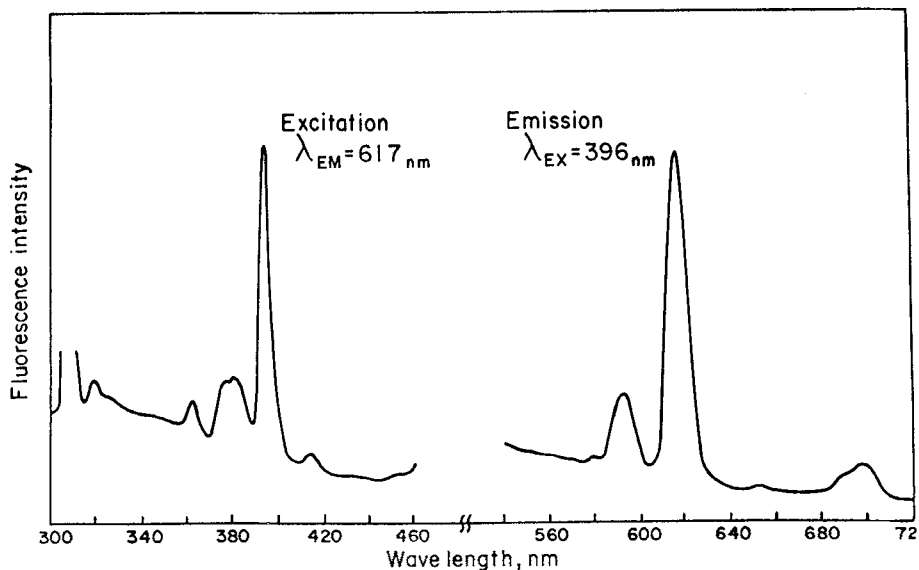


FIG. 1. Fluorescence spectra of poly(acrylic acid)  $\text{Eu}^{3+}$  salt. Eu, 5.0 mol%.

Considerable effort has been devoted to the study of nonradiative energy transfer between fluorescent lanthanide donor-acceptor pairs in the solid state [9-13]. When the emission spectrum of the donor overlaps the absorption spectrum of the acceptor, excitation energy absorbed by the donor can be transferred to the acceptor over considerable distances [14]. Thus, we attempted to elucidate the size of the ion aggregates using Tb-Eu and Tb-Co metal probes. The energy transfer from  $\text{Tb}^{3+}$  to  $\text{Co}^{2+}$  and  $\text{Eu}^{3+}$  were measured by the  $\text{Tb}^{3+}$  fluorescence quenching behavior.

In the poly(styrene-acrylic acid) system, effective  $\text{Tb}^{3+}$  fluorescence quenching by  $\text{Co}^{2+}$  and also by  $\text{Eu}^{3+}$  was observed (Figs. 4 and 5). The results show that  $\text{Tb}^{3+}$  fluorescence is completely quenched by the presence of less than equimolar amounts of  $\text{Co}^{2+}$ . The  $\text{Tb}^{3+}$  fluorescence was also found to be effectively quenched by  $\text{Eu}^{3+}$ . We calculated that the distance between the two metals must be smaller than the critical transfer distance, which is of the order of 1.0 nm [11]. Neither similar energy transfer between these metal ions nor the fluorescence quenching pattern (see Figs. 6 and 7) in the polymer systems, such as partially sulfonated or carboxylated styrene, were detected. These results provided further evidence that the sulfonated or carboxylated polystyrene

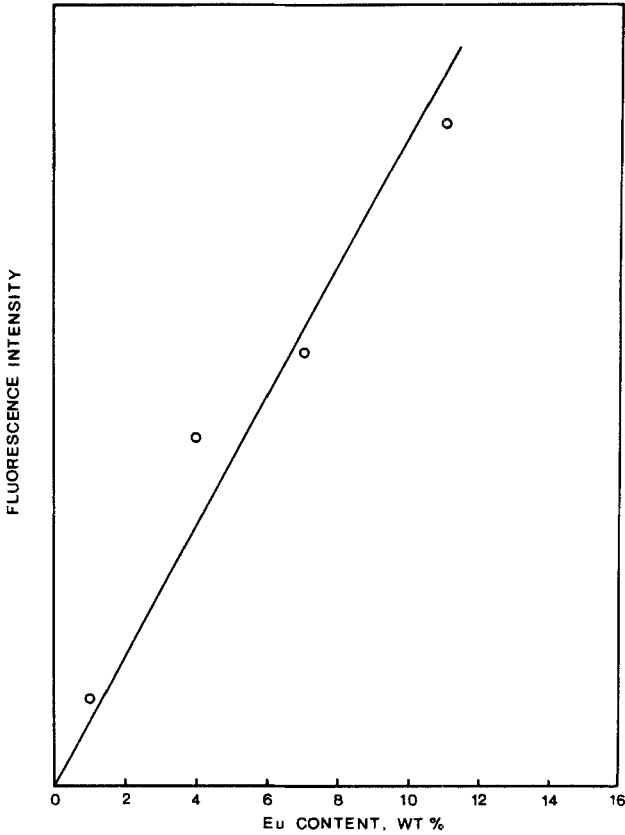


FIG. 2. Relationship between fluorescence intensity and Eu content in Eu acetate-polystyrene composite.

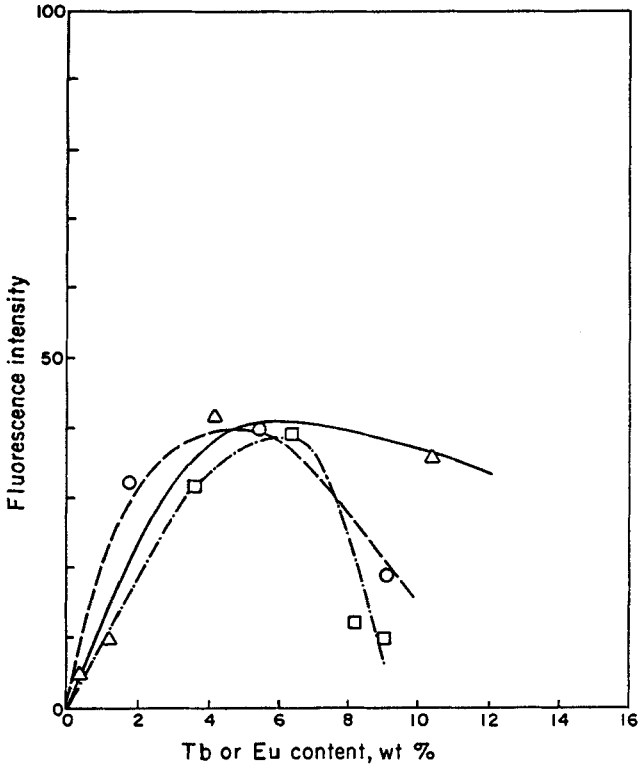


FIG. 3. Relationship between fluorescence intensity and metal content. (○) PSAA-Eu salt (COOH content 13 mol%), (△) PSAA-Eu salt (COOH content 9 mol%), (□) PSAA-Tb salt (COOH content 13 mol%).

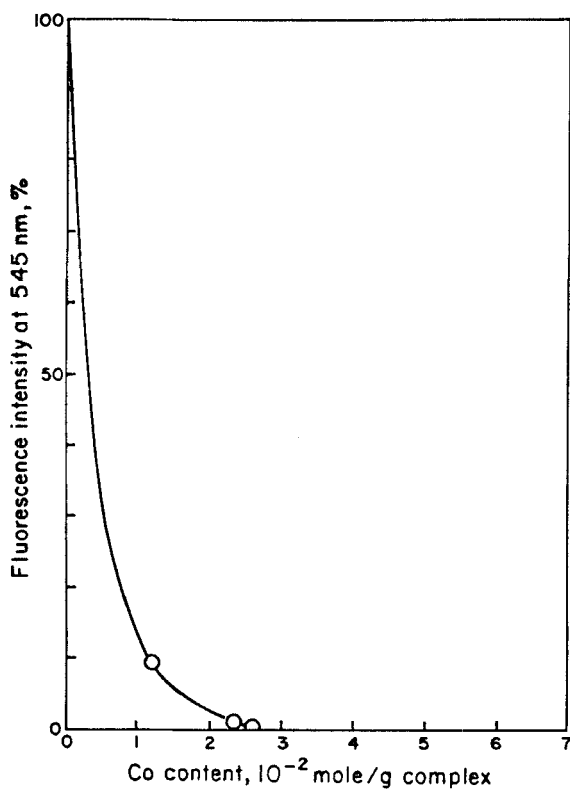


FIG. 4. Energy transfer from  $Tb^{3+}$  to  $Co^{2+}$  in PSAA.

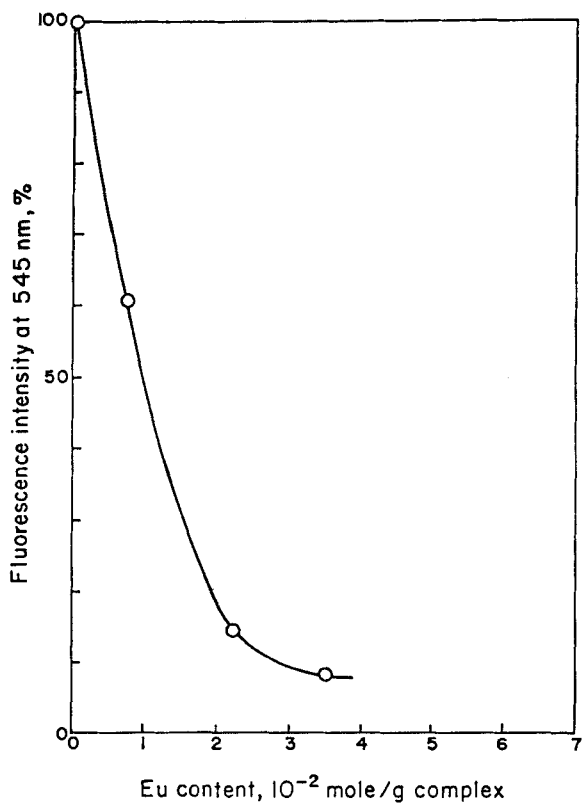


FIG. 5. Energy transfer from  $Tb^{3+}$  to  $Eu^{3+}$  in PSAA.



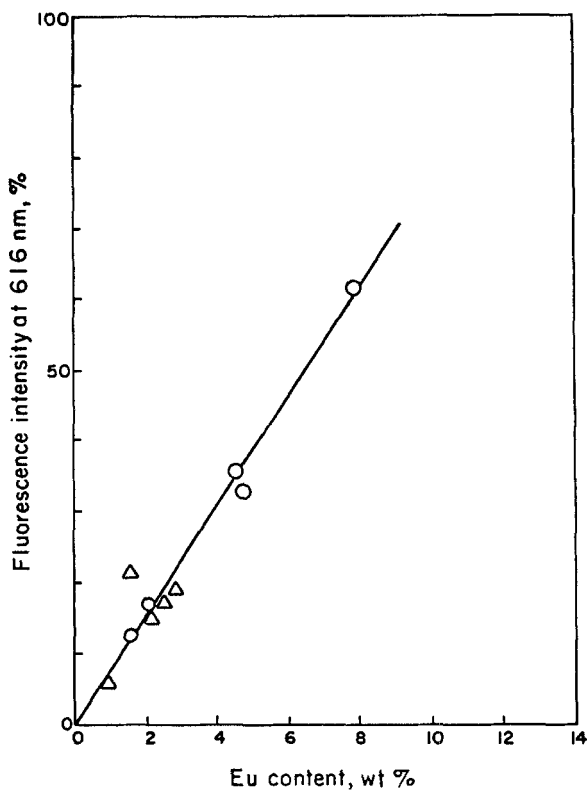


FIG. 6. Fluorescence intensity vs Eu content in sulfonated polystyrene-Eu<sup>3+</sup> salt: (Δ) sulfonic acid content, 2.6 mol%; (○) sulfonic acid content, 6.1 mol%.

ionomers do not contain ion aggregates [15] and that the acrylic copolymers contain ionic cluster structure.

The emitting level of the UO<sub>2</sub> ion is about 480 nm and the fluorescence extends from 480 to about 570 nm. Three transitions of Eu<sup>3+</sup> ion are observed at room temperature within this energy range. It has been found that UO<sub>2</sub><sup>2+</sup> transfers energy to Eu<sup>3+</sup> in borosilicate glass, resulting in a fivefold increase in the Eu fluorescence [16]. If the ion-containing polymer forms ion aggregates, it is very likely that Eu<sup>3+</sup> and UO<sub>2</sub><sup>2+</sup> pairs are located close together within the aggregates and that efficient energy transfer would be observed. Thus, we prepared Eu<sup>3+</sup> and UO<sub>2</sub><sup>2+</sup> mixed salts of PSAA and PMMA/

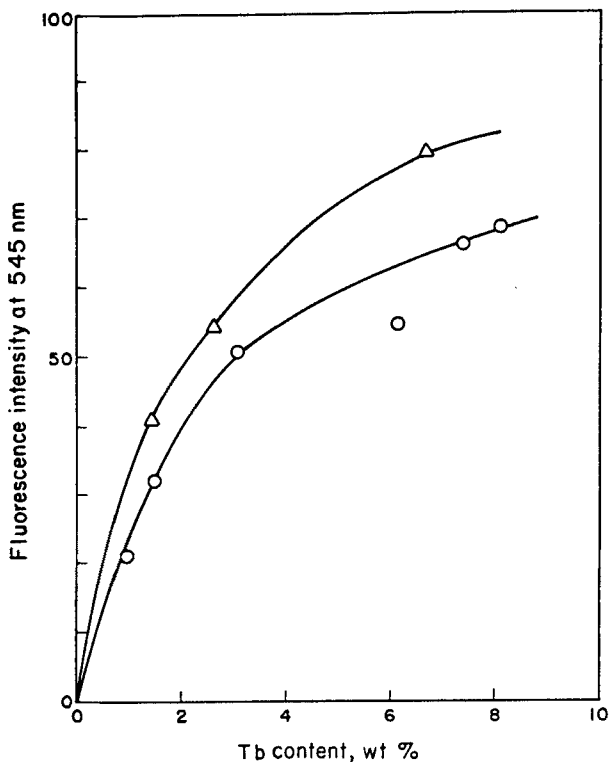


FIG. 7. Fluorescence intensity vs Tb content in carboxylated polystyrene-Tb<sup>3+</sup> salt: (○) carboxylic acid content, 5.0 mol%; (△) carboxylic acid content, 6.4 mol%.

MA. The fluorescence intensity was found to be greatly increased (~30 fold) when equal molar concentrations of UO<sub>2</sub><sup>2+</sup> and Eu<sup>3+</sup> were present in these polymer systems [17].

These results further support the existence of ion aggregate structures in the ionomers such as PMM/MA and PSAA in which Eu<sup>3+</sup> and UO<sub>2</sub><sup>2+</sup> are located close together, facilitating the energy transfer between these ions.

We have also investigated the fluorescence behavior of the lanthanide-metal salts of Nafion membranes [18], which consist of perfluorinated sulfonate. When Eu<sup>3+</sup> was bound to the Nafion membrane, the fluorescence of Eu<sup>3+</sup> was greatly enhanced due to formation of asymmetric bonding between Eu<sup>3+</sup> and

locally concentrated  $\text{SO}_3^-$  groups in the membrane. The fluorescence intensities of  $\text{Eu}^{3+}$  were also greatly increased when  $\text{UO}_2^{2+}$  was present (on excitation of  $\text{UO}_2^{2+}$ ). These findings indicate the existence of ion-cluster structures in the membrane in which  $\text{Eu}^{3+}$  and  $\text{UO}_2^{2+}$  are located close together, facilitating energy transfer between these ions. On heating a Nafion membrane containing  $\text{Eu}^{3+}$  and  $\text{UO}_2^{2+}$ , the fluorescence intensity of  $\text{Eu}^{3+}$  decreased sharply at around  $130^\circ\text{C}$ . This indicates that the distance between  $\text{Eu}^{3+}$  and  $\text{UO}_2^{2+}$  had increased with increasing temperature due to thermal deformation of the cluster structure of the membrane. The Nafion-Tb sample showing the concentration quenching was heated, resulting in an increase in fluorescence intensity of  $\text{Tb}^{3+}$  at around  $130^\circ\text{C}$ . These results also indicate that the structure of the cluster began to deform at around  $130^\circ\text{C}$ , and the average distance between  $\text{Tb}^{3+}$  ions was increased by about 0.1-0.15 nm. This behavior was reproducible on thermal cycling [19].

These investigations suggest that the lanthanide fluorescence probe technique is simple and useful for studying ionomer structure.

## II. Use of Lanthanide-Metal Probes to Study the Ion-Binding Properties of Polyelectrolytes

Interest in the absorption and fluorescence of lanthanide metal ions in solution has been greatly stimulated because of their possible use as lasers. In an effort to obtain stronger fluorescence, two general approaches appear possible. The first involves the addition to the solution of an agent, usually an organic ligand, that will absorb energy and transfer it to the lanthanide ion. An alternative method is to enhance the absorption and fluorescence of the lanthanide ion itself by suitable changes in its environment.

The extreme sensitivity of certain lanthanide absorption bands to their detailed solution environment is well documented, and the phenomenon is referred to as "hypersensitivity" [20]. Hypersensitive absorption is greatly increased by three factors: increasing the basic character of the coordinating ligand, decreasing the metal ion-ligand bond distance, and increasing the number of coordinated ligands.

Recently, we observed that an excitation peak (310 nm) and the fluorescence intensity (545 nm) of  $\text{Tb}^{3+}$  ions are greatly enhanced when they are bound to synthetic polyelectrolytes in aqueous solution (Fig. 8) [21]. These results suggest that the absorption band (310 nm) corresponds to the hypersensitive transition of  $\text{Tb}^{3+}$  ion and that the ions are site-bound on the poly-anions.

The excitation peak (310 nm) and the fluorescence intensity (545 nm) of

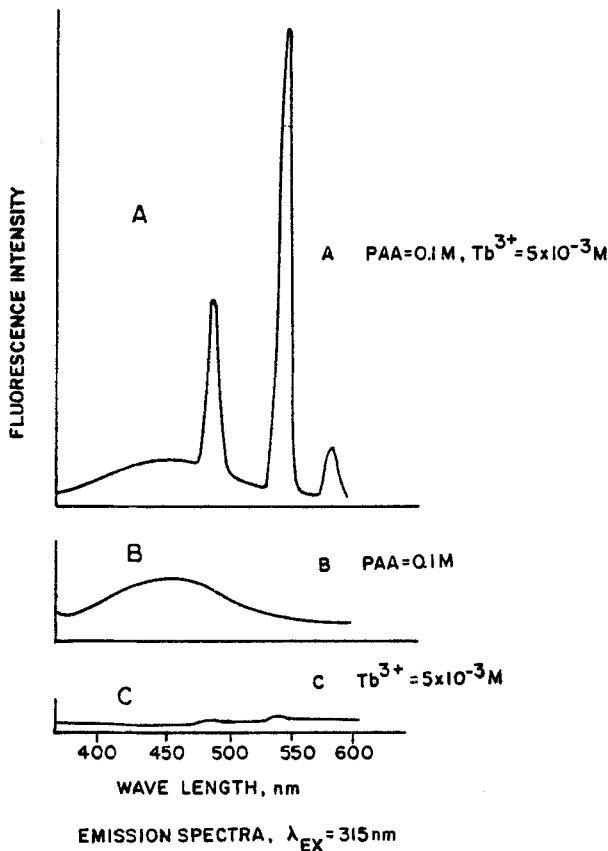


FIG. 8. Enhancement of the fluorescence intensity in PAA- $Tb^{3+}$  aqueous solution at 25°C.

$Tb^{3+}$  ion in aqueous polyacrylate solution do not change upon standing at room temperature. However, it was found that, when the solution was irradiated with ultrasonic waves, the intensities were greatly enhanced (Fig. 9). These intensities increased with increasing duration of the irradiation. However, it was found that, when the irradiated solution was allowed to stand at room temperature, these intensities gradually decreased toward the preirradiation intensities. Typical data are plotted in Fig. 10 [22]. These phenomena suggest that the polyacrylate chain was compressed and disturbed by

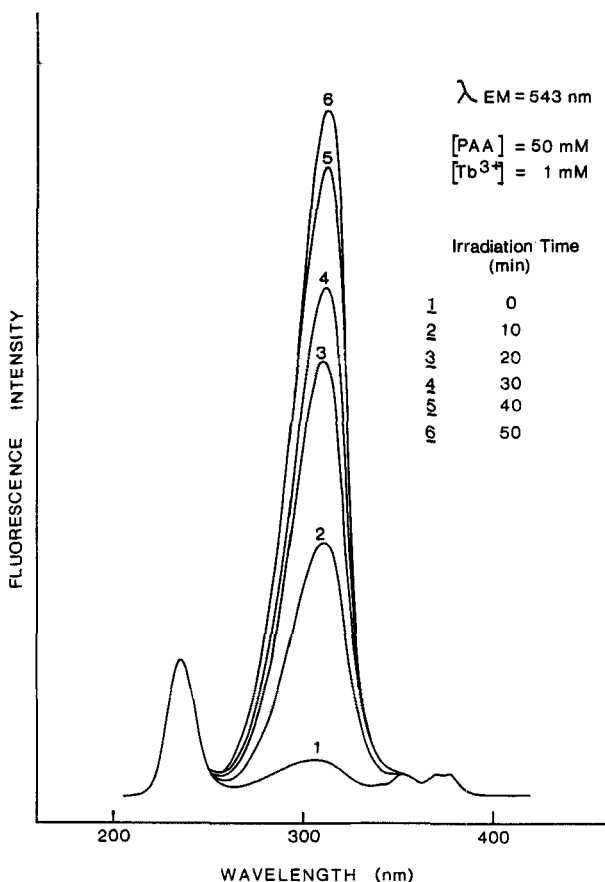


FIG. 9. Effects of ultrasonic irradiation on fluorescence of Tb<sup>3+</sup> in aqueous PAA solution at 25°C.

ultrasonic irradiation, resulting in increasing binding of Tb<sup>3+</sup> ions to the nearest carboxylates.

The resulting structure may have a greater coordination number and decreased ion-ligand bond distance, leading to a further increase in the absorption and fluorescence intensity. However, the complex has an internal stress, rendering it thermodynamically unstable. As a result, when the sample was aged at room temperature, the structure rearranged gradually to a more strain-free form, leading to a decrease in the absorptions and fluorescence intensity.

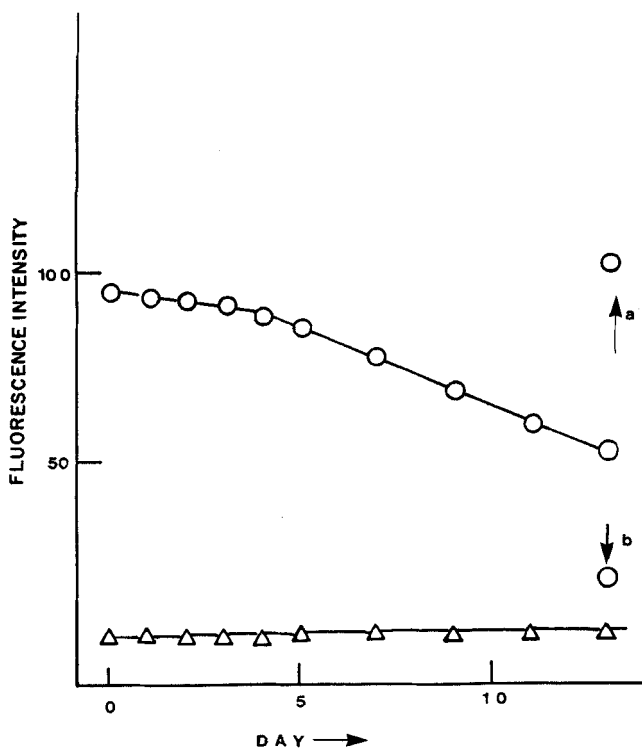


FIG. 10. Fluorescence intensity of  $Tb^{3+}$  ion in aqueous polyacrylate solution. (○) After 20 min ultrasonic irradiation at  $10^{\circ}C$ . (△) Without ultrasonic irradiation. (a) After additional 20 min ultrasonic irradiation at  $10^{\circ}C$ . (b) After heating 15 min at  $75^{\circ}C$ . The fluorescence was measured at  $25^{\circ}C$ .

When  $Tb^{3+}$  ion was added to a solution of the sodium salt of poly(methyl acrylate) (PMA), only moderate enhancement of the fluorescence intensity was obtained.

The complex formation of polyanions with metal ions usually results in an intramolecular coordination (cooperative binding) which leads to contraction of the polymer chain [23]. When methyl groups are attached to the polymer chain, the polymer is less flexible, and multidentate complex formation becomes more difficult [24]. Thus, when the PMA- $Tb^{3+}$  system was irradiated with ultrasonic waves, the coordination structure of the  $Tb^{3+}$  with respect to the carboxylates did not change and, as a result, no effect of ultrasonic irradiation on the absorption and fluorescence intensity could be detected.

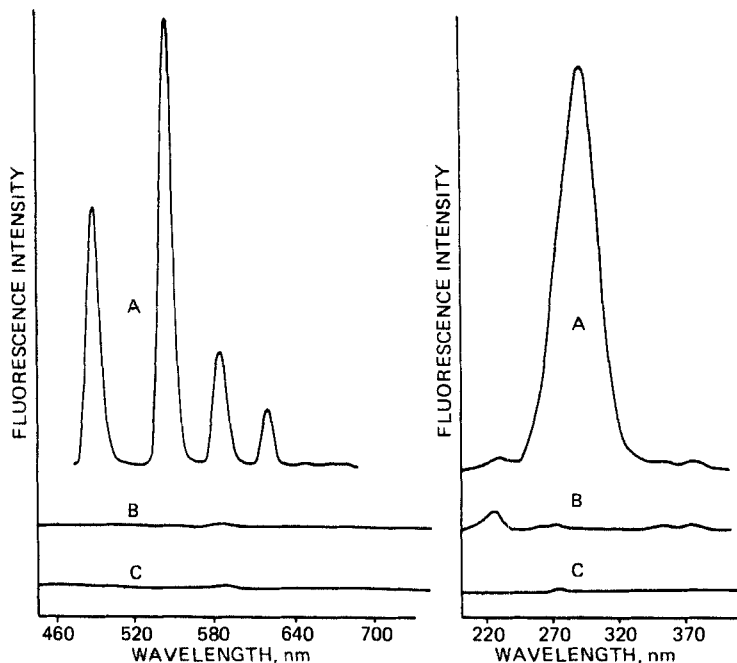


FIG. 11. Effect of dextran sulfate on the excitation spectrum (left, emission wavelength 545 nm) and luminescence spectrum (right, excitation wavelength 290 nm) of Tb(III) in aqueous solution. Spectra labeled A correspond to Tb(III) and dextran sulfate, both at concentrations of 10 mM. Spectra labeled B correspond to 10 mM  $TbCl_3$ , and spectra C correspond to 10 mM dextran sulfate.

We have also observed that an absorption peak for the hypersensitive transition (310 nm) and the fluorescence intensity (545 nm) of  $Tb^{3+}$  ion are greatly enhanced when it is bound to polysaccharides, such as heparin and carrageenan (Fig. 11) [25]. These results indicate that not only lanthanide ions form complexes with polysaccharides in the electrostatic manner of polyelectrolytes, but that specific chelating groups can further influence the metal-ion binding characteristics. This hypothesis can be tested by examination of the chiroptical properties of the Tb/polysaccharide complexes. One of the most useful techniques for the study of chiral lanthanide compounds is that of circularly polarized luminescence (CPL) spectroscopy [26, 27].

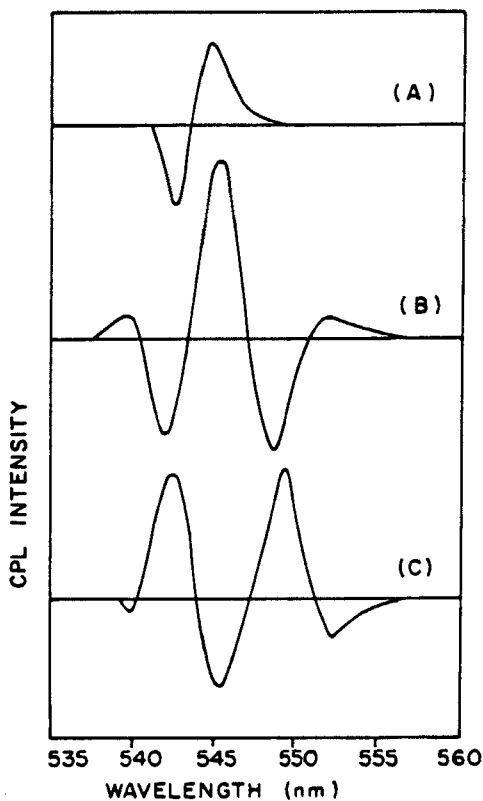


FIG. 12. Circularly polarized luminescence spectra obtained for the Tb(III) complexes with heparin (A), carboxymethyl cellulose (B), and sclerox (S-1.0) (C).

While formation of Tb-polysaccharide invariably led to enhanced Tb-fluorescence, this emission was always found to yield CPL. The fluorescence of Tb complexes with aqueous dextran sulfate, i- or k-carrageenan, and amylose sulfate was not found to exhibit any measurable optical activity. On the other hand, quite strong CPL was observed in the Tb complexes of heparin (sodium salt), carboxymethylcellulose (CMC), and sclerox (S-1.0) (Fig. 12). The latter group of polysaccharides differs from the former in that its members contain carboxylate groups. It appears that the presence of carboxylate groups in the polysaccharide chain produces well-defined binding sites for the



Tb ions, and that these sites are very chiral. When the Tb binding is affected by sulfate groups, the sites are more random. Random binding of Tb ions on the polysaccharide chain would not be expected to yield strong CPL, as the chiralities of the many sites could partially cancel. This investigation shows that combined study of the fluorescence and chirality of lanthanide ion salts of polysaccharides can yield important information regarding the metal-ion binding sites of these polymers.

These results showed that the lanthanide-ion fluorescence-probe technique is also useful for the elucidation of the ion-binding properties in aqueous poly-electrolyte solutions.

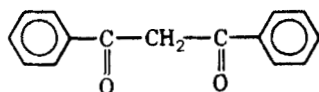
### III. Investigation of the Fluorescence Properties of Lanthanide-Polymer Complexes Containing $\beta$ -Diketone and Keto-Carboxyl Ligands

The fluorescent characteristics of europium chelates are of considerable interest in connection with electronic energy-transfer processes and with their use in laser systems [28, 29]. The most successful laser systems have demonstrated the use of compounds of the  $[(\beta\text{-diketonato})_4 \text{Eu} \cdot \text{P}^+]$  system as the active species, where  $\text{P}^+$  is a cation such as piperidinium or substituted ammonium.

The chelate system is interesting because the pump energy is absorbed by the organic molecule and then is efficiently transferred to the lanthanide ion. This differs from conventional systems where the optical pump energy is absorbed by the lanthanide ion itself. Because of this energy-transfer process in the chelate system, the lanthanide ion is pumped more effectively than in the conventional crystal and glass lasers. The europium chelate laser emits at a wavelength of 613 nm in the red portion of the visible spectrum. However, the tetrakis chelates tend to dissociate in organic solution into lower chelate forms, tris- and bischelates and free diketones [30].

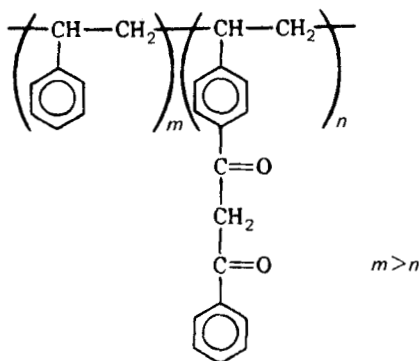
The dissociation may be minimal in the solid polymer complexes where the chelate should be, to a certain extent, locked into a specific configuration. Thus we investigated the fluorescence properties of  $\text{Eu}^{3+}$ -polymer complexes containing  $\beta$ -diketone ligands (2 and 3) [31]. Their fluorescence properties were compared with those of the corresponding complex of  $\text{Eu}^{3+}$  with dibenzoylmethane (1).

We have prepared the  $\text{Eu}^{3+}$ -dibenzoylmethane (DBM) complex,  $\text{Eu}(\text{DBM})_4 \cdot \text{P}^+$  ( $\text{P}^+$  is the piperidinium ion). The complexes were uniformly dispersed in a polystyrene matrix. The fluorescence emission intensity was found to increase linearly with increasing Eu content (Fig. 13). However, for the Eu-coordination polymers of 2 and 3, the intensity was found to reach a maximum

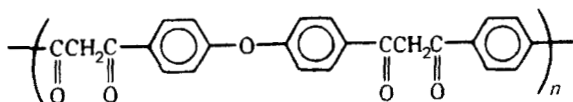


1

dibenzoylmethane



2

poly(*p*-benzoylacetlylstyrene)

3

poly(aryl  $\beta$ -diketone)

at an Eu content as small as 1 wt% (Fig. 14) [31]. The fluorescence intensity of the lower numbered coordination complexes such as tris- (Eu(DBM)<sub>3</sub>) and bis- (Eu(DBM)<sub>2</sub>) are much weaker compared to the same amount of Eu content in Eu(DBM)<sub>4</sub>. Thus, these results (Fig. 14) show that, when the  $\beta$ -diketone group is incorporated in the polymer chain, the formation of multiple coordination Eu<sup>2+</sup> ion with  $\beta$ -diketone ligands is restricted by the increasing steric hindrance and decrease of the freedom of bond rotation [31, 32].

In order to obtain the maximum fluorescent efficiency for the Eu<sup>3+</sup> content, a monomer (Eu<sup>3+</sup> tetradibenzoylmethide) was synthesized in which a polymerizable vinyl group (D') was bonded to one of the phenyl groups (EuD'D<sub>3</sub>)-P<sup>+</sup> (4).

Monomer (4) was dissolved in methylene chloride and methyl methacrylate

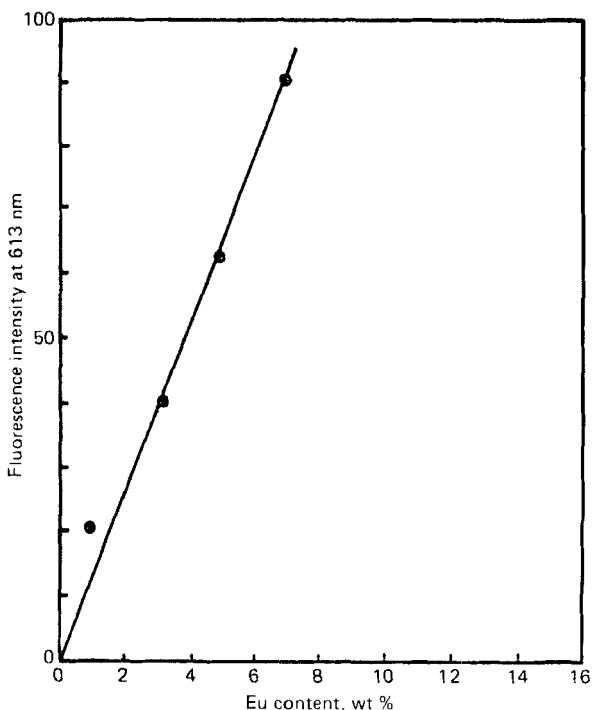


FIG. 13. Relationship between fluorescence intensity and Eu content of  $\text{Eu}(\text{DBM})_4$  in polystyrene. Slit  $E_x/E_m = 1.5/1.5$ ,  $\lambda_{E_x} = 398 \text{ nm}$ .

(MMA), and then copolymerized by AIBN initiator at  $60\text{--}65^\circ\text{C}$ . The polymer obtained was repeatedly purified by reprecipitating the methylene chloride solution of copolymer into hexane (Scheme 1).

Various composition ratios of  $\text{Eu}^{3+}$  to MMA were prepared, and the relationship between the fluorescence intensity at 613 nm and Eu content in the copolymers is shown in Table 1 and Fig. 15.

In order to demonstrate the laser action and the energy transfer within the copolymer of  $(\text{D}'\text{EuD}_3)\text{-P}^+\text{-MMP}$ , rod-shaped samples were prepared and both ends were polished. In pursuit of possible laser action in the polymers,

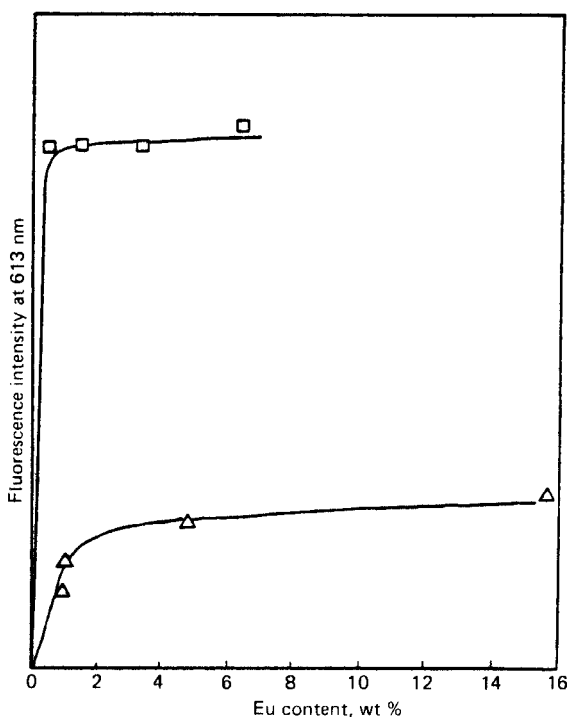
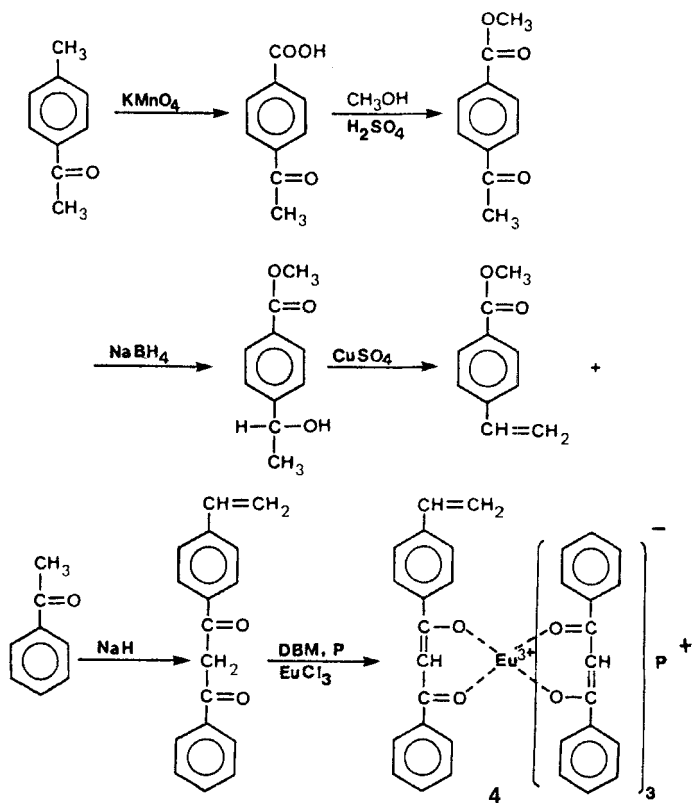
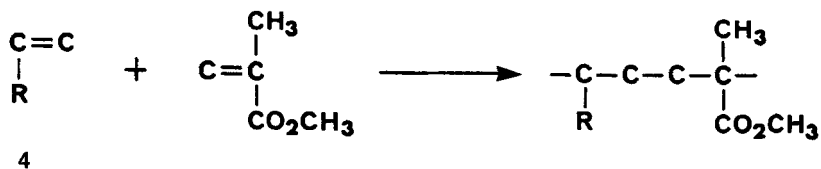


FIG. 14. Relationship between fluorescence intensity and Eu content of Polymer 2-Eu complex ( $\square$ ) and Polymer 3-Eu complex ( $\triangle$ ).

the fluorescence lifetime was monitored. The samples were excited by a pulse from a xenon flashlamp at room temperature. Since the sample was cooled only by a nitrogen stream, the polymer began to degrade due to the heat produced after several pulses. However, when a threshold excitation energy was reached, a considerable shortening of the fluorescence lifetime was observed, followed by a return to the characteristic lifetime profile. Such lifetime shortening is typical of the phenomenon of superfluorescence, which is a precursor to laser action [33].



Synthesis of (p-vinylphenyl)-3-phenyl-1,3-propanediones, europium chelates, ( $\text{D}'\text{EuD}_3\text{P}$ ) and copolymer with MMA.

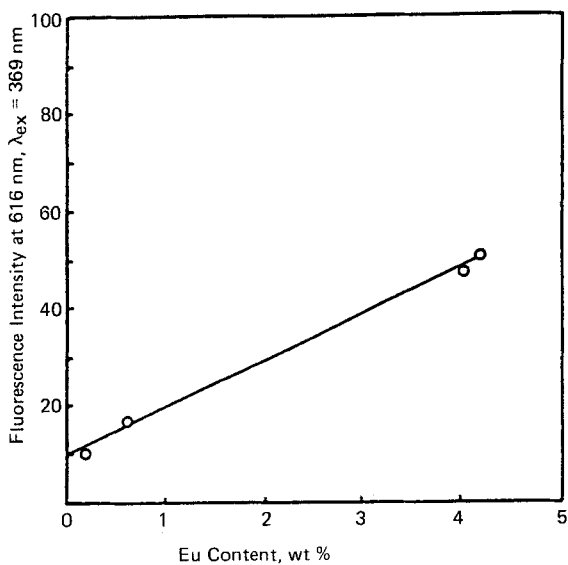


R = tetrakis coordinated compounds

SCHEME 1.

TABLE 1. Fluorescence Intensity at 613 nm vs Eu Content in D'EuD<sub>3</sub>P:MMA Copolymer Powder

Copolymerization ratio of copolymer (D'EuD <sub>3</sub> P:MMA)	Eu contents in polymer produced, %	Fluorescence intensity
1:4	4.18	51
1:6	4.04	47
1:40	0.61	17
1:100	0.19	10

FIG. 15. Fluorescence intensity at 613 nm vs Eu<sup>+3</sup> content in D'EuD<sub>3</sub>P:MMA copolymer powder. Slit Ex/Em = 2/2, sensitivity 3,  $\lambda_{ex}$  = 396 nm.

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