

Investigation on the Synthesis and Characterization of Rare Earth Metal-Containing Polymers. II. Fluorescence Properties of Eu^{3+} -Polymer Complexes Containing β -Diketone Ligand

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Synopsis

Europium(III) chelates of dibenzoylmethane (DBM) (1) and β -diketone-containing polymers, i.e., poly(*p*-benzoylacetylstyrene) (2) and poly(aryl β -diketone) (3), were prepared. In the polymer 2 the β -diketone moiety is attached to the phenyl ring, and for polymer 3 the β -diketone group is incorporated in the linear chain. The chelate structures were confirmed by measuring IR spectra, TGA, and DTA. The fluorescence emission intensity was measured on fine powder samples. For the composite samples of $\text{Eu}(\text{DBM})_4$ in polystyrene, the fluorescence intensity was found to increase linearly with increasing Eu content. However, for Eu coordination polymers, the intensity reached a maximum at Eu^{3+} content as small as 1 wt % and remained constant on further increasing the Eu^{3+} content. When the fluorescence intensities of Eu complexes were compared under the same conditions, namely, 1 wt % Eu, at which Eu-2 and Eu-3 show nearly maximum intensity, the order was found to be Eu-1 > Eu-2 > Eu-3. These phenomena were accounted for by the differences in the coordination number of the Eu complexes.

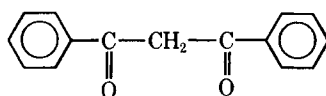
INTRODUCTION

The fluorescent characteristics of europium chelates are of considerable interest in connection with electronic energy transfer processes and with their use in laser systems.^{1,2} Chelating compounds containing the β -diketone moiety were widely used for this purpose.³ An attempt to utilize a polymer as a matrix was reported by Wolff and Pressley.⁴ They found that a solid solution of europium-tris[4,4,4-trifluoro-1-(2-thienyl)-1,3-butenedione] in poly(methyl methacrylate) had optical maser action. However, polymeric systems in which rare earth metals are directly bonded to the polymer have not yet been investigated.

Recently, in our laboratory, we synthesized rare earth complexes of ionomers and reported the fluorescent properties of the polymers.⁵ They were homogeneous, glassy phases with no grain boundaries to scatter the light. Thus, we have been investigating the fluorescent properties of Eu^{3+} -polymer complexes. The polymers investigated in this study contain the β -diketone moiety and are linear and branched types described by structures 2 and 3. Their fluorescent properties were compared with those of the corresponding complex of Eu^{3+} with the

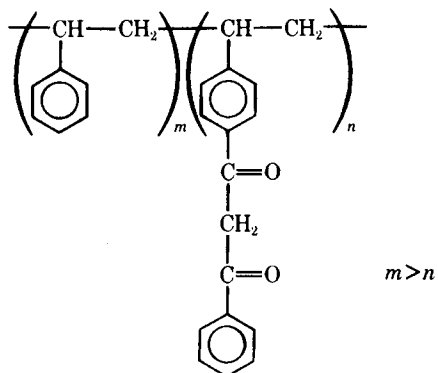
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monomeric chelating compound dibenzoylmethane (1):

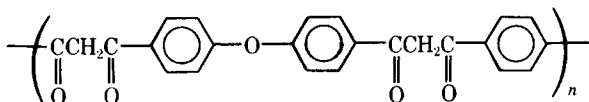


1

dibenzoylmethane



2

poly(*p*-benzoylacetylstyrene)

3

poly(aryl β -diketone)

EXPERIMENTAL

Materials

Europium chloride ($\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$) was purchased from Ventron Co. and used without further purification. Dibenzoylmethane was obtained from Aldrich Chemical Co.

*Eu*³⁺-Tetrakisdibenzoylmethide Piperidinium Salt, *Eu*(DBM)₄P

The Eu^{3+} -tetrakisdibenzoylmethide chelate was prepared by the method described in the literature.⁶ $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (2.24 g, 0.006 mole) was dissolved in 30 ml of 95% ethanol and added to the ethanol solution (100 ml) of dibenzoylmethane (6.68 g, 0.03 mole) and piperidine (2.55 g, 0.03 mole). The precipitate was washed three times with 95% ethanol and dried under vacuum at 50°C overnight. Eu content was found to be 13.7 wt %, calculated for the tetrakis chelate $\text{Eu}(\text{DBM})_4\text{P}$, 13.4 wt %.

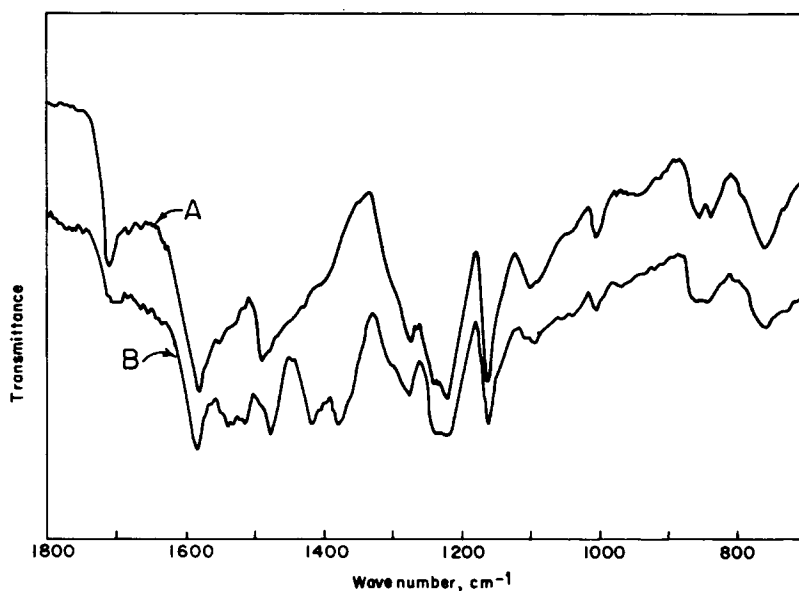


Fig. 1. Infrared spectra of poly(aryl β -diketone) (A) and poly(aryl β -diketone)-Eu³⁺ complex (B).

Eu³⁺-Trisdibenzoylmethide, Eu(DBM)₃

The Eu³⁺-trisdibenzoylmethide was prepared by following the method in the literature.⁷ A solution of 1.67×10^{-3} mole EuCl₃·6H₂O in 30 ml water was added to a solution of 8.93×10^{-3} mole dibenzoylmethane in 50 ml of 95% ethanol. The suspension was stirred and neutralized with aqueous ammonia. The resulting precipitate was filtered and dried under vacuum at room temperature. The chelating compound was confirmed by IR spectrum; Eu content was found to be 18.0 wt %, calculated for Eu(DBM)₃, 18.4 wt %.

Eu³⁺-Bisdibenzoylmethide, Eu(DBM)₂OAc

The bis chelate was prepared by the method reported in the literature.⁸ A solution of CH₃COONa (1.50×10^{-3} mole) in 15 ml water was added to 10 ml water solution of EuCl₃·6H₂O (2.50×10^{-3} mole). This solution was added to 100 ml 95% ethanol solution of dibenzoylmethane (8.26×10^{-3} mole) with vigorous stirring. The mixture was heated on the hot plate for 10 min. After cooling, the precipitate was filtered, washed with 95% ethanol, and then dried under vacuum at room temperature. The IR spectrum of the product showed the characteristic absorption for the chelate formation. Eu content was found to be 25.8 wt %, calculated for Eu(DBM)₂OAc, 23.1 wt %.

Poly(aryl β -Diketone) (3)

Poly(aryl β -diketone) was prepared by a method similar to that described in the literature.⁹ The molecular weight of the polymer was reported to be 3300. The structure of polymer was identified by measuring the IR spectrum.

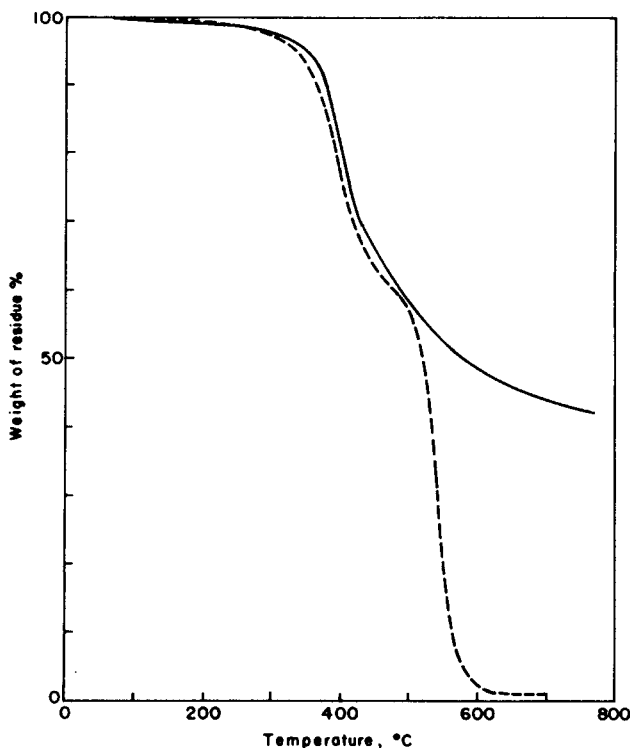


Fig. 2. TGA for poly(aryl β -diketone): (—) under N₂; (---) under air atmosphere; 10°C/min.

Poly(p-benzoylacetylstyrene) (2)

Polymer 2 was prepared from a partially acetylated polystyrene by the condensation with methyl benzoate. The typical preparation of the polymer was as follows. Polystyrene (Dow Chemical Co., M.W. 30,000) was acetylated by acetyl chloride using AlCl₃ as catalyst in CS₂ solution. The acetyl moiety in the polymer was found to be about 20 mole % (calculated by IR spectra). The substitution occurred mainly on the para position. The acetylated polystyrene, 8.00 g, was dissolved into 150 ml anhydrous tetrahydrofuran. To this solution, methyl benzoate, 2.79 g, and then sodium amide were added. The mixture was stirred at 50°C for 90 hr. The product was poured into 800 ml water. After the precipitate was filtered and washed with dilute HCl, water, and then methanol, the solid was dried under vacuum at 50°C for a couple of days. The polymer showed a characteristic absorption at 1585 cm⁻¹ owing to the β -diketone moiety. The dibenzoylmethane group in the polymer was calculated to be about 5 mole % from IR spectra measurement.

Preparations of Eu³⁺ Complexes of 2 and 3

EuCl₃ solution of tetrahydrofuran and methanol (1:1 volume ratio) was added to the tetrahydrofuran solution of polymers 2 or 3 (1–2% solution). The pH of the solution was adjusted to slightly basic (~pH 8) by adding piperidine, and the solution was stirred for 1 hr. After the precipitate was filtered, the solid was washed continuously with methanol and dried under vacuum at 50°C for two

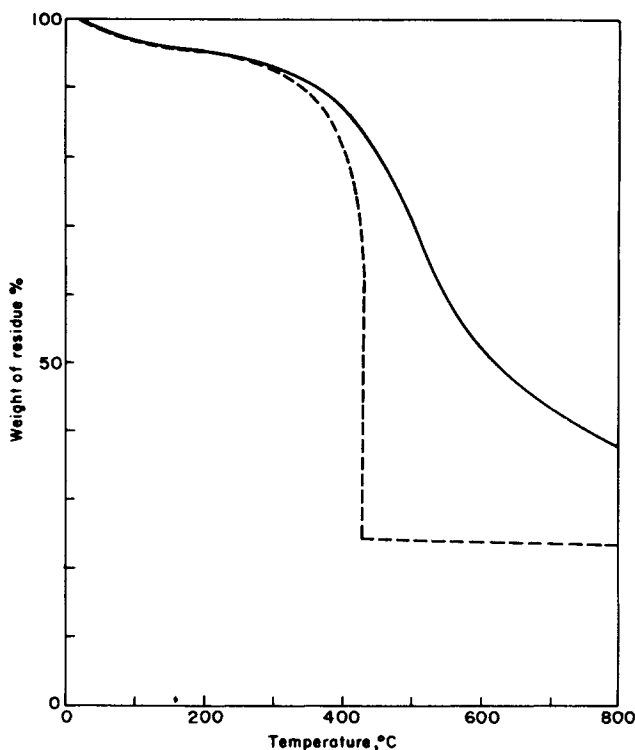


Fig. 3. TGA for poly(aryl β -diketone)-Eu³⁺ complex: (—) under N₂; (- - -) under air atmosphere; 10°C/min.

days. No chlorine was detected from the Eu³⁺ complexes of 2 and 3 by Beilstein test.

Eu(DBM)₄P-Polymer Mixture

A commercial polystyrene (Dow Chemical Co., MW 30,000) was purified by reprecipitating from methyl ethyl ketone solution with methanol. The weighed polystyrene and Eu(DBM)₄P were dissolved in benzene. The solvent was removed under vacuum and the mixture was dried under vacuum at 50°C. The solid was ground into fine powder and further dried under vacuum.

Determination of Eu Content in Polymer

The amounts of Eu in chelating polymers were determined by a method (ashing method) similar to that described in the previous article.⁵

Fluorescence Measurement

A Hitachi-Perkin-Elmer model MPF-2A fluorescence spectrophotometer was used to measure fluorescence spectra of Eu³⁺-polymer systems. Powder samples were used for the measurements.⁵

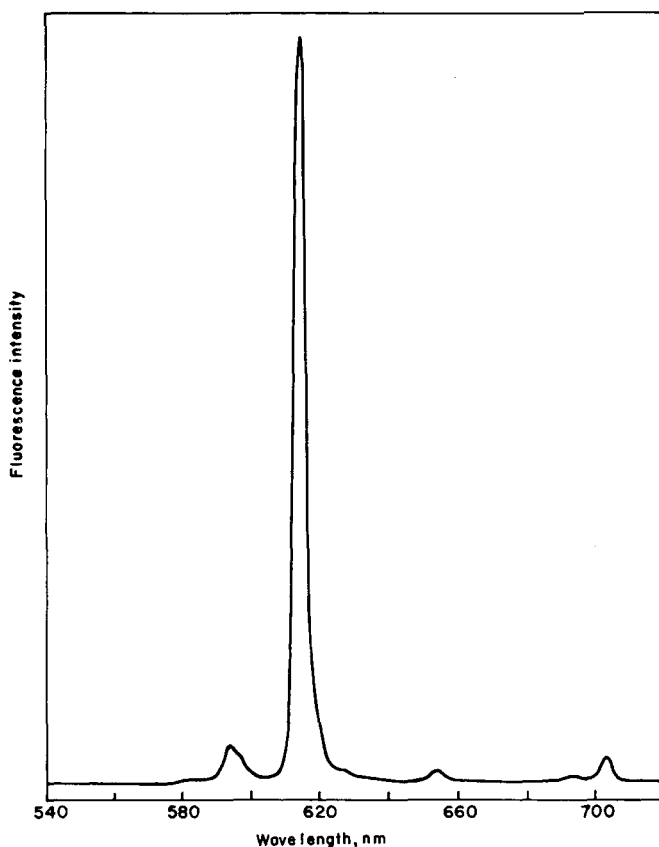


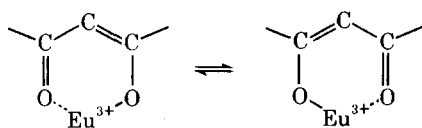
Fig. 4. Emission spectrum of $\text{Eu}(\text{DBM})_4\text{P}$, $\lambda_{\text{ex}} = 396 \text{ nm}$.

DSC and TGA Measurements

DSC and TGA measurements were carried out using a du Pont 990 thermal analyzer.

RESULTS AND DISCUSSION

The coordination structure of Eu^{3+} -polymer complexes was investigated by measuring the IR spectra. Typical spectra of the polymer and the Eu^{3+} chelate are shown in Figure 1. The polymer has mostly enol structure and a wide absorption band between 1350 and 1600 cm^{-1} because of the overlap of two effects—intramolecular hydrogen chelation and conjugated double bond. Upon the formation of the chelate with Eu^{3+} , new strong bands appeared at around 1400 and 1530 cm^{-1} corresponding to the asymmetric and symmetrical vibration of two $\text{C}=\text{O}$ links in the resonating structures:



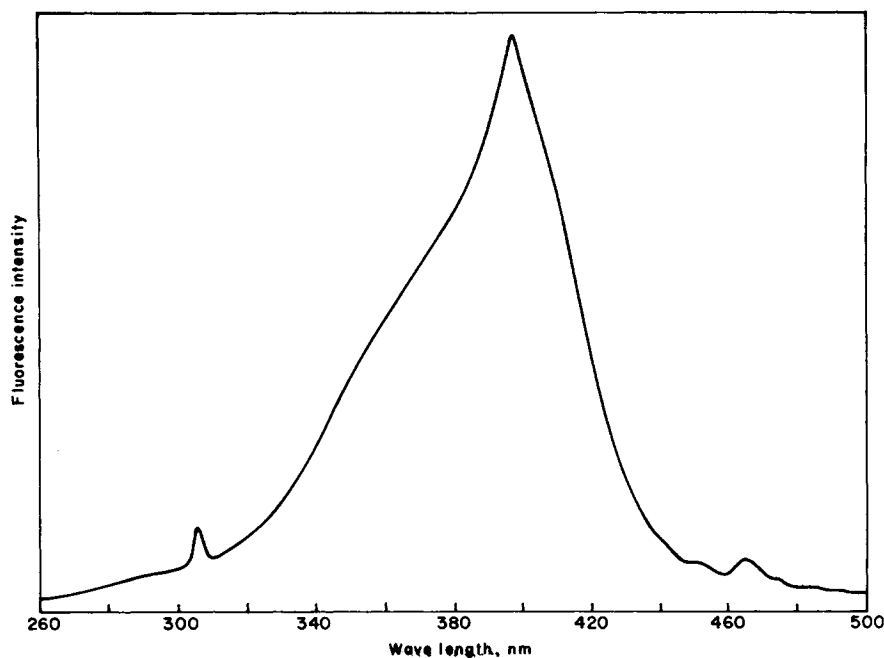


Fig. 5. Excitation spectrum of poly(*p*-benzoylacetylstyrene)-Eu complex (Eu 1.5 wt %), $\lambda_{em} = 613$ nm.

These bands have been assigned in the copper chelates of acetylaceton¹⁰ and in the corresponding polymer.⁹

The polymers and their Eu³⁺ complexes were thermally stable and started to decompose at around 350°C. Typical TGA data of these compounds are shown in Figures 2 and 3. It is of interest that 3 has unusually high char yield (~45%) (Fig. 2). This may be due to formation of crosslinkages via dehydration during heating. When the Eu-polymer complex was heated in nitrogen or air atmosphere, piperidine was initially eliminated from the complex, resulting in gradual decrease of weight (Fig. 3).

Rare earth ions are incorporated in organic chelates by coordination through a donor atom such as oxygen; when excited with light absorbed by the ligand, they exhibit narrow-line emission at approximately the same frequencies as the inorganic crystal system. This phenomenon is the result of an intramolecular energy transfer from the electronic states associated with the organic complex to localized intra-4f shell energy levels of the ions.¹¹ The fluorescent properties of europium dibenzoylmethides have been intensively investigated.¹² The sharp emission spectrum is detected at 613 nm even at room temperature (Fig. 4). The peak is due to the ⁵D₀ → ⁷F₂ transition.

We have prepared several Eu³⁺-containing coordination polymers and mixtures in which Eu³⁺-dibenzoylmethide, Eu(DBM)₄, is uniformly dispersed in a polystyrene matrix. The preparation of transparent films became difficult for the polymers containing high metal concentrations. Thus, in order to investigate the fluorescent properties of a wide range of metal-containing polymers, we decided to study the properties on pressed powders. The fluorescence intensity measurements on solid samples are known to be difficult. Various factors, such as particle size and reabsorption of the Eu³⁺ emission, may influence

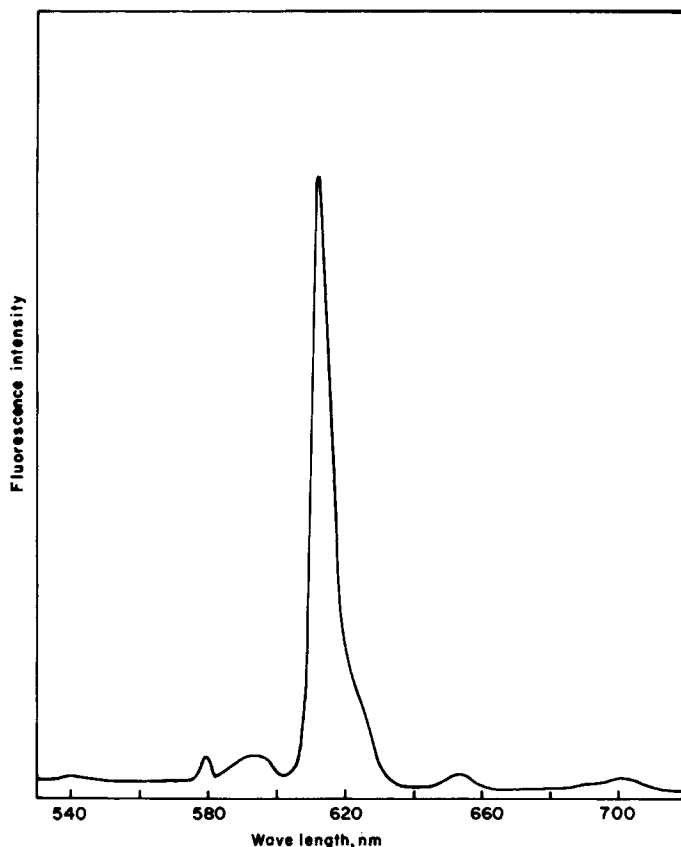


Fig. 6. Emission spectrum of poly(*p*-benzoylacetylstyrene)-Eu complex (Eu 1.5 wt %), $\lambda_{\text{ex}} = 398$ nm.

the intensity. Thus, we took three measurements on a sample and took the average value. The scatter of these values was at times as much as 15%. The typical excitation and emission spectra of the polymers are shown in Figures 5 and 6. The sharp emission peak at 613 nm was detected in those Eu-polymer systems at room temperature (Fig. 6).

In addition to the lines of the emission spectrum in the $\text{Eu}(\text{DBM})_4$ (Fig. 4), as shown in Figure 6, a line at 580 nm was detected for the Eu-polymer complex, corresponding to the forbidden $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition.¹³ The appearance of the $\text{O} \rightarrow \text{O}$ transition has been explained in terms of low symmetry around Eu^{3+} .¹⁴ Thus, the spectrum indicated that the Eu-polymer complex may have more asymmetric structure around Eu^{3+} than that of the $\text{Eu}(\text{DBM})_4$.

For the composite sample of $\text{Eu}(\text{DBM})_4$ in polystyrene, the fluorescence emission intensity was found to increase linearly with increasing Eu content (Fig. 7). However, for the Eu-coordination polymer complexes, the intensity reached a maximum at Eu^{3+} content as small as 1 wt % and remained constant on further increasing the Eu^{3+} content (Figs. 8 and 9).

When the fluorescence intensities of these Eu complexes were compared under the same conditions, viz., 1 wt % Eu, at which Eu-2 and Eu-3 show nearly maximum fluorescence intensity, the order was found to be $\text{Eu}(\text{DBM})_4 > \text{Eu-2} > \text{Eu-3}$. The samples' intensities differed by a factor of about 20–30. This was far larger

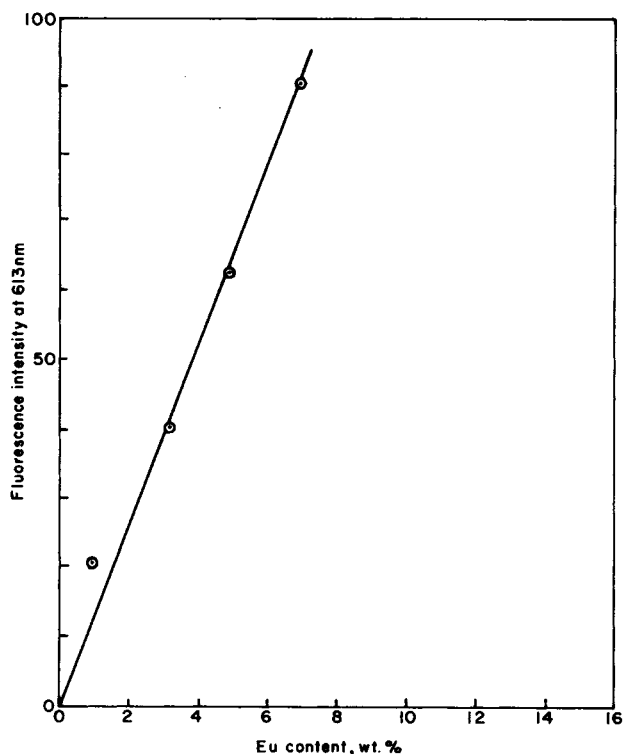


Fig. 7. Relationship between fluorescence intensity and Eu content of Eu(DBM)₄P in polystyrene; sensitivity 1, slit ex/em = 1.5/1.5, $\lambda_{\text{ex}} = 398$ nm.

than the experimental error for each sample. The fluorescence emission intensity is known to vary with environmental factors such as the nature of coordination bond, solvent, and temperature.¹⁵

In order to obtain data on the effect of the coordination number on the fluorescence intensity in the Eu-dibenzoylmethide system, we prepared Eu-tetrakis-, tris-, and bisdibenzoylmethides and found that the fluorescence intensities were in the order Eu(DBM)₄ > Eu(DBM)₃ > Eu(DBM)₂. The intensity ratios were 40- to 50-fold among these complexes.

When Eu ion reacts with excess dibenzoylmethane in basic solution, generally the tetrakis coordination complex is obtained. However, when β -diketone groups are incorporated into the polymer chain, the formation of multiple coordination bonding between Eu and the β -diketone may be restricted by the increasing steric hindrance and the decrease of the freedom of bond rotation.

The fluorescence intensity data discussed above suggest that polymer 2 forms tris-coordination complexes with a small amount of Eu³⁺, (~1 wt % Eu) and subsequently forms bis- and mono-coordination complexes with excess Eu³⁺. Since the fluorescence intensity of the tris-coordination compound Eu(DBM)₃ was far greater than those of bis- and mono-coordination compounds, the intensity remained essentially constant after reaching a maximum at low Eu³⁺ concentration, as shown in Figure 9. In other words, the maximum intensity obtained is due mostly to the tris-coordination-diketone complex between Eu³⁺ and polymer 2. In the case of the polymer 3, the β -diketone groups are incorporated

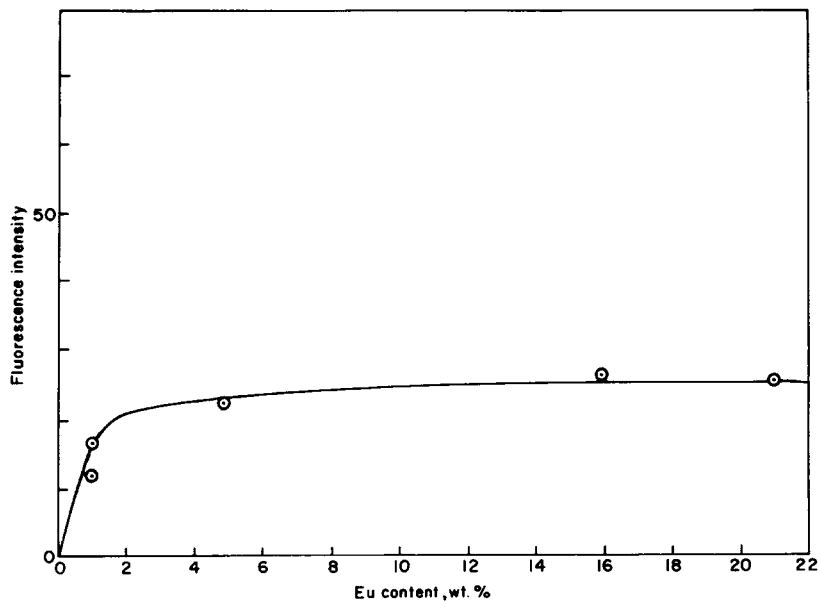


Fig. 8. Relationship between fluorescence intensity and Eu content of poly(aryl β -diketone)-Eu complex; sensitivity 1, slit ex/em = 6/6, λ_{ex} = 396 nm.

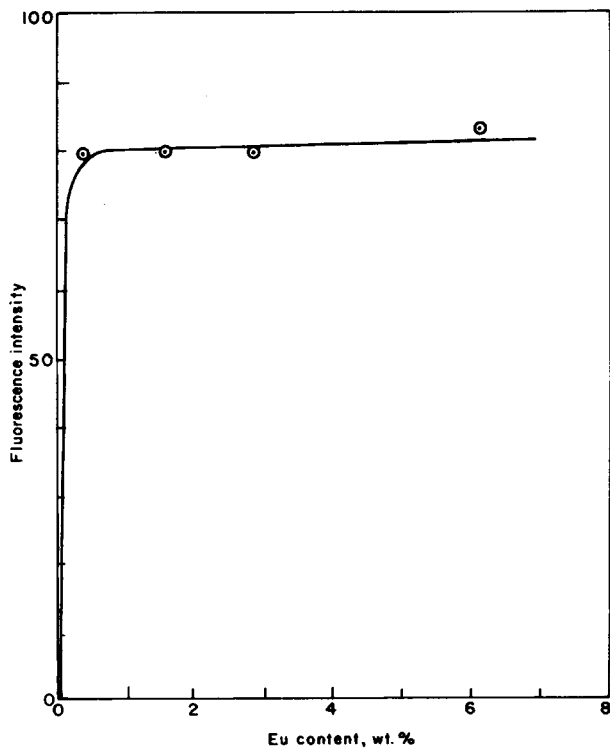


Fig. 9. Relationship between fluorescence intensity and Eu content of poly(*p*-benzoylacetyl-styrene)-Eu Complex; sensitivity 1, slit ex/em = 3/3.5, λ_{ex} = 398 nm.

in the linear chain; consequently, the formation of multiple coordination bonds between Eu ion and β -diketone moiety is expected to be more restricted as compared with polymer **3**, in which β -diketone is attached on the side chain. Therefore, polymer **3** may form mainly the bis-coordination complex with limited amounts of Eu³⁺, followed by the formation of mono-coordination complex with excess Eu³⁺.

Thus, the maximum fluorescence intensity obtained in the Eu-polymer **3** system may be due to that of Eu-bisdiketone complex, and the intensity remained nearly constant even with increasing Eu content (Fig. 8). In order to clarify the above hypothetical arguments, we are currently studying the phosphorescence properties of Cr complexes at low temperature, using the well-known sharp-line luminescence of Cr³⁺.¹⁶

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