

Synthesis and Characterization of Rare Earth Metal-Containing Polymers. I. Fluorescent Properties of Ionomers Containing Dy^{3+} , Er^{3+} , Eu^{3+} , and Sm^{3+}

E. BANKS, Y. OKAMOTO, and Y. UEBA, *Department of Chemistry, Polytechnic Institute of New York, Brooklyn, New York 11201*

Synopsis

Rare earth metal (Dy^{3+} , Er^{3+} , Eu^{3+} , and Sm^{3+}) salts of copolymers of methyl methacrylate-methacrylic acid, styrene-acrylic acid, 1-vinylnaphthalene-acrylic acid and 1-vinylanthracene-styrene-acrylic acid were prepared. The fluorescence of these polymer salts under ultraviolet excitation was investigated. The fluorescent intensity of polymer- Eu^{3+} films varied with film thickness because of incomplete absorption of exciting light, hence most of the measurements were made on pressed fine powders. The fluorescent intensity of mixed samples of $\text{Eu}(\text{III})$ acetate in a polymer matrix increased linearly with Eu content. However, the Eu^{3+} -polymer complex system displayed typical concentration-quenching behavior, reaching a maximum at 4–5 wt % Eu and decreasing with further increases in Eu content. This suggests that the ionomer contains ionic aggregates, in agreement with a recently proposed model. Such aggregates would create locally high Eu ion concentrations, whose interactions lead to concentration quenching at low nominal concentrations. The fluorescent intensity of the acrylic copolymers decreased in the order methacrylate > styrene > naphthalene > anthracene. This sequence is explained by increasing competition for the exciting light by the aromatic groups with negligible energy transfer from the aromatic groups to the Eu^{3+} ions. This is also consistent with the hypothesis that the ionic regions of the polymer are segregated.

INTRODUCTION

The properties of synthetic polymers containing salt groups have been extensively investigated in recent years.^{1,2} An important class of these polymers are 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 rare earth metals have unique and interesting properties. Interest in rare earth complexes has been stimulated by their fluorescent and laser properties.³ Polymers were utilized as a matrix for these complexes, and their fluorescent and laser properties have been investigated.^{4,5} However, polymeric systems in which rare earth metals are directly bonded to the chain have been studied only slightly. Recently, in our laboratory we synthesized Eu^{3+} salts of styrene-maleic acid and ethylene-methacrylic acid copolymers. The polymers exhibited characteristic reddish-orange Eu^{3+} fluorescence under UV excitation, even with a Eu^{3+} content as small as 2 wt % in the polymers. The polymers were dissolved in certain organic solvents, formed clear films upon the evaporation of the solvent, and were thermally stable up to about 300°C.

TABLE I
Styrene-Acrylic Acid Copolymer^a

Feed, mole % ^b		Found, mole %		
Styrene	Acrylic acid	Styrene	Acrylic acid	Yield, %
90	10	91	9	69

^a The polymer obtained may be highly heterogeneous. The polymer formed during the early stages of polymerization would have an acrylic acid content of about 20%, while the material polymerized toward the end would probably be pure polystyrene. We have investigated various compositions of styrene-acrylic acid copolymers and found that the tendency of the fluorescence data of these polymers was about identical. We will report in the future the effects of the polymer compositions and structures on fluorescence properties.

^b Azobisisobutyronitrile, 0.1 mole %, was used.

Thus, we have initiated a detailed study of fluorescent properties of various polymeric systems containing rare earth metals. The effects of polymer structures on the fluorescent properties were investigated.

EXPERIMENTAL

Styrene-Acrylic Acid Copolymer (PSAA). Distilled styrene and acrylic acid and recrystallized azobisisobutyronitrile were weighed and placed in a polymerization tube (Table I). The tube was sealed after replacing air with nitrogen and removing dissolved gas. Polymerization was carried out at 60°C for 20 hr. The polymer obtained was purified by precipitating the polymer-methyl ethyl ketone solution into methanol. The copolymer was dried under vacuum at 50°C for three days. The polymer composition was determined by UV absorption.

Methyl Methacrylate-Methylmethacrylic Acid Copolymer (HPMMA). Forty grams poly(methyl methacrylate) (medium molecular weight polymer

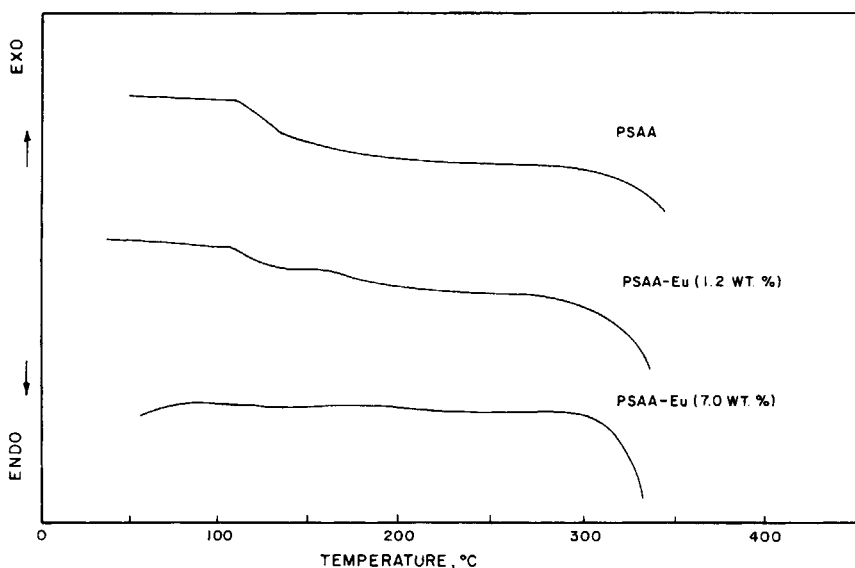


Fig. 1. DSC curves for PSAA-Eu³⁺ complexes.

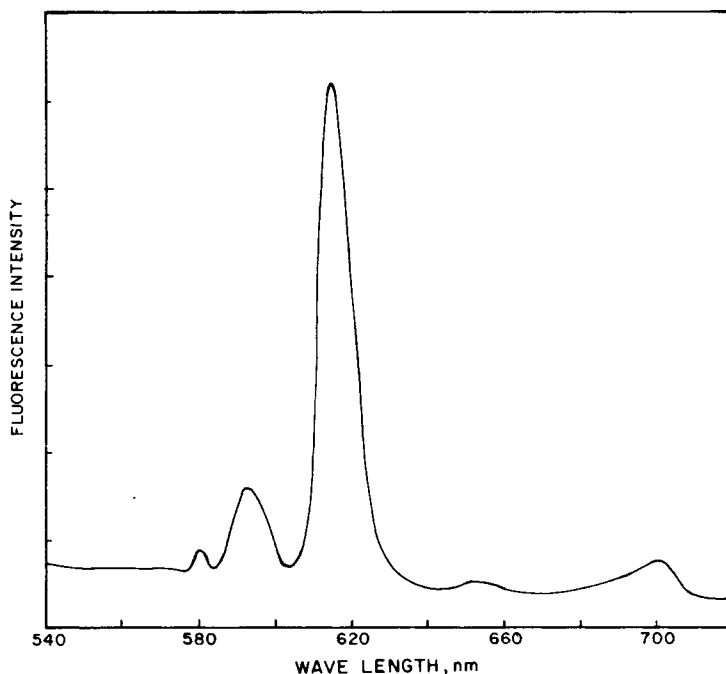


Fig. 2. Emission spectrum of PSAA-Eu complex (Eu, 7.0 wt %), $\lambda_{\text{Ex}} = 0.396$ nm.

obtained from Polysciences, Inc.) was stirred with 16 g NaOH in water (7.2 ml) and isopropanol (350 ml) for 45 min. The reaction mixture was cooled to room temperature. Partially hydrolyzed PMMA was filtered and then washed with dilute HCl and water, and dried under vacuum at 60°C for three days. The acid content of HPMMA was determined by titrating HPMMA solution in acetone and methanol (1:1 volume ratio) with standardized sodium ethoxide using phenolphthalein as an indicator. The methacrylic acid content in the polymer was found to be 6.8 mole %.

1-Vinylnaphthalene-Acrylic Acid Copolymer (PNAA). 1-Vinylnaphthalene, 0.063 mole (obtained from Polysciences, Inc.), was copolymerized with 0.007 mole acrylic acid using azobisisobutyronitrile (0.07 mmole) as initiator at 60°C for 140 hr. The polymer obtained was purified and dried by the same procedure described in PSAA. The yield was 22%. The vinylnaphthalene content was determined by UV measurement and calculated to be in the range of 70 mole % in the polymer.

1-Vinylnanthracene-Styrene-Acrylic Acid Terpolymer (PASA). 1-Vinylnanthracene was prepared and purified by the methods described in the literature.^{6,7} 1-Vinylnanthracene (0.002 mole), styrene (0.048 mole), and acrylic acid (0.004 mole) were copolymerized using azobisisobutyronitrile as an initiator at 60°C for 88 hr. The polymer obtained was purified and dried as described before. The yield was 18%. The IR spectrum of the polymer was similar to that of PSAA. The vinylnanthracene moiety content was determined by UV absorption and estimated as 5 mole % in the polymer.

Lanthanides. Europium chloride, $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, and erbium chloride, $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, were purchased from Ventron Co. Samarium nitrate, $\text{Sm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, and dysprosium nitrate, $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, were obtained from Research

TABLE II
Fluorescence Emission Lines of PSAA-Eu Complexes

Wavelength, ^a nm	SBW ^b nm	Peak intensity ^c	Transition
616	11.5	100	$^5D_0 \rightarrow ^7F_2$
592	9.0	24.2	$^5D_0 \rightarrow ^7F_1$
700	13.0	11.0	$^5D_0 \rightarrow ^7F_4$
580	4.0	2.9	$^5D_0 \rightarrow ^7F_0$
653	11.0	2.4	$^5D_0 \rightarrow ^7F_3$

^a Excitation at $\lambda_{EX} = 396$ nm.

^b The width of band at 50% intensity.

^c Normalized to the most intense emission $^5D_0 \rightarrow ^7F_2$.

Organic/Inorganic Chemical Co. These chlorides and nitrates were used without further purification.

Europium Acetate [Eu(AcO)₃]. Europium acetate was synthesized by the method described in the literature.⁸ The europium content in the acetate prepared was determined by ashing. (Found: 47.0 wt %, calcd.: 42.6 wt %).

Polymer-Lanthanide Complexes. The polymer-lanthanide salts were prepared by two different methods. Typical procedures are as follows:

(1) Styrene-acrylic acid copolymer (PSAA), 2.5 g, was dissolved into 100 ml methyl ethyl ketone. A solution of the weighed EuCl₃ in methanol and methyl

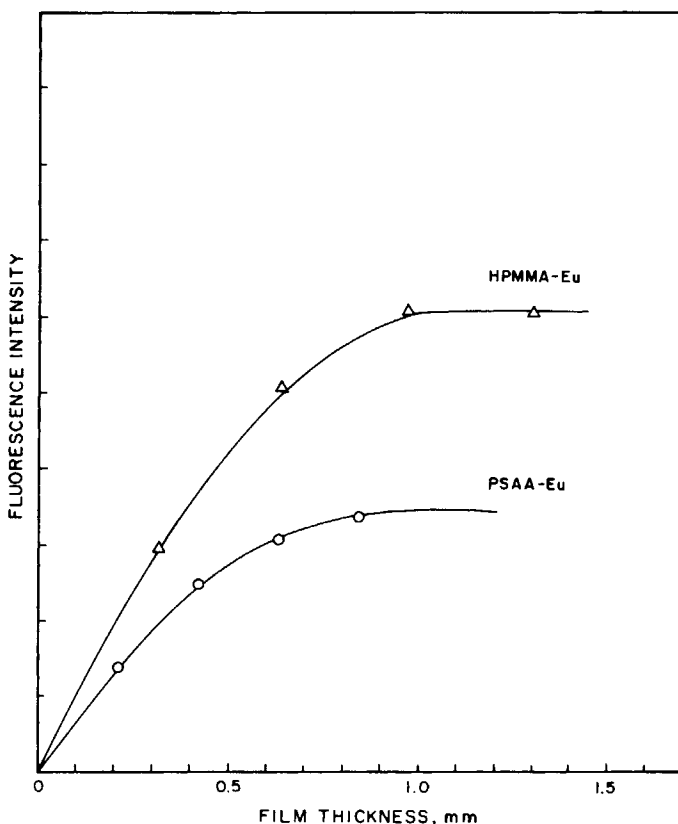


Fig. 3. Effect of film thickness on fluorescence intensity.

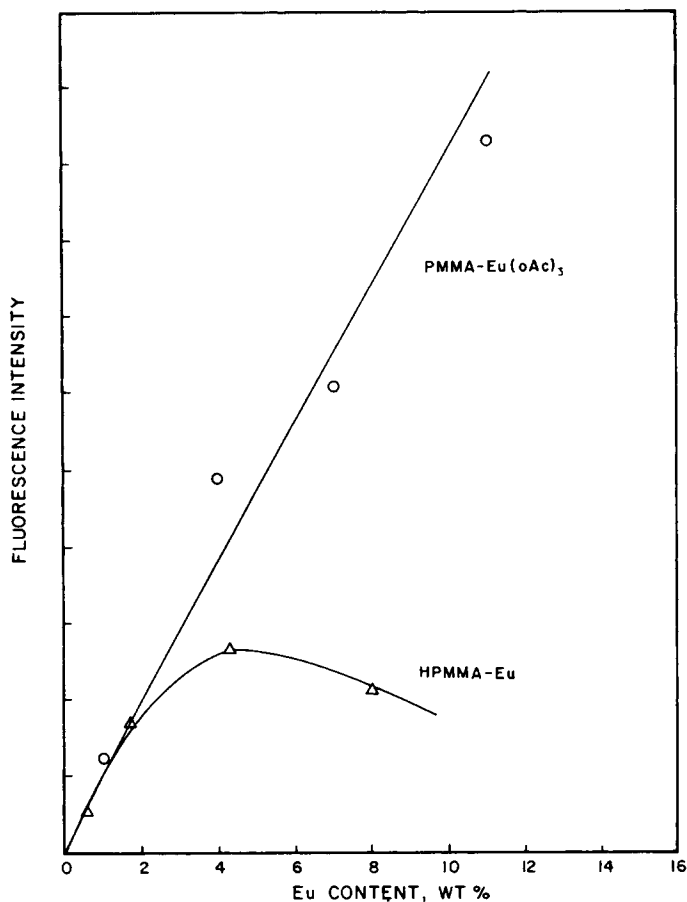


Fig. 4. Relationship between fluorescence intensity and Eu content in HPMMA-Eu and PMMA-Eu (OAc)₃ systems.

ethyl ketone (1:1) was prepared and added to the copolymer solution. After the solution was stirred for 1 hr, the mixture was poured into a large amount of distilled water. The precipitate was filtered, washed with water and methanol, and dried under vacuum at 60°C for one day.

(2) Sodium acetate or ammonium hydroxide was added to the solution of EuCl₃-polymer. The resulting precipitate and solution were further stirred for 1 hr. The precipitate was purified as described in procedure (1).

Polymer-Europium Acetate Systems. Commercial polystyrene (Dow Chemical Co., MW 30,000) was purified by reprecipitating from methyl ethyl ketone into methanol. The weighed polystyrene and europium acetate-methyl ethyl ketone solution was stirred overnight. After removing the solvent, the mixture was dried at 60°C for one day. The mixed system of poly(methyl methacrylate)-europium acetate was also prepared by the procedure described above.

Determination of Lanthanide Content in Polymers. Lanthanide contents in polymer systems were determined by an ashing method. A sample was weighed in Pt or porcelain crucibles and placed in a furnace. The temperature was raised to 600°C at a rate of 200°C/hr and maintained at 600°C for 1 hr. The

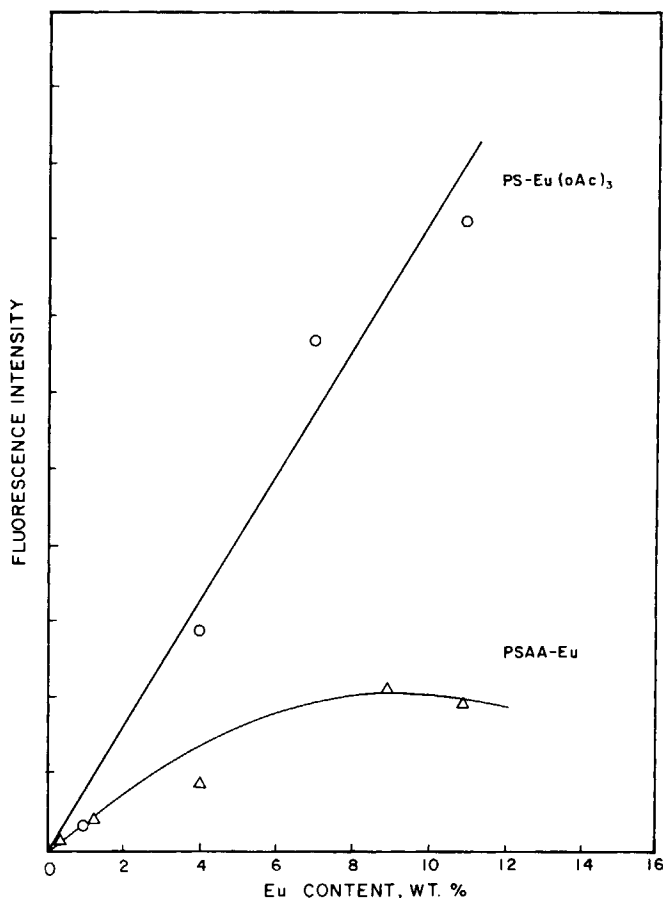


Fig. 5. Relationship between fluorescence intensity and Eu content in PSSA-Eu and PS-Eu (OAc)₃ systems.

metal oxide residue was weighed and the content was calculated on the basis of the stoichiometry of M_2O_3 . The identity of the lanthanide oxide was confirmed by x-ray powder diffraction.

Fluorescence Measurement. A Hitachi-Perkin-Elmer model MPF-2A fluorescence spectrophotometer was used to measure fluorescence spectra of lanthanide-containing polymers. Film and powder samples were placed in the sample holder attached to the instrument, which measures the fluorescence at 90°C to the exciting beam.

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 the polymer-rare earth metal complexes was investigated by measuring the IR spectra. The spectra of the ionomers have an absorption at around 1700 cm^{-1} due to the carbonyl group. Upon formation of the salts, this absorption decreased and a new peak appeared at around 1550 cm^{-1} , corresponding to carboxylate ion absorption. The polymers investigated

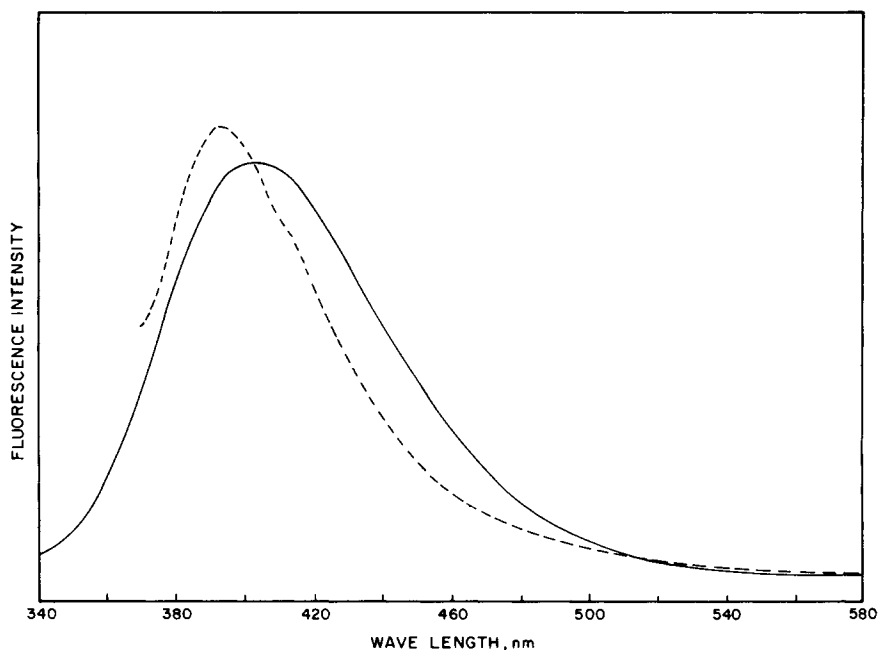


Fig. 6. Emission spectra of poly(1-vinylnaphthalene-acrylic acid): —, $\lambda_{Ex} = 325$ nm; - - -, $\lambda_{Ex} = 360$ nm.

were thermally stable and started to decompose at around 300°C. Improvement of the thermal stability upon salt formation was not apparent from the TGA measurements. However, in DSC measurements, the glass transition points of the ionomers were found to have disappeared upon complex formation. Typical data on the thermal properties for the polymer-Eu³⁺ complex is shown in Figure 1.

The transparent films could be prepared by casting either from organic solution or from compressed melt. The typical emission spectrum of the polymer-Eu³⁺ complex is shown in Figure 2. The bright-red fluorescence lines of Eu³⁺ at around 600 nm were assigned to transitions from the ⁵D₀ levels to all the multiplet levels of ⁷F (Table II). This emission spectrum was obtained under excitation at 395 nm (25340 cm⁻¹), corresponding to the Eu³⁺⁵L₇ level.

It was observed that the fluorescence intensity depends on the film thickness. The intensity increased parabolically with increasing thickness (Fig. 3). Since the film samples were transparent, this may be due to the reflection of the fluorescence emission from the various depths in the film. The preparation of transparent film became difficult for the polymers containing high metal concentrations and also for the mixed systems of low molecular weight organic salts and polymers. Thus, in order to investigate the fluorescent properties of a wide range of metal-containing polymers and composite materials, we decided to study mostly the properties on pressed fine powders. The fluorescence spectra of film and powder samples were found to be identical. The major fluorescence excitation and emission lines of PSAA-Dy, -Er, -Eu, and -Sm are summarized in Table III. It is known that the relative positions of these lines vary only slightly with the changes of environment, but the intensities are changed drastically with the changes of environment.⁹

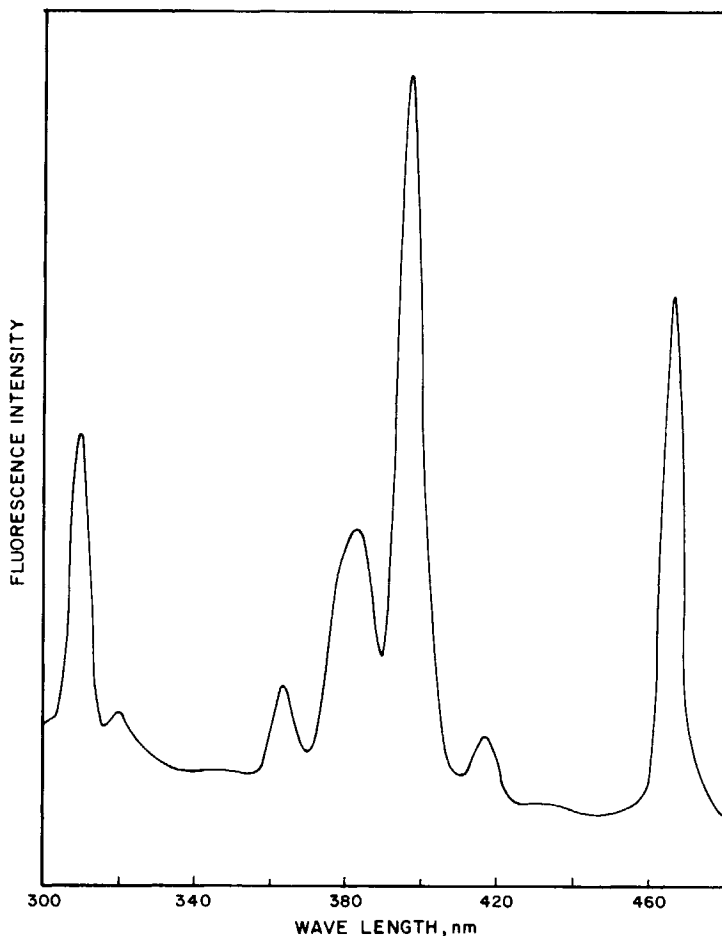


Fig. 7. Excitation spectra of PSAA-Eu complex (7.4 wt %), $\lambda_{Ex} = 613$ nm.

Recently, the structures of ionomers have been extensively studied by several investigators.¹⁰ It is proposed that there are submicroscopic regions of the polymer in which lamellar domains are interspersed with ionic aggregates. In these ionic regions there may be several intermolecular associations involving carboxyl, carboxylate, and the metal cations. If such structures exist in the currently investigated polymer systems, the metal ions in the ionic aggregate would be expected to be strongly coupled, and, as a result, concentration quenching of the fluorescence emission would be observed. Thus, we prepared several Eu^{3+} -containing polymers and samples in which europium acetate is uniformly dispersed in a polymer matrix. In both cases, Eu^{3+} was coordinated with carboxylates. As shown in Figures 4 and 5, for the europium acetate system the fluorescence intensity was found to increase linearly with Eu content. However, in the polymer- Eu^{3+} complex system the fluorescence intensity reached a maximum at a Eu content as small as 4 ~ 5 wt % and subsequently decreased with increasing Eu content.

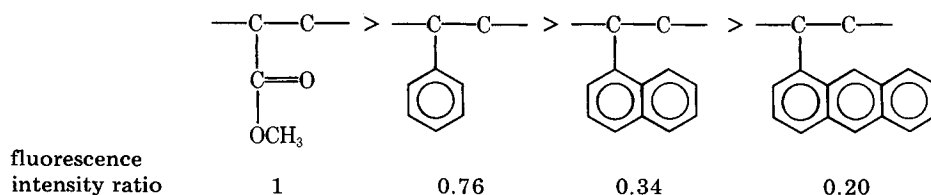
Fluorescence intensity measurements on solid samples are known to be difficult. Various factors such as particle size and reabsorption of the Eu^{3+} emission

TABLE III
Fluorescence Excitation and Emission Lines of PSAA-Eu, -Dy, -Er, and -Sm Complexes

Complex	Excitation, nm	Emission, nm	Metal content wt %	Mole Ln/mole % COOH ^a
PSAA-Eu	396	616	5.2	0.41
		592		
		700		
PSAA-Dy	356	414	5.5	0.40
		348		
PSAA-Er	413	482	6.5	0.47
		495		
		514		
		545		
PSAA-Sm	356	414	5.2	0.41
		348		

^a When Ln ion coordinates with three moles of the COOH group, the ratio is 0.33.

may influence the intensity. Thus, we have taken the average value of three measurements on different samples. The tendency of fluorescence intensity with increasing Eu^{3+} content is a typical fluorescence quenching pattern,¹¹ and the result may provide supporting evidence that ionomers have ionic aggregates in which metal ions are close together. In other words, the local concentration of Eu^{3+} ions in these regions is much higher than the overall range concentration. The polymer structure was varied by copolymerization of acrylic acid with styrene, 1-vinylnaphthalene, and 1-vinylanthracene. The fluorescence emissions were measured on these Eu^{3+} salts containing the same Eu^{3+} wt %. The intensities were found to decrease in the following order:



Nonradiative energy transfer in rare-earth-containing solids has been extensively studied.¹² Intermolecular energy transfer was observed from organic excited donors to a europium or terbium chelate or salt.¹³ Thus, if organic groups whose emission spectra overlap the absorption spectrum of Eu^{3+} are located within a critical distance, nonradiative energy transfer may be observed.¹⁴ Especially in the case of naphthalene, the emission spectrum has a maximum around 400 nm, which strongly overlaps the absorption spectrum of Eu^{3+} (see Figs. 6 and 7). Thus, an increase in the fluorescence intensity of the polymer- Eu^{3+} system should be detected. However, the intensity was found to be smaller than those in the methyl methacrylate and styrene copolymers.

Anthracene also has a broad emission spectrum at 420–460 nm. Although the anthracene content in the polymer was small (see experimental section), the intensity was found to be the smallest one in this series. Therefore, the aromatic groups in these polymers are located too far from the ionic aggregate region in the ionomers, and energy transfer from the organic moiety to Eu^{3+} may be undetectably small. Thus, the above fluorescence intensity sequence may be due to the absorption of excitation energy by the aromatic groups. The absorption

at 400 nm by the aromatic groups decreases in the order anthracene > naphthalene > phenyl, and Eu^{3+} competes in absorption of energy with those organic groups; the more absorption of energy by the organic moiety, the less excitation energy available for Eu^{3+} . As a result, the above fluorescence intensity sequence was obtained.

This work was supported by the National Science Foundation under Polymer Program Grant DMR 78-09764.

References

1. L. Holliday, Ed., *Ionic Polymers*, Applied Science, London, 1975.
2. A. Eisenberg and M. King, *Ion-Containing Polymers*, Academic, New York, 1977.
3. S. I. Weissman, *J. Chem. Phys.*, **10**, 214 (1942).
4. N. E. Wolff and R. J. Pressley, *Appl. Phys. Lett.*, **2**, 152 (1963).
5. M. Nellay, *J. Electrochem. Soc.*, **111**, 1253 (1964).
6. P. H. Gore, *J. Org. Chem.*, **22**, 135 (1957).
7. M. Stolka, Y. F. Yonus, and J. M. Pearson, *Macromolecules*, **9**, 374 (1976).
8. J. R. Witt and E. I. Orstott, *J. Inorg. Nucl. Chem.*, **24**, 637 (1962).
9. S. P. Sinha, *Europium*, Springer-Verlag, New York, 1967, p. 126.
10. A. Eisenberg, *ACS Polym. Prepr.*, **20**, 286 (1979).
11. L. G. Van Uitert, *J. Electrochem. Soc.*, **107**, 803 (1960).
12. E. Matorich and C. K. Suzuki, *J. Chem. Phys.*, **39**, 1442 (1963).
13. A. Heller and E. Wasserman, *J. Chem. Phys.*, **42**, 949 (1965).
14. H. Morawetz, *Science*, **203**, 405 (1979).

Received July 2, 1979

Revised September 1979