ENERGY TRANSFER FROM COPOLYMERS OF STYRENE-MALEIC ACID TO EU(III) IONS IN TETRAHYDROFURAN

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Abstract The sensitization of Eu(III) ion emission in tetrahydrofuran by copolymers of styrene-maleic anhydride, styrene-maleic acid (PSMA), and europium salt of PSMA (PSMA-Eu) was studied. When excited at 260 nm in the presence of PSMA, the emission of Eu(III) at 618 nm exhibited large enhancement compared with that in the absence of PSMA. The enhancement was even greater for PSMA-Eu and accompanied by the decrease in monomer and excimer emission of polymers, suggesting that energy is transferred from the excited polymer to Eu(III) ions.

Key words energy transfer, Eu(III) ion, styrene-maleic acid copolymer

INTRODUCTION

The properties and structures of synthetic polymers containing lanthanide ions have been studied recently[1]. Interests in lanthanides have been stimulated by their fluorescence and laser properties. However, since lanthanides exhibit low absorptivities, luminescence from the lanthanide under direct illumination is weak. A route to overcome this drawback is complexation of the lanthanide ion with ligands which transfer the absorbed energy to the lanthanide ion to produce intense luminescence. The energy transfer process may take place by either intramolecular or intermolecular step. The intermolecular process is, however, often much less efficient than intramolecular process owing to the exponential distance dependence of energy transfer[1b]. The energy transfer process can be applied to the spectrofluorimetric analysis of lanthanides. Fluorimetric measurements offer particular advantages since they are sensitive and can be employed at low concentration of its luminescent species. Fluorimetric methods are also used to obtain information about the structure of lanthanide complexes, their formation constants, and symmetry among other things[1b]. However most of the energy transfer studies have been concerned with the samples in the form of solid, powder or film.

Thus the present study was conducted in tetrahydrofuran (THF) solutions of the copolymers of styrene-maleic anhydride (PSMA), styrene-maleic acid, and Eu(III) complex of PSMA for the purpose of obtaining high sensitized Eu(III) luminescence.

EXPERIMENTAL

Reagents The random copolymers of PSMA with styrene contents of 50%, 67%, and 75% and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were purchased from Aldrich. Sodium salt of PSMA was prepared by refluxing PSMA with 0.25M NaOH for 48 hours, followed by precipitating the reaction mixture into a large amount of ethanol. To obtain PSMA, the sodium salt was dissolved in distilled water, followed by precipitation in 1M HCl. A mixed solution of PSMA and Eu(III) was stirred for 10 hours and precipitated in distilled water to produce PSMA-Eu.

Apparatus A Hitachi 650-60 spectrofluorimeter was used to record fluorescence spectra of copolymer samples in THF at room temperature. Absorption spectra were measured with a Hewlett Packard 8542 diode array spectrophotometer. An Analet fx-6160 FT-IR spectrometer, a Labtest plasmascan 710 ICP, and a DuPont 910 DSC were employed to characterize the polymers.

RESULTS AND DISCUSSION

The structure of the polymer was identified by measuring the IR spectra, DSC curves, and fluorescence characteristics. The IR spectrum of PSMA has the characteristic absorption peaks at 1856cm^{-1} and 1782cm^{-1} . On forming PSMA these peaks disappeared and a new peak at 1713cm^{-1} was observed due to the carboxylic acid groups, whereas PSMA-Eu complex showed a new absorption at 1550cm^{-1} . DSC measurements showed the m.p. of PSMA and PSMA-Eu derived from 75% PSMA increased to 175°C and 178°C , respectively, from 155°C for PSMA. The absorption spectra of the polymers has the absorption maximum at 260 nm. Upon excitation at 396 nm, the wavelength of maximum absorption for Eu(III) ion, PSMA-Eu complex showed the characteristic fluorescence emissions at 593 nm, 618 nm, 650 nm, and 697 nm corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$, and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions, respectively[1d]. Eu content in PSMA-Eu was measured to be 2.8 wt % by ICP.

The fluorescence spectra of random vinylaromatic polymers show monomer and excimer bands. The ratio of excimer to monomer fluorescence intensities, I_e/I_m , is often used to characterize the luminescence properties of the polymer[2]. In particular, the ratio reveals whether the excimer formation is due to intramolecular or intermolecular process.

An increase in the polymer concentration resulted in an increase of the monomer and excimer fluorescence intensities. However, beyond $4.0 \times 10^{-3}\text{M}$ styrene unit concentration both the monomer and excimer intensities declined. Since the resolution of the monomer and excimer bands becomes difficult for these vinylaromatic copolymers, the values of I_e/I_m contain comparatively large experimental errors. Fig.1 shows the dependence of I_e/I_m on the polymer concentration

Fig.1 Comparison of I_e/I_m values vs styrene unit concentration for PSMA (dotted line) and PSMA (solid line). Mole fraction of styrene unit: 75% ($\square$); 67% ($\bullet$); 50% ($\blacktriangle$).

and the mole fraction of styrene unit expressed in %. The monomer and excimer intensities were taken at 285 nm and 330 nm, respectively, to avoid possible overlap. Within experimental error essentially no change in the ratio was observed up to $8.0 \times 10^{-3}\text{M}$ styrene unit concentration regardless of the styrene mole fraction for those two different polymers. This result indicates that the excimer formation of PSMA and PSMA in THF is strictly an intramolecular process up to the concentration studied[3]. PSMA yielded larger I_e/I_m for all styrene concentrations than PSMA of same styrene mole fraction. In PSMA the segments are apparently more flexible and undergo a conformational change more easily than those in PSMA during the lifetime of the excited state to bring the two phenyl rings into the suitable orientation for excimer formation.

When PSMA-Eu complex in THF was ir-

TABLE 1. Effect of triethylamine (TEA) on the relative fluorescence intensities of Eu(III) and of excimer (at 330 nm) and monomer (at 285 nm) of PSMA. $\lambda_{\text{ex}} = 260\text{ nm}$.

Solution	I_{330}	I_{285}	I_{618}	I_{593}	I_{618}/I_{593}
Eu(III)	-		4.0	0.64	6.3
Eu(III)+PSMA	85	25	20	3.6	5.5
Eu(III)+PSMA+[TEA]	76	21	30	5.5	5.4
Eu(III)+PSMA+2·[TEA]	63	15	41	8.0	5.1
Eu(III)+PSMA+3·[TEA]	54	13	43	8.2	5.2
Eu(III)+PSMA+4·[TEA]	53	12	56	11	5.0

Concentrations: [Eu(III)]; $2.2 \times 10^{-4}\text{M}$; [styrene unit] = $1.1 \times 10^{-3}\text{M}$; [TEA] = $5.6 \times 10^{-5}\text{M}$.

TABLE 2. Effect of polymer composition on the relative fluorescence intensities of Eu(III), excimer, and monomer. $\lambda_{\text{ex}}=260$ nm.

Solution	I ₃₃₀	I ₂₈₅	I ₆₁₈	I ₅₉₃	I ₆₁₈ /I ₅₉₃
Eu(III)	-	-	4.3	0.7	6.1
67% PSMA	35	14	-	-	-
Eu(III)+67% PSMA	26	7	9.7	2.0	4.9
50% PSMA	29	36	-	-	-
Eu(III)+50% PSMA	17	14	22	4.5	4.9

Concentrations : [Eu(III)]= 2.2×10^{-4} M; [styrene unit]= 1.1×10^{-3} M.

Fig.2 Comparison of fluorescence emission spectra of PSMA-Eu at two different excitation wavelengths. [styrene unit]= 4.0×10^{-3} M.

radiated at 260 nm, the fluorescence intensity of Eu(III) at 618 nm showed 13 fold increase compared with that at $\lambda_{\text{ex}}=396$ nm as presented in Fig.2. Since the molar absorptivity of Eu(III) at 396 nm is 12 times larger than that at 260 nm[4], the 13 fold enhancement implies that the energy absorbed by styrene unit was transferred to Eu(III). To confirm the energy transfer, the fluorescence properties under various conditions were studied.

First, the fluorescence emission spectra were measured with three samples of equal concentrations of Eu(III) and styrene unit: Eu(III) only, a mixture of Eu(III) and PSMA, and PSMA-Eu. As expected all three solution gave equal Eu(III) emissions at $\lambda_{\text{ex}}=396$ nm. However, when the polymer solutions were irradiated to 260 nm radiation, the weak Eu(III) emission was replaced by a brighter red glow. Compared with

the Eu(III) only solution, PSMA-Eu and the mixed solution resulted in a 12-fold and 6-fold increase in Eu(III) fluorescence, respectively. Thus the energy transfer is apparently more efficient when Eu(III) ions are bound to the polymer. Concurrently both the monomer and the excimer intensities were declined, confirming again that the energy absorbed by styrene unit was transferred.

If a complex formation is important in the energy transfer process, the addition of a base into the mixed solution of Eu(III) and PSMA was considered enhancing the complex formation, followed by the increase in energy transfer. This expectation is clearly demonstrated in Table 1 using triethylamine (TEA) as a base. Over the concentration range of TEA the Eu(III) fluorescence intensity increased almost linearly.

However, the ratio of Eu(III) fluorescence at 618 nm to that at 593 nm, I_{618}/I_{593} , exhibited a slight decrease as the concentration of TEA increased as indicated in Table 1. The decrease may not be significant, but it is likely related to the enhanced complex formation. The $^5D_0 \rightarrow ^7F_2$ transition at 618 nm is a hypersensitive transition[1c], which is more sensitive to the chemical environment than the normal $f \rightarrow f$ transitions such as $^5D_0 \rightarrow ^7F_1$ at 593 nm. Thus the exchange in the type of ligands around Eu(III) ions may cause the I_{618}/I_{593} ratios to vary. The I_{618}/I_{593} value of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in THF was measured 6.0 ± 0.3 . Upon exchanging nitrate and/or aquo ligands of Eu(III) with the carboxylate ligand of PSMA, the fluorescence intensity of $^5D_0 \rightarrow ^7F_2$ transition is apparently reduced slightly with respect to that of $^5D_0 \rightarrow ^7F_1$.

The addition of 1.1×10^{-3} M succinic acid or malonic acid to the THF solution of 2.2×10^{-4} M $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ did not alter the ratio. On the other hand, the addition of PSMA containing 1.1×10^{-3} M carboxylic acid decreased the ratio to 4.8.

The PSMA containing more carboxylic acid group was more efficient in forming the complex as noted in Table 2. At a given styrene unit concentration 50% PSMA contains twice as much carboxylic acid groups as 67% PSMA.

Fig. 3 Fluorescence intensity of Eu(III) at 618 nm vs molar ratio of carboxylic acid (L) in PSMA to Eu(III). $[Eu(III)]$: $2.2 \times 10^{-4} M$ ($\blacksquare$); $1.3 \times 10^{-4} M$ ($\bullet$); $1.1 \times 10^{-4} M$ ($\blacktriangle$).

Fig. 4 Fluorescence intensities of monomer at 285 nm (I_m), excimer at 330 nm (I_e), and ratio (I_e/I_m) vs concentration of Eu(III) at constant PSMA. [styrene unit] = $2.2 \times 10^{-3} M$.

Now, the effect of PSMA on Eu(III) emission was examined and is summarized in Fig. 3. At a given concentration of Eu(III), the intensity increased continuously, although the initial rise is rather sharp at higher concentration of Eu(III) ions reflecting abrupt increase in the complex formation. It appears that no definite stoichiometry exists between Eu(III) and carboxylic acid of PSMA and the coordination of Eu(III) to PSMA is not completed over the concentration range studied. Inversely, when the concentration of Eu(III) was varied at a given concentration of PSMA, the monomer and excimer fluorescence were diminished, but I_e/I_m increased as shown in Fig. 4. This result probably suggests that some conformational change in PSMA occur upon the addition of Eu(III) because the mechanism for excimer formation predicts I_e/I_m to be constant unless intermolecular excimer forms [5]. Under certain conditions such as at high ionic strength [3] or at high solvent viscosity [6], the excimer formation can be enhanced by the participation of non-nearest neighbors. In the present system, however, an increase in the concentration of Eu(III) is suspected to increase the polymer chain coiling [6,7], which increases the probability of forming the sandwich conformation needed for excimer formation. This result may be considered to provide a supporting evidence to the proposal that ion-containing polymers have ionic aggregates in which the local concentration of metal ions is larger than the overall range concentration [7].

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