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Rare Earth Metal Containing Polymers. 4. Energy Transfer from Uranyl to Europium Ions in Ionomers

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ABSTRACT: Various ratios of europium and uranyl acetates were prepared by dissolving europium and uranyl acetates in acetic acid and removing acetic acid under vacuum. The fluorescence intensities at 616 nm of these mixed acetates were measured under an excitation wavelength of 420 nm. Strong energy transfer from UO_2^{2+} to Eu^{3+} was observed. This result indicated that these ions were in very close proximity in this system. Various concentrations of Eu^{3+} and UO_2^{2+} salts of polymer containing carboxyl ligands were prepared and fluorescence properties of these polymers were investigated. The polymers investigated were poly(methacrylic acid) (PMA) and styrene–acrylic acid (PSAA) and methyl methacrylate–methacrylic acid (PMM/MA) copolymers. When Eu^{3+} and UO_2^{2+} were introduced to the polymers of PSAA and PMM/MA, very effective energy transfer from UO_2^{2+} to Eu^{3+} was observed because of the proximity of these metal ions in ionic aggregates of these ionomers. However, the PMA-UO_2 and -Eu salts did not show such energy transfer even when a large excess of UO_2^{2+} was added to the polymer. The PMA salts are reported to have no ion aggregate structure; it is concluded that Eu^{3+} and UO_2^{2+} ions were uniformly dispersed throughout the polymer system so that the distances between these ions were far beyond the energy transfer range.

Energy transfer occurs from a donor to an acceptor when the fluorescence spectrum of the donor overlaps the absorption spectrum of the acceptor.[1] The emission of UO_2^{2+} ion extends from 480 to about 570 nm. Three absorptions of Eu^{3+} ion observed at room temperature lie within this energy range.[2] It has previously been shown that UO_2^{2+} transfers energy to Eu^{3+} in borosilicate glass, resulting in a fivefold increase in the Eu fluorescence.[3] Kropp investigated energy transfer from UO_2^{2+} to Eu^{3+} in several solutions and suggested that the energy transfer involves electric dipole transition or electron exchange interaction.[4] In both cases, the transfer is short range, of the order of the collision diameters.

The structures of synthetic polymers containing metal ions have been extensively investigated in recent years.[5,6] It is proposed that there are submicroscopic reigons of the polymer in which lamellar domains are interspersed with ionic aggregates. We have also initiated a study of the structures of ionomers, using trivalent lanthanide ions as fluorescent probes.[7,8] The results support the proposed model of ionomers consisting of clusters or aggregates of ionic groups dispersed throughout the system. Thus, if Eu^{3+} and UO_2^{2+} ions are introduced into an ionomer having an ion aggregate structure, it would be expected that these ions should concentrate in these ionic aggregate sites and that very effective energy transfer should take place because of the proximity of Eu^{3+} and UO_2^{2+} ion aggregates.

In this paper, the results of energy transfer between Eu^{3+} and UO_2^{2+} ions in methyl methacrylate–methacrylic acid (PMM/MA) and styrene–acrylic acid (PSAA) copolymers are described and the results are compared with those in poly(methacrylic acid) (PMA), as a further test of the existence of ion aggregates in the former two and their absence in the latter.

Experimental Section

Materials. Polymers. Methyl methacrylate–methacrylic acid (PMM/MA) copolymer was prepared by partial hydrolysis of poly(methyl methacrylate) (Polysciences Inc., high molecular weight) as described in the literature.[9] A typical preparation procedure for PMM/MA (MA content 4.1 mol %) is as follows: Fine-powdered poly(methyl methacrylate) (40 g) was suspended in 350 mL of 2-propanol in a 1-L three-necked flask equipped with a mechanical stirrer and a condenser. To this solution was added 16 g of NaOH in 8 mL of water, followed by heating for 35 min at 70 °C. The product was poured into water and the precipitate was filtered, washed with dilute HCl and water several times, and dried under vacuum at 60 °C for 2 days.

The acid content of the polymer obtained was determined by titration in 1:1 (v/v) acetone–methanol solvent with standardized sodium methoxide, using phenolphthalein as an indicator. Polymers with two different acid contents (4.1 and 13 mol %) were used in this study.

Styrene–acrylic acid copolymer (PSAA) was prepared in the same manner as described in our previous report.[7] The acid content was 9 mol %.

Lanthanides. Europium chloride ($EuCl_3{\cdot}6H_2O$) (Ventron), $UO_2(NO_3)_2{\cdot}6H_2O$ (J. T. Baker), and $UO_2(OAc)_2{\cdot}2H_2O$ (Mallinckrodt Chemical Works) were used without further purification. $Eu(OAc)_3$ was prepared by the method described in the literature.[9]

Lanthanide–Polymer Salts. Various lanthanide-containing polymers were prepared similarly. The typical procedure of the preparations is as follows: Five grams of PMM/MA (acid content 4.1 mol %) was dissolved in butanone (250 mL). A solution in 1:1 (v/v) butanone–methanol of the weighed $EuCl_3$ and $UO_2(NO_3)_2$ was added to the polymer solution. After the solution was stirred for 1 h, sodium acetate was added to the solution until the pH reached about 7. The solution was poured into a large amount of distilled water, and the precipitate was washed with water and methanol several times and dried under vacuum for 2 days at 60 °C. To determine the metal content of the polymer, a sample (0.2 g) was weighed in a porcelain crucible and ashed in a furnace heated to 600 °C at a rate of 200 °C/h. The Eu content was determined by atomic absorption measurement.[7] The uranium content was calculated by subtraction of Eu content (as Eu_2O_3) from the oxide residue. The uranium was calculated on the basis of U_3O_8.[10]

Fluorescence Measurements. Perkin-Elmer Model MPF-2A and MPF-44B fluorescence spectrophotometers were used to measure fluorescence spectra of samples. The powder sample was placed in the solid sample holder attached to the instruments, which measures the fluorescence emission at 60° with the exciting beam at 30° to the sample surface. The powder samples were dried at 60 °C under vacuum and kept in a desiccator containing P_2O_5 until ready to be loaded into the sample holder.

X-ray Powder Diffraction. Samples were placed in the sample holder of a Norelco high-angle diffractometer equipped with a monochromator. Diffraction patterns were run over a 2θ range of 10–50°, using Cu Kα radiation.

Results and Discussion

Since Eu^{3+} has a strong emission peak at 616 nm while UO_2^{2+} emits very weakly at that wavelength, the fluorescence excitation spectra at 616 nm of Eu^{3+} and UO_2^{2+} salts of PSAA (9.0 mol % of acrylic acid) were recorded. The spectra for various concentrations of these metal ions are shown in Figure 1. The excitation spectra have peaks at

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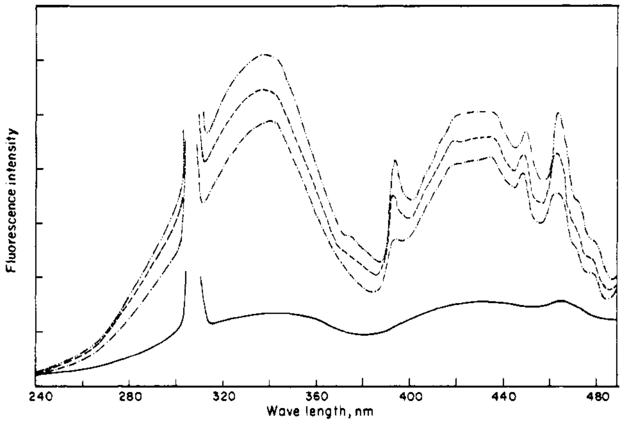

Figure 1. Fluorescence excitation spectra of Eu^{3+} and UO_2^{2+} salts of styrene–acrylic acid copolymer (acid content 9 mol %) monitored at 616 nm: (- - -) $[UO_2^{2+}]/[Eu^{3+}] = 4.7{:}0.36$ mol %; (—) $[UO_2^{2+}]/[Eu^{3+}] = 1.2{:}0.68$ mol %; (-·-) $[UO_2^{2+}]/[Eu^{3+}] = 1.2{:}1.58$ mol %; (-··-) $[UO_2^{2+}]/[Eu^{3+}] = 1.2{:}2.30$ mol %.

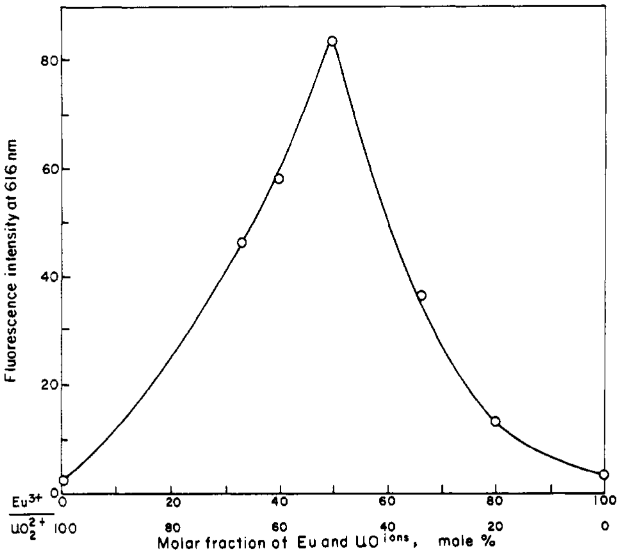

Figure 2. Fluorescence intensity of mixtures of $Eu(OAc)_3$ and $UO_2(OAc)_2$ at 616 nm. Excitation wavelength 420 nm.

335, 396, and 412–425 nm and the intensities of these peaks increased on increasing the Eu^{3+} concentration in the polymer.

The absorptivities of UO_2^{2+} ion in aqueous solution at 335 and 420 nm were found to be 14.0 and 9.0 M^{-1} cm^{-1}, respectively, whereas Eu^{3+} showed negligible absorption at these wavelengths. Therefore, the strong excitation peaks at 335 and 420 nm shown in Figure 1 suggest that the energy absorbed by UO_2^{2+} was transferred to Eu^{3+} in the polymer system. In order to obtain further information about the energy transfer process, various concentrations of UO_2^{2+} and Eu^{3+} acetates were prepared and the fluorescence properties were studied. Samples containing different ratios of $Eu(OAc)_3$ and $UO_2(OAc)_2$ were first dissolved in acetic acid, which was then removed under vacuum. The fluorescence intensities at 616 nm of these mixed acetates were measured at an excitation wavelength of 420 nm. Strong energy transfer from UO_2^{2+} to Eu^{3+} was observed and the maximum value was found in the sample having the two ions in equimolar proportions, as shown in Figure 2. However, when the sample was prepared by mechanically mixing without dissolving in acetic acid, no energy transfer was observed. This result indicates that the emission due to energy transfer between UO_2^{2+} and Eu^{3+} can be observed only when these ions are in very close proximity. An X-ray powder diagram showed that the material obtained by drying the mixed acetates contained a phase different from the uranyl and europium acetates. Thus, it may be assumed that a double salt was formed, similar to $RbUO_2(NO_3)_2$ described previously.[11] This would bring the two ions into the proximity required for nonradiative energy transfer. The acetate double salt may be considered as a primitive model for the ion aggregates proposed to exist in the polymer salts.

Table I
Energy Transfer from UO_2^{2+} to Eu^{3+} in Polymer Systems

	metal ion content		fluorescence intensity		
			area	peak	
	Eu^{3+}	UO_2^{2+}	320–500 nm	330 nm	430 nm
PMM/MA (4 mol %)	0.33		21	4	1
PMM/MA (4 mol %)	0.35	0.30	129	33	34
PMM/MA (4 mol %)	0.41	0.81	118	31	35
PMM/MA (4 mol %)	0.36	1.39	115	24	25
PMM/MA (13 mol %)	0.52		27	4	2
PMM/MA (13 mol %)	0.52	0.53	221	37	52
PMM/MA (13 mol %)	0.48	1.10	196	31	45
PMA	0.33		10	1	1
PMA	0.32	0.28	10	2	1
PMA	0.32	0.96	9	1	1
PMA	0.34	5.41	9	1	1
PMA	0.34	9.84	2	0.5	0.5

This interpretation is also supported by a change in the IR spectrum. In the infrared spectra of the acetic acid treated acetates, the 950-cm^{-1} absorption, which corresponds to U=O stretching,[12] was shifted by 5–10 cm^{-1} to a lower wavenumber.

In the PSAA system, a similar arrangement of Eu^{3+} and UO_2^{2+} with carboxyl ligand in the ion aggregate is also expected. This may account for the effective energy transfer between these ions.

For further investigation of the effect of the concentration of UO_2^{2+} on the energy transfer to Eu^{3+} in the polymer matrix, several Eu^{3+}- and UO_2^{2+}-containing salts of methyl methacrylate–methacrylic acid copolymers (PMM/MA) were prepared. In these systems, the concentrations of Eu^{3+} were kept constant and the UO_2^{2+} concentrations were varied. The excitation spectra from 300 to 500 nm at an emission wavelength of 616 nm of these samples were recorded and the results are summarized in Table I.

The fluorescence intensities of Eu^{3+} at 330 and 430 nm were found to be increased up to 35-fold when equal molar concentrations of UO_2^{2+} and Eu^{3+} were added. This is apparently due to the effective energy transfer from UO^{2+} to Eu^{3+}. However, further increases in UO_2^{2+} concentration decreased slightly the Eu^{3+} fluorescence intensity. This may be due to concentration quenching of UO_2^{2+}.[13] In other words, as the UO_2^{2+} concentration in the polymer matrix is increased, the probability of the interactions between UO_2^{2+} ions is also increased, which may reduce the efficiency of energy transfer of UO_2^{2+} to Eu^{3+}.

When Eu^{3+} and UO_2^{2+} were introduced into poly(methacrylic acid) (PMA), no enhancement in the Eu^{3+} fluorescence intensity was observed even when a large excess of UO_2^{2+} ion was added. There is apparently no energy transfer between these ions. The PMA salt has no ion aggregate structure and Eu^{3+} and UO_2^{2+} were expected to be uniformly dispersed throughout the polymer system so that the distances between Eu^{3+} and UO_2^{2+} were far beyond the energy transfer range.

These results further support the existence of ion aggregate structures in the PMM/MA system in which Eu^{3+} and UO_2^{2+} are located close together, facilitating the energy transfer between these ions.

The above conclusions attributing the loss of Eu^{3+} fluorescence activity at higher UO_2^{2+} concentration to UO_2^{2+} self-quenching can only be confirmed by a simultaneous study of the concentration dependence of both emissions and by measuring decay and build-up times of both. These experiments are now in progress and will be the subject of a future report.

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References and Notes

(1) Förster, Th. *Discuss. Faraday Soc.* **1959**, *27*, 7.
(2) Sinha, S. P. "Europium"; Springer-Verlag: New York, 1967; p 123.
(3) De Shager, L. G.; Cabeza, A. Y. *Proc. IEEE* **1964**, *52*, 1355.
(4) Kropp, J. L. *J. Chem. Phys.* **1967**, *46*, 843.
(5) Eisenberg, A. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1979**, *20* (1), 286.
(6) Eisenberg, A.; King, M. "Ion-Containing Polymers"; Academic Press: New York, 1977; p 23.
(7) Banks, E.; Okamoto, Y.; Ueba, Y. *J. Appl. Polym. Sci.* **1980**, *25*, 359.
(8) Okamoto, Y.; Ueba, Y.; Dzhanibekov, N. F.; Banks, E. *Macromolecules* **1981**, *14*, 17.
(9) Witt, J. R.; Orstott, E. J. *J. Inorg. Nucl. Chem.* **1962**, *24*, 637.
(10) Taha, I. A.; Morawetz, H. *J. Am. Chem. Soc.* **1971**, *93*, 829.
(11) Barclay, G. A.; Sabine, T. M.; Taylor, J. C. *Acta Crystallogr.* **1965**, *19*, 205.
(12) Ohwada, K. *Spectrochim. Acta, Part A* **1968**, *24*, 595.
(13) Van Uitert, L. G. *J. Electrochem. Soc.* **1960**, *107*, 803.

Effect of Filament Flexibility on the Dynamic Light-Scattering Spectrum with Special Reference to fd Virus and Muscle Thin Filaments[†]

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ABSTRACT: The field correlation function, $g^{(1)}(\tau)$, of light scattered from very long, semiflexible filaments in dilute solution was simulated for various values of filament length (L), flexibility (γL), friction constant (ζ), temperature (T), and length of the scattering vector (K). For a given γL, $g^{(1)}(\tau)$'s for different temperatures scaled with T/η (η is solvent viscosity). In the stiff limit ($\gamma L \ll 1$), profiles of the present $g^{(1)}(\tau)$'s closely resembled those based on a rigorous formula for a rigid rod. In the semiflexible range ($0 \ll \gamma L \leq 0.5$), the profiles of $g^{(1)}(\tau)$'s strongly depended on γL at large K, indicating that if γL changes with temperature, $g^{(1)}(\tau)$'s do not scale with T/η at large K. The model was applied to the analysis of experimental data available in the literature and it was suggested that both fd virus and the muscle thin filament are not rigid but have γL values of the order of 0.1.

Introduction

Considerable effort has been expended in recent years in extracting the contributions of internal motions of large flexible macromolecules from the intensity autocorrelation functions of polarized Rayleigh scattered light. Pecora[1,2] was the first to give theoretical expressions for the field correlation function of light scattered from flexible-coil macromolecular chains as a sum of exponential terms with time constants corresponding to the lifetimes of the internal fluctuation normal modes. Fujime[3] and Fujime and Maruyama[4] gave formulas for the intensity fluctuation spectrum of light scattered from semiflexible filaments also as a sum of exponentials.

In earlier days of dynamic light-scattering studies, one used spectrum analyzers. More recently, however, one uses digital correlators. Since the power spectrum and the time correlation function are connected with each other by the Fourier transform, both techniques should provide the same information. However, the real situation is very different for these two techniques. Consider a model situation composed of four components:

$$g^{(1)}(\tau) = \sum_n P_n \exp(-\tau/\tau_n) \qquad \text{with} \qquad \sum_n P_n = 1$$

The so-called average decay rate $\bar{\Gamma}$ of $g^{(1)}(\tau)$ is given by $\bar{\Gamma} = \sum_n P_n/\tau_n$. Even if $P_1 > P_2 > P_3 \gg P_4$ and $\tau_1 > \tau_2 > \tau_3 \gg \tau_4$, the ratio P_4/τ_4 is not necessarily small compared with P_1/τ_1. Roughly speaking, the short-time behavior of correlation functions is sensitively affected by components having short time constants. On the other hand, the power spectrum corresponding to the above $g^{(1)}(\tau)$, in the heterodyne case for simplicity of discussion, has the form

$$S(\omega) = (1/\pi)\sum_n\{(1/\tau_n)P_n/[\omega^2 + (1/\tau_n)^2]\}$$

In the above situation of P_n and τ_n, the fourth Lorentzian in $S(\omega)$ will hardly be detected because $\pi S(0) = \sum_n P_n \tau_n$ and $\pi S(\omega_h)\omega_h^2 = \bar{\Gamma}$, where $\omega_h \gg 1/\tau_4$. Of course, $P_1\tau_1 > P_2\tau_2 > P_3\tau_3 \gg P_4\tau_4$ and only at frequencies $\omega \gtrsim \omega_h$, where $S(\omega)$ will be close to or below the noise level, will all components contribute to the power spectrum in the same way as to the correlation function. The power spectrum is insensitive to components having short time constants. From an experimental point of view, *we have to take into account many more components in the correlation technique than in the spectral technique.*

[†] A part of this work was presented at the NATO ASI on scattering techniques, Wellesley College, Mass., August 1980.