nitude of k_D in ternary solutions is less than or equal to that in pure solvent, and no substantial error is incurred by equating $D_{\rm measd}$ and $D_{\rm tr}$. Specifically, for the 3.0×10^5 PS used in the DLS/FRS comparison, k_D is approximately 40 mL/g in pure oFT, and the product $k_D c_{\rm PS}$ was at most 0.02. These results also justify, a posteriori, the use of the assumption $D_{\rm measd} \approx D_{\rm tr}$ in our previous work.[3,6-10]

A remarkable feature of these data is that the transition from good to apparently θ-like quality occurs at very low PVME concentrations; the onset of semidilute conditions is expected to occur at $c_{\rm PVME} = 1.3\%$. Conversely, when the matrix concentration is semidilute, k_D is at most a weak function of $c_{\rm PVME}$. In contrast, in binary PS solutions, the decrease from good solvent to θ solvent conformation with increasing concentration occurs over the semidilute region.[28-30] This observation of decreasing solvent quality is mirrored in the dependence of R_g (from static light scattering[25]) and R_h (from $D_{\rm tr}$ corrected for solution viscosity) on $c_{\rm PVME}$, both of which decrease significantly in the same concentration range. This behavior contradicts an assumption invoked in current theories for the thermodynamic properties of ternary polymer solutions[31] and will be reported on in more detail in a future publication.[32] This PS coil contraction with increasing $c_{\rm PVME}$ was also inferred previously from the low $c_{\rm PVME}$ behavior of $D_{\rm measd}$, for both linear and star PS.[9,10] The conclusions from the results presented here may be summarized as follows. 1. Within the accuracy of the experiments, both FRS and DLS yield equivalent values for D, confirming the identification of D measured by DLS as the translational diffusion of the PS component. 2. The finite PS concentrations used for DLS measurements lead to negligible differences between $D_{\rm measd}$ and $D_{\rm tr}$. 3. The dependence of k_D on $c_{\rm PVME}$ is quite interesting and is under further investigation. Although these results justify a posteriori the interpretation of our previous results, the universality of these conclusions has not been established. In other words, it would be desirable to perform similar measurements for other ternary systems.

Acknowledgment. This work was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also appreciate the assistance of Professor H. Yu in the dye-labeling procedure.

Registry No. PS, 9003-53-6; PVME, 9003-09-2.

References and Notes

(1) Hadgraft, J.; Hyde, A. J.; Richards, R. W. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 1495.
(2) Cotts, D. B. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1381.
(3) Lodge, T. P. *Macromolecules* **1983**, *16*, 1393.
(4) Martin, J. E. *Macromolecules* **1984**, *17*, 1279.
(5) Martin, J. E. *Macromolecules* **1986**, *19*, 922.
(6) Hanley, B.; Tirrell, M.; Lodge, T. P. *Polym. Bull. (Berlin)* **1985**, *14*, 137.
(7) Lodge, T. P.; Wheeler, L. M.; Hanley, B.; Tirrell, M. *Polym. Bull. (Berlin)* **1986**, *15*, 35.
(8) Lodge, T. P.; Wheeler, L. M. *Macromolecules* **1986**, *19*, 2983.
(9) Wheeler, L. M.; Lodge, T. P.; Hanley, B.; Tirrell, M. *Macromolecules* **1987**, *20*, 1120.
(10) Markland, P.; Lodge, T. P. *Polymer* **1987**, *28*, 1377.
(11) Numasawa, N.; Hamada, T.; Nose, T. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 19.
(12) Numasawa, N.; Kuwamoto, K.; Nose, T. *Macromolecules* **1986**, *19*, 2593.
(13) Nemoto, N.; Inoue, T.; Makita, Y.; Tsunashima, Y.; Kurata, M. *Macromolecules* **1985**, *18*, 2516.
(14) Chu, B.; Wu, D.-Q.; Liang, G.-M. *Macromolecules* **1986**, *19*, 2665.
(15) Nose, T.; Chu, B. *Macromolecules* **1979**, *12*, 590.
(16) Amis, E. J.; Han, C. C. *Polymer* **1982**, *23*, 1403.
(17) Amis, E. J.; Janmey, P. A.; Ferry, J. D.; Yu, H. *Macromolecules* **1983**, *16*, 441.
(18) Candau, S. J.; Butler, I.; King, T. A. *Polymer* **1983**, *24*, 1601.
(19) Balloge, S.; Tirrell, M. *Macromolecules* **1985**, *18*, 819.
(20) Brown, W. *Macromolecules* **1986**, *19*, 1083.
(21) Hanley, B.; Balloge, S.; Tirrell, M. *Chem. Eng. Commun.* **1983**, *24*, 93.
(22) Bauer, B. J.; Hanley, B.; Muroga, Y., to be submitted for publication.
(23) Kim, H.; Chang, T.; Yohanan, S. M.; Wang, L.; Yu, H. *Macromolecules* **1986**, *19*, 2737.
(24) Tran-Cong, Q.; Chang, T.; Han, C. C.; Nishijima, Y. submitted for publication in *Macromolecules*.
(25) Markland, P. M.S. Thesis, University of Minnesota, 1987.
(26) Mandema, W.; Zeldenrust, H. *Polymer* **1977**, *18*, 835.
(27) Han, C. C. *Polymer* **1979**, *20*, 259.
(28) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(29) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P.-G. *Macromolecules* **1975**, *8*, 804.
(30) King, J. S.; Boyer, W.; Wignall, G.; Ullman, R. *Macromolecules* **1985**, *4*, 709.
(31) Joanny, J.-F.; Leibler, L.; Ball, R. *J. Chem. Phys.* **1984**, *81*, 4640.
(32) Kent, M.; Markland, P.; Wheeler, L. M.; Lodge, T. P.; Tirrell, M. to be submitted for publication in *Macromolecules*.

Investigation of Ion Binding Properties of Synthetic Polyelectrolytes Using a Terbium(III) Probe: Elucidation of the Number of Coordinated Water Molecules on Metal Polyelectrolyte Complexes[1]

J. KIDO,[†] H. G. BRITTAIN,[‡] and Y. OKAMOTO*[†]

Department of Chemistry and Polymer Research Institute, Polytechnic University, Brooklyn, New York 11201, and Squibb Institute for Medical Research, P.O. Box 191, New Brunswick, New Jersey 08903. *Received April 24, 1987*

Introduction

The extremely low activity coefficients of counterions in polyelectrolyte solutions are attributed to two types of association of counterions to polyions. One type of binding is referred to as "diffuse" or "ion atmosphere binding", where the counterions are located in the area of the polyelectrolyte domain due to the large electrostatic forces and have some mobility. Another type of binding is "site binding", where the counterions are attracted to specific sites of the polyions through the formation of the complex.[2] Evidence for site binding has been accumulated from studies of dialysis equilibrium,[3] dilatometric measurements,[4,5] UV spectroscopy,[6,7] and potentiometric titrations of synthetic polyelectrolytes.[8] The ion binding can be characterized quantitatively by phenomena which are directly related to the release of water molecules coordinated to the cations. Since the hydration shell is compressed by electrostriction, this release leads to an increase in volume[4,5] and characteristic decrease in refractive index.[9]

The fluorescence properties of lanthanide ions in aqueous solution are known to be strongly influenced by their immediate coordinative environment.[10,11] The fluorescence intensity of the ions is normally quite weak in aqueous solution since the coordinated water molecules serve as efficient quenchers of the emission.[12] Recently, we have observed that the fluorescence intensities and excitation spectra of Tb(III) are greatly enhanced upon binding of this ion to either polyacrylate[13] or to polysaccharides such as carboxymethylcellulose or heparin.[14]

[†] Polytechnic University.

[‡] Squibb Institute for Medical Research.

0024-9297/88/2221-1872$01.50/0 © 1988 American Chemical Society

These results indicate that Tb(III) ions were bound strongly and asymmetrically in aqueous solution by the polymeric systems and that some or all of the coordinated water molecules were expelled upon binding.

The existence of a deuterium isotope effect in the fluorescence properties of lanthanide compounds has been known for some time and has been studied in detail by a number of investigators.[15-18] The OH vibration (3500 cm^{-1}) of coordinated water molecules presents an efficient mechanism whereby the Tb(III) excited state may undergo radiationless deactivation, but the OD vibration (2800 cm^{-1}) is far less efficient. Horrocks and Sudnick placed these observations on a quantitative scale and developed a method whereby the hydration state of a lanthanide complex could be determined.[17] Fluorescence lifetimes measured in H_2O and D_2O are used to obtain the apparent rate constants for radiative decay, and the difference between these two constants is used to obtain the number of coordinated water molecules.

Determination of the hydration state of a metal ion bound in a polymer matrix can be used to deduce its coordinative environment. Consequently, we have studied the fluorescence properties of Tb(III) bound to polycarboxylates, as well as to simpler monomeric carboxylate ligands. The results of these investigations are the subject of the present work.

Experimental Section

Materials. Poly(acrylic acid) (MW 450 000) and 1:1 copolymer of maleic anhydride and ethylene (MW 250 000) were obtained by Polyscience Inc. and Monsant Co., respectively. Poly(methacrylic acid) was prepared by a radical polymerization of methacrylic acid using potassium persulfate as an initiator. The polymer obtained was dialyzed by using cellophane tubes for 4 days and was then freeze-dried. The molecular weight of the polymer was determined to be 470 000 by viscosity measurements. Poly(acrylic acid-*co*-acrylamide) was prepared by copolymerization at 70 °C of the benzene solution of acrylic acid and acrylamide with AIBN as an initiator under nitrogen atmosphere. The composition of the copolymer was determined to be 2.5:1 molar ratio of acrylamide and acrylic acid by the titration of the acrylic acid moiety. Monomeric acids used in this study were purchased from Aldrich and used without further purification. Terbium chloride ($TbCl_3 \cdot 6H_2O$) was obtained from Research Chemicals.

Fluorescence Measurements. Tb(III) fluorescence and excitation spectra were obtained on a Perkin-Elmer MPF-44B instrument. Measurements of the fluorescence lifetime were obtained on an apparatus assembled for this purpose. Tb(III) samples were excited by the 337-nm output of a pulsed nitrogen laser (Model LN-1000, Photochemical Research Associates). The resulting emission was analyzed at 545 nm by a 0.1-m grating monochromator (Model H-10, Instruments SA) and detected by a 1P2B photomultiplier tube. The fluorescence decay curve was captured by using a boxcar averager (Model SR265, Stanford Research Systems), with the radiative rate constant being obtained by means of the SR265 software. Reproducibility of the rate constants was better than to within 5%.

The concentrations of carboxylic acid unit and Tb(III) ion used for all work were 50 and 2 mM, respectively.

Results and Discussion

Upon addition of poly(sodium acrylate) to an aqueous solution of Tb(III), it was found that the Tb(III) fluorescence intensity was greatly increased.[13] Repeat of the same experiment in D_2O led to an approximate order of magnitude increase in emission intensity. These data are summarized in Figures 1 and 2. Addition of simple carboxylic acids leads to the observation of similar effects, although the magnitudes are not as dramatic. These experiments demonstrate that the binding of both simple and polymeric carboxylates significantly perturbs the Tb(III) emission properties, enabling these quantities to be used in studies of complex formation.

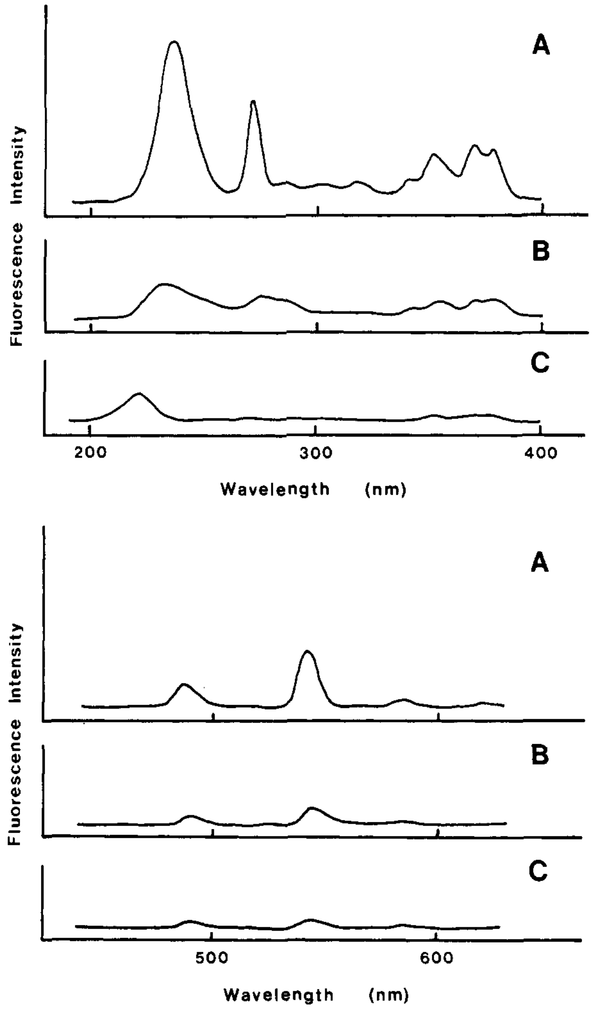

Figure 1. (Top) Fluorescence excitation spectra of Tb(III) complexes in H_2O solution, λ_{em} = 543 nm. (Bottom) Fluorescence emission spectra of Tb(III) complexes in H_2O solution, λ_{ex} = 368 nm. (A) PAA/Tb; (B) PrA/Tb; (C) Tb alone.

The observed fluorescence decay constant, k_{obsd}, is the reciprocal of the measured emission lifetime. In a mixed H_2O/D_2O solvent, this quantity may be expressed as[17]

$$k_{obsd} = k_0 + CX(H_2O) \qquad (1)$$

is the portion of the rate constant consisting of all nonradiative decay processes not involving solvent deactivation of the excited state. $X(H_2O)$ is the mole fraction of H_2O in the H_2O/D_2O solvent mixture, and C is a constant of proportionality. Horrocks and Sudnick have plotted k_{obsd} against $X(H_2O)$ for a wide variety of Tb(III) complexes and have obtained values for C from the slopes of these plots. The best value of C obtained by these workers was 0.24 ms^{-1}.[17]

The fluorescence lifetimes of Tb(III) bound to poly(acrylic acid) (PAA), poly(maleic acid-*co*-ethylene) (MAE), poly(methacrylic acid) (PMA), and poly(acrylic acid-*co*-acrylamide) (PAAm) were obtained in both H_2O and D_2O solutions. In addition, analogous data were obtained on several simple carboxylate monomers which could be taken as model compounds for the polymers: propionic acid (PrA), glutaric acid (GA), 2,3-dimethylsuccinic acid (DSA), and dimethylmalonic acid (DMA). All pertinent data and computed results are summarized in Tables I and II.

The number of water molecules bound to Tb(III) in its polyacrylate complex was found to be 3.5. The analogous carboxylate monomer to PAA was propionate, and it was

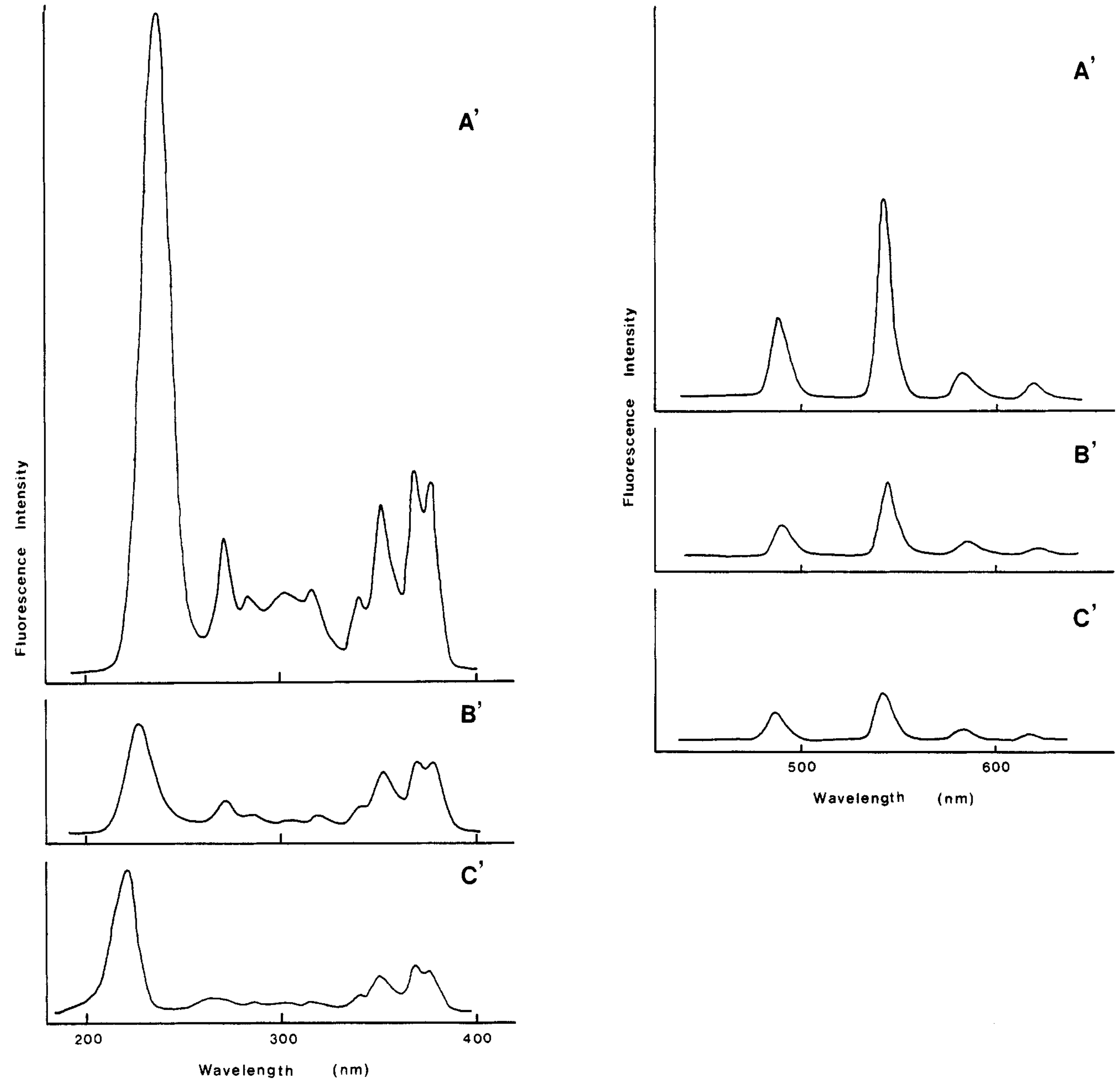

Figure 2. (Left) Fluorescence excitation spectra of Tb(III) complexes in D_2O solution, λ_{em} = 543 nm. (Right) Fluorescence emission spectra of Tb(III) complexes in D_2O solution, λ_{ex} = 368 nm. (A′) PAA/Tb; (B′) PrA/Tb; (C′) Tb alone.

Table I
Number of Coordinated Water Molecules and Photophysical Parameters for Tb(III)-Monomeric Carboxylate Complexes

ligand[a]	solvent	τ, μs	k_{obsd}, ms^{-1}	Δk_{obsd}, ms^{-1}	no. of H_2O[b]
PrA[c]	H_2O	530	1.87	1.45	6.0
	D_2O	2370	0.42		
DMA[d]	H_2O	460	2.17	1.52	6.3
	D_2O	1550	0.65		
DSA[e]	H_2O	550	1.83	1.39	5.8
	D_2O	2260	0.44		
Ga[f]	H_2O	550	1.83	1.35	5.6
	D_2O	2100	0.48		

[a] [COOH] = 50 mM, degree of ionization = 1, [Tb] = 2 mM. [b] 0.24 ms^{-1} used as the constant of proportionality. [c] PrA, propionic acid. [d] DMA, dimethylmalonic acid. [e] DSA, 2,3-dimethylsuccinic acid. [f] GA; glutaric acid.

Table II
Number of Coordinated Water Molecules and Photophysical Parameters for Tb(III)-Polymeric Carboxylate Complexes

ligand[a]	solvent	τ, μs	k_{obsd}, ms^{-1}	Δk_{obsd}, ms^{-1}	no. of H_2O[b]
PAA[c]	H_2O	780	1.28	0.84	3.5
	D_2O	2300	0.44		
PMA[d]	H_2O	760	1.32	0.93	3.9
	D_2O	2560	0.39		
MAE[e]	H_2O	740	1.36	0.85	3.5
	D_2O	1980	0.51		
PAAm[f]	H_2O	690	1.44	0.91	3.8
	D_2O	1900	0.53		

[a] [COOH] = 50 mM, degree of ionization = 1, [Tb] = 2 mM. [b] 0.24 ms^{-1} used as the constant of proportionality. [c] PAA, poly(acrylic acid). [d] PMA, poly(methacrylic acid). [e] MAE, poly(maleic acid-*co*-ethylene). [f] PAAm, poly(acrylic acid-*co*-acrylamide).

observed that the Tb/PrA complex contained 6.0 coordinated waters. If it is assumed that the Tb(III) aquo complex contains nine waters of hydration,[17] then the data of tables imply that about five or six water molecules are expelled upon formation of the Tb/PAA complex while only three are expelled when the Tb/PrA complex is formed. The larger amount of water expelled by the PAA ligand indicates that the Tb(III) ion is more strongly bound in the polymer, and this increase in binding ability could be attributed to the polymer cooperative effect.[19]

The copolymer of maleic acid–ethylene (MAE) is also known to exhibit excellent metal ion binding properties.[20] A Tb(III) hydration number of 3.5 was measured from the fluorescence lifetime determinations, which is quite close in magnitude to the value obtained for the PAA complex. The relative magnitudes of Tb(III) emission intensities in the PAA and MAE systems were also quite similar, indicating that the metal ion binding properties were comparable in the two polymers. These observations agree with the results of the dilatometric investigation by Begala and Strauss.[5] They found that the volume changes upon the binding of alkaline-earth metal ions such as Mg^{2+} and Ba^{2+} to PAA and MAE were fairly close. They concluded that the chelate formation of the metal ions with two adjacent carboxyl groups is of minor importance and the seven- or eight-membered rings would be involved in chelation for these polyelectrolytes.

When Tb(III) is bound to poly(methacrylate) (PMA), slightly less enhancement of Tb(III) fluorescence intensity (relative to the Tb/PAA complex) was observed. At the same time, the number of coordinated water molecules was found to be 3.9. These effects indicate that the Tb(III) binding property of PMA is slightly different from the analogous binding properties of PAA or MAE. Strauss and Leung also found that the volume changes on complexation of alkaline-earth metal ions with PMA were smaller than those with PAA.[4] When a methyl group is attached to the polymer chain, the polymer becomes less flexible.[21] This property is evident in the high absolute values observed for the Tb(III) emission lifetimes, since the absolute values appear to be reliable indicators for chain flexibility. This inflexibility of the PMA chain interferes somewhat with the formation of a multidentate metal ion binding site, since the polymer cannot fold in such a manner to present an equivalent site. Interaction with a Tb(III) ion becomes more difficult, and hence PMA cannot form the strongest Tb(III) complexes like those of PAA and MAE.

In the case of the Tb/PAAm complex, the number of coordinated water molecules was found to be 3.8, and the enhancement of Tb(III) fluorescence intensity was comparable to that found in PAA- and MAE–Tb(III) complexes. These results indicate that although the carboxylic groups are randomly distributed in the polymer chain, the Tb(III) ion binding site of the copolymer is similar to that of the homopolymer, PAA. This is probably because at this monomer composition (AAm/AA = 2.5), spacing between carboxylates is not large enough to prevent strong complex formation. But the spacer, acrylamide, reduces electric repulsion among the carboxylates and consequently makes the polymer chain of the copolymer more flexible than that of the homopolymer. As a result, the copolymer shows strong binding ability to Tb(III), comparable with that of the homopolymer of acrylic acid.

The Tb(III) binding properties of several monomeric dicarboxylic acid ligands were also studied, and the results are summarized in Table I. The Tb(III) complexes of glutaric, 2,3-dimethylsuccinic, and dimethylmalonic acids all contain approximately six waters of hydration, as did the propionic acid complex. The fluorescence intensities of these were all comparable, and the results of these investigations imply the formation of similar complexes in each case. The fluorescence lifetime results indicate that probably three waters of hydration are expelled upon formation of the complex.

The results reported in this paper show that the number of water molecules bound to Tb(III)–monomeric carboxylate complexes is significantly larger than to the polymeric carboxylate. These values provide strong evidence that the flexible polymers wrap around the Tb(III) ion, forming a strong and definite metal ion binding site. Thus, the large enhancement of the fluorescence intensity of Tb(III) in the flexible polymer–Tb(III) complexes in the aqueous solution can be accounted for by (1) the decrease of coordinated water molecules on Tb(III) and (2) the strong and also asymmetrical binding of carboxylate to Tb(III).

Registry No. H_2O, 7732-18-5.

References and Notes

(1) Part 13 of "Rare Earth Metal Containing Polymers".
(2) Morawetz, H. "Macromolecules in Solution", 2nd ed.; Robert E. Krieger: Malabar, FL, 1983; Chapter VII.
(3) Kotliar, A. M.; Morawetz, H. *J. Am. Chem. Soc.* **1955**, *77*, 3692.
(4) Strauss, U. P.; Leung, Y. P. *J. Am. Chem. Soc.* **1965**, *87*, 1476.
(5) Begala, A. J.; Strauss, U. P. *J. Phys. Chem.* **1972**, *76*, 254.
(6) Walls, F. T.; Gill, S. J. *J. Phys. Chem.* **1954**, *58*, 1128.
(7) Eldridge, R. J.; Treloar, F. I. *J. Phys. Chem.* **1970**, *74*, 1446.
(8) Morawetz, H.; Gobran, R. H. *J. Polym. Sci.* **1954**, *12*, 133.
(9) Ikegami, A. *J. Polym. Sci., Part A* **1964**, 907.
(10) Gallagher, R. K. *J. Chem. Phys.* **1964**, *41*, 3061.
(11) Yoshino, N.; Paoletti, S.; Kido, J.; Okamoto, Y. *Macromolecules* **1985**, *18*, 1515.
(12) Kropp, J. L.; Windsor, M. W. *J. Phys. Chem.* **1967**, *71*, 477.
(13) Nagata, I.; Okamoto, Y. *Macromolecules* **1977**, *77*, 773.
(14) Crescenzi, V.; Brittain, H. G.; Yoshino, N.; Okamoto, Y. *J. Polymer Sci., Polym. Phys. Ed.* **1985**, *23*, 437.
(15) Heller, Y.; Stein, G. *J. Am. Chem. Soc.* **1966**, *88*, 2058.
(16) Haas, Y.; Stein, G. *J. Phys. Chem.* **1971**, *75*, 3677.
(17) Horrocks, W. D., Jr.; Sudnick, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 334.
(18) Brittain, H. G.; Spaulding, L. *Inorg. Chem.* **1984**, *23*, 2165.
(19) Kaneko, M.; Tsuchida, E. *Macromol. Rev.* **1980**, *36*, 1844.
(20) Paoletti, S.; Delben, F.; Crescenzi, V. *J. Phys. Chem.* **1976**, *30*, 2564.
(21) Shirai, M.; Nagatsuka, T.; Tanaka, M. *Makromol. Chem.* **1977**, *178*, 37.