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## INVESTIGATION OF ION-BINDING PROPERTIES OF SYNTHETIC POLYELECTROLYTES WITH THE Tb(III) LUMINESCENCE PROBE

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### ABSTRACT

The binding properties of trivalent metal ions to polyelectrolytes were investigated through the use of Tb(III) luminescence studies. The condensation of Tb(III) with the homopolymers poly(acrylic acid) and poly(methacrylic acid) was studied in detail. In addition, the 1:1 copolymers of maleic acid with ethylene, isobutene, and 2,4,4-trimethyl-1-pentene were also examined. The emission intensity of the 305 nm Tb(III) hypersensitive excitation band was found to correlate with the size of the alkyl group on the polymer chains. Tb(III) luminescence lifetime studies indicated that the metal ion binding site was equivalent over a wide range of Tb(III)/polymer ratios. The number of solvent molecules coordinated by Tb(III) in the various polymer complexes was determined and found to range between 3.5 and 4 molecules of water of hydration.

## INTRODUCTION

The luminescence properties of Tb(III) and Eu(III) have been extremely useful for the study of metal-ion coordination within biological systems [1-4] and for the characterization of metal-ion-binding polymers [5]. It has been recently observed that the luminescence intensity of Tb(III) is greatly enhanced upon complex formation with poly(acrylate) and poly(styrene-sulfonate), and that this intensity enhancement is useful in the definition of metal-ion-binding tendencies [6, 7]. Although these early studies demonstrated the strength of polyelectrolyte binding to Tb(III), they did not address the question of the nature of the metal-ion-binding site.

In the present work we report the results of further investigations into the utility of Tb(III) luminescence probe studies of polymer systems. The chain structure of the polycarboxylates has been systematically varied to deduce the relation between polymer structure and Tb(III) luminescence properties. In addition, the number of water molecules coordinated by the Tb(III) ion in the various binding sites has been determined to obtain full characterization of the coordination chemistry. The results were compared to studies carried out on model complexes containing propionic acid, and evidence was obtained demonstrating that the flexible polymers were capable of wrapping around the Tb(III) ion, expelling more water molecules than could the simple ligands.

## EXPERIMENTAL

### Materials

Poly(acrylic acid) (PAA), molecular weight 450 000, was obtained from Polyscience, Inc. The 1:1 copolymer of maleic acid with ethylene (MAE), molecular weight 250 000, was obtained from the Monsanto Company. The 1:1 copolymers of maleic acid with isobutene (MAiB) and 2,4,4-trimethyl-1-pentene (MA3MPE) were gifts of Professor E. Bianchi (University of Genoa, Italy).

Poly(methacrylic acid) (PMA) was prepared by free-radical polymerization of methacrylic acid with potassium persulfate as an initiator. The polymer thus obtained was dialyzed for 4 days in cellophane tubes and then freeze dried. The molecular weight of polymer prepared in this fashion was found to be 470 000 by viscosity measurements.

Propionic acid (PrA) was obtained from Aldrich Chemical Co. and purified by distillation. Hydrated terbium chloride (99.9%) was obtained from

Research Chemicals. The pH of all complex solutions was adjusted to approximately 9 by the addition of NaOH, and all work was carried out in fluid solution at room temperature.

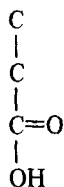
### Luminescence Measurements

Tb(III) excitation and emission spectra were recorded on a Perkin-Elmer MPF-44B fluorimeter. Excitation spectra were obtained by monitoring the emission intensity of the  $^5D_4 \rightarrow ^7F_5$  Tb(III) band at 545 nm. The most important excitation features were the hypersensitive transitions near 300 nm, and the normal f-f excitation features at 370 nm.

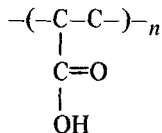
Luminescence lifetimes were obtained by using the pulsed output (337 nm) of a nitrogen laser (Model LN-1000, Photochemical Research Associates) and capturing the emission-decay curves with a boxcar averager system (Model SR-265, Stanford Research Systems). The emission was analyzed by a 0.1-m grating monochromator (Model H-10, Instruments SA) and detected by a side-on photomultiplier tube (Type RCA 1P28). Comparison of theoretically calculated and experimentally determined decay curves indicated the existence of single exponential decays, which in turn signifies the presence of essentially one type of Tb(III) emitting species. The rate constants for luminescence decay obtained in this fashion were reproducible to within 5%.

## RESULTS AND DISCUSSION

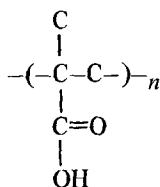
The Tb(III) complexes studied in the present work form a series of structural variations in which the stiffness of the polymer chain is gradually increased. The structure of the polycarboxylate system is as follows:



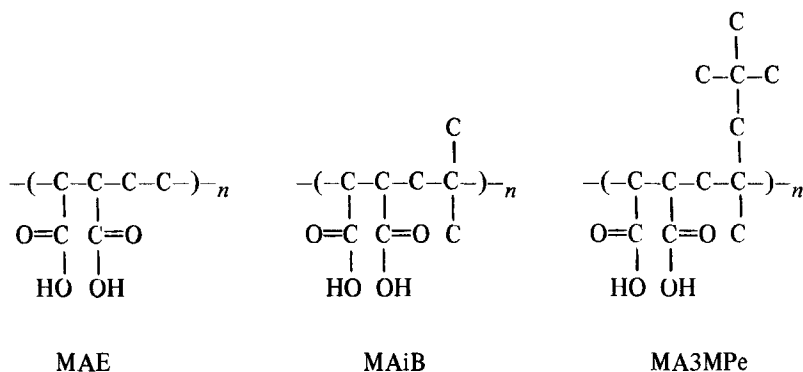
PrA



PAA



PMA



It is anticipated that an increase in the stiffness of the polymer backbone would affect the nature of any metal-ion-binding site which could be formed through a polymer conformational change.

### Tb(III) Excitation Spectra

The binding of Tb(III) by polycarboxylates induces marked changes in the luminescence properties of the Tb(III) ion. This behavior is illustrated in Fig. 1, where the Tb(III) excitation spectra obtained for Tb(MAE) and Tb(PMA) are contrasted with that of the aquo ion. Binding of Tb(III) by all polycarboxylate ligands resulted in a strong increase in the luminescence intensity, but the most dramatic effects were noted in the excitation spectra. In most of the Tb(polymer) complexes, a strong excitation feature located around 300 nm was observed. It has been shown elsewhere that observation of a broad band in this spectral region is linked to the binding of Tb(III) in an oligomeric environment [8]. This band appears to be a hypersensitive Tb(III) absorption ( ${}^7F_6 \rightarrow {}^5H_4$ ), which is only observed when the metal-ion coordination sphere becomes highly asymmetric as happens when the ion is bound by a polymer. The hypersensitive nature of this excitation band is consistent with the accepted view of these transitions [9]. The Tb(III) excitation bands around 370 nm correspond to nonhypersensitive f-f absorption bands, whose intensity remains relatively constant regardless of the nature of the Tb(III) binding site.

The relative intensities of Tb(III) excitation peaks measured at 305 nm, as observed for the different polycarboxylate complexes, are shown in Table 1. With the exceptions of Tb(PAA) and Tb(PMA), all of the complex systems exhibited higher luminescence intensities when excited at 305 nm than when excited at 370 nm. The intensity order (for 305 nm excitation) was found to be

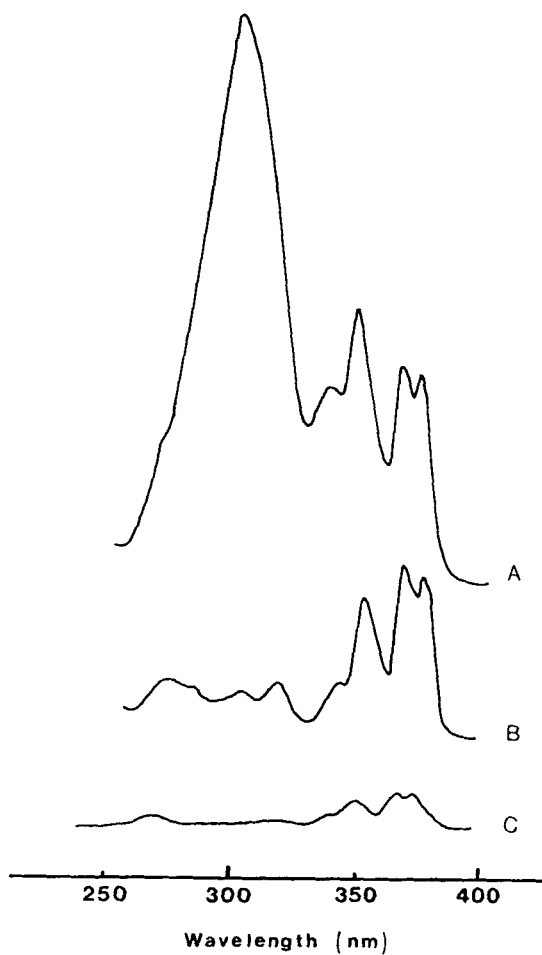


FIG. 1. Luminescence excitation spectra of Tb(MAE) (Trace A), Tb(PMA) (Trace B), and TbCl<sub>3</sub> (Trace C) aqueous solutions obtained at an analyzing emission wavelength of 545 nm. In all traces, [Tb<sup>3+</sup>] = 2 mmol/L; and for the polymer complexes, [-COOH] = 50 mmol/L at pH 9. The intensity scale is arbitrary.

TABLE 1. Relative Luminescence Intensity of Tb(III) Complexes

Polycarboxylate system <sup>a</sup>	Relative luminescence intensity <sup>b</sup>
PMA	0.2
PAA	1
MAE	2
MAiB	5
MA3MPe	8

<sup>a</sup>Obtained at  $[-\text{COOH}] = 10 \text{ mmol/L}$ ,  $[\text{Tb}^{3+}] = 1 \text{ mmol/L}$ , and pH 9.

<sup>b</sup>Excitation wavelength 305 nm, and emission wavelength 545 nm.

$\text{MA3MPe} > \text{MAiB} > \text{MAE} > \text{PAA} > \text{PMA}$ . Since the linear charge density of all polymers was the same, it follows that it was the actual distribution of the carboxylate groups on the chain and their mutual orientation that led to the excitation trend.

On passing from MAE to MAiB and to MA3MPe, several effects take place which can be summarized as follows: a) In the alkaline region, the second acid dissociation constant of the MA copolymers becomes increasingly weaker [10, 11]. b) The chelating ability of MA copolymers for divalent cations increases [12]. c) The rigidity of the chain increases strongly due to increasing steric hindrance associated with interaction among side chains. d) The increase in the bulk of the alkyl side chains results in an increase in the hydrophobicity of the chain.

In regard to Points a) and b), it should be noted that the increase in bulkiness of the alkyl residues on the olefinic comonomer decreases the  $\text{p}K_a$  of the first dissociation constant while it increases the second  $\text{p}K_a$ . From these observations it becomes reasonable to assume that the order of Tb(polymer) complex stability would be  $\text{MA3MPe} > \text{MAiB} > \text{MAE} > \text{PAA} > \text{PMA}$ .

Yoshino et al. reported that the hypersensitive excitation band (305 nm) of Tb(PAA) was greatly enhanced by ultrasonic irradiation of aqueous solutions [14]. This observation led these workers to suggest that a PAA conformation change was induced by the ultrasound and that the new conformation provided a more asymmetric binding site for the Tb(III) ion. This, in turn, may imply that not only does Tb(III) form stronger complexes with the MA copolymers (especially MAiB and MA3MPe), but that the ion-binding site of

these is more asymmetric than in the other polymers. This conclusion is supported by the fact that the MAiB and MA3MPe polymers would be more rigid than the other polymers, and less likely to adjust their conformational preference to suit the Tb(III) ion.

### Water Coordination Numbers

Dissolution of Tb(III) salts into water results in production of the aquo species, where it is probable that nine solvent molecules are bound at the inner coordination sphere [4]. Kropp and Windsor reported the existence of effective radiationless deactivation of the emissive  $^5D_4$  Tb(III) excited state by means of energy transfer to the  $-OH$  vibrational manifold of the coordinated water molecules [15, 16]. This quenching of the Tb(III) luminescence results in greatly shortened Tb(III) emission lifetimes, with a value of  $400 \mu s$  normally being observed for the aquo ion. The formation of Tb(III) complex species with carboxylate ligands results in the expulsion of some of the coordinated water. This situation usually results in increased Tb(III) emission intensities and in longer Tb(III) emission lifetimes.

### Tb(III) Hydration Numbers

The Tb(III) aquo ion is known to contain nine water molecules in its inner coordination sphere as long as no cation-anion association takes place [4]. It has been established by Kropp and Windsor [15, 16] that the emissive  $^5D_4$  excited state could experience effective nonradiative quenching via energy transfer to the  $-OH$  vibrational manifold of the coordinated water molecules. Since complexation of the Tb(III) ion with suitable ligands must result in the expulsion of some or all of the coordinated water molecules, it follows that formation of a stable Tb(III) complex must be accompanied by enhanced luminescence intensities and lifetimes [17].

The effect of Tb(III) concentration on the magnitudes of luminescence intensity and lifetime in the Tb(PAA) complex are illustrated in Fig. 2. The Tb(III)/polymer ratio ranged from 0.006 to 0.1, and the data were acquired by using an excitation wavelength of 370 nm and an emission wavelength of 545 nm. It was observed that, although the emission intensity increased linearly with the Tb(III) concentration, the luminescence lifetime remained constant at  $780 \mu s$  over the entire range. This value may be compared to the lifetime of  $420 \mu s$  measured for the Tb(III) aquo ion. The insensitivity of the emission lifetime to the total Tb(III) concentration is strong evidence for the existence of a well-defined metal-ion-binding site [17] whose nature is independent of the amount of Tb(III) condensed on the polymer.



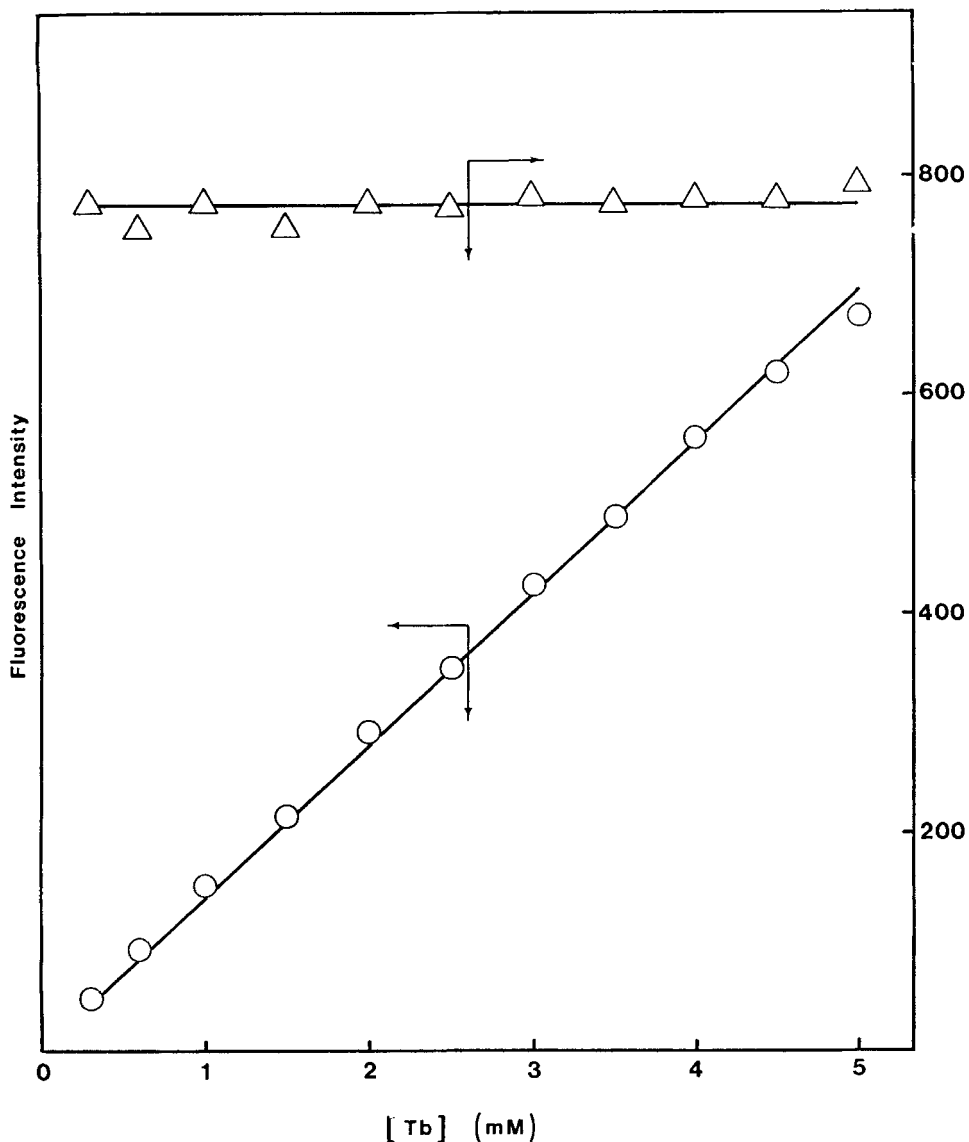


FIG. 2.  $\text{Tb}^{3+}$  luminescence intensity (excitation wavelength 370 nm and emission wavelength 545 nm) and luminescence lifetime as a function of  $\text{Tb}^{3+}$  concentration in the presence of PAA. The data were obtained in aqueous solution at  $[-\text{COOH}] = 50$  mmol/L and pH 9. The scale associated with the intensity trace is arbitrary.

As mentioned above, the nonradiative quenching pathway through energy transfer to the  $-\text{OH}$  vibrational manifold of coordinated water molecules represents the dominant mode of radiationless deactivation of the emissive  $^5\text{D}_4$  Tb(III) state [15, 16]. It was observed at this same time that the  $-\text{OD}$  oscillator was essentially totally ineffective in promoting the same type of radiationless quenching [17]. Horrocks and Sudnick were able to quantitate this deuterium isotope effect and produced a spectroscopic method by which the number of coordinated water molecules could be determined from lifetime measurements made in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  [18]. They derived an equation in which the number of water molecules,  $q$ , bound at the inner coordination sphere of the Tb(III) ion is given by

$$q = [k(\text{H}_2\text{O}) - k(\text{D}_2\text{O})] / 0.24. \quad (1)$$

In Eq. (1),  $k(\text{H}_2\text{O})$  and  $k(\text{D}_2\text{O})$  are the observed radiative rate constants (given in units of  $\text{ms}^{-1}$ ) for  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  solution, respectively.

The Tb(III) emission lifetimes in both  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  solution were obtained for the polymeric systems Tb(PAA), Tb(PMA), and Tb(MAE), and for the model Tb(PrA) system. The data and results are summarized in Table 2.

It was found that an average of 3.5 waters of hydration were bound by the central Tb(III) ion in the Tb(PAA) complex. In the analogous carboxylate Tb(PrA) monomer system,  $q$  was found to be 6.0. These observations indicate the expulsion of only three coordinated waters upon formation of the model Tb(PrA) system, while either five or six are expelled upon formation of the Tb(PAA) complex. The more extensive binding noted in the polymeric system can be attributed to the polymer cooperative effect [19].

The maleic acid copolymers are also known to exhibit excellent metal-ion-binding properties [12]. Once again,  $q$  was found to be 3.5 for the Tb(MAE) complex, and a similar interpretation may be invoked to explain the nonintegral value. The relative magnitudes observed for the Tb(III) emission were found to be similar for the Tb(PAA) and Tb(MAE) complex systems, indicating that the metal-ion-binding properties must be comparable for the two polymers. These observations are in accord with the dilatometric results obtained by Begala and Strauss [20], who found that the volume changes which occurred upon binding of Mg(II) and Ba(II) to PAA and MAE were fairly close. These workers concluded that the formation of a chelate ring with the metal ions and two adjacent carboxyl groups is of minor importance, and that seven- or eight-membered rings would be formed in the chelation.

In the case of the Tb(PMA) complex, the enhancement of Tb(III) luminescence intensity was slightly less than that observed for the Tb(PAA) complex. The average number of water molecules coordinated to the Tb(III) ion was

TABLE 2. Photophysical Parameters Obtained for the Tb(III) Complexes<sup>a</sup>

Ligand system	Solvent	Emission lifetime, $\mu\text{s}$	Observed rate constant, $\text{ms}^{-1}$	Difference in rate constant, $\text{ms}^{-1}$	Number of coordinated water molecules
PAA	H <sub>2</sub> O	780	1.28	0.84	3.5
	D <sub>2</sub> O	2300	0.44		
PMA	H <sub>2</sub> O	760	1.32	0.93	3.9
	D <sub>2</sub> O	2560	0.39		
MAE	H <sub>2</sub> O	740	1.36	0.85	3.5
	D <sub>2</sub> O	1980	0.51		
PrA	H <sub>2</sub> O	530	1.87	1.45	6.0
	D <sub>2</sub> O	2370	0.42		

<sup>a</sup>The data were obtained at  $[-\text{COOH}] = 50 \text{ mmol/L}$ ,  $[\text{Tb}^{3+}] = 2 \text{ mmol/L}$ , and pH 9.

found to be 3.9, indicating that the majority of the metal-ion-binding sites contained four waters of hydration. These results indicate that the Tb(III) site in Tb(PMA) must be slightly different from the analogous sites in either Tb(PAA) or Tb(MAE) complexes. Strauss and Leung also found that the volume changes which took place upon complexation of alkaline earth cations with PMA were smaller than those observed with PAA [21]. Since it is known that attachment of a methyl side group on a polymer chain results in a less flexible polymer [22], it follows that the observed difference in Tb(III) binding is related to the difference in chain flexibility. A less flexible chain would not be as able to adopt its conformation to fit around a Tb(III) ion and would consequently not be able to expel as many solvent molecules as would a more flexible chain.

It was also found that the overall Tb(III) emission intensity was significantly higher for the Tb(MAE) complex than for the Tb(PAA) complex. Aside from quenching associated with the  $-\text{OH}$  vibrational manifold of the solvent, a second Tb(III) quenching mechanism is associated with the ability of the

coordinated polymer to act as an energy trap through its own vibrational modes. A change in the polymer backbone flexibility would perturb the vibrational modes of the chain, and this effect would in turn affect the non-radiative quenching of the Tb(III) ion. It is evident from the data shown in Table 1 that, as the degree of substitution on the polymer side chains increases (PAA < MAE < MAiB < MA3Pe), the Tb(III) emission intensity undergoes a concomitant enhancement. These observations indicate that Tb(III) emission intensities may serve as reliable indicators of chain flexibility.

### SUMMARY

The results obtained in this work demonstrate that the number of coordinated water molecules in Tb(III) monomeric carboxylate model complexes is significantly larger than hydration numbers existing in Tb(polymer) complexes. Polymers characterized by less flexible backbone structures (as induced by side chain substitution) were found to be less efficient at expelling water molecules. These observations provide strong evidence that the flexible polymers alter their conformation to wrap around the Tb(III), thus forming a strong and definite metal-ion-binding site.

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