

# Use of Terbium(III) as a Probe for the Ion-Binding Properties of Tactic Polyacids and Triacidic Model Compounds

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The binding properties of Tb(III) ions in configurationally different environments were investigated using luminescence intensity and lifetime measurements. The emission intensity of Tb(III) ( $^5D_4$ – $^7F_5$  transition) is directly dependent upon the number of coordinated water molecules (quenchers) bound in the inner coordination sphere. The more efficiently a ligand coordinates to Tb(III) ion, the more water molecules are expelled from the coordination sphere, thereby enhancing the luminescence intensity and lifetime of the ion. Isotactic and syndiotactic poly(methacrylic acids) (PMAs) were neutralized and complexed with Tb(III) ions in aqueous solutions. The luminescence intensities and lifetimes were monitored with  $\lambda_{exc} = 265$ , the hypersensitive excitation band at 286 and 370 nm. The isotactic PMA/Tb(III) complex exhibited a six times greater luminescence intensity than the syndiotactic PMA complex. Lifetime measurements showed 2.4 water molecules coordinated to Tb(III) ion in the isotactic PMA complex, while 3.4 water molecules were found to remain in the syndiotactic complex. Similar studies were also conducted on small organic model compounds such as Kemp's triacid and its configurational isomer. These data supported the polymeric results where the isotactic model, Kemp's triacid, exhibited a higher luminescence intensity and a longer lifetime than the Kemp's isomer. Lifetime results showed the Kemp's molecule retained approximately 2.7 water molecules, compared to four water molecules for the isomer. The validity of using the Kemp's molecules as polymeric models is also discussed.

**KEY WORDS:** Terbium; poly(methacrylic acid); Kemp's triacid; tacticity; luminescence; lifetime.

## INTRODUCTION

Terbium metal ion, Tb(III), is a lanthanide whose size, luminescence, and paramagnetic properties have allowed it to be used as a substitutional probe for calcium ion,  $Ca^{2+}$ , and magnesium ion,  $Mg^{2+}$ , in many biological systems [1–6]. Terbium(III) also has a well-defined emission and excitation spectra at room temperature and has a relatively long emissive lifetime. Essentially, all emissions of aqueous Tb(III) complexes emanate from

the  $^5D_4$  excited state when an excitation wavelength shorter than 490 nm is used. The transition regions  $^3D_4 \rightarrow ^7F_J$  ( $J = 0, 1, 2, 3, 4, 5$ , or  $6$ ) all display emissions with the relative intensities being, in descending order,  $^5D_4 \rightarrow ^7F_5 > ^7F_6 > ^7F_4 > ^7F_3 > ^7F_2 > ^7F_1 > ^7F_0$ . The  $J = 1$  and  $0$  are the weakest of these emissive transitions. The wavelengths corresponding to the previous order are 540–555, 485–500, 580–595, 615–625, and 645–655 nm, respectively ( $J = 1, 0$  are not included) [7,8]. All of the transition regions of Tb(III) show fine structuring, with the sharpest structure exhibited by the  $^5D_4$ – $^7F_5$  and  $^7F_3$  emissions. The  $^5D_4 \rightarrow ^7F_5$  transition is the most intense transition and remains remarkably intense under a wide variety of solution conditions [2].

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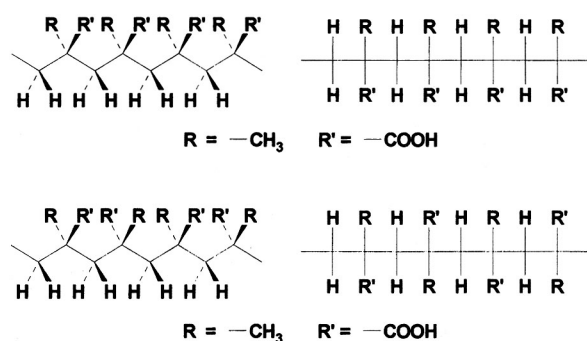


Fig. 1. Structures of tactic poly(methacrylic acids). Top: Isotactic PMA. Bottom: Syndiotactic PMA.

The transition is also extremely sensitive to the detailed nature of the ligand environment, making it the best transition to use as a fluorescent probe [9–15]. The intensity of the emission depends on three things: the degree of binding to the Tb(III), the site symmetry of the complex, and the mode of binding, whether direct or indirect excitation is involved [4].

Tb(III) prefers to interact with “hard” bases such as oxygen and fluorine rather than with “soft” bases such as nitrogen, sulfur, and phosphorus. Its ligand binding preferences are  $O > N > S$  [2]. Aqueous salt solutions of Tb(III) exist as an aquo complex  $[Tb(OH_2)_n]^{3+}$  with nine water molecules ( $n = 9$ ), bound to the inner coordination sphere. These coordinated water molecules serve as efficient quenchers of intrinsic Tb(III) ion luminescence, and consequently, the emissive intensity of aqueous terbium solutions is normally very weak [16,17]. The OH stretching mode of coordinated  $H_2O$  is effective at quenching the terbium  $^5D_4$  excited state via nonradiative energy transfer. Replacement of any of these water molecules with “hard” ligands, especially those containing carboxylate anions, increases both the luminescence intensity and the lifetime of the complexed Tb(III) by decreasing the concentration of quenchers in the coordination sphere [4,18–20]. Once the ligating groups occupy specific coordination sites on the Tb(III) ion once held by water molecules, these sites are no longer accessible to quencher water molecules, thereby increasing the luminescence intensity of the Tb(III) ion [4,21,22]. The luminescence intensities of Tb(III) are greatly enhanced upon binding to carboxy-containing polymers such as polyacrylates and polysaccharides [23,24].

The addition of simple carboxylate compounds also leads to the observation of similar effects. Upon complexation with certain carboxylate compounds, a hypersensitive excitation peak which most closely resembles

the  $^7F_6 \rightarrow ^5H_5$  transition is observed at 286 nm [25–27]. Hypersensitive transitions are more sensitive to the local environment around the lanthanide ion than normal f–f transitions. They experience relatively large changes in shape and intensity when modifications occur in the coordination sphere of the ion [8,28]. The observation of a broad band in this region is linked to the presence of Tb(III) ion in a very asymmetric local environment, as is the case when bound to a polymer [18,20,23]. This type of hypersensitive band tends to be too weak to be observed in monomeric Tb(III) complexes but becomes evident and strongly allowed in certain polymeric environments.

The word “tacticity” describes a region of ordered domains within a polymer possessing regularity in configuration of successive pseudo-chiral centers. Polymers exhibiting such order are said to be “stereoregular” (Fig. 1) [29]. The effect of tacticity on the solution properties of poly(methacrylic acid) has been investigated for many years. It was recognized that isotactic PMA behaves as a weaker polyacid than syndiotactic PMA [30]. In addition, the dissociation of isotactic PMA is more endothermic than that of the syndiotactic sample [31]. The interaction with divalent metal ions such as  $Cu^{2+}$  and  $Mg^{2+}$  were also found to be different for the two polymers. Dialysis equilibria measurements indicate that the isotactic sample binds copper more strongly than syndiotactic PMA, whereas the reverse is true for the binding of magnesium and sodium [30,32,33]. No one, however, has yet measured the binding affinity of these polymers to Tb(III). Our goal was to measure the ion affinity of these polymers using straightforward static Tb(III) luminescence intensity and lifetime measurements.

Lifetime measurements were based on the following information by Horrocks and Sudnick. They have developed a quantitative method by which the number of water molecules surrounding the Tb(III) ion can be determined based on a deuterium isotope effect [4,15]. Water serves as a quencher of intrinsic terbium luminescence through dissipation of the excitation energy by way of the OH manifold. Deuterium oxide,  $D_2O$ , does not quench as efficiently due to the greater reduced mass of the OD manifold [16,17]. When all of the competing processes of an excited-state lanthanide ion are considered, the reciprocal excited-state lifetime,  $\tau_{obsd}^{-1}$ , is the sum of the following terms:

$$\tau_{obsd}^{-1} = \tau_{nat}^{-1} + \tau_{nonrad}^{-1} + \tau_{OH}^{-1} \quad (1)$$

where  $\tau_{nat}^{-1}$  is the natural rate constant for photon emission,  $\tau_{nonrad}^{-1}$  is the rate constant for all other nonradiative processes not involving the OH manifold, and  $\tau_{OH}^{-1}$  ac-

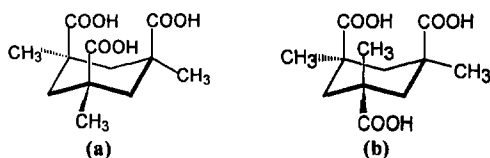


Fig. 2. Kemp's molecules: (a) Kemp's triacid; (b) Kemp's configurational isomer.

counts for the deexcitation of photons attributable to nonradiative processes involving only the OH oscillator in the first coordination sphere. The parameters for the quenched aqueous terbium solutions are  $\tau_{\text{nat}}^{-1} = 0.11 \text{ ms}^{-1}$ ,  $\tau_{\text{nonrad}}^{-1} = 0.19 \text{ ms}^{-1}$ , and  $\tau_{\text{OH}}^{-1} = 2.15 \text{ ms}^{-1}$ . The number of OH oscillators can be determined by conducting lifetime measurements in both  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  since the quenching pathway of the  $-\text{OH}$  vibrational manifold represents the dominant mode of radiationless deactivation of the emissive  ${}^5\text{D}_4$  Tb(III) state [16,17]. The number of coordinated water molecules,  $q$ , is then directly related to the difference in the emissive lifetimes as given by

$$q = A(\tau_{\text{H}_2\text{O}}^{-1} - \tau_{\text{D}_2\text{O}}^{-1}) \quad (2)$$

where  $A$  is the slope of the linear relationship between the mole fraction ( $\chi$ ) of  $\text{H}_2\text{O}$  in the first coordination sphere and  $\tau_{\text{obsd}}^{-1}$ . Experimentally,  $A$  can be determined by varying the ratio of  $\text{D}_2\text{O}/\text{H}_2\text{O}$  in Tb(III) solutions. Thus, quantification of the number of water molecules bound to Tb(III)'s first coordination sphere upon complexation can be approximated using lifetime decay measurements. Since the luminescence intensity of Tb(III) is extremely sensitive to changes in its coordinative environment, we investigated the effect of microstructure using isotactic and syndiotactic PMA. We also used Tb(III) ion as a probe for similar effects in smaller organic molecules such as Kemp's triacid (1,3,5-trimethyl-1,3,5-cyclohexanetricarboxylic acid) and its configurational isomer (Fig. 2). Our interest in the molecule is based on its unique conformational structure which resembles a monomeric subunit of isotactic PMA, with all carbonyl moieties on one side. Its isomer resembles syndiotactic PMA. These molecules can serve as model systems for the aforementioned polymers [34].

In our study we monitored the effect that configurational differences had on the binding properties of the terbium ion by observing the luminescent behavior of its complexes in both polymeric and monomeric molecules. The polymeric system used isotactic and syndiotactic PMAs. These differ in their spatial arrangement and, consequently, in the nearest-neighbor distance between

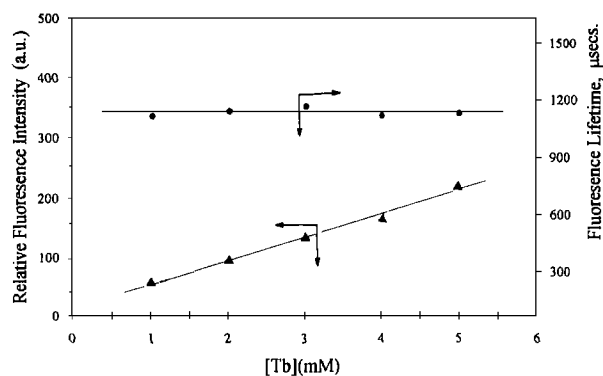
ligating carboxylate anions. These differences should strongly affect the complexation behavior of the Tb(III) ion, which possesses a specific coordination geometry. The atactic, or random form of PMA was also investigated. A similar set of experiments was conducted using Kemp's molecules as the nonpolymeric system.

## EXPERIMENTAL

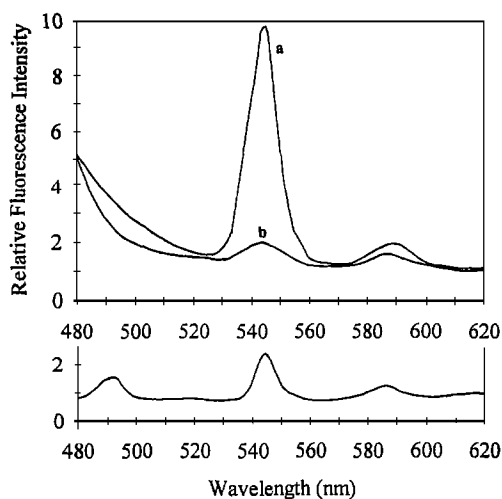
The isotactic and syndiotactic poly(methacrylic acids) were obtained from Professor G. Challa's laboratory, Department of Chemistry, University of Groningen. Tacticity information was determined by  ${}^1\text{H}$ NMR and was follows: 0.97 (mm), 0.03 (mr), 0 (rr) for isotactic PMA and 0.01 (mm), 0.07 (mr), 0.92 (rr) for syndiotactic PMA. The (rr) notation refers to the isotactic triads in the sample, (mm) to the syndiotactic domains, and (mr) represents areas of an atactic region. The molecular weights for the polyacids were approximately 500 K (iso) and 193 K (syndio) as determined by solution viscometry.

Titration of the tactic PMAs was done in order to determine the concentration of carboxylic acid groups per gram of polymer (to account for water absorption). A detailed procedure can be found in our previous paper [35]. Kemp's triacid and its isomer [(1 $\alpha$ ,3 $\alpha$ ,5 $\beta$ )-1,3,5-trimethyl-1,3,5-cyclohexanetricarboxylic acid] were also titrated in order to obtain fully ionized structures (see reference for a detailed procedure) [36]. Ionization of the acids is necessary because the carboxylate group is a much better ligand for Tb(III) than is the acid. All acid-containing molecules used in this study were titrated to the endpoint in order to obtain the maximum number of carboxylate ligands for complexation. All ligand/Tb(III) ion complexes should be taken to be maximally ionized.

In order to obtain an optimal operational [ligand]/[Tb] ratio, the following solution ratios were made: 0.3/1, 0.9/1, 1.5/1, 3/1, 6/1, 9/1, 10/1, and 15/1 for both the polymeric and Kemp's systems. Deionized water was used for all solutions. Excitation spectra were obtained by holding the emission wavelength fixed at 545 nm, the  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$  Tb(III) band, while scanning the wavelengths between 200 and 400 nm. Emission was measured by fixing the absorption transition at 286 nm for the tactic PMA/Tb(III) solutions while scanning the wavelengths from 400 to 640 nm. The emission spectra of the Kemp's complexes were measured by fixing the absorption transition at 240 nm, while scanning the aforementioned wavelength domains. These excitation wavelengths were chosen because they were the most



**Fig. 3.** Plot of luminescence intensity and lifetime vs Tb(III) concentration. Aqueous Kemp's solutions were used, where [COOH] was held constant at [50 mM], 25°C. (▲) Static measurements; (●) lifetime measurements.  $\lambda_{exc}$  = 240, 265, and 370 nm.



**Fig. 4.** Emission spectra of isotactic and syndiotactic PMA/Tb(III) complexes. Top: (a) Isotactic PMA/Tb(III) complex; (b) syndiotactic PMA/Tb(III) complex. [COOH]/Tb = (50 mM/5 mM),  $\lambda_{exc}$  = 286 nm, room temperature. Gain = 1×. Bottom: Aqueous terbium(III) chloride (5 mM).  $\lambda_{exc}$  = 286 nm, room temperature. Gain = 10×.

intense for each system. These investigations showed that in both cases, a ratio of [COOH]/[Tb(III)] = 10/1 gave the highest luminescence intensity without exhibiting any turbidity (a serious problem with the Kemp's compounds). Therefore, this concentration ratio was chosen for our investigations. At higher ligand/terbium ratios precipitation has made solution measurements invalid. At a 10/1 ratio this problem is minimal (a millipore filter was used for every solution except the 15/1 concentration, which was obviously turbid). A representative plot of these experiments appears as Fig. 3 (triangles).

Based on these data polymer/Tb(III) complex solutions were prepared by mixing 0.005 M TbCl<sub>3</sub> (Rhône Poulenc) with a 0.05 N solution of the polymeric ligand in order to obtain a concentration ratio of 10/1 [COOH]/[Tb]. Similarly, aqueous solutions of 0.05 M (with respect to acid moieties) of the Kemp's molecules were used to complex with aqueous TbCl<sub>3</sub> (0.005 M).

Lifetime measurements were conducted on both polymeric and triacidic model compounds in solution using final concentrations of 50 mM ligand, [COOH], and 5 mM Tb(III) ion. The excitation wavelengths used in the lifetime measurements for the polymers and model compounds were 265, 286, 370 and 240, 265, and 370 nm, respectively. The method of Jackson was used in which the luminescence intensity was measured as a function of various delay times (the time from the end of the exciting pulse until the emission decay is monitored) [37]. All experiments were done on the same day to reduce the possibility of instrumental error/deviation.

A Perkin Elmer MPF-44B and a Perkin Elmer LS50B luminescence spectrophotometer were used to measure the emissive intensity of all the lanthanide complexes at ambient temperature. The lifetime measurements were performed on the Perkin Elmer LS50B machine at room temperature. The slits widths were set at 5–6 nm for both the excitation and the emission. The instrument was calibrated using a phosphorescent sample block made of europium (III) thenoyltrifluoroacetate (EuTTFA) dissolved in a transparent matrix of poly(methylmethacrylate) (Perkin Elmer). The major emission peak for this standard is at 615 nm (other bands occur at 580, 595, and 653 nm) with an excitation at 350 nm. The average lifetime for phosphorescence decay is 0.322 ms.

## RESULTS

The emission spectra of the aqueous tactic PMA–Tb(III) complexes at  $\alpha$  = 0.75 (degree of ionization) are shown in Fig. 4. The  $^5D_4 \rightarrow ^7F_5$  transition in the isotactic polymer is approximately six times larger than the corresponding peak in the syndiotactic polymer. The luminescent properties for the atactic PMA–Tb(III) complexes were found to be similar to those of the syndiotactic PMA–Tb(III) complex. This is reasonable since the atactic PMA sample possessed a great deal of syndiotactic character (>70%).

Steady-state luminescence measurements carried out on the complexes of Tb(III) with fully neutralized Kemp's triacid and its isomer also showed a marked enhancement in the emission intensity of Tb(III) (Fig.

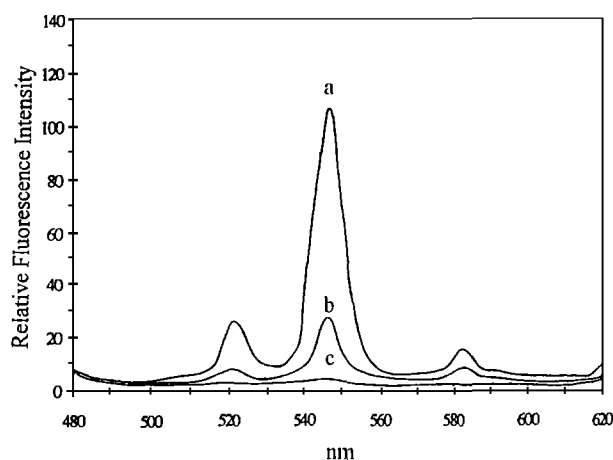


Fig. 5. Emission spectra for Tb(III) complexed with Kemp's compounds in H<sub>2</sub>O at 25°C. [COOH]/Tb = (50 mM/5 mM),  $\lambda_{ex}$  = 240 nm. (a) Kemp's compound/Tb(III); (b) Kemp's isomer/Tb(III); (c) aqueous TbCl<sub>3</sub>·6H<sub>2</sub>O (5 mM).

5). The neutralized Kemp's acid/Tb(III) complex was approximately four times higher in luminescence intensity than the complex formed with its isomer. Since the luminescence intensity of Tb(III) is directly proportional to the number of water molecules replaced by the carboxylate ligands, the trianionic Kemp's complex appears to have displaced more water molecules than its isomer. Hence, Kemp's tricarboxylate binds to Tb(III) ion more efficiently than its isomer.

In order to quantify our intensity results, lifetime measurements were conducted on both types of complexes, the one with the tactic PMA's and Tb(III) as well as the one Tb(III) made with the Kemp's molecules. Lifetimes were monitored as a function of excitation wavelength and ligand/Tb(III) ratio. A typical experimental plot of the stability of the lifetime with ligand/metal ratio appears as Fig. 3 (circles). Since the ligand used was always in excess, it is not surprising that the lifetime of the system did not change with varying ligand-to-metal ratios. These data denotes the presence of only one type of complex. The lifetime emissive data, once plotted (semilog) against the delay times, were all linear, thereby exhibiting single-exponential behavior. Hence, the existence of only one "type" of terbium carboxylate complex is proposed from these data. Using the method of Horrocks, the number molecules bound to the terbium ion in each system was determined and these results appear in Table I.

The lifetime measurements of the polymers correlate with the intensity data showing that fewer O–H oscillators remained bound to the terbium ion in the

isotactic PMA/Tb(III) complex than in the syndiotactic PMA/Tb(III) complex. Several lifetime measurements were performed at excitation wavelengths of 265, 286, and 370 nm. In all cases the isotactic complex exhibited longer lifetimes, indicating the presence of fewer water molecules remaining coordinated to the metal ion. Quantitative calculations on the number of water molecules bound to each complex were based upon an excitation wavelength of 265 nm. The data obtained at 370 nm were near the sensitivity limitations of the machine and were therefore not used for quantitative purposes. Finally, the hypersensitive transition of 286 nm was not used in calculations because we wished to compare the behavior of the polymeric systems with the Kemp's molecules and a simple carboxylic acid system (used as the control). The control, a propanoic acid/Tb(III) complex, showed that there remained approximately 6.5 water molecules bound to the Tb(III) ion. This result proved to be an excellent control, as it exactly matched those obtained previously by Okamoto *et al.* [38]. The short lifetime observed for the control, propanoic acid, is as expected and is explained by a polymeric cooperative effect, which is also discussed in detail by Okamoto *et al.* The lifetime measurements support the intensity data and prove that the isotactic PMA binds to the Tb(III) ion more efficiently than the syndiotactic polymer.

The lifetimes of the Tb(III) complex with the Kemp's isomers also exhibited the behavior observed with the tactic polymers. The Tb(III) complex with the Kemp's compound (the isotactic model) disclosed fewer O–H oscillators than the isomeric Tb(III) complex (see Table I). All complexes in Table I show a fractional number of O–H oscillators. One interpretation of this fractional number of water molecules is that it reflects an equilibrium process between the ligands in other coordinative spheres and the water molecules bound to the inner coordination sphere [39]. Another point of view accounts for the fractional number of waters as due to quenching of the excited state from the complexing moiety's other bonds [40]. Oudes Wolbers *et al.* offer this explanation citing discrepancies between the experimentally obtained O–H oscillators and MD calculations. However, although lanthanides were used in the Oudes Wolbers study in a manner very similar to our investigation, the ligands used by this group were of a highly aromatic nature. Our data showed that the Tb(III)/isomeric Kemp's complex retained fewer O–H oscillators than did its isomeric complex. Several lifetime measurements were performed at excitation wavelengths of 265, 286, and 370 nm, and in all cases the Kemp's trianion/Tb(III) complex (isotactic model) exhibited longer lifetimes, indicating the presence of fewer water

Table I. Summary of Lifetime Measurements

| Ligand <sup>a</sup>          | Solvent          | Emission lifetime ( $\mu\text{s}$ ) | Observed rate constant ( $\text{ms}^{-1}$ ) | Difference in rate constant ( $\text{ms}^{-1}$ ) | Number of coordinated water molecules <sup>b</sup> |
|------------------------------|------------------|-------------------------------------|---|--|--|
| <i>Iso</i> -PMA <sup>c</sup> | D <sub>2</sub> O | 3237                                | 0.31  | 0.56   | 2.4  |
|                              | H <sub>2</sub> O | 1147                                | 0.87  |  |  |
| <i>Syn</i> -PMA <sup>d</sup> | D <sub>2</sub> O | 3290                                | 0.30  | 0.80   | 3.4  |
|                              | H <sub>2</sub> O | 913                                 | 1.10  |  |  |
| Kemp's trianion              | D <sub>2</sub> O | 3382                                | 0.30  | 0.63   | 2.7 <sup>e</sup>                                   |
|                              | H <sub>2</sub> O | 1083                                | 0.92  |  |  |
| Isomeric trianion            | D <sub>2</sub> O | 3149                                | 0.32  | 0.94   | 4.0 <sup>e</sup>                                   |
|                              | H <sub>2</sub> O | 795                                 | 1.26  |  |  |
| PrA <sup>f</sup>             | D <sub>2</sub> O | 1609                                | 0.62  | 1.52   | 6.5  |
|                              | H <sub>2</sub> O | 468                                 | 2.14  |  |  |

<sup>a</sup> [COOH] = 50 mM for polymers ( $\alpha = 0.75$ ) and Kemp's systems (pH = 9.5). PrA, propanoic acid (pH = 9.2); [Tb] = 5 mM.

<sup>b</sup> The constant of proportionality used was 4.3 ms<sup>-1</sup>.

<sup>c</sup> Isotactic poly(methacrylic acid);  $\lambda_{\text{ex}} = 265$ ,  $\lambda_{\text{em}} = 545$ .

<sup>d</sup> Syndiotactic poly(methacrylic acid);  $\lambda_{\text{ex}} = 265$ ,  $\lambda_{\text{em}} = 545$ .

<sup>e</sup> Average of 10 runs, with each set done at  $\lambda_{\text{ex}} = 240, 265$ , and 370 and  $\lambda_{\text{em}} = 545$ .

<sup>f</sup> Propanoic acid;  $\lambda_{\text{ex}} = 265$  nm,  $\lambda_{\text{em}} = 545$ .

molecules in the immediate local environment of the metal. The lifetime measurements support the intensity data showing that Kemp's trianion binds to the Tb(III) ion more efficiently than its isomer.

## DISCUSSION

This study was initiated in order to investigate if the emissive properties of terbium ion were sensitive to such subtle coordination differences as found in tactic polyacids and some small organic molecules. The difference between isotactic and syndiotactic poly(methacrylic acid) is in the relative positions of the nearest-neighbor ligating moieties, that is, the carboxylate groups. If the complexation behavior is of an intramolecular nature, then Tb(III) should coordinate differently to each tactic polymer. This hypothesis was also tested on a nonpolymeric configurational model, Kemp's triacid. Derivatives of this compound were also studied.

Kemp's molecule could serve as a configurational model for isotactic PMA if several conditions were met. These criteria are discussed in detail in a previous publication [34]. However, to summarize, Kemp's triacid is known to undergo a ring flip in basic media to make the trianion. Once the Tb(III) ion is introduced, a ring flip reversal is observed upon complexation, restoring the carboxylate groups to their axial positions. This has been proven by Menger *et al.* using <sup>1</sup>HNMR experiments [41]. His group reported observing ring reversals when Mg<sup>2+</sup>, Ca<sup>2+</sup>, and Al<sup>3+</sup> ions complex with Kemp's mole-

cule. The latter was critical so that this molecule could serve as the model compound for the isotactic polymer once Tb(III) is introduced. Due to the similarities in charge (aluminum) and ionic radius (calcium ion), it is probable that a conformational ring flip also occurs when Tb(III) is complexed to Kemp's triacid. Hence, Kemp's molecule can serve as a model for the isotactic polymer.

Additionally, the torsional, angular, steric, and dipolar interactions among the carboxylate groups of Kemp's acid and the isotactic polymer were proven comparable [36]. It has been reported that the nearest-neighbor carboxylate group distances in the preferred half-chair conformation of Kemp's molecule is 5.04 Å [41]. In order for Kemp's triacid to act as a model for isotactic PMA, the nearest-neighbor distances between carboxyl groups in the polymer should approximate this value. These distances can be calculated, since the rotational angles and bond distances of the tactic PMAs are known [42]. The neutralized polymers are known to retain the same conformation as the acids, so the repulsion between carboxylate anions can be neglected [43]. Simple geometric calculations give the nearest-neighbor carboxylate distance at 2.55 Å for the syndiotactic polymer and 5.16 Å for the isotactic PMA [36]. The coordination site bond distances in the isotactic polymer agreed within 5% of the preferred half-chair carboxylate bond distances of Kemp's molecules. Therefore, Kemp's triacid could be used as a viable model for the complexation of the tactic PMAs with terbium ion.

The relative intensities for the steady-state measurements of the ionized Kemp's compounds complexed

to Tb(III) were compared. The results indicate that although both compounds complex strongly with the Tb(III) ion, the luminescence of Kemp's isomer is approximately four times weaker than that of the complex formed with Kemp's molecule. The contribution to the overall luminescence intensity of excess Tb(III)-aquo complex is minimal due to quenching by the -OH manifold of water. The luminescence differences between these two compounds is probably due largely to their configurations. This parallels the static luminescence intensities of the tactic PMA polymers and illustrates the effect of configurational isomerism on the Tb(III) complex. Static luminescence measurements on the complexes of Tb(III) with neutralized isotactic and syndiotactic poly(methacrylic acids) also showed a configurational effect. The luminescence intensity of both tactic PMA/Tb(III) complexes showed enhancement in the hypersensitive region. The isotactic polymer was approximately six times more fluorescent than the syndiotactic PMA under the same conditions. These data support our hypothesis concerning the importance of the relative position of the nearest-neighbor ligating species.

The presence of a hypersensitive transition in the terbium/polymer complex system indicates that the terbium ion exists in a highly asymmetric environment. This stands in contrast to the luminescence data obtained from the Tb(III) complexes of Kemp's compounds, which did not exhibit hypersensitive transitions of this type (known to be due to the polymer cooperative effect). The Tb(III) ion therefore, occupies a highly symmetric site in these complexes.

Finally, in support of our findings, a recent study on the luminescence behavior of dimeric and trimeric models of poly(acrylic acid), PAA complexed with Tb(III) showed that in all cases the models with an isotactic-type configuration always enhanced the luminescence of the Tb(III) over that which mimicked the syndiotactic-type model [44].

## CONCLUSION

The purpose of this study was to determine whether Tb(III) ion is sensitive to the distance between ligating carboxylate anions in a polymer, such as in a tactic situation. Isotactic and syndiotactic poly(methacrylic acids) were chosen to complex with the metal since they each possess a definite microstructure with respect to the nearest-neighbor ligand distance. Steady-state luminescence intensities of Tb(III) ion complexed to each polymer showed that there was a six-to-one preference

for binding with the isotactic polymer over the syndiotactic poly(methacrylic acid). This preference is believed to be due to the relative distance between nearest-neighbor ligating species. Lifetime measurements supported this result and indicated that the isotactic polymer was more efficient at expelling water from the inner coordination sphere of the metal ion. Hence, an enhancement of the fluorescence intensity of this complex.

In order to confirm the nearest-neighbor effect, Kemp's triacid was used as a monomeric model for the isotactic polymer. Calculations involving simple geometry using bond angles and lengths based on energy minimizations calculations for the isotactic polyacid and Kemp's molecule showed a common nearest-neighbor ligating distance of approximately 5.0 Å. The complexation behavior of Kemp's triacid could therefore be used as a model for polymeric chelation. The results of luminescence studies on the terbium/Kemp's trianion complex and its isomeric analogue corresponded to those of the tactic PMA systems. The luminescence intensity of Kemp's trianion/terbium complex was four times as intense as that of the isomeric complex. This was explained by the fact that, in Kemp's triacid, Tb(III) can complex with three axial carboxylates, while in the case of its isomer, only two axial carboxylates exist to complex to the lanthanide ion. It can be concluded that the binding efficiency of a chelating species with Tb(III) ion is very strongly influenced by the nearest-neighbor distances of the ligating sites on the molecule. Lifetime measurements on complexes of the Kemp's molecules supported the intensity results.

The binding efficiency of a ligand is directly correlated with the number of water molecules bound to the coordination sphere of a metal ion. Our study has proven that the binding efficiency of stereoregularly identical ligands is highly dependent upon the immediate configuration of the ligand(s). Therefore, Tb(III) ion can be effectively used to probe for configurational differences in polymeric systems as well as in smaller molecules.

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