Macromolecules **1996,** *29,* 3511−3514

Ion Binding Properties of Polycarboxylates Using Terbium(III) as a Fluorescent Probe: Viscosities and Coordinated Water Molecules in Polycarboxylate−Terbium(III) Complexes in Aqueous Solutions

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Received February 15, 1996; Revised Manuscript Received February 20, 1996[⊗]

ABSTRACT: The binding properties of trivalent ions to polyacrylate and its low molecular weight analogs (monomer, dimer, and trimer) were investigated in dilute aqueous solution (10^{-2}−10^{-3} M) using Tb^{3+} ion as a fluorescent probe. The fluorescence intensity and lifetime of the Tb^{3+} ion depend directly on the number of water molecules bound to their inner coordination sphere. The more efficiently ligands coordinate to Tb^{3+} ion, the more water molecules are expelled and, consequently, the greater the fluorescence intensity and lifetime observed. Lifetime measurements in H_2O and D_2O showed that the number of water molecules coordinated to the Tb^{3+} ion are 6.5, 6.1, 4.9, and 3.6 for monomer, dimer, trimer model compounds, and polyacrylate, respectively. The viscosities of Tb^{3+}−polyacrylate complexes were measured in the presence of a large excess of sodium bromide. Viscosities (η_{sp}/c) of the polyacrylate solutions follow Huggins' equation, and on addition of Tb^{3+} ion, the intrinsic viscosities decrease abruptly from 700 to 40 mL/g. The mean end-to-end distances, $\langle r^2\rangle^{1/2}$, for polyacrylate in Tb^{3+}−polymer complexes were calculated using the Flory−Fox equation and were found to be reduced from 125 to 48 nm on addition of Tb^{3+}. These results indicate that of the nine water molecules coordinated to Tb^{3+} ion in aqueous solution, five to six are replaced with carboxylate groups attached to the polymer chain wrapped around the Tb^{3+}.

Introduction

Fluorescence techniques have an advantage over other experimental methods in that emission can be detected with high sensitivity, which allows studies to be carried out at relatively low concentrations of the fluorescent species (10^{-5}−10^{-6} M).[1] Lanthanide metal ions such as Tb and Eu exist as stable trivalent ions and exhibit their characteristic fluorescence properties in aqueous solution. The fluorescence properties of lanthanide ions in aqueous solution are known to be strongly influenced by their immediate coordinated environments.[2,3] 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.[4] Recently we have observed that the fluorescence intensities of excitation spectra for the Tb^{3+} ion are greatly enhanced upon binding to polycarboxylates[3] and polysaccharides.[5] The results indicated that Tb^{3+} ions were strongly bound to these polyanions in aqueous solution and that some or all of their inner coordinated water molecules were expelled upon binding. Here we have studied in detail the fluorescence and viscosity of dilute aqueous solutions (10^{-2}−10^{-3} M) of Tb^{3+} complexes with poly(acrylic acid) and its low molecular weight analogs.

Experimental Section

Propionic acid and 2,4-pentanedicarboxylic acid (hereafter referred to as the monomer and dimer models, respectively) were purchased from Aldrich Chemical Co. The stereoisomers of 2,4-pentanedicarboxylic acid were obtained by Allinger's method.[6] 2,4,6-Heptanetricarboxylic acid (trimer model) was prepared via the condensation product of methyl methacrylate and methyl cyanoacetate.[7] The detail synthesis of this compound is as follows. Methyl cyanoacetate (50 mL) was added in several portions to a methanol solution of sodium methoxide (4.2 g). Methyl methacrylate (120 mL) was added dropwise under cooling, and the solution was stirred at room temperature for 12 h. After the yellow solid was filtered off, the filtrate was acidified by acetic acid. The solution was evaporated under reduced pressure and extracted with ether. The extract solution was washed with water repeatedly and dried over anhydrous magnesium sulfate. The product (bp 153 °C/7 mmHg) obtained was hydrolyzed by boiling for 15 h with 20 mL of concentrated hydrochloric acid and 75 mL of water. On cooling, the almost pure product was separated and recrystallized from acetonitrile (mp 142 °C). The stereoisomers of 2,4,6-heptanetricarboxylic acid were prepared by separation of the corresponding methyl ester by liquid chromatography. The trimeric diastereomers were identified by ^1H 500 MHz NMR (Figure 1). Poly(acrylic acid) was obtained from Polysciences Inc. The intrinsic viscosity of the poly(acrylic acid) was found to be 700 mL/g in the presence of 0.1 M sodium bromide at 25 °C, which corresponds to $M_v = 580\,000$.[8] Terbium chloride hexahydrate was purchased from Rhône-Poulenc Basic Chemicals Co. Distilled and deionized waters were used throughout. Deuterium oxide 99.9% was purchased from Aldrich Chemical Co. The stock aqueous solutions (10^{-2}−10^{-3} M) of poly(acrylic acid) were neutralized with sodium hydroxide to pH 9, which leads to an ionization degree $\alpha > 0.9$.[9] The solutions of low molecular weight analogs were completely neutralized with sodium hydroxide. Exact amounts of the polyacrylate, terbium chloride, and sodium bromide solutions were mixed to obtain various ratios of carboxylate to Tb^{3+} ion. No precipitation was observed from the solutions investigated.

Fluorescence spectra and lifetime measurements were recorded on a Perkin Elmer LS50B instrument at ambient temperature. The slit widths were set at 2.5−10 nm for both excitation and emission. The fluorescence intensity was reported in arbitrary units. The viscosities of the polymer solutions in the presence of 0.1 M sodium bromide were measured with a Ubbelohde viscometer at 25 °C in a thermostated water bath. The ^1H NMR spectra were recorded on a JEOL JNM-GSX-500 spectrometer operating at 500 MHz.

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[⊗] Abstract published in *Advance ACS Abstracts*, April 1, 1996.

S0024-9297(96)00251-3 CCC: $12.00

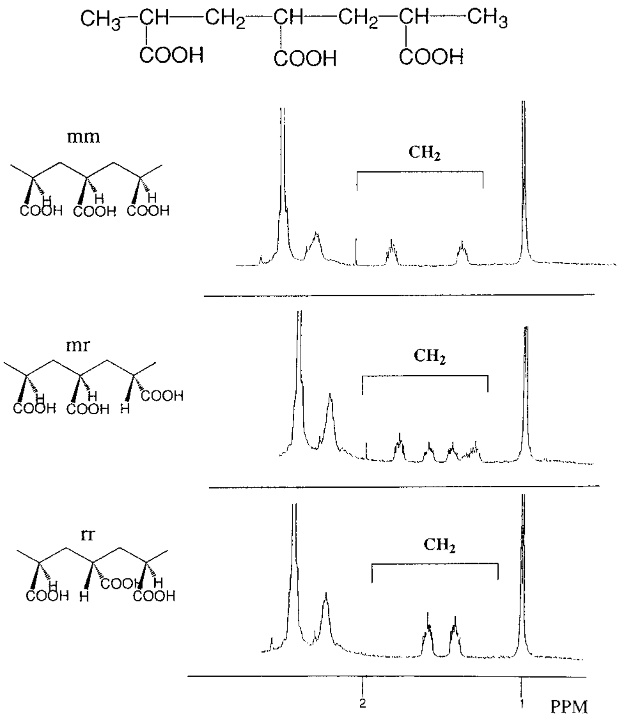

Figure 1. ^{1}H NMR spectra of the stereoisomers of 2,4,6-heptanetricarboxylic acids.

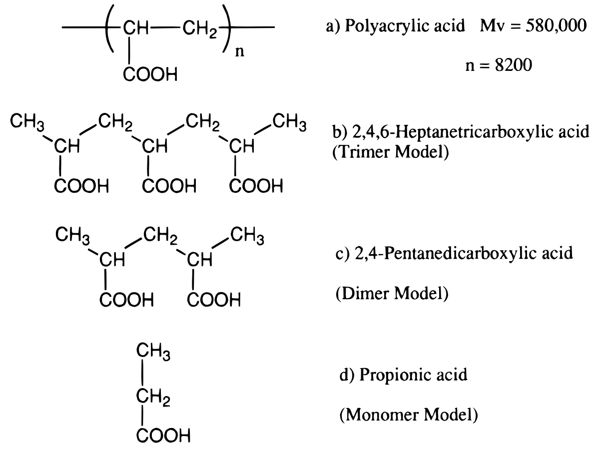

Figure 2. Chemical structures of carboxylates used in this study.

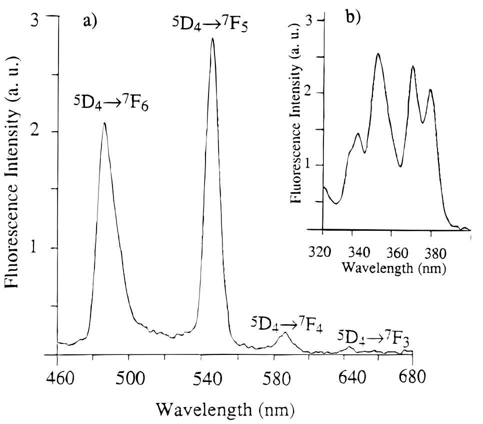

Figure 3. Fluorescence excitation and emission spectra of trimer–Tb^{3+} complexes in H$_2$O solution: (a) emission spectra (λ_{ex} = 354 nm) and (b) excitation spectra (λ_{em} = 545 nm).

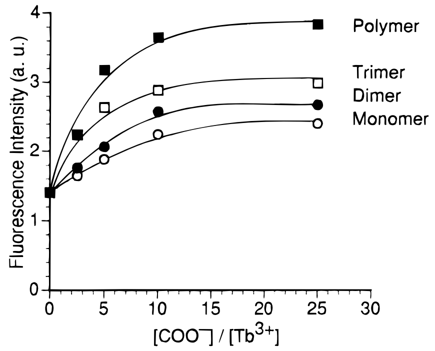

Figure 4. Variations of fluorescence intensities at 545 nm against the ratio [COO$^-$]/[Tb^{3+}] for Tb^{3+}–carboxylate complexes. [Tb^{3+}] is constant at 0.005 M.

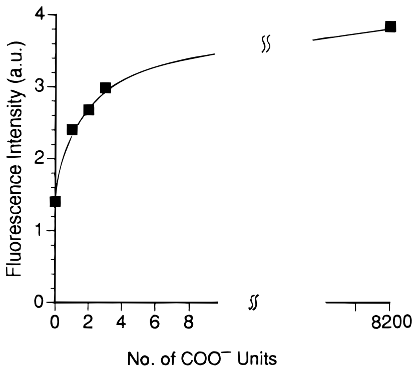

Figure 5. Plot of fluorescence intensity at 545 nm versus number of COO$^-$ units measured at a constant ratio, [COO$^-$]/[Tb^{3+}] = 25.

Results and Discussion

The excitation and emission spectra of Tb^{3+} complexes of poly(acrylic acid) and its low molecular weight analogs (Figure 2) were initially studied. Typical spectra of Tb^{3+}-carboxylate complexes in aqueous solution are shown in Figure 3. The highest emission peak at 545 nm corresponds to the $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+} ion.[4,10] Figure 4 shows the fluorescence intensities plotted against the ratio of the ligand concentration to the Tb^{3+} ion, [COO$^-$]/[Tb^{3+}]. At a [COO$^-$]/[Tb^{3+}] ratio = 10, the fluorescence intensities reach a limiting value and remain constant up to a ratio of 25 without exhibiting any turbidity in the solution. As shown in Figure 5, the emission intensities are polymer $\gg$ trimer > dimer > monomer, suggesting that the Tb^{3+} ion is most strongly bound to polyacrylate. This increase in binding to polyacrylate is attributed to the "polymer cooperative effect", i.e., the high local ligand concentration in the polymer domain.[11,12] In our previous study, polymethacrylate (PMA) was found to be strongly complexed with Tb^{3+} ions in aqueous solution. Also, the fluorescence intensity of the isotactic PMA-Tb^{3+} complex was about 6 times greater than that of the syndiotactic PMA-Tb^{3+} complex.[13] The isotactic and syndiotactic PMAs differ in the spatial arrangement of nearest-neighbor carboxylates, and this difference may affect strongly the complexation behavior of the Tb^{3+} ion. To demonstrate this effect, we have synthesized stereoregular dimer and trimer models of polyacrylate and investigated the fluorescent properties of their Tb^{3+} ion complexes. The results are summarized in Figure 6. The fluorescence intensities of Tb^{3+} complexes of these stereoisomeric models differ much less from each other than the Tb^{3+} complexes of stereoisomeric PMA, although the dimer and trimer having m and mm structures, respectively (consistent with the behavior of isotactic PMA), exhibited slightly higher emission in-

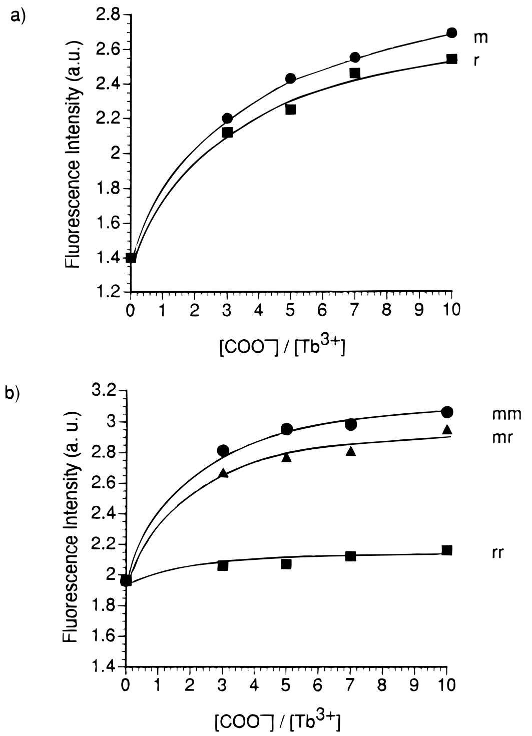

Figure 6. Variations of fluorescence intensities at 545 nm against the ratio $[COO^-]/[Tb^{3+}]$ for stereoisomers of (a) dimer and (b) trimer models; $[Tb^{3+}]$ are 0.005 M (for the dimer) and 0.007 M (for the trimer).

tensities. The results suggest that the complexation with the first two ligands involves nearest neighbors and the third and successive ligands may complex with the most geometrically (thermodynamically) favorable position on the polymer chain. This is apparently more favorable in the isotactic than in the syndiotactic polymer. Thus, the carboxylates in isotactic PMA can be more strongly complexed with Tb^{3+} ion than that of syndiotactic PMA.

The fluorescence intensity of the Tb^{3+} strongly depends on the number of water molecules replaced by carboxylate ligands. Horrocks and Sudnick[14] have developed a quantitative method by which the number of water molecules surrounding the Tb^{3+} ion can be determined based on a deuterium isotope effect. As mentioned above, water is a quencher of the intrinsic terbium fluorescence 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. Hence, the number of coordinated water molecules is directly related to the difference in the emission lifetimes as given by

$$\text{no. of coordinated water molecules} = q(\tau_{H_2O}^{-1} - \tau_{D_2O}^{-1}) \tag{1}$$

where $q = 4.26\ \text{ms}^{-1}$ for Tb^{3+} and τ is the observed lifetime of the complex in H_2O or D_2O.

Typical semilog plots of the exponential decay of the fluorescence intensity of the Tb^{3+} complexes of monomer, trimer, and polymer are shown in Figure 7. The method of Horrocks[14] was used to determine the number of water molecules bound to the Tb^{3+}, and the results are summarized in Table 1 and Figure 8. The lifetime measurements correlate with the intensity data showing an average of 3.6 waters bound to the Tb^{3+} in polyacrylate, while 4.9, 6.1, and 6.5 remain bound to the trimer, dimer, and monomer model, respectively. These results indicate that since nine water molecules are coordinated to Tb^{3+} ion in aqueous solution,[14] five to six hydrated water molecules to Tb^{3+} are replaced with carboxylate groups of polyacrylate.

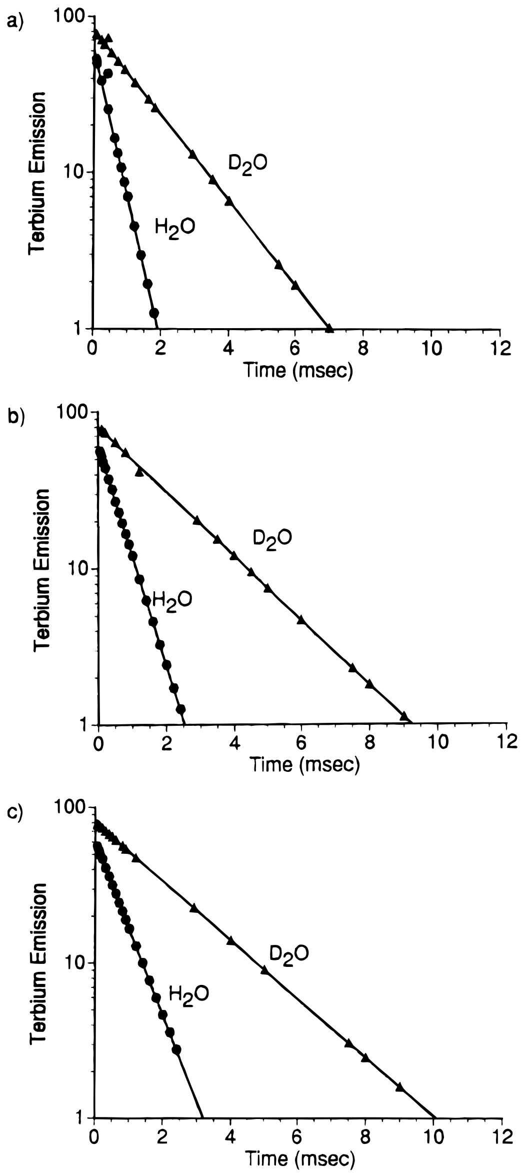

Figure 7. Decay of the fluorescence intensity at 545 nm of the Tb^{3+}–carboxylate complexes: (a) monomer; (b) trimer; and (c) polymer.

Table 1. Summary of Lifetime Measurements

ligand	solvent	emission lifetime (μs)	observed rate constants (ms^{-1})	no of coordinated water molecules[a]
monomer[b]	D_2O	1609	0.622	6.5
	H_2O	468	2.137	
dimer[c]	D_2O	1701	0.588	6.1
	H_2O	496	2.016	
trimer[c]	D_2O	2100	0.476	4.9
	D_2O	617	1.621	
polymer[d]	D_2O	2300	0.435	3.6
	H_2O	780	1.282	

[a] Aqueous Tb^{3+} ion is coordinated with nine water molecules at 25 °C.[14] [b] Reference 13. [c] $[COO^-]/[Tb^{3+}] = 25$. [d] Reference 3c.

The polyacrylate anion is highly expanded due to repulsion between polymer-bound ionic charges.[15] When

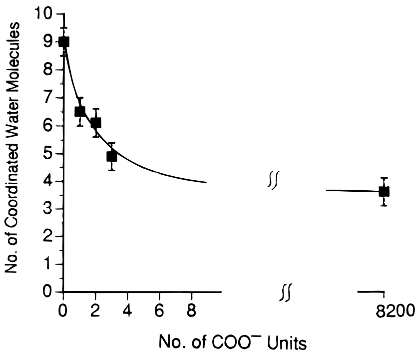

Figure 8. Number of waters elucidated from lifetime measurements against number of COO^- units.

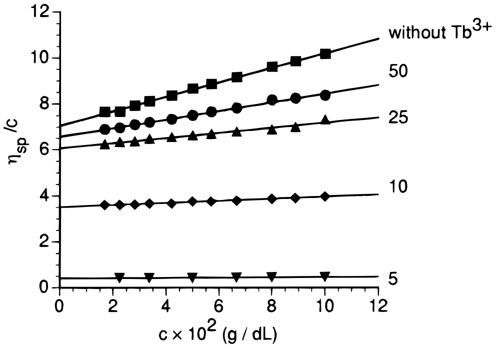

Figure 9. Dependencies of viscosities on polymer concentration at various ratios, $[COO^-]/[Tb^{3+}]$, in the presence of 0.1 M sodium bromide.

an excess of a simple salt such as sodium bromide is added to the solution, the repulsion between these charges is screened,[16] the chain expansion decreases, and the reduced viscosity (η_{sp}/c) behavior of the polymer solution becomes similar to that of nonionic polymers, following the Huggins equation:

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2 c \tag{2}$$

As shown in Figures 9 and 10, on addition of Tb^{3+} ion, the intrinsic viscosities decreased abruptly from 700 to 40 mL/g, and the mean end-to-end distances, $\langle r^2\rangle^{1/2}$, for polyacrylate in these solutions, calculated from the Flory–Fox equation:[17]

$$[\eta] = \phi \frac{\langle r^2\rangle^{3/2}}{M} \tag{3}$$

were reduced as shown in Table 2. For $[COO^-]/[Tb^{3+}] = 5$, the $\langle r^2\rangle^{1/2}$ value was reduced to about one-third. These results indicate that several carboxylate groups on a polyacrylate chain are intramolecularly bound to a Tb^{3+} ion and that this forces the polyacrylate chain to be wrapped around the Tb^{3+} ions.

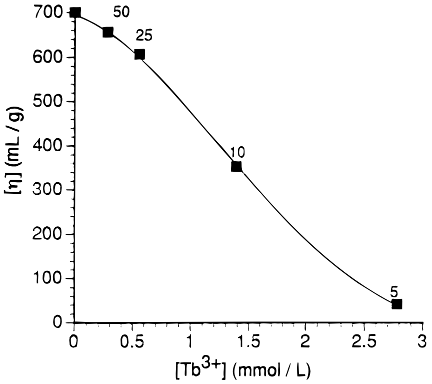

Figure 10. Intrinsic viscosity versus Tb^{3+} concentration. The corresponding ratios, $[COO^-]/[Tb^{3+}]$, are indicated.

Table 2. Intrinsic Viscosity, [η], and End-to-End Distance, $\langle r^2\rangle^{1/2}$, Data for PAA–Tb^{3+} Complex Aqueous Solutions at 25 °C in the Presence of 0.1 M Sodium Bromide

sample[a] PAA:Tb^{3+}	[η] (cm^3/g)	$\langle r^2\rangle^{1/2}$ (nm)
without Tb^{3+}	700	125
50:1	655	122
50:2	606	119
50:5	352	99
50:10	41	48

[a] The ratios of $[COO^-]$ to $[Tb^{3+}]$ are 50, 25, 10, and 5, respectively.

Acknowledgment. We acknowledge the advice and suggestions of Professor H. Morawetz throughout the course of the work.

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