Synthesis and Characterization of *N,N′,N″,N‴*-Tetrasalicylidene-3,3′-diaminobenzidine Schiff-Base Coordination Polyelectrolytes of Yttrium(III), Lanthanum(III), Gadolinium(III), and Ytterbium(III)

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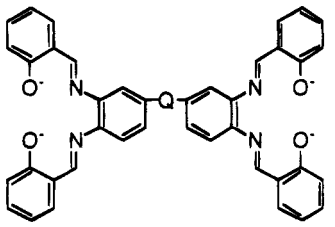
ABSTRACT: A series of linear coordination polyelectrolytes formed by lanthanide(III) ions (Ln^{3+} = La^{3+}, Gd^{3+}, Y^{3+}, or Yb^{3+}) with the anion of the Schiff-base *N,N′,N″,N‴*-tetrasalicylidene-3,3′-diaminobenzidine (H_4tsdb) have been synthesized. This new series has the formula $[MLn(tsdb)]_n$ (M^+ = an alkali metal ion). Some can dissolve in polar organic solvents with high dielectric constants, such as DMSO, NMP, and DMF, and they exhibit the typical properties of polyelectrolytes, i.e., an apparent increase in inherent viscosity for dilute solutions; the formation of colloidal precipitates when water is added to the solutions; smaller solution conductivity relative to simple electrolytes; high thermal stability (>773 K); and high glass transition temperatures. Molecular weights of $[NaY(tsdb)]_n$ have been estimated by NMR end-group analysis to be as high as 18 500. The Mark–Houwink constants for $[NaY(tsdb)]_n$ are $a = 0.510$ and $K = 8.12 \times 10^{-2}$ cm³/g. The molecular weights of the other polyelectrolytes have been estimated from their intrinsic viscosities. The solubilities of the polyelectrolytes are strongly affected by the counterions. Only the sodium salts of the polyelectrolytes are soluble in polar organic solvents, except for La(III), for which the lithium salt also has some solubility. The La(III) compounds give a behavior somewhat different from that of the other polyelectrolytes.

Introduction

Although several kinds of lanthanide (Ln) Schiff-base complexes have been prepared previously,[1–5] the soluble linear coordination polymers $[Ce(tsdb)]_n$, $[Ce(tstm)]_n$, and $[Ce(tsts)]_n$ containing Ce(IV) in their backbones [and where $tsdb^{4-}$ (**1**), $tstm^{4-}$ (**2**), and $tsts^{4-}$ (**3**) are bis-

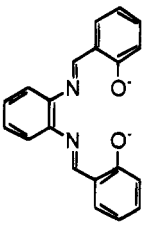


1 $tsdb^{4-}$ Q = —
2 $tstm^{4-}$ Q = CH_2
3 $tsts^{4-}$ Q = SO_2

tetradentate Schiff-base ligands] are the only examples and were prepared in our laboratory previously.[6,7] In most reports involving lanthanide(III or IV) ions in polymeric systems, either the polymers are used as matrices for the lanthanide complexes[8–10] or the lanthanide ions are bonded directly to branches of the polymer chains.[11–15] Attempts to use the Ln(III) ions in the polymer backbones normally result in insoluble compounds.[16,17] Soluble linear polymers or polyelectrolytes from Ln(III) ions and Schiff-base ligands similar to the Ce(IV) polymers were unknown prior to this paper.

The impetus for this research on coordination polymers formed by lanthanide(III) ions with Schiff-base ligands, such as H_4tsdb, includes their potential applications as conducting materials based on both the electronic conjugation of the polymer chains and the ionic conductivity properties of polyelectrolytes[18] and as models for analogous luminescent lanthanide(III) ion polymers. The strong narrow-line emission from many lanthanide(III) compounds is coordination number dependent, and previous attempts to obtain luminescence materials with lanthanide(III) polymer systems provided only the decreased luminescence obtained for Ln(III) ions with low coordination numbers.[19,20] Lanthanide(III) Schiff-base coordination polymers or polyelectrolytes with 8-coordinate ligand structures should alleviate that problem.

Based on our research with $[MLn(dsp)_2]$ coordination complexes formed by the lanthanide ions Y^{3+}, La^{3+}, Gd^{3+}, and Yb^{3+} with the anion of the Schiff-base *N,N′*-disalicylidene-1,2-phenylenediamine (dsp^{2-}, **4**) in the



4 dsp^{2-}

presence of alkali-metal ions (M^+),[21] a series of coordination polyelectrolytes with the formula $[MLn(tsdb)]_n$ (Ln = La, Gd, Y, and Yb; M = alkali ions) have now been prepared. La, Gd, and Yb were chosen in our research to represent the entire series of lanthanide elements. Yttrium was investigated initially because of its availability, its similarities in size and hardness with the lanthanides, and the easy characterization of its diamagnetic compounds by proton nuclear magnetic resonance. Yttrium is considered as a lanthanide (Ln) in the general discussions herein. Two methods have been used to prepare the Y(III) polyelectrolytes as

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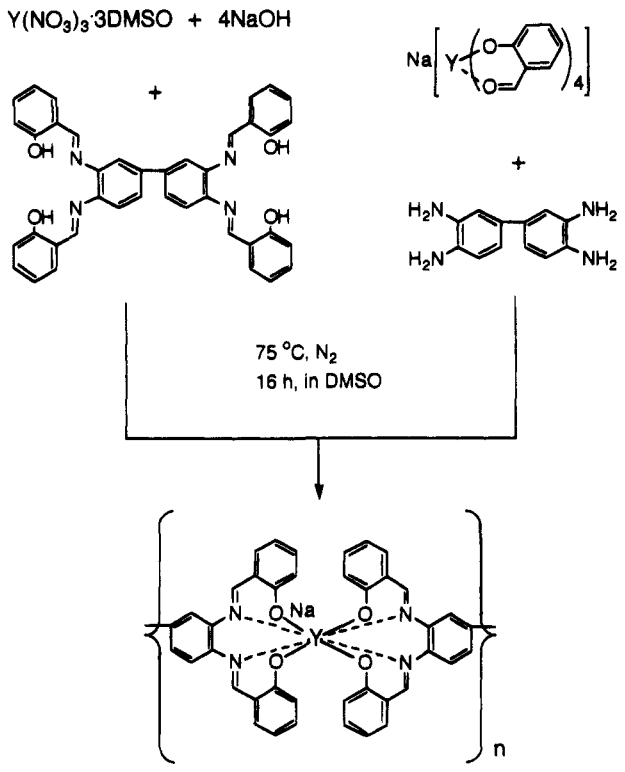

Figure 1. Two methods for synthesizing $[NaY(tsdb)]_n$ polyelectrolytes.

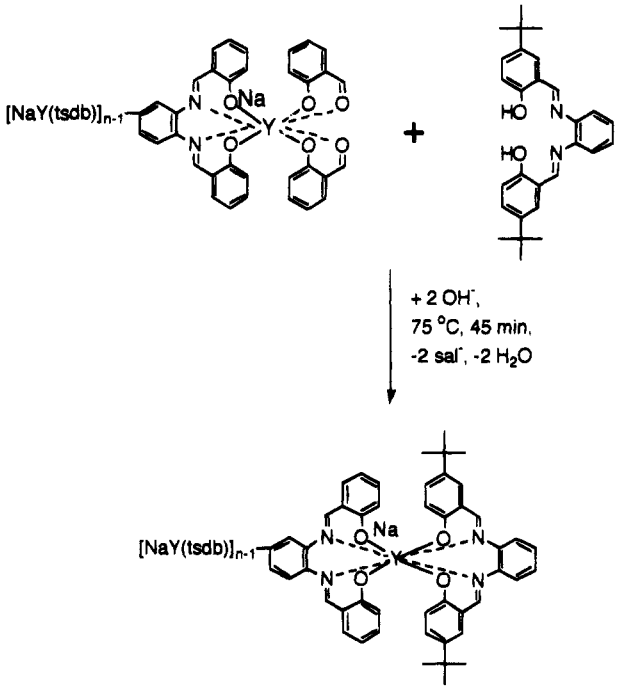

Figure 2. End-capping reaction for polyelectrolytes prepared by method b. An analogous reaction replaces NO_3^- ligands from polyelectrolytes prepared by method a.

shown in Figure 1, and the molecular weights of the Y(III) polyelectrolytes have been estimated by end-group analyses similar to those used for the neutral $[Ce(tsdb)]_n$ coordination polymer.[7] The *N,N'*-bis(5-*tert*-butylsalicylidene)-1,2-phenylenediaminato (bsp^{2-}) end groups have been introduced by the end-capping reactions shown in Figure 2. The other polyelectrolytes have been synthesized based on the yttrium results, although some modifications have been necessary as noted below.

Experimental Section

Syntheses. Reagent-grade and HPLC-grade solvents and chemicals were used throughout. Prior to use, dimethyl sulfoxide (DMSO) was stirred for 2 days with barium oxide and fractionally distilled over calcium hydride under reduced pressure. *N*-methylpyrrolidone (NMP) and dimethylformamide (DMF) were purified following literature procedures.[22] Salicylaldehyde (Hsal) was distilled under reduced pressure. 3,3'-Diaminobenzidine (db) was purified just prior to use by using the method of Vogel and Marvel.[23,24] The purified db was kept under an inert atmosphere of N_2 or Ar to avoid oxidation of the amine groups.

Dimethyl Sulfoxide Complexes of Lanthanide and Yttrium Nitrates, $Ln(NO_3)_3 \cdot n$DMSO (Ln = La, n = 4; Ln = Gd, Yb, and Y, n = 3). The $Ln(NO_3)_3 \cdot n$DMSO reagents were prepared as reported previously.[21,25]

Schiff Bases. *N,N'*-Bis(5-*tert*-butylsalicylidene)-1,2-phenylenediamine (H_2bsp) and *N,N',N'',N'''*-tetrasalicylidene-3,3'-diaminobenzidine (H_4tsdb) were prepared as reported previously.[7]

Sodium Tetrakis(salicylaldehydato)yttriate(III), Na[Y(sal)$_4$]. $Na[Y(sal)_4]$ was prepared as reported previously.[21]

Sodium *catena*-Poly[yttriate(III)-μ-*N,N',N'',N'''*-tetrasalicylidene-3,3'-diaminobenzidinato-*O,N,N',O',O'',N'',N''',O'''*], [NaY(tsdb)]$_n$. Method a. NaOH (0.1524 g, 3.810 mmol) in 5 mL of methanol was added to a solution of 0.5000 g (0.7937 mmol) of H_4tsdb and 0.4040 g (0.7937 mmol) of $Y(NO_3)_3 \cdot 3$DMSO in 25 mL of DMSO at 75 °C under N_2. The resulting solution was allowed to react at 75 °C under N_2 for 16 h with magnetic stirring. The end-capping reagent H_2bsp (0.0700 g, 0.1636 mmol) and 0.0262 g (0.6560 mmol) of NaOH in 5 mL of methanol were added at the end of the reaction. The end-capping reaction proceeded at the same conditions for another 45 min before 100 mL of methanol was added to the solution. A yellow precipitate was obtained after the solution was stirred for about another 45 min at 75 °C. The product was filtered, washed with methanol and ether, and dried at 100 °C *in vacuo*. Yield: 0.30 g (45%).

Method b. Diaminobenzidine (db) (0.1440 g, 0.6730 mmol) was added to a solution of $Na[Y(sal)_4]$ (0.4011 g, 0.6730 mmol) in 25 mL of DMSO in 75 °C under N_2. The resulting solution was allowed to react at 75 °C under N_2 with magnetic stirring for 16 h. The end-capping reagent H_2bsp (0.0700 g, 0.1636 mmol) and 0.0262 g (0.6560 mmol) of NaOH in 5 mL of methanol were added. The end-capping reaction proceeded for another 45 min at the same conditions before 100 mL of methanol was added to the solution. A yellow precipitate was obtained after the solution was stirred for about 45 min more at 75 °C. The product was filtered, washed with methanol and ether, and dried at 100 °C *in vacuo*. Yield: 0.25 g (45%). Anal. Calcd for $NaYC_{40}H_{26}O_4N_4 \cdot 1.2C_2H_6SO$: Y, 10.7; C, 61.2; H, 3.99; N, 6.74; DMSO, 11.3. Found: Y, 10.4; C, 61.0; H, 4.02; N, 6.83; DMSO, 11.5.

End-Capping Confirmation for Y(III) Compounds. (a) Two Y(III) per Bridging Ligand. H_4tsdb (0.2240 g, 0.3556 mmol) in 10 mL of DMSO and 0.0569 g (1.422 mmol) of NaOH in 5 mL of methanol were slowly added at 75 °C under N_2 to a solution of $Y(NO_3)_3 \cdot 3$DMSO (0.3620 g, 0.7112 mmol) in 15 mL of DMSO. The resulting solution was allowed to react for 1 h at 75 °C under N_2 before 0.3040 g (0.7103 mmol) of H_2bsp and 0.0682 g (1.705 mmol) of NaOH were added to it. The reaction was allowed to proceed for another 1 h under the same conditions. A yellow precipitate formed after about 30 min. At the end of the reaction 70 mL of methanol was added to the solution to obtain more precipitate. The product was filtered, washed with methanol, and dried *in vacuo* at 100 °C. Yield: 0.45 g (74%).

(b) Polymerization Reaction end-Capped at Different Times. NaOH (0.2651 g, 0.6629 mmol) in 10 mL of methanol was added at 75 °C under N_2 to a solution of 0.8700 g (1.381 mmol) of H_4tsdb and 0.7029 g (1.381 mmol) of $Y(NO_3)_3 \cdot 3$DMSO in 50 mL of DMSO. The resulting solution was allowed to react at 75 °C under N_2. Twelve (12.0) milliliter portions were pipetted out after 30 min, 1 h, 2 h, 4 h, and 7 h. End capping was accomplished by adding 0.0350 g (0.0818 mmol) of H_2bsp

and 0.0079 g (0.1963 mmol) of NaOH to each solution and allowing the end-capping reaction to proceed at 75 °C under N_2 for 45 min. The precipitates obtained by adding 45 mL of methanol to each solution and stirring for 30 min were filtered, washed with methanol, and dried *in vacuo* at 100 °C.

Sodium *catena*-Poly[gadoliniate(III)-μ-*N,N',N'',N'''*-tetrasalicylidene-3,3'-diaminobenzidinato-*O,N,N',O',O'',N'',N''',O'''*], [NaGd(tsdb)]$_n$. NaOH (0.1317 g, 3.292 mmol) in 5 mL of methanol was added to a solution of H_4tsdb (0.4320 g, 0.6857 mmol) and 0.3956 g (0.6857 mmol) of $Gd(NO_3)_3$·DMSO in 25 mL of DMSO at 75 °C under N_2. The resulting solution was allowed to react for 16 h at 75 °C under N_2. A yellow precipitate started to appear after about 4 h. The product was filtered, washed with methanol, and dried *in vacuo* at 100 °C. Yield: 0.35 g (59%). Anal. Calcd for $NaGdC_{40}H_{26}N_4O_4 \cdot 0.8C_2H_6SO$: Gd, 18.1; C, 57.5; H, 3.54; N, 6.45; DMSO, 7.18. Found: Gd, 17.8; C, 57.0; H, 3.16; N, 6.45; DMSO, 7.37.

Sodium *catena*-Poly[ytterbiate(III)-μ-*N,N',N'',N'''*-tetrasalicylidene-3,3'-diaminobenzidinato-*O,N,N',O',O'',N'',N''',O'''*], [NaYb(tsdb)]$_n$. NaOH (0.1280 g, 3.200 mmol) in 5 mL of methanol was added to a solution of H_4tsdb (0.4200 g, 0.6667 mmol) and 0.3953 g (0.6667 mmol) of $Yb(NO_3)_3$·3DMSO in 25 mL of DMSO at 75 °C under N_2. The resulting solution was allowed to react for 16 h at 75 °C under N_2. A precipitate was obtained by adding 80 mL of methanol and then stirring for 30 min. The product was filtered, washed with methanol, and dried *in vacuo* at 100 °C. Yield: 0.33 g (55%). Anal. Calcd for $NaYbC_{40}H_{26}N_4O_4 \cdot C_2H_6SO$: Yb, 19.2; C, 56.0; H, 3.55; N, 6.22; DMSO, 8.67. Found: Yb, 19.4; C, 55.8; H, 3.46; N, 6.18; DMSO, 8.47.

Sodium and Lithium *catena*-Poly[lanthanate(III)-μ-*N,N',N'',N'''*-tetrasalicylidene-3,3'-diaminobenzidinato-*O,N,N',O',O'',N'',N''',O'''*], [NaLa(tsdb)]$_n$ and [LiLa(tsdb)]$_n$. LiOH or NaOH (3.848 mmol) in 5 mL of methanol was added to a solution of H4tsdb (0.5050 g, 0.8016 mmol) and $La(NO_3)_3$·4DMSO (0.5106 g, 0.8016 mmol) in 25 mL of DMSO at 75 °C under N_2. The resulting solution was allowed to react for 16 h at 75 °C under N_2. End capping was accomplished analogous to [NaY(tsdb)]$_n$. A precipitate was obtained by adding 80 mL of methanol and then stirring for 30 min. The product was filtered, washed with methanol, and dried *in vacuo* at 100 °C. Yield: ~50%. Anal. Calcd for $LiLaC_{40}H_{26}N_4O_4 \cdot 1.4C_2H_6SO$: La, 15.8; C, 58.3; H, 3.91; N, 6.36; DMSO, 12.4. Found: La, 15.9; C, 58.3; H, 3.96; N, 6.46; DMSO, 12.5. Calcd for $NaLaC_{40}H_{26}N_4O_4 \cdot 0.5C_2H_6SO$: La, 16.8; C, 59.5; H, 3.51; N, 6.77; DMSO, 4.71. Found: La, 17.1; C, 58.9; H, 3.34; N, 6.80; DMSO, 4.95.

End-Capping Confirmation for La(III) Compounds. (a) Two La(III) per Bridging Ligand. H_4tsdb (0.2110 g, 0.3349 mmol) in 10 mL of DMSO was slowly added to a solution of $La(NO_3)_3$·4DMSO (0.4267 g, 0.6698 mmol) in 15 mL of DMSO at 75 °C under N_2, followed by adding 0.054 g (1.340 mmol) of NaOH in 5 mL of methanol. The resulting solution was allowed to react for 1 h at 75 °C under N_2 before 0.2867 g (0.6698 mmol) of H_2bsp and 0.064 g (1.608 mmol) of NaOH were added to it. The reaction proceeded for another 1 h before 70 mL of methanol was added to the solution. The precipitated product was filtered, washed with methanol, and dried *in vacuo* at 100 °C. Yield: 0.15 g.

(b) Polymerization Reaction End-Capped at Different Times. NaOH (0.305 g, 7.642 mmol) in 10 mL of methanol was added to a solution of H_4tsdb (1.0030, 1.592 mmol) and $La(NO_3)_3$·4DMSO (1.0141 g, 1.592 mmol) in 55 mL of DMSO at 75 °C under N_2. The resulting solution was allowed to react at 75 °C under N_2. Twelve (12.0) milliliter portions were pipetted out after 30 min, 1 h, 2 h, 4 h, and 7 h. End capping was accomplished by adding 0.0400 g (0.0935 mmol) of H_2bsp and 0.0089 g (0.224 mmol) of NaOH to each solution and allowing the reaction to proceed at 75 °C under N_2 for 45 min. The precipitates obtained by adding 45 mL of methanol to each solution and stirring for 30 min were filtered, washed with methanol, and dried *in vacuo* at 100 °C.

Reaction Stoichiometry. The best stoichiometry for Y(III), Yb(III), and La(III) was verified by varying the mole ratios of $Ln(NO_3)_3$·*n*DMSO:H_4tsdb {and also Na[Y(sal)$_4$]:db for Y(III)} with ratios of 0.98:1.00, 0.99:1.00, 1.00:1.00, 1.00:0.99, and 1.00:0.98 for each. All reactions were conducted under the same conditions as above.

Analyses. C, H, and N were analyzed by standard microanalytical methods in the University of Massachusetts Microanalysis Laboratory. The Ln^{3+} ions were analyzed by EDTA titration by using Eriochrome Black T as the indicator and DMSO as the solvent. The percent of DMSO in the compounds was determined from the weight loss obtained by heating 0.2000 g of [MLn(tsdb)]$_n$·*n*DMSO at 230 °C to a constant weight.

Physical Measurements. Proton Fourier transform nuclear magnetic resonance (FT-NMR) measurements were taken with Varian models XL-200 and XL-80. The bsp-end-capped-polymer *tert*-butyl protons (average of 18 per chain) were integrated against the aromatic and aldehydic protons in the $tsdb^{4-}$ ligands (26 protons per $tsdb^{4-}$ unit). The average number of monomeric units (n_{mer}) *vs* the average number of bsp end groups (n_e) was obtained from the ratio of intensities adjusted for the number of protons in each. The average degree of polymerization was calculated by $\overline{DP} = 2(n_{mer}/n_e)$.[26] Several thousand acquisitions were used to obtain reliable results for the high $\overline{M}_n$ polymers.

Viscosity measurements were conducted in an Ubbelohde type viscometer in NMP solution at 30.00 ± 0.02 °C.

Infrared spectra were obtained as KBr pellets with a Mattsen Cygnus 100 Fourier transform infrared (FT-IR) spectrometer.

Ultraviolet–visible spectra were obtained with a Perkin-Elmer Model 3840 Lambda-array spectrophotometer coupled with an IBM personal computer using software supplied by Perkin-Elmer.

Thermal analyses were conducted with Perkin-Elmer TGS-2 and DSC-7 thermal analyzers under nitrogen gas with heating rates of 10–20 °C/min. Systems include Perkin-Elmer thermal analysis data stations and system 4 and 7 microprocessors, respectively.

Molar conductances were measured with a YSI Model 34 conductance–resistance meter in DMF at 30.0 ± 0.2 °C.

Results

Synthesis of [MLn(tsdb)]$_n$. The successful preparation of the [MLn(tsdb)]$_n$ polyelectrolytes depends mostly on the alkali-metal bases used to remove the protons from the H_4tsdb Schiff base. Besides alkali-metal hydroxides, many other bases including sodium methoxide, sodium hydride, and alkylamines were tried in the syntheses. The alkali-metal hydroxides gave the most satisfactory results, as was also observed in the preparations of the M[Ln(dsp)$_2$] monomers.[21] A slight excess of alkali-metal hydroxide is important to ensure complete removal of all the protons from the Schiff base. Synthetic reactions between $tsdb^{4-}$ and the lanthanide(III) nitrates proceed rapidly. The products obtained after 1 h exhibit the same infrared and NMR spectra as the product obtained after 16 h. However, the synthesis of [NaY(tsdb)]$_n$ by the condensation reaction between Na[Y(sal)$_4$] and diaminobenzidine requires a much longer time for complete reaction; otherwise, impure products are obtained in which some of the $tsdb^{4-}$ ligands have their oxygen atoms coordinated to two Y(III) ions at the same time (based on infrared evidence as noted below). When methanol was used as a precipitant, the precipitates do not come out immediately for products with high molecular weights (>10 000 based on the end-group analysis) as in the case of the neutral [Ce(tsdb)]$_n$ and [Ce(tstm)]$_n$ coordination polymers. No matter how much methanol is added to the solution, precipitation takes place only after the solution is heated. However, for products with low molecular weights (<8K from results of the end-group analysis) some precipitate comes out as soon as metha-

Table 1. Characterization of [MLn(tsdb)]$_n$ Polyelectrolytes

compd	$\overline{M}_n$[d]	viscosity[e]	T_g(°C)[f]	conductivity[g]	dec temp (°C)[h]
[NaY(tsdb)]$_n$ (a)[a]	18 500	12.5	162 (154)	34	530
[NaY(tsdb)]$_n$ (b)[b]	16 500	11.5		33	
$Na_2[Y_2(tsdb)(bsp)_2]$[c]	1 500	3.84			515
[NaGd(tsdb)]$_n$	10 500[i]	9.1	143 (125)	34	562
[NaYb(tsdb)]$_n$	22 000[i]	13.4	179 (169)	28	502
[LiLa(tsdb)]$_n$		9.5	103 (80)	60	502
[NaLa(tsdb)]$_n$		8.9	100 (87)	62	568

[a] Compound prepared by synthetic method a. [b] Compound prepared by synthetic method b. [c] Compound from the end-capping confirmation reaction (a). [d] Molecular weight from the end-group analysis by proton NMR assuming an average of one bsp^{2-} ligand per chain. [e] Intrinsic viscosity in cm^3/g in NMP at 30.00 ± 0.02 °C. [f] Glass transition temperature; heating rate of 20 °C/min; onset temperature in parentheses. [g] Ionic conductivity in DMF at 30.0 ± 0.2 °C (cm^2 mol^{-1} Ω^{-1}) for 1 mM (formula weight) solutions. [h] Decomposition temperature in N_2; heating rate of 10 °C/min. [i] Molecular weight based on the Mark–Houwink equation for [NaY(tsdb)]$_n$.

nol is added to the solution. If H_2O is used as the precipitant, colloidal suspensions are obtained, which are difficult to handle. However, the addition of an electrolyte such as sodium nitrate destroys the colloidal suspension and an easily filtered precipitate is obtained. This is a typical behavior for polyelectrolytes.[27]

Another good synthetic precipitant is a mixed solvent of ether and toluene (3:1). A sticky oil sinks to the bottom of the flask when the mixed solvent is added to the solution, and the oil is immediately transformed to a precipitate by the addition of methanol. Thin films can be obtained by careful evaporation of DMSO from the [MLn(tsdb)]$_n$ solutions.

Similar to the M[Ln(dsp)$_2$] monomers,[21] the solubility of [MLn(tsdb)]$_n$ depends on two factors. One is the countercation. The sodium salts have a moderate solubility in polar solvents such as DMSO, DMF, and NMP, and heating greatly increases their solubility. All of the other alkali-metal salts have very limited solubility and precipitate out during synthesis except for the lithium salt of the lanthanum polyelectrolyte, which has good solubility, too. Among the soluble sodium salts of the polyelectrolytes, [NaGd(tsdb)]$_n$ has the smallest solubility. It precipitates out as polymer chains increase in length, but it redissolves when the temperature is raised or more solvent is added.

End-Group Analysis for Molecular Weight. End-group analyses of [NaY(tsdb)]$_n$ have been obtained by FT-NMR spectroscopy from the intensity of the *tert*-butyl proton signal of the end-capping bsp^{2-} at about 1.1–1.3 ppm (18 protons per bsp^{2-}) *vs* the signals associated with the Schiff-base protons ranging from 5.5 to 8.5 ppm (26 protons per repeating unit) as shown in Figure 3. The highest molecular weights obtained for [NaY(tsdb)]$_n$ are 18 500 with a $\overline{DP}$ of 50 for synthetic method a (of Figure 1) [for the trial with the ratio of $Y(NO_3)_3$·3DMSO:H_4tsdb = 1.00:1.00] and 16 500 with a $\overline{DP}$ of 45 for method b {for Na[Y(sal)$_4$]:db = 1.00:0.99} (Table 1).

Results from the end-capping confirmation method a show that the product has the composition [(bsp)Y(tsdb)Y(bsp)]$^{2-}$ based on an NMR end-group analysis (Table 1). Results from method b where [NaY(tsdb)]$_n$ was end-capped at different reaction times are given in Table 2. The apparent molecular weights from the end-group analyses and the viscosities of the products increase as the reaction time increases.

Similar end-capping reactions for [NaLa(tsdb)]$_n$ gave negative results. No signal from the end-group bsp^{2-} in the area 1.1–1.3 ppm was observed in the product from the end-capping reaction (a), and no end group was found even for the product which was end-capped after a short 1-h reaction. Intrinsic viscosities found for the La products from different reaction times are all about

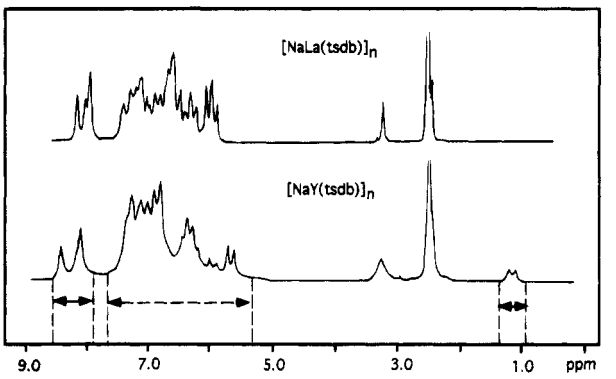

Figure 3. ^{1}H NMR spectra for the end-capped polyelectrolytes [NaLa(tsdb)]$_n$ and [NaY(tsdb)]$_n$. The molecular weight of [NaY(tsdb)]$_n$ is 18 500 from the end-group analysis. No signal from the *tert*-butyl of the end group was found for [NaLa(tsdb)]$_n$.

Table 2. Results for [NaY(tsdb)]$_n$ Polymers End-Capped after Different Reaction Times

reaction time (h)	$\overline{M}_n$[a]	viscosity[b]
0.5	4500	5.63
1	5000	6.37
2	7700	8.08
4	9200	8.38
7	14000	10.5

[a] Molecular weight from the end-group analysis by proton NMR. [b] Intrinsic viscosities in cm^3/g in NMP at 30.00 ± 0.02 °C.

8.5 cm^3/g. No end-capping reaction was performed for Gd(III) and Yb(III) compounds because both ions are paramagnetic, which greatly shifts and broadens the peaks of the proton signals and makes it impossible to estimate the molecular weights by this method.

The inherent viscosities of the [NaY(tsdb)]$_n$ polymers have been determined using Kraemer's approximation:[28] $[\eta]_{inh} = (1/c)\ \ln(t_{soln}/t_{solv})$, where $[\eta]_{inh}$ is the inherent viscosity, c is the concentration in g/cm^3, and t is the time in seconds for the solution (soln) or solvent (solv). Inherent viscosity values between 4×10^{-3} and 1×10^{-3} cm^3/g have been extrapolated to zero concentration to obtain the intrinsic viscosities. No salts were added to the solutions (i.e., to maintain ionic strength) because simple inorganic salts do not dissolve in NMP. When the concentrations are below 1×10^{-3} g/cm^3, apparent increases in the inherent viscosity are observed (see Figure 4). Viscosity results for the [MLn(tsdb)]$_n$ polyelectrolytes are given in Table 1. For [NaGd(tsdb)]$_n$ the products which spontaneously precipitate during the syntheses have viscosities in the range of 8.8–9.1 cm^3/g. For Yb, the highest viscosity of 13.4 cm^3/g was obtained for the $Yb(NO_3)_3$·3DMSO:H_4tsdb ratio of 1.00:0.99. Viscosities obtained for different trials are all close to 9 cm^3/g for [NaLa(tsdb)]$_n$ and 9.5 cm^3/g for [LiLa-

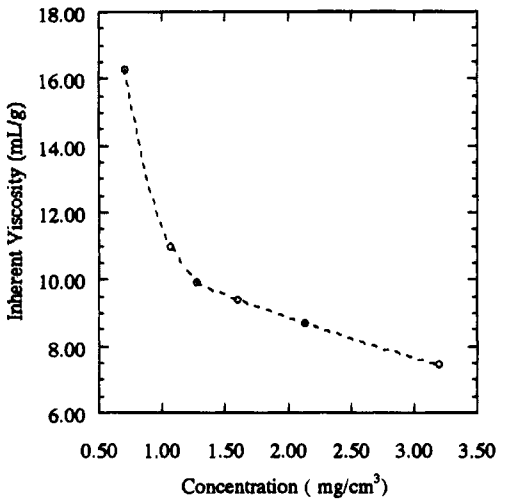

Figure 4. Inherent viscosities of $[NaY(tsdb)]_n$ polyelectrolytes at 30.00 ± 0.02 °C in NMP.

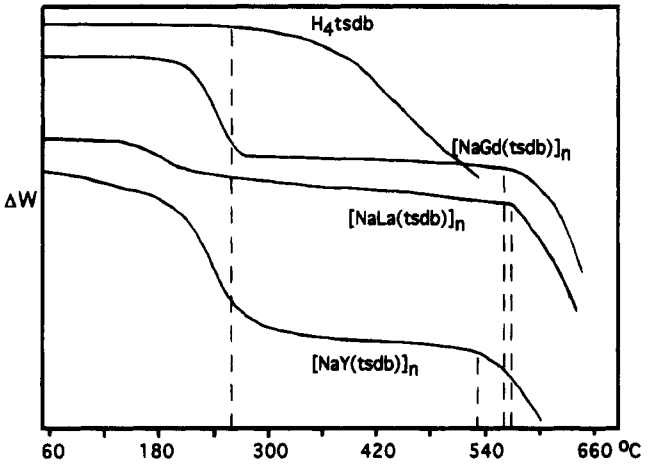

Figure 5. Thermal gravimetric weight-loss plots for H_4tsdb and some $[NaLn(tsdb)]_n$ polyelectrolytes.

$(tsdb)]_n$. Greatly reduced viscosities were observed when protonic acids were introduced to $[MLn(tsdb)]_n$ solutions, consistent with polymer chain scission.

Thermal analyses of the polyelectrolytes have included thermal gravimetry (TGA) and differential scanning calorimetry (DSC). The $[MLn(tsdb)]_n$ polyelectrolytes show excellent thermal stability (>773 K or 500 °C) (Table 1). The $[MLn(tsdb)]_n$ products containing DMSO lose it around 493 K (220 °C; Figure 5). The glass transition temperatures (T_g) have been calculated from DSC measurements to be 469 and 462 K for $[NaY(tsdb)]_n$ from synthetic methods a and b with onset temperatures of 441 and 445 K, 455 K for $[NaGd(tsdb)]_n$ with an onset temperature of 444 K, 491 K for $[NaYb(tsdb)]_n$ with an onset temperature of 486 K (Table 1), and 411 and 407 K for $[LiLa(tsdb)]_n$ and $[NaLa(tsdb)]_n$ with onset temperatures of 393 and 391 K, respectively.

Results from conductivity measurements are shown in Table 1. In comparison to the molar conductances of the monomeric $M[Ln(dsp)_2]$ 1:1 electrolytes, which are about 70 $cm^2\ mol^{-1}\ \Omega^{-1}$,[21] the molar conductances of the $[MLn(tsdb)]_n$ polyelectrolytes are about 33 $cm^2\ mol^{-1}\ \Omega^{-1}$ {for a 1 mM concentration, calculated by using the formula weight of $[MLn(tsdb)]_n$}. Note that the La(III) compound molar conductance values for both $[LiLa(tsdb)]_n$ and $[NaLa(tsdb)]_n$ are much closer to the values observed for simple 1:1 electrolytes.

The spectral characterization of the $[MLn(tsdb)]_n$ polyelectrolytes is provided in Table 3.

Discussion

Synthesis. Both synthetic methods used in this study have used DMSO as the solvent. DMSO is an effective solvent for polymers,[29,30] and strong hydrogen bonding with water makes it an excellent water scavenger in Schiff-base condensation polymerization reactions.[7,21,31] Step-growth polymerization reactions are affected by both the extent of reaction and the ratio of reactants as discussed in some detail in a recent paper.[7] Both reactions used in this study appear to go essentially to completion without side reactions, except when solubility limits the extent of reaction. Even so, both the purity and the exact stoichiometry of the reactants are critical for obtaining polymers with reasonable molecular weights.

The coordination polymers formed between the Ln(III) ions and the $tsdb^{4-}$ ligand (synthetic method a) use a reaction similar to that used for synthesizing the analogous Ce(IV) polymer.[7] However, whereas the 4+ charge of the Ce(IV) ion matches the 4− charge on $tsdb^{-4}$ and yields a neutral coordination polymer, the 3+ charge on the Ln(III) ions does not match the 4−

Table 3. Spectral Characterization of $[NaLn(tsdb)]_n$ Polyelectrolytes

H_4tsdb	$[NaLa(tsdb)]_n$	$[NaGd(tsdb)]_n$	$[NaY(tsdb)]_n$	$[NaYb(tsdb)]_n$	assignment
		Infrared (cm^{-1})[a]			
3450					OH
1615	1609	1611	1612	1613	C=N
1278	1340 (sh)	1341 (sh)	1344 (sh)	1345 (sh)	CO
	1322	1323	1325	1327	CO
		Ultraviolet–Visible (nm)[b]			
374 (4.70,sh)	404 (4.66)	408 (4.68)	406 (4.67)	404 (4.65)	$n-\pi^*$
350 (4.73)	302 (4.51)	302 (4.48)	302 (4.50)	302 (4.47)	$\pi-\pi^*$
275 (4.73)	268 (4.51)	268 (4.48)	268 (4.47)	268 (4.46)	$\pi-\pi^*$

H_4tsdb	$[NaLa(tsdb)]_n$	$[NaY(tsdb)]_n$	assignment
	Nuclear Magnetic Resonance[c]		
12.94 (s) (2.7)			OH
9.08 (d) (4)	8.34 (s)	8.4 (s)	aldimine
	8.20 (s, sh)	8.1 (s)	
	8.13 (s)		
7.9–7.3 (m) (14)	7.6–5.6 (m, b)	7.3–5.4 (m, b)	aromatic
6.9 (m) (9.3)			

[a] KBr pellets; sh = shoulder. [b] log ε (molar extinction coefficient in $M^{-1}\ cm^{-1}$) in parentheses; DMSO solvent. [c] DMSO-d_6 solvent; s = singlet; d = doublet; m = multiplet; b = broad band, relative intensities in parentheses; also see Figure 3 for $[NaY(tsdb)]_n$ and $[NaLa(tsdb)]_n$.

charge on the $tsdb^{4-}$ ligand and requires a countercation to balance the charge for each repeating unit of the polymer chain. Our initial synthetic attempts with yttrium using both small ions (H^+ and Li^+) and large ions (K^+, Cs^+, NH_4^+, and R_4N^+) to balance the charge were unsuccessful and led only to oligomers.

A digression to monomer syntheses between Y(III) [and other Ln(III) ions] and the dianion of disalicylidene-1,2-phenylenediamine (dsp^{2-})[21] determined that only the sodium salts of the $M[Ln(dsp)_2]$ complexes have reasonable solubility in polar organic solvents with yttrium and most of the lanthanide ions and that a strong base (e.g., NaOH) is required to remove the last proton from the tetradentate Schiff base. When the base strength is insufficient, $[Ln_2(dsp)]_3$ species are formed that contain ligands that bridge two lanthanide ions instead of producing the $M[Ln(dsp)_2]$ species, which has only nonbridging tetradentate Schiff-base ligands.

Assuming that only the fully deprotonated $tsdb^{4-}$ ligand can act as a good bistetradentate ligand to coordinate with Y(III) ions to form a linear coordination polymer, method a was devised to prepare these polymers. In fact, this method does provide a convenient way to synthesize these polyelectrolytes. *Caution*! NaOH absorbs H_2O from the air so the true mass of NaOH is always less than measured; thus, the small stoichiometric excess of NaOH in the preparation is used to ensure enough base to remove all of the protons from the H_4tsdb. This method provides a rapid polymerization reaction because the neutralization reaction between the alkali hydroxide and H_4tsdb proceeds rapidly and the replacement of nitrate ions by tetradentate Schiff-base ligand $tsdb^{4-}$ can also take place quickly. The IR and NMR found for products obtained at 1 h are virtually indistinquishable from those taken after long reaction times. However, end-capping the products for the yttrium polyelectrolyte at different reaction times (Table 2) shows that maximum molecular weight is not obtained even after 7 h. The highest molecular weight obtained for $[NaY(tsdb)]_n$ by NMR end-group analysis is 18 500 after 16 h. This method was also used to prepare the other polyelectrolytes as well.

Method b for preparing $[NaY(tsdb)]_n$ is a condensation polymerization reaction between $Na[Y(sal)_4]$ and the tetraamine. This method works well for preparing coordination polymers of zirconium(IV) and cerium(IV).[7,31,32] The difference in this reaction from those with $M^{IV}(sal)_4$ is the possibility of partial dissociation of $[Y(sal)_4]^-$ to $Y(sal)_3$ and sal^- in DMSO solution as happens to the analogous $acac^-$ complex, $[Ln(acac)_4]^-$, in some solvents.[33] Any dissociation would increase the difficulty in controlling the reactant ratios and increase the difficulty in preparing high molecular weight polyelectrolytes. The stability of $[Y(sal)_4]^-$ to hydrolysis in DMSO in the presence of small quantities of water[21] ensures that the polymerization reaction proceeds smoothly. The conditions for this synthetic method were set to maximize polymerization. Stoichiometric ratios of reactants were controlled by varying the ratio of starting materials to reach the ideal 1:1 ratio. This condensation polymerization reaction is expected to be slower relative to the direct ligand coordination polymerization. However, the molecular weight of 16 500 obtained by end-group analysis for $[NaY(tsdb)]_n$ from the condensation method b is only marginally below the 18 500 obtained for the same reaction time and temperature by the direct ligand reaction (method a).

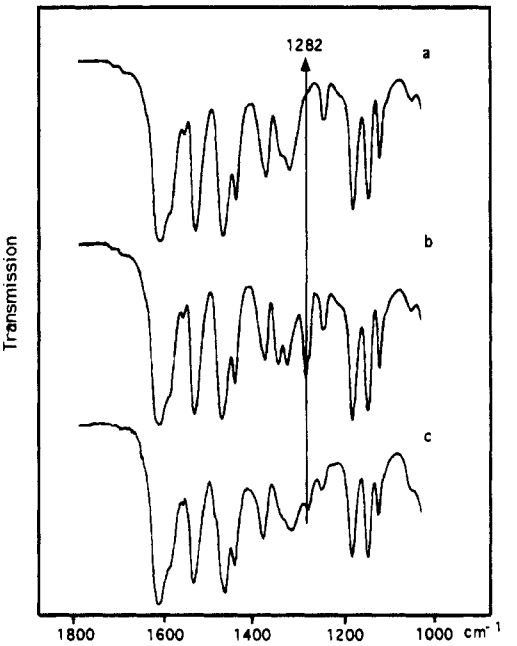

Figure 6. Infrared spectra for (a) the $[NaY(tsdb)]_n$ polyelectrolyte prepared properly, (b) the product of $Y(acac)_3$ and H_4tsdb without added base, and (c) the attempted preparation of $[LiY(tsdb)]_n$ using the method that was successful for $[NaY(tsdb)]_n$.

Structure of Polyelectrolytes. As mentioned previously,[21] the formation of lanthanide(III) 8-coordinate Schiff-base complexes can be followed by changes in their infrared spectra. The infrared spectra of the polymers show that the phenolic C–O stretch moves from 1278 cm^{-1} in H_4tsdb to around 1340–1320 cm^{-1} in the soluble linear polymers (Figure 6a) and the C=N stretching vibration moves from 1615 cm^{-1} to 1611 ± 2 cm^{-1}; both shifts are analogous to those of the lanthanide(III) Schiff-base monomers $M[Ln(dsp)_2]$.[21] A phenolic C–O stretch at 1282 cm^{-1} (that can be distinguished from the phenolic C–OH stretch at 1278 cm^{-1} in high-resolution FTIR) occurs in species in which some of the oxygen atoms are coordinated to two lanthanide ions at the same time [as occurs in Ln_2(tetradentate-Schiff-base-ligand)$_3$ systems][21] and its disappearance coincides with the formation of 8-coordinate complexes with two tetradentate ligands per lanthanide(III) ion {as in the $[Ln(tetradentate\text{-}Schiff\text{-}base\text{-}ligand)_2]^-$ ions}.[21] The $[MLn(tsdb)]_n$ polyelectrolytes show this same phenomenon. For example, when $Y(acac)_3$ and H_4tsdb react without added base, the product has a peak at 1282 cm^{-1} in its IR spectra (Figure 6b). We interpret this to mean that some of the oxygen donor atoms of this "base-free" product are coordinated to two Y(III) at the same time as in the case of Y_2dsp_3,[21] and the product has a nonlinear cross-linked structure. However, when NaOH removes the protons from H_4tsdb, the IR spectrum of the soluble reaction product has no peak at 1282 cm^{-1} (Figure 6a), consistent with a linear 8-coordinate structure for the polyelectrolyte.

The NMR spectra of the soluble polymers exhibit no phenolic proton peaks, which is consistent with anionic coordination. The data for the electronic spectra are given in Table 3 with the bands assigned analogous to the monomeric Schiff-base species.[21] The formation of films, rather than powders, upon solvent evaporation gives further evidence for the formation of soluble polyelectrolytes.

Although no X-ray structural information is available at this time for the analogous monomers, a nonrigid antiprismatic structure similar to the structure of Ce(dsp)$_2$[34] is assigned to M[Ln(dsp)$_2$] complexes (Ln = Gd, Y, and Yb)[21] based on the similar sizes[35] of the Ln(III) ions (94, 90, and 87 pm for Gd^{3+}, Y^{3+}, and Yb^{3+}, respectively) relative to Ce^{4+} (88 pm). The similarities in the spectral properties of the [NaLn(tsdb)]$_n$ polyelectrolytes to those of [Ce(tsdb)]$_n$[7] hint that the polyelectrolytes of Gd(III), Y(III), and Yb(III) should have a linear structure similar to that of polymeric [Ce(tsdb)]$_n$. Recent spectroscopic results obtained for analogous Eu(III) monomers and polyelectrolytes further confirm that the preceding structural suggestions are correct.[36]

Polyelectrolyte Solubility. The solubilities of the polyelectrolytes are greatly affected by the counterions. The fact that the solubility of the polyelectrolytes decreases when alkali-metal ions increase in size from Na^+ to K^+ to Cs^+ is expected because large cations tend to form less soluble compounds with large anions. However, lithium ions show an exception to this rule by forming insoluble products for all Ln(III) ions used in these syntheses except for La(III). The very low solubility of the lithium polyelectrolytes may be due to the small lithium ions possessing an ability to attract oxygen atoms from two polyelectrolyte chains to form a three-dimensional structure and is similar to the situation for the Li[Ln(dsp)$_2$] monomers.[21] The solubilities of the lithium salts of $[Y(tsdb)]^-$, $[Gd(tsdb)]^-$, and $[Yb(tsdb)]^-$ are so low that the synthesis reactions are incomplete when the products precipitate, as is evident in the IR spectra of the products (e.g., the small peak at 1282 cm^{-1} for the Y(III) compound is evident in Figure 6c). The only way to get pure [LiLn(tsdb)]$_n$ (Ln = Gd, Y, and Yb) is to add lithium salts such as lithium chloride to a solution of the appropriate sodium polyelectrolyte, which quickly provides a lithium electrolyte precipitate. If the lithium polyelectrolyte is prepared in this manner, no peak exists at 1282 cm^{-1}. The lithium precipitate retains the linear 8-coordinate structure of the sodium polyelectrolyte, but the strong attraction for the oxygen atoms reduces the solubility and causes a small shift in the CO peak (from about 1325 cm^{-1} for the sodium salts to between 1317 and 1320 cm^{-1} for the lithium products). The sodium polyelectrolytes show the best solubility among all the alkali-metal ions. The solubility is also affected by the degree of polymerization of the compounds. The longer the chains grow, the less soluble the polyelectrolytes become. Although reasonably soluble for short chain lengths, [NaGd(tsdb)]$_n$ precipitates from the DMSO solution after the reaction has proceeded for several hours. The abnormalities of the La(III) compound, including solubilities, are discussed below.

Polyelectrolyte Molecular Weights. The end-capping reactions work quite well for [NaY(tsdb)]$_n$ as indicated by the results of end-capping confirmation reaction a where two yttrium ions coordinate to one $tsdb^{4-}$ bridging ligand. Two tetradentate bsp^{2-} ligands easily replace the remaining nitrate groups stoichiometrically and give the anticipated Na_2[(bsp)Y(tsdb)Y(bsp)] product. In the polyelectrolyte end-capping reactions, the concentration of the end-capping bsp^{2-} group added to the solutions greatly surpasses the concentration of polymer-chain ends which are coordinated by the nitrate ions. Therefore, a complete replacement of the nitrate ions by tetradentate bsp^{2-} is expected. Results from end-capping reactions for [NaY(tsdb)]$_n$ at different reaction times (Table 2) further confirm this conclusion. Longer reaction times yield higher molecular weight polyelectrolytes (as determined by NMR of the end-group *tert*-butyl protons), and the molecular weight increases are consistent with the increases in viscosity that are observed for these same products.

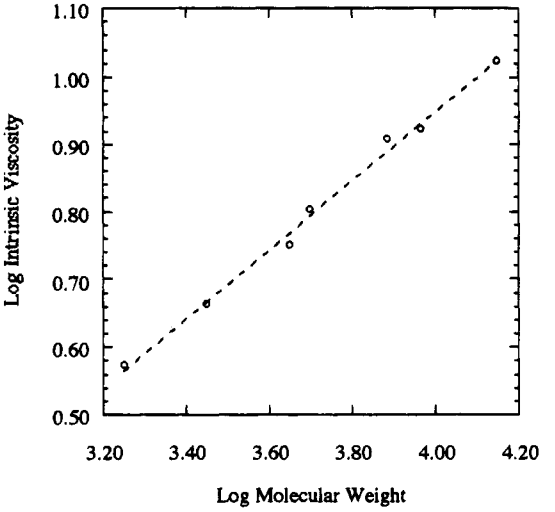

Figure 7. Composite Mark–Houwink plot for the [NaY(tsdb)]$_n$ polyelectrolytes.

The property of sharp increases in the viscosity of dilute solutions of [MLn(tsdb)]$_n$ (Figure 4) is one of the typical properties of polyelectrolytes.[37,38] Lower molecular weight species that have ionic groups show similar behavior, as noted recently in DMF for telechelic ionomers.[39] In polar solvents such as NMP, DMF, and DMSO, ionization of the polyelectrolytes takes place to a greater extent in dilute solution and the ions tend to order the solvent molecules and increase the viscosity.[40] From the ionic conductivity measurements, it is evident that appreciable ion pairing still occurs at 0.8 mg/L (1 mM) because of the low dielectric constant of DMF (ϵ = 37) relative to water (ϵ = 80).

In order to estimate the molecular weights of the Gd(III) and Yb(III) polyelectrolytes, the Mark–Houwink equation[26] $\eta = K\bar{M}^a$ for [NaY(tsdb)]$_n$ was obtained by plotting logarithms of the $\bar{M}_n$ values from the NMR end-group analysis of a series of [NaY(tsdb)]$_n$ polymers against the logarithms of their intrinsic viscosities (in cm^3/g). The plot gives $a = 0.51$ and $K = 8.1 \times 10^{-2}$ cm^3/g after linear regression, with $R^2 = 0.99$ (Figure 7). These data may be somewhat in error because constant ionic strength was not maintained during the viscosity measurements[37] but should be self-consistent for use with the Gd(III) and Yb(III) polyelectrolytes handled in an analogous fashion. The a value of 0.51 is quite close to 0.50, the value expected for a θ solvent, which means that at 30 °C NMP is not a good solvent for this type of polyelectrolyte.[38,41] The K value of 8.1×10^{-2} cm^3/g is consistent with polymer–solvent interactions.[42] This result is quite different from those for the analogous neutral coordination polymers of cerium(IV)[6,7] and zirconium(IV).[32] For them, higher a values (0.65–0.79) were found. The highest molecular weights obtained for [NaGd(tsdb)]$_n$ and [NaYb(tsdb)]$_n$ based on the Mark–Houwink equation are 10 500 ($\overline{DP}$ = 26) and 22 000 ($\overline{DP}$ = 53) (Table 1).

Attempts to use gel permeation chromatography (GPC) to find the molecular weights failed to give significant results because of the ionization of the

polyelectrolytes in the polar solvents in which they are soluble.[40] In order to use GPC to solve the molecular weight of the polyelectrolytes, it would be better to convert the polyelectrolytes to neutral polymers;[43] however, it is impossible to do so for this kind of polyelectrolyte without breaking down the polymer chain.

The ionic conductivity of the polyelectrolytes (Table 1) indicates that ionization takes place in the DMF solution to a considerable extent, but the conductivities of the $[NaLn(tsdb)]_n$ polyelectrolytes are somewhat lower than normal 1:1 electrolytes of the monomeric $M[Ln(dsp)_2]$ species in the same solvent,[21] except for the La(III) compound. The lower conductivity relative to simple salts is another typical property of polyelectrolytes[44] and is caused by ion binding to the polyions,[14,44-46] and the conjugated system in $[NaLn(tsdb)]_n$ can further increase this tendency. In conjugated systems the sharing of the negative charge from the ionization of the polyelectrolyte increases the strong field within which the counterions are restricted.

Lanthanum(III) Compound Abnormalities. Several anomalies have been observed for the $[MLa(tsdb)]_n$ species relative to the other polyelectrolytes. First, $[LiLa(tsdb)]_n$ dissolves in DMSO, DMF, and NMP, whereas none of the other lithium polyelectrolytes are soluble in these solvents; second, the end-capping reaction for determining molecular weights does not work for $[MLa(tsdb)]_n$ although it works well for $[NaY(tsdb)]_n$ and for the neutral Ce(IV) and Zr(IV) polymers; third, the molar conductances of the soluble $[MLa(tsdb)]_n$ species are higher than those of the other soluble electrolytes.

The larger radius of the La(III) ion relative to Ga(III), Y(III), and Yb(III) (103 pm for La^{3+} *vs* 94, 90, and 87 pm for Gd^{3+}, Y^{3+}, and Yb^{3+} respectively[35]) may mean a higher coordination number for La(III), which is not at all uncommon, and should provide more flexibility to the growing polyelectrolyte chains. Although no conclusive evidence exists for a coordinate number of greater than 8 in the La(III) species, the larger radius of La(III) could provide a difference in structure through greater flexibility of the coordination sphere. The good solubility of $[LiLa(tsdb)]_n$ in polar organic solvents may come from a structure difference combined with coordinated DMSO to the Li^+ in this species which prevents Li^+ from further attracting oxygen atoms from the other polymer chains analogous to the $Li[La(dsp)_2]$ monomer.[21]

The lack of bsp^{2-} end groups on the $[MLa(tsdb)]_n$ polyelectrolytes after the attempted end-capping reaction was performed on these compounds can be explained in two ways. First, $[MLa(tsdb)]_n$ might have a ring structure. If so, all Ln(III) ions are coordinated by $tsdb^{4-}$ ligands in the solution and no replaceable nitrate ends exist. A second explanation is that the bsp^{2-} end-capping groups do replace nitrate groups and form complexes at the ends of some La(III) polyelectrolyte species but that they can not be precipitated from a DMSO solution by the addition of methanol. The second explanation seems unreasonable because the end groups in the polymer chains do not affect the solubility of polyelectrolytes that much with any of the other lanthanide ions, although the *tert*-butyl groups in bsp^{2-} do increase the solubility of Ln(III) Schiff-base compounds in some organic solvents.[3] Experimental results seem to prefer the first explanation. The result from the end-capping confirmation reaction a designed to form a dimeric La(III) species analogous to the $[(bsp)Y(tsdb)Y(bsp)]^{2-}$ ion gave a low yield of products with no bsp^{2-} end groups. This result is most consistent with the first reason. Otherwise, the short-chain product expected from this reaction should have been obtained analogous to the yttrium experiment. The viscosities of the products from all of the lanthanide reactions are all very close to 9 cm^3/g, which also suggests a specific product is being formed in the attempted synthesis of a linear polyelectrolyte. This compound must either exist in a DMSO solution before methanol is added or be derived from other compounds because of its relatively smaller solubility after methanol is added through a rapid rearrangement of the bistetradentate species, which seems unlikely. The possibility of forming $[M_2La_2(tsdb)_2]$ with a sandwich structure appears to be energetically unlikely because of the repulsion of the two $tsdb^{4-}$ ligands (according to CAChe molecular modeling results). The viscosities of the La(III) compounds (*ca.* 9 cm^3/g) and the observation of T_g values for both soluble species further rule out this possibility because a dimeric structure is not expected to have viscosities of this magnitude or to form a glass. However, a definitive explanation of the anomalous behavior of the $[MLa(tsdb)]_n$ polyelectrolytes would be helped by structural information on monomeric $M[La(dsp)_2]$ species, for which only twinned crystals have been obtained to date.

Stabilities of Polyelectrolytes. The polyelectrolytes have high thermal stability. The decomposition temperatures of ≥785 K (512 °C) are higher than those of the similar neutral polymers of Ce(IV) and Zr(IV). High thermal stabilities are expected for polyelectrolytes. The high glass transition temperatures found for these $[MLn(tsdb)]_n$ polyelectrolytes (Table 1) are reasonable because solid-state interactions between the ions in different chains occurs, which reduces the flexibility of the polymer chains and increases the glass transition temperatures. The increases in T_g from La(III) to Gd(III) to Y(III) to Yb(III) species can be due to the differences in structures and molecular weights. Even with the smallest radius among the Ln(III) ions used, Yb^{3+} appears to have the size to form a linear coordination polymer with two $tsdb^{4-}$ ligands attached to each Yb^{3+} ion. In fact, $[MYb(tsdb)]_n$ has the highest $\overline{DP}$ of any of the polyelectrolytes. It is uncertain whether this result is due to Yb(III)'s highest charge to radius ratio causing a slightly higher extent of reaction or whether a slight difference in stoichiometry existed in the Yb(III) reaction that gave the high $\overline{DP}$.

In conclusion, a series of lanthanide(III) Schiff-base polyelectrolytes have been prepared and characterized. The compounds exhibit the typical properties of polyelectrolytes in polar solvents such as DMSO, NMP, and DMF. Further work emphasizing applications of this type of compound is being conducted in our laboratory, and the results will be reported later.

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References and Notes

(1) Fenton, D. E.; Vigato, P. A. *Chem. Soc. Rev.* **1988**, *17*, 69.
(2) Vigato, P. A.; Fenton, D. E. *Inorg. Chim. Acta* **1987**, *139*, 39.
(3) Afshar, S.; Bullock, J. *Inorg. Chim. Acta* **1980**, *38*, 145.
(4) Dutta, R. L.; Das, B. R. *J. Sci. Ind. Res.* **1988**, *47*, 547.

(5) Liu, G.; Na, C.; Li, B.; Mao, K. *Polyhedron* **1990**, *9*, 2019.
(6) Chen, H.; Cronin, J. A.; Archer, R. D., manuscript in preparation.
(7) Chen, H.; Cronin, J. A.; Archer, R. D. *Macromolecules* **1994**, *27*, 2174.
(8) Li, W.; Mishima, T.; Adachi, G.; Shiokawa, J. *Inorg. Chim. Acta* **1986**, *121*, 97.
(9) Nellay, M. *J. Electrochem. Soc.* **1964**, *111*, 1253.
(10) Wolff, N. E.; Pressley, R. J. *Appl. Phys. Lett.* **1963**, *2*, 152.
(11) Nishide, H.; Izusshi, T.; Yoshioka, N.; Tsuchida, E. *Polym. Bull.* **1985**, *14*, 387.
(12) Ueba, Y.; Zhu, K. J.; Banks, E.; Okamoto, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1271.
(13) Okamoto, Y.; Ueba, Y.; Dzhanibekov, N. F.; Banks, E. *Macromolecules* **1981**, *14*, 17.
(14) Nagata, I.; Okamoto, Y. *Macromolecules* **1983**, *16*, 749.
(15) Okamoto, Y. *J. Macromol. Sci., Chem.* **1987**, *A24*, 455.
(16) Dwivedi, D. K.; Shukla, B. K.; Shukla, R. K. *Orient. J. Chem.* **1991**, *7*, 99.
(17) Dwivedi, D. K.; Shukla, B. K.; Shukla, R. K. *Acta Cienc. Indica* **1991**, *17C*, 383.
(18) Shimidzu, T. *Applications of Electroactive Polymers*; Scrosati, B., Ed.; Chapman & Hall: New York, 1993; pp 283–309.
(19) Ueba, Y.; Banks, E.; Okamoto, Y. *J. Appl. Polym. Sci.* **1980**, *25*, 2007.
(20) Okamoto, Y.; Ueba, Y.; Nagata, I.; Banks, E. *Macromolecules* **1981**, *14*, 807.
(21) Chen, H.; Archer, R. D. *Inorg. Chem.* **1994**, *33*, 5195.
(22) Vogel, A. *Textbook of Practical Organic Chemistry*, 4th ed.; Longman Group Limited: New York, 1978; p 277.
(23) Vogel, H.; Marvel, C. S. *J. Polym. Sci., Polym. Chem. Ed.* **1963**, 1531.
(24) Vogel, H.; Marvel, C. S. *J. Polym. Sci.* **1961**, *50*, 511.
(25) Ranalingam, S. K.; Soundararajan, S. *J. Inorg. Nucl. Chem.* **1967**, *29*, 1763.
(26) Young, R. J.; Lovell, P. A. *Introduction to Polymers*, 2nd ed.; Chapman & Hall: New York, 1991; p 25.
(27) Eisenberg, A.; King, M. *Ion-Containing Polymers: Physical Properties and Structure*; Academic Press: New York, 1977; Vol. 2, p 216.
(28) Kraemer, E. O. *Ind. Eng. Chem.* **1938**, *30*, 1200.
(29) Conciatori, A. B.; Chenevey, E. C.; Bohrer, T. C.; Prince, A. E., Jr. *J. Polym. Sci., Part C* **1967**, *19*, 49.
(30) Reynolds, W. L. *Prog. Inorg. Chem.* **1970**, *12*, 1.
(31) Archer, R. D.; Illingsworth, M. L.; Rau, D. N.; Hardiman, C. J. *Macromolecules* **1985**, *18*, 1371.
(32) Archer, R. D.; Wang, B. *Inorg. Chem.* **1990**, *29*, 39.
(33) Lempicki, A.; Samelson, H.; Brecher, C. *Appl. Opt.* **1965**, *Supplement 2*, 205–213.
(34) Terzis, A.; Menrzafos, D.; Tajmir-riahi, H. A. *Inorg. Chim. Acta* **1984**, *84*, 187.
(35) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984; pp 1105, 1430. Other sets of relative ionic radii could be given; e.g., the 8-coordinate crystal radii compiled by Shannon, R. D. (*Acta Crystallogr.* **1976**, *A32*, 751) and rounded to the nearest pm are as follows: La^{3+}, 130 (136 for 9 coordinate); Gd^{3+}, 119; Y^{3+}, 116; Yb^{3+}, 112; Ce^{4+}, 111.
(36) Chen, H., unpublished results.
(37) Billmeyer, F. W. J. *Textbook of Polymer Science*, 2nd ed.; John Wiley & Sons, Inc.: New York, 1971; pp 95 and 96.
(38) Eisenberg, A.; King, M. *Ion-Containing Polymers: Physical Properties and Structure*; Academic Press: New York, 1977; Vol. 2; pp 265–272.
(39) Wu, J.-L.; Wang, Y.-M.; Hara, M.; Granville, M.; Jerome, R. J. *Macromolecules* **1994**, *27*, 1195.
(40) Lundberg, R. D.; Phillips, R. R. *J. Polym. Sci., Polym. Phys.* **1982**, *20*, 1143.
(41) Young, R. J.; Lovell, P. A. *Introduction to Polymers*, 2nd ed.; Chapman & Hall: New York, 1991; p 162.
(42) Seefried, J. C. G.; Koleske, J. V.; Critchfield, F. E.; Pfaffenberger, C. R. *J. Polym. Sci., Polym. Phys.* **1980**, *18*, 817.
(43) Denton, F. R., III; Lahti, P. M.; Karasz, F. E. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 2223.
(44) Rice, S. A.; Nagasawa, M. In *Polyelectrolyte Solutions*; Kaplan, N. O., Scheraga, H. A., Eds.; Academic Press: New York, 1961; Vol. 2; pp 427–494.
(45) Oosawa, F. *Polyelectrolytes*; Marcel Dekker: New York, 1971.
(46) Hara, M.; Lee, A. H.; Wu, J. *J. Polym. Sci., Polym. Phys.* **1987**, *25*, 1407.

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