2306 *Inorg. Chem.* **1995,** *34,* 2306−2315

Synthesis and Characterization of Two New Schiff-Bases and Their Soluble Linear Cerium(IV) Polymers

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Received September 14, 1994®

Two new linear Ce^{IV} Schiff-base coordination polymers, *catena*-poly[cerium(IV)-*μ*-*N,N',N'',N'''*-tetrasalicylidene-3,3',4,4'-tetraaminodiphenylmethanato-*O,N,N',O',O'',N'',N''',O'''*], $[Ce(tstm)]_n$, and *catena*-poly[cerium(IV)-*μ*-*N,N',N'',N'''*-tetrasalicylidene-3,3',4,4'-tetraaminodiphenylsulfonato-*O,N,N',O',O'',N'',N''',O'''*], $[Ce(tsts)]_n$, have been successfully synthesized using step growth chelation polymerizations between cerium(IV) octoxide or tetrakis-(acetylacetonato)cerium(IV) and new, premade Schiff-bases. Both new polymers exhibit excellent solubility in organic solvents with high dielectric constants, such as DMSO, NMP, and DMF. The $[Ce(tstm)]_n$ polymer fractions with low molecular weights (<9000) also have moderate solubility in THF and dichloromethane. The molecular weights of the polymers have been characterized by end group analysis based on proton NMR, by gel permeation chromatography, and by intrinsic viscosities. The highest $\overline{M}_n$ values reach 28 000 for $[Ce(tstm)]_n$ and 31 500 for $[Ce(tsts)]_n$ after fractionation. The polymers are thermally stable to 340 °C and exhibit high T_g values. Mark−Houwink constants of $a = 0.79$ and $K = 5.84 \times 10^{-3}$ cm^3/g for $[Ce(tstm)]_n$ and $a = 0.70$ and $K = 1.25 \times 10^{-2}$ cm^3/g for $[Ce(tsts)]_n$ have been established from the intrinsic viscosities and the NMR $\overline{M}_n$ values. A side reaction in the condensation polymerization between tetrakis(salicylaldehydato)cerium(IV) and 3,3',4,4'-tetraaminodiphenylmethane results in some insoluble polymeric material along with some of the desired soluble polymer. $[Ce(tstm)]_n$ provides greater solubilities and lower T_g values than either $[Ce(tsts)]_n$ or $[Ce(tsdb)]_n$, the analogous *N,N',N'',N'''*-tetrasalicylidene-3,3'-diaminobenzidine cerium polymer.

Introduction

Polymers containing lanthanide elements have been investigated for quite some time in order to explore their potential application as new luminescence materials.[1−3] Different polymer systems containing lanthanide elements such as the polymers used as matrixes for lanthanide compounds,[4−6] polymers in which the lanthanide ions are bonded to branches of the polymer chain,[7−10] and intractable polymers formed with lanthanide ions in the main chain[11,12] have been reported previously.

The first soluble linear lanthanide coordination polymer, *catena*-poly[cerium(IV)-*μ*-*N,N',N'',N'''*-tetrasalicylidene-3,3'-diaminobenzidinato-*O,N,N',O',O'',N'',N''',O'''*] or $[Ce(tsdb)]_n$ with Ce^{IV} ions in the polymer backbone, was synthesized and characterized in our laboratory.[13] The $[Ce(tsdb)]_n$ polymer is thermally stable to 400 °C and is appreciably soluble in organic solvents with high dielectric constants such as DMSO, NMP, and DMF. Whereas traditional coordination polymers with flat unsaturated chains are typically quite intractable[14,15] as a consequence of the bulk and irregularity of the square antiprismatic coordination geometry of the organic ligand donors around the Ce^{IV} ions, interchain stacking forces are minimized for this ceric coordination polymer. Although the solubility of this new type of coordination polymer has been dramatically improved, the $[Ce(tsdb)]_n$ polymer does not dissolve in organic solvents with low dielectric constants, such as THF and dichloromethane. The advantages of solubility in such solvents would include more facile characterization of the polymers and convenient means for the preparation of polymer films, which should greatly expand the potential applications of lanthanide polymers. One way to further improve the solubility of such polymers is to increase the flexibility of the polymer chains by incorporating aliphatic or inorganic spacing groups into the chain by modifying the Schiff-base ligands as has been done in this study (Chart 1).

Effective ways to prepare the two tetraamines 3,3',4,4'-tetraaminodiphenylmethane (TAPM) and 3,3',4,4'-tetraaminodiphenylsulfone (TAPSONE) and the two Schiff-bases *N,N',N'',N'''*-tetrasalicylidene-3,3',4,4'-tetraaminodiphenylmethane (H_4tstm) and *N,N',N'',N'''*-tetrasalicylidene-3,3',4,4'-tetraaminodiphenylsulfone (H_4tsts) are delineated herein along with different methods (Figure 1) for synthesizing the two new coordination polymers $[Ce(tstm)]_n$ and $[Ce(tsts)]_n$. Methods using a chelation displacement reaction between cerium(IV) octoxide, $Ce(OR)_4$, or tetrakis(acetylacetonato)cerium(IV), $Ce(acac)_4$, and the pre-

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® Abstract published in *Advance ACS Abstracts,* April 1, 1995.

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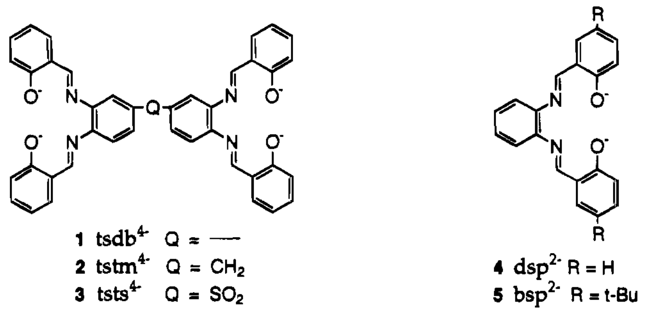
Chart 1. Ligand Structures



made Schiff-bases have been confirmed to be efficient ways to prepare these polymers. The polymers have been fractionated by methods commonly employed for organic polymers with molecular weights of the polymers determined by ^{1}H-NMR end-group analysis where *tert*-butyl groups introduced by an end capping reaction (Figure 2) act as spectroscopic handles. Molecular weight estimates have also been obtained by gel permeation chromatography and intrinsic viscosity in NMP.

Experimental Section

Syntheses. Reagents. Reagent grade and HPLC grade solvents and chemicals were used throughout; dimethyl sulfoxide, DMSO, was stirred for 2 days with barium oxide and then fractionally distilled over calcium hydride under reduced pressure; *N*-methylpyrrolidone, NMP, and *N,N*-dimethylformamide, DMF, were purified following literature procedures;[16] and salicylaldehyde, Hsal, was distilled under reduced pressure.

***N,N'*-Disalicylidene-1,2-phenylenediamine, H$_2$dsp.** H$_2$dsp was prepared by the condensation of 1,2-phenylenediamine with salicylaldehyde (1:2 mol stoichiometric ratio) in methanol at room temperature similar to earlier procedures.[17-19] ^{1}H-NMR (CDCl$_3$) [δ, ppm (relative intensity)]: 12.4 (singlet [s], 2), 8.6 (s, 2), 7.5–7.1 (multiplet [m], 8), 7.1–6.8 (m, 4).

***N,N'*-Bis-5-*tert*-butylsalicylidene-1,2-phenylenediamine, H$_2$bsp.** The preparation of H$_2$bsp is provided in our earlier reference.[13] ^{1}H-NMR (CDCl$_3$): 12.03 (s, 2), 8.63 (s, 2), 7.4–6.9 (m, 10), 1.31 (s, 18).

Tetrakis(2,4-pentanedionato)cerium(IV), Ce(acac)$_4$. This compound, where acac$^-$ is the anion of 2,4-pentanedione, was prepared according to the literature.[20] Mp: 150–151 °C. ^{1}H-NMR (CDCl$_3$): 5.3 (s, 1), 1.9 (s, 6).

Tetrakis(salicylaldehydato)cerium(IV), Ce(sal)$_4$. This compound, where sal$^-$ is the anion of salicylaldehyde, was prepared according to the literature.[13] ^{1}H-NMR (DMSO-*d*$_6$): 10.1 (s, 4), 7.6–7.3 (m, 8), 6.9–6.3 (m, 8).

Cerium(IV) *n*-Octoxide, Ce(OR)$_4$. This compound, where OR$^-$ is the octoxide anion, was prepared by a modified literature method.[21] *n*-Octanol (5.2 g, 40 mmol) was added to a solution of 5.48 g (10 mmol) of (NH$_4$)$_2$Ce(NO$_3$)$_6$ in 20 mL of dry methanol. Then, a 25% sodium methoxide solution (60 mmol of NaOCH$_3$ freshly prepared by dissolving 1.4 g of Na metal in 15 mL of dry methanol) was added to the solution under N$_2$. A bright yellow precipitate formed immediately. The mixture was diluted with 25 mL of dry toluene and stirred at 50 °C for 8 h. Methanol was completely removed from the reaction mixture by distillation of the system at 73 °C under N$_2$ overnight, and 25 mL of dry toluene was added to the solution, which was then stirred at 50 °C for an additional 2 h. Sodium nitrate was removed by filtration and washed with toluene (five 8-mL portions). The toluene was completely removed by distillation at 40 °C under reduced pressure for 1 day. The resulting product, an orange-red oil, was obtained with a yield of 6.5 g, 99%. Anal. Calcd for Ce(OC$_8$H$_{17}$)$_4$: C, 58.50; H, 10.43. Found: C, 58.48; H, 11.09. ^{1}H-NMR (CDCl$_3$): 0.89 (triplet[t], 3); 1.29 (s, 12), 3.62, (t, 2).

3,3',4,4'-Tetraaminodiphenylmethane, TAPM. With stirring, 4,4'-diaminodiphenylmethane (75.0 g, 383 mmol, Aldrich) was dissolved in 300 mL of glacial acetic acid at 70 °C, and then 75 mL of acetic anhydride was added dropwise. Then the mixture was heated under reflux conditions for 2 h. The mixture was cooled to room temperature and filtered to isolate the white precipitate of 4,4'-diacetamidodiphenylmethane, which was washed with methanol (100 mL) followed by diethyl ether (50 mL) and dried *in vacuo* at 100 °C. Yield: 93 g (90%). Mp: 232–236 °C (lit. 228–230, 234–236 °C).[22] ^{1}H-NMR (DMSO-*d*$_6$): 2.02 (s, 6); 3.81 (s, 2); 7.10 (doublet [d], 4); 7.48 (d, 4); 9.82 (s, 2).

4,4'-Diacetamidodiphenylmethane (75.0 g, 256 mmol) was stirred in 600 mL of acetic anhydride at 10 °C. With magnetic stirring and external cooling, 68 mL of concentrated HNO$_3$ was added at a rate such that the temperature in the reaction flask did not exceed 15 °C. (Precise thermal control is necessary to avoid polynitration.) Filtration of the canary yellow slurry allowed isolation of the 3,3'-dinitro-4,4'-diacetamidodiphenylmethane product. The crude product was washed with methanol until the filtrate was acid free and was then allowed to air dry. Yield: 100 g (containing some acetic anhydride). [The solid can be recrystallized from 500 mL of hot dimethylacetamide, washed with 150 mL of methanol and dried *in vacuo*. Yield: 47.9 g (48%). However, a much higher overall yield results when the crude product is deacetylated directly.] ^{1}H-NMR (DMSO-*d*$_6$): 2.05 (s, 6); 4.09 (s, 2); 7.56 (s, 4); 7.88 (s, 2); 10.17 (s, 2).

The previously isolated 3,3'-dinitro-4,4'-diacetamidodiphenylmethane (100 g of crude product) was added to a methanolic KOH solution (47.5 g of KOH in 150 mL of methanol) with magnetic stirring, and the mixture was heated under reflux conditions. After 30 min, 65 mL of distilled water was added and the system heated under reflux conditions for another hour. The mixture was then chilled with an external ice bath. Filtration of the mixture gave the maroon deacetylated 3,3'-dinitro-4,4'-diaminodiphenylmethane product. Yield: 67.0 g (68% based on 4,4'-diacetamidodiphenylmethane). ^{1}H-NMR (DMSO-*d*$_6$): 3.67 (s, 2); 5.23 (s, broad, 4); 6.79 (d, 2); 7.16 (d of d, 2); 7.73 (d, 2).

Under argon, 60 g (316 mmol) of SnCl$_2$ was stirred in 100 mL of concentrated HCl at 0 °C. 3,3'-Dinitro-4,4'-diaminodiphenylmethane (10.0 g, 34.7 mmol) was added with stirring. After heating the solution under reflux for 1 h, about 1 g of decolorizing carbon (Nuchar) was added and reflux was continued for 30 min more. The hot mixture was filtered and the pale yellow acidic filtrate containing the hydrochloride salt of the tetraamine was treated dropwise, with stirring and external cooling, with a degassed solution of 110 g of NaOH in 200 mL of distilled H$_2$O. The final pH of the mixture was about 12. The resulting gray solid, which contained the crude tetraamine and occluded tin hydroxide, was filtered. The solid was recrystallized from 250 mL of degassed H$_2$O after the addition of decolorizing carbon, dried at 100 °C *in vacuo*, and kept under an inert atmosphere of N$_2$ or Ar to avoid oxidation of the amine groups. Yield: 6.5 g (82%). Mp = 132 °C (uncorrected); lit.[23] mp = 137–139 °C. ^{1}H-NMR (DMSO-*d*$_6$): 3.42 (s, 2); 4.25 (s, broad, 8); 6.2 (m, 6).

***N,N',N'',N'''*-Tetrasalicylidene-3,3',4,4'-tetraaminodiphenylmethane, H$_4$tstm.** 3,3',4,4'-Tetraaminodiphenylmethane (0.838 g, 3.67 mmol) was added to neat salicylaldehyde (10 mL, 95.5 mmol) at 75 °C. After the mixture was heated at this temperature for 2 h, 30 mL of methanol was introduced to the yellow reaction solution and the resulting mixture was heated under reflux conditions for 30 min. The system was then chilled to below 0 °C and filtered to isolate the crude Schiff-base ligand. Purification was accomplished by dissolution of the ligand in 25 mL of CH$_2$Cl$_2$ and precipitation with 100 mL of petroleum ether. Yield: 2.07 g (87%, or 43% overall, based on the original diamine). Anal. Calcd for C$_{41}$H$_{32}$N$_4$O$_4$: C, 76.36; H, 5.01; N, 8.70. Found: C, 76.44; H, 5.14; N, 8.74. Mp = 195 °C (uncorrected). ^{1}H-NMR (DMSO-*d*$_6$): 4.10 (s, 2); 6.91–7.68 (m, 22); 8.92 (s, 4); 12.89–13.04 (m, <4).

3,3',4,4'-Tetraaminodiphenylsulfone, TAPSONE, was prepared via a modification of a literature method.[24] 4,4'-Diaminodiphenylsulfone

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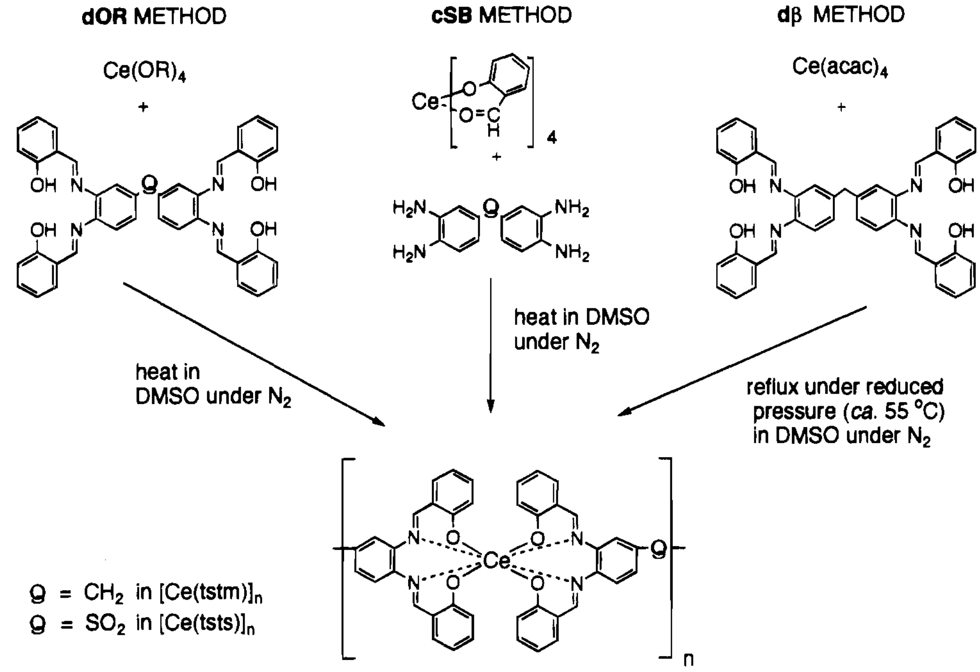

Figure 1. Three methods for the preparation of cerium(IV) coordination polymers.

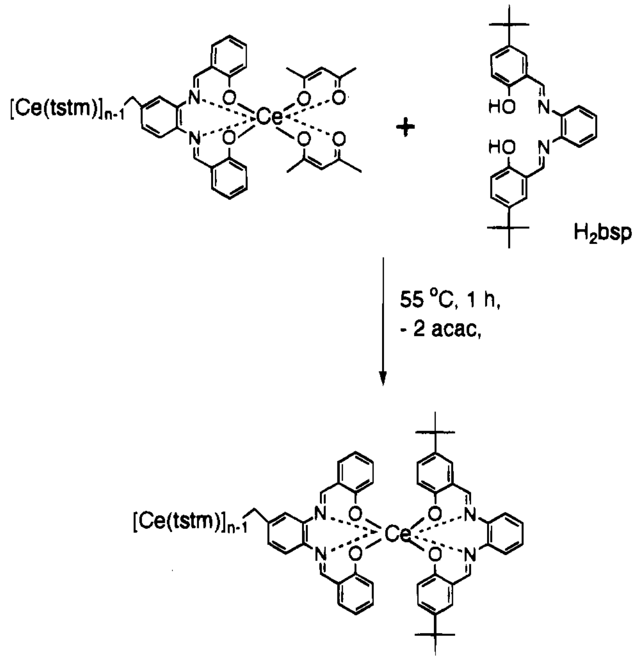

Figure 2. End-capping reaction of $[Ce(tstm)]_n$ polymers synthesized by the **dβ** method. Analogous reactions replace the two sal$^-$ ligands from the "cerium" ends of polymers prepared by the **cSB** method and the two *n*-octoxide ligands from polymers prepared by the **dOR** method.

(Aldrich) was acetylated by dissolving 50.00 g (202 mmol) of the diamine in 200 mL of glacial acetic acid at 75 °C and the subsequent addition of 40 mL of acetic anhydride. The resulting mixture was heated under reflux conditions for 2 h, cooled to room temperature, and filtered. The yield of the diacetamidodiphenylsulfone product after washing with diethyl ether and air drying was 65.8 g, 98%. ^{1}H-NMR (DMSO-d_6): 2.07 (s, 6); 7.74–7.85 (m, 6); 10.32 (s, 2).

Nitration and subsequent deprotection of the acetylated substrate was accomplished by the method of Stille and Arnold.[24] Yield: 77% of the dinitrodiamine product. ^{1}H-NMR (DMSO-d_6): 7.09 (d, 2); 7.77 (d, 2); 8.08 (s, broad, 2); 8.44 (s, 2).

Reduction of the above dinitro compound with tin(II) chloride yielded the corresponding tetraamine as follows: $SnCl_2{\cdot}2H_2O$ (20 g, 88.65 mmol) was dissolved in concentrated HCl (35 mL) in a 200-mL Schlenk flask under argon. To this solution, 3,3′-dinitro-4,4′-diamidodiphenylsulfone dihydrochloride (3.00 g, 7.3 mmol) was added and the reaction mixture was heated under reflux conditions under argon for 2 h. Approximately 1 g of decolorizing carbon was added to the reaction solution and the system was heated under reflux for 1 h more. The mixture was filtered while hot, and the colorless acidic filtrate was cooled to room temperature under argon and added dropwise to a degassed solution of 25 g of NaOH in 50 mL of H_2O in a 250-mL Schlenk flask under argon via a pressure equalizing dropping funnel with magnetic stirring while being cooled externally with an ice bath. The resulting gray mixture was filtered to obtain the crude 3,3′,4,4′-tetraaminodiphenylsulfone product. This solid was recrystallized from 125 mL of degassed H_2O with activated charcoal treatment to yield 1.61 g (79%) of the tan product. Mp = 174 °C (uncorrected), lit.[24] mp = 175–177 °C. ^{1}H-NMR (DMSO-d_6): 4.79 (s, broad, 4H); 5.20 (s, broad, 4H); 6.45–6.89 (m, 6H).

***N,N′,N″,N‴*-Tetrasalicylidene-3,3′,4,4′-tetraaminodiphenylsulfone, H_4tsts.** 3,3′,4,4′-Tetraaminodiphenylsulfone (0.7461 g, 2.68 mmol) was added to 10 mL (95.5 mmol) of neat salicylaldehyde at 100 °C. After 30 min, 30 mL of methanol was added to the yellow solution, which was heated under reflux for 30 min and then chilled to below 0 °C and filtered. The crude ligand was purified by sequential washes with hot absolute ethanol, toluene, and diethyl ether (20 mL each). Yield: 1.58 g, 85%. Anal. Calcd for $C_{40}H_{30}N_4O_6S$: C, 69.15; H, 4.35; N, 8.07; S, 4.61. Found: C, 68.9; H, 4.16; N, 8.08; S, 4.52. Mp = 254 °C (uncorrected). ^{1}H-NMR (DMSO-d_6): 6.83–8.17 (m, >22H); 8.94 (s, 2H), 9.06 (s, 2H); 12.34, (s, <2H); 12.62, (s, <2H).

$[Ce(tstm)]_n$ Polymers. The Alkoxide Displacement (dOR) Method in DMSO. $Ce(OR)_4$ (1.0000 g, 1.524 mmol) in 5 mL of dry dichloromethane was added dropwise to a solution of 0.9916 g (1.540 mmol) of H_4tstm [H_4tstm:$Ce(OR)_4$ mole ratio = 1.00:0.99] in DMSO (40 mL) at 70 °C under N_2. A dark red solution was obtained immediately. The mole ratio of H_4tstm:$Ce(OR)_4$ was adjusted to 1.00:1.00 and then to 1.00:1.01 by the addition of 0.0101 g (0.0154 mmol) aliquots of $Ce(OR)_4$ at 8 h intervals. After a total reaction time of 24 h, the cerium ends of the polymer chains were capped by the addition of a solution of 0.1500 g (0.3505 mmol) of H_2bsp in 5 mL of dichloromethane to the reaction solution. The end-capping reaction was allowed to proceed for 40 min at 70 °C. Precipitation of the polymer was accomplished by dilution of the reaction system to 250 mL with methanol. The product was filtered, washed with methanol, and dried at 100 °C *in vacuo*. Yield: 0.84 g, 70%.

The crude polymer was fractionated by dissolving 0.80 g of product in DMSO (20 mL) followed by precipitation with a methanol/toluene nonsolvent (2:1 by vol), which was added slowly until a persistent

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Table 1. Synthetic Results for $[Ce(tstm)]_n$ and $[Ce(tsts)]_n$

method[a]	fractionation batch	% yield[b]	$\overline{M}_n$[c]	viscosity[d]	$\overline{DP}$[e]
		$[Ce(tstm)]_n$			
dOR	1	31	28 000	18.9	72
	2	19	21 500	15.4	55
	3	18	18 000	14.0	46
cSB	1	35	13 000	11.0	33
d*β* (trial 1)	1	24	22 800	16.8	58
	2	14	15 600	12.5	40
	3	12	12 500	9.80	32
	4	14	10 700	9.40	27
	1*[f]		26 500	18.0	68
d*β* (Trial 2)	1	16	20 000	14.7	51
	2	16	16 500	12.7	42
	3	20	13 000	10.8	33
	4	20	12 900	10.5	33
		$[Ce(tsts)]_n$			
dOR	1	38	31 500	18.5	76
	2	18	20 000	12.0	48
	3	15	13 000	9.65	31
cSB	1	28	21 000	12.6	51
	2	35	12 500	9.35	30

[a] $\overline{M}_n$ from NMR end group analysis before fractionation; for $[Ce(tstm)]_n$, 14 500 by **dOR**, 7000 by **cSB**, and 12 000 and 10 500 for trials 1 and 2 by **d*β*** method, respectively; for $[Ce(tstm)]_n$, 13 500 by **dOR** and 11 000 by **cSB**. [b] Yield based on weight of sample used for fractionation. [c] $\overline{M}_n$ based on results from NMR end group analysis. [d] Intrinsic viscosity (cm^3/g) in NMP at 30.00 ± 0.02 °C. [e] Average degree of polymerization based on NMR end-group analysis. [f] Sample 1* obtained by stirring sample 1 in trial 1 in THF.

precipitate was observed, and then an additional 15 mL of the nonsolvent was added and the first fraction of the $[Ce(tstm)]_n$ polymer was filtered. To the filtrate, 20 mL more of nonsolvent was added to induce the precipitation of another fraction of $[Ce(tstm)]_n$. The above technique was repeated several times to isolate fractions with different molecular weights. The results are listed in Table 1.

The Alkoxide Displacement (dOR) Method in THF. $Ce(OR)_4$ (0.5244 g, 0.7993 mmol) in 5 mL of THF was added dropwise to a solution of 0.5200 g (0.8074 mmol) of H_4tstm [$H_4tstm:Ce(OR)_4$ mole ratio = 1.00:0.99] in 80 mL of THF at 65 °C under N_2. A dark red solution was obtained immediately, and the formation of a brown precipitate in the reaction system was observed after 10 min of reaction. At 8-h intervals the $H_4tstm:Ce(OR)_4$ mole ratio was adjusted to 1.00: 1.00 and then to 1.00:1.01 by the addition of aliquots of $Ce(OR)_4$. After 24 h, the mixture was filtered, washed with methanol, and dried at 65 °C *in vacuo*. Yield: 0.20 g, 32%. The mother liquor was placed in a beaker, and the solvent was allowed to evaporate at 1 atm in air. A lustrous dark red film was obtained.

The Schiff-Base Condensation (cSB) Method. 3,3′,4,4′-Tetraaminodiphenylmethane (0.3480 g, 1.513 mmol) was added to a solution of $Ce(sal)_4$ (0.9347 g, 1.495 mmol) [$TAPM:Ce(sal)_4$ mole ratio = 1.00: 0.99] at 55 °C under N_2. The mole ratio of $TAPM:Ce(sal)_4$ was adjusted to 1.00:1.00 and then to 1.00:1.01 by the addition of 0.0101 g (0.0162 mmol) of $Ce(sal)_4$ at 8-h intervals. After 24 h, the cerium ends of the polymer chains were capped by the addition of a solution of 0.2000 g of H_2bsp (0.4672 mmol) in 5 mL of DMSO to the reaction solution. The end-capping reaction was allowed to proceed for 1 h under the same conditions. Precipitation of the polymer was accomplished by the addition of 100 mL of methanol. The product was filtered, washed with methanol, and dried at 100 °C *in vacuo*. Yield: 0.78 g, 66%.

For fractionation, 0.700 g of the crude polymer was stirred in 20 mL of DMSO. The resulting mixture was filtered, and 50 mL of methanol was added to the filtrate to precipitate the high molecular weight fraction. The materials isolated were washed with methanol and dried at 100 °C *in vacuo*. Yield: 0.10 g, 14% (insoluble product); 0.30 g, 42% (precipitated from methanol).

The *β*-Diketone Displacement (d*β*) Method. Trial 1. $Ce(acac)_4$ (1.2369 g, 2.3059 mmol) was added to a solution of H_4tstm (1.5000 g, 2.3291 mmol) in 70 mL of DMSO at 55 °C under N_2 ($H_4tstm:Ce(acac)_4$ mole ratio = 1.00:0.99). The resulting solution was heated under reflux for 8 h at 55 °C under reduced pressure. At 8 h intervals, $Ce(acac)_4$ (0.0124 g, 0.0232 mmol) was added to the solution to adjust the ratio of $H_4tstm:Ce^{IV}$ to 1.00:1.00 and then to 1.00:1.01. After 24 h, 0.4000 g (0.9346 mmol) of H_2bsp in 5 mL of DMSO was added to cap the cerium ends of the polymer chains. The end-capping reaction was allowed to proceed for 1 h under these conditions. The polymer was precipitated by the addition of 200 mL of methanol, filtered, washed with methanol, and dried *in vacuo* at 100 °C. Yield: 1.4 g, 81%. The resulting polymer was fractionated by dissolution in 45 mL of DMSO and precipitated in portions using a toluene/methanol nonsolvent precipitant as described in the alkoxide displacement (dOR) method. Results for the fractionated polymers are listed in Table 1.

Trial 2. All conditions and reagents are the same as in trial 1. In this case, however, the amount of $Ce(acac)_4$ was kept constant and the previously delineated mole changes were affected by the gradual addition of H_4tstm. The results are listed in Table 1.

Anal. Calcd for $CeC_{41}H_{28}N_4O_4{\cdot}0.15C_2H_6SO$: C, 62.6; H, 3.65; N, 7.07, DMSO, 1.48. Found: C, 62.8, H, 3.87; N, 7.05; DMSO, 1.63.

$[Ce(tsts)]_n$ Polymers. The Alkoxide Displacement (dOR) Method. $Ce(OR)_4$ (1.0320 g, 1.5731 mmol) dissolved in 5 mL of dichloromethane was added to a solution of H_4tsts (1.1029 g, 1.589 mmol) in 40 mL of DMSO at room temperature under N_2. [$H_4tsts:Ce(OR)_4$ mole ratio = 1.00:0.99] Under these conditions, H_4tsts remains insoluble; after 30 min at 95 °C, however, a dark red solution was obtained. The temperature was reduced to 55 °C and a solution was maintained. The reaction was allowed to proceed at this temperature for another 8 h before the ratio of $H_4tsts:Ce(OR)_4$ was adjusted to 1.00: 1.00 and then to 1.00:1.01 by adding $Ce(OR)_4$ to the solution at 8-h intervals. After 24 h, 0.1800 g (0.421 mmol) of H_2bsp in 5 mL of dichloromethane was added to cap the cerium ends of the polymer chains. After 40 min of end capping, precipitation of the polymer was accomplished by dilution of the reaction system to 250 mL with methanol. The product was filtered, washed with methanol, and dried in vacuo at 100 °C. Yield: 0.80 g, 60%.

The Schiff-Base Condensation (cSB) Method. 3,3′,4,4′-Tetraaminodiphenylsulfone (0.5118 g, 1.8278 mmol) was added to a solution of 1.1521 g (1.8463 mmol) of $Ce(sal)_4$ in 40 mL of DMSO at 65 °C under N_2 [$Ce(sal)_4$:TAPSONE mole ratio = 1.00:0.99]. At 8-h intervals, TAPSONE was added to the solution to adjust the ratio of $Ce(sal)_4$:TAPSONE to 1.00:1.00 and then to 1.00:1.01. After 24 h, the cerium ends of the polymer chains were capped by the addition of 0.2000 g (0.4672 mmol) of H_2bsp in 5 mL of dichloromethane to the reaction solution. The end-capping reaction was allowed to proceed for 40 min at 65 °C. Precipitation of the polymer was accomplished by dilution of the reaction system to 250 mL with methanol. The product was filtered, washed with methanol, and dried *in vacuo* at 100 °C. Yield: 0.76 g, 50%.

Fractionation of $[Ce(tsts)]_n$ was similar to that for $[Ce(tstm)]_n$ described above. The results are given in Table 1. Anal. Calcd for $CeC_{40}H_{26}N_4O_4SO_2{\cdot}0.4C_2H_6SO$: C, 56.9; H, 3.30; N, 6.50, DMSO, 3.62. Found: C, 58.0, H, 3.36; N, 6.47; DMSO, 3.74.

Extent of the Reaction of $Ce(OR)_4$ and H_2dsp. $Ce(OR)_4$ (0.1868 g, 0.2848 mmol) and 0.1800 g (0.5696 mmol) of H_2dsp were dissolved in 5 mL of $CDCl_3$ or DMSO-d_6 with stirring. The resulting solutions were periodically checked by ^1H-NMR to follow the extent of this reaction in which $Ce(dsp)_2$ is formed. In the case of DMSO-d_6 as solvent, temperatures of 50 and 70 °C were used.

Physical Measurements. Proton Fourier-transform nuclear magnetic resonance (FT-NMR) measurements were taken with Varian Model XL 80 and XL 200 spectrometers. The bsp^{2-} end-capped polymer *tert*-butyl protons (average of 18 per chain at 1.1−1.3 ppm) were integrated against the aromatic and aldimine protons in the $tstm^{4-}$ or $tsts^{4-}$ ligands (26 protons per $tstm^{4-}$ or $tsts^{4-}$ unit). The average number of monomeric units (n_{mer}) vs the average number of bsp^{2-} 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 $\overline{DP} = 2(n_{mer}/n_e)$.[25] Several thousand aquisitions were used to obtain reliable results for the high $\overline{M}_n$ polymers.

Gel permeation chromatography (GPC) measurements were conducted in NMP with a Waters Model 6000A pump, a Model R 401

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differential refractometer, and a linear 7 mm pore size ultrastyragel column. The column was calibrated with polystyrene standards in NMP.

Viscosity measurements were conducted in an Ubbelohde type viscometer in NMP solution at 30.00 ± 0.02 °C. Kraemer's approximation,[26] $[\eta]_{inh} = (1/c)\ln(t_{soln}/t_{solv})$ [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)], was used to determine the inherent viscosities of the $[Ce(tstm)]_n$ and $[Ce(tsts)]_n$ polymers. The intrinsic viscosities have been obtained by extrapolation of the inherent viscosity values to zero concentration.

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 a heating rate of 20 °C/min. Both systems include Perkin-Elmer thermal analysis data stations and system 4 and 7 microprocessors, respectively.

Results and Discussion

Synthesis of Ce(OR)$_4$. Cerium(IV) alkoxides have been reported previously,[21,27,28] but several factors are necessary for the successful preparation of cerium(IV) octoxide from ceric ammonium nitrate:

$$[Ce(NO_3)_6]^{2-} + 4CH_3O^- \rightarrow Ce(OCH_3)_4 + 6NO_3^- \tag{1}$$

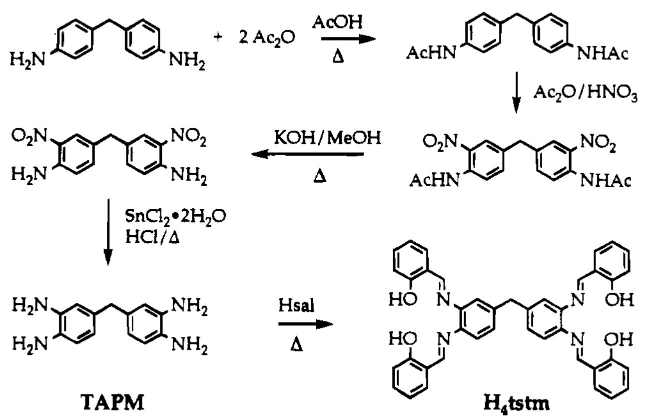
$$2NH_4^+ + 2CH_3O^- \rightarrow 2CH_3OH + 2NH_3\uparrow \tag{2}$$

$$Ce(OCH_3)_4 + 4C_8H_{17}OH \rightarrow Ce(OC_8H_{17})_4 + 4CH_3OH \tag{3}$$

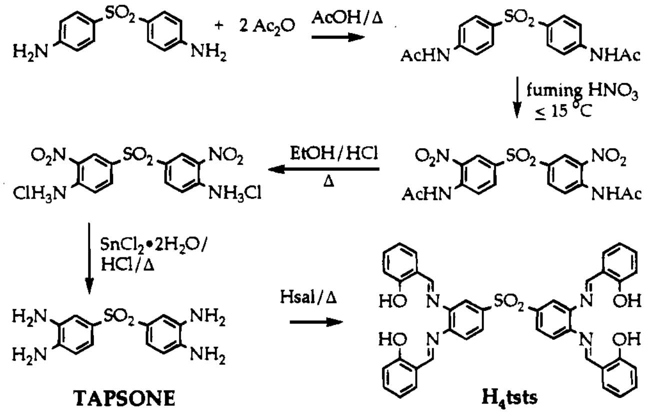
The purity of the sodium methoxide used in the synthesis is important; e.g., a fresh sodium methoxide solution prepared from freshly cut sodium metal dissolved in dry methanol is suitable. The methanol produced by reaction of the cerium methoxide intermediate with *n*-octanol must be completely removed to drive reaction 3 to completion. We used an overnight distillation at 73 °C. Pure product from this stoichiometrically exact synthesis can only be obtained after all the methoxide is replaced by octoxide. Otherwise, the residual *n*-octanol, which has a high boiling point, is difficult to separate from the product, which is an orange oil. The complete removal of toluene from the product can be accomplished by vacuum distillation at about 40 °C. The complete removal of toluene from the product can be confirmed by ^{1}H-NMR.

Ligand Synthesis. The two tetraamines were synthesized using modified literature procedures as noted in the experimental section. The details are shown in reaction Schemes 1 and 2. The most difficult step proved to be the nitration of the methylene bridged system. In order to get one nitro group on each ring of the protected diaminodiphenylmethane in good yield, concentrated nitric acid was necessary, but to avoid multinitration on either ring, the temperature had to be kept below 15 °C. Also, in order to get the tetrasalicylidene Schiff-bases from the tetraamines, the Schiff-base condensation reactions were conducted in neat salicylaldehyde. Precipitation of partially condensed materials with less than four salicylidenes/ligand occurred when the reactions were attempted in a variety of alcohols or toluene. It also proved difficult to remove the desired product from DMSO, when it was used as a solvent; thus, the neat aldehyde proved the best solvent.

Scheme 1



Scheme 2



Synthesis of Polymers. The syntheses of the $[Ce(tstm)]_n$ and $[Ce(tsts)]_n$ coordination polymers involve either ligand displacement or Schiff-base condensation polymerizations. Three different byproducts, i.e. octyl alcohol, H_2O, and Hacac, are formed in the alkoxide displacement (dOR), Schiff-base condensation (cSB), and β-diketone displacement (dβ) methods, respectively. Two factors greatly affect displacement and condensation polymerizations.[25] One is the extent of reaction, which should be as close to 100% as possible; the other is the stoichiometric ratio of reactants, which should be as close to 1:1 as possible in these systems. Reaction conditions in different methods in our syntheses were designed to maximize the extent of reaction. Stoichiometric control of reactants was accomplished by gradually changing the ratio of reactants during the reactions to experimentally reach the theoretically best stoichiometric ratio of 1:1. A fundamental concept of this synthetic technique is based on the fact that the complexes formed by tetradentate ligands with Ce^{IV} ions are inert toward further substitution in solution. When the ratio of starting reactants reaches 1:1 and enough time is allowed for the reaction to go to completion, further addition of small amounts of either reactant will not significantly effect the molecular weights of the polymers. Normal fractionation methods used for organic polymers work quite well for the new coordination polymers. Polymer fractions with higher molecular weights precipitated from solution before those with smaller ones when nonsolvent is added. The polymers fractionated by the methods described here have narrow molecular weight distributions as shown by GPC (Figure 3); thus more reliable results can be obtained when using the viscosity data from these fractionated polymers for determining the Mark–Houwink equation constants.

DMSO was used as a solvent for these syntheses because of its good ability as a polymer solvent[29,30] and its excellent water

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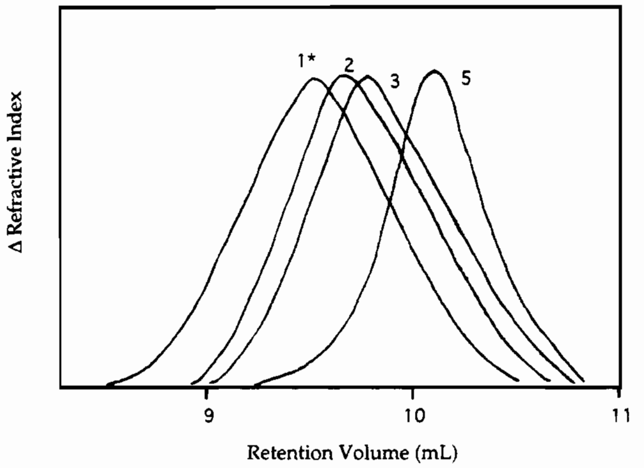

Figure 3. Gel permeation chromatographic results for the fractionated [Ce(tstm)]$_n$ polymers by the **dβ** method (Trial 1). On the basis of the polystyrene standards, $\overline{M}_n$ = 22 700 (1*), 15 000 (2), 12 000 (3), and 6500 (5). On the basis of NMR end-group analysis, $\overline{M}_n$ = 26 500 (1*), 15 600 (2), 12 500 (3), and 7500 (5).

scavenging ability derived from its tendency to form strong hydrogen bonds with water.[13,31,32]

Syntheses by Alkoxide Displacement. The Alkoxide Displacement (dOR) Method. The preparation of [Ce(tstm)]$_n$ and [Ce(tsts)]$_n$ using the ligand displacement reaction between Ce(**OR**)$_4$, specifically Ce(OC$_8$H$_{17}$)$_4$, and the preformed Schiff-base (the **dOR** method) gave the most satisfactory results for both species, even though the synthesis of lanthanide coordination polymers through a metal alkoxide and a premade Schiff bases had not been reported previously. This facile method also avoids any reduction of Ce^{IV} even though the temperature was kept at 70 °C in the [Ce(tstm)]$_n$ synthesis and initially at 95 °C in the [Ce(tsts)]$_n$ synthesis. The other advantage is that after the tetradentate Schiff-bases replace the monodentate alkoxides, the reverse reaction is highly unfavorable, a result of the so-called chelate effect. Cerium(IV) octoxide was chosen because of its high stability to hydrolysis. Although alkoxides are usually thought to be good leaving groups and a high reactivity was reported for ceric alkoxides (addition of acetylacetone instantly converts the alkoxides into ceric acetylacetonate),[21] the results from the extent of reaction study between Ce(OR)$_4$ and H$_2$dsp show that high temperatures (at least 65 °C) are required to complete this reaction in a reasonable time frame (Figure 4). The bulky *n*-octylalkoxy groups provide an effective barrier to the Ce^{IV} ions, which presumably accounts for this inertness to hydrolysis and displacement reactions.

Molecular weight analyses (Tables 1 and 2) show that the **alkoxide displacement (dOR)** method is a very effective way to prepare Ce^{IV} coordination polymers. The [Ce(tstm)]$_n$ polymers prepared by this method were determined to have $\overline{M}_n$ values of around 14 000 to 14 500 **prior** to fractionation. A similar $\overline{M}_n$ value (13 500) was also obtained for the [Ce(tsts)]$_n$ polymer synthesis by this method, although the reaction temperature was kept at 55 °C after an initial 30 min at a higher temperature to help dissolve the ligand. Results from the electronic spectra vs time (not shown) provide evidence that the polymers are much more stable in solution than the corresponding Schiff-bases, especially at high temperatures.

An attempt to estimate $\overline{M}_n$ for the polymers by end-group analyses using the original *n*-octoxy end group (instead of introducing the bsp^{2-} end group) led to $\overline{M}_n$ results of greater than 30 000, again prior to fractionation. Apparently, a sizable fraction of the alkoxide end groups had hydrolyzed prior to the NMR experiment.

When the **alkoxide displacement (dOR)** reaction was attempted in THF, the spontaneously precipitated product contained some THF that could not be removed, even at 100 °C *in vacuo*, as confirmed by IR and ^{1}H-NMR spectroscopies. This product, when redissolved in NMP with heating, has an intrinsic viscosity of 9.6 cm^3/g, or a $\overline{M}_n$ of 11 000 based on the Mark–Houwink constants for [Ce(tstm)]$_n$. However, this method provides an excellent way to make polymer films because of the ease of evaporation of the THF solvent.

Syntheses by Schiff-Base Condensation. The Schiff-Base Condensation (cSB) Method. The condensation reaction providing a Schiff-base from the tetraamine and M(sal)$_4$ (the **cSB** method) works well for zirconium(IV) polymers and [Ce(tsdb)]$_n$.[13,31,32] However, the same polymerization reaction fails to give good results when applied to the [Ce(tstm)]$_n$ polymer synthesis. Reduction of Ce^{IV} always occurs with this method and is detectable by a fading of the dark red color of the cerium(IV) charge-transfer transitions during the reaction under N$_2$. This reduction cannot be avoided by lowering the reaction temperature. The dark red color returns when O$_2$ or dry air is introduced into the system and is accompanied by a dark brown precipitate in the reaction vessel. This precipitate does not redissolve in DMSO even at temperatures exceeding 100 °C. If O$_2$ or dry air are not introduced to system at the end of the reaction, adding methanol to the solution yields a precipitate that does not completely redissolve in DMSO. The molecular weight of the soluble polymer portion obtained by this method was only 7000 before fractionation and 13 000 after fractionation.

In the case of [Ce(tsdb)]$_n$, lowering the temperature below 55 °C avoided the reduction of cerium in the Schiff-base condensation (cSB) method.[13] On the other hand, the synthesis of [Ce(tsts)]$_n$ gave satisfactory results ($\overline{M}_n$ = 11 000 before fractionation) by this method, and no reduction was observed during the reactions, even though the temperature was kept as high as 65 °C. These results indicate a variable susceptibility to the oxidation/reduction reaction between Ce^{IV} ions and the tetraamines. The unavoidable oxidation of 3,3′,4,4′-tetraaminodiphenylmethane arises from the fact that it is the most vulnerable to oxidation among the three tetraamines, followed by 3,3′-diaminobenzidine and finally by 3,3′,4,4′-tetraaminodiphenylsulfone due to different functionalities on the amines. Reoxidation of Ce^{III} to Ce^{IV} by introducing O$_2$ or dry air into the system proceeds quickly because Ce^{IV} ions are greatly stabilized in the presence of tetradentate Schiff-base ligands as shown by a shift in the reduction potential of Ce(dsp)$_2$/Ce(dsp)$_2^-$ = −0.529 V [aqueous Ce^{IV}/Ce^{III} = +1.20 V].[33]

The precipitate which forms spontaneously after reoxidation has a different structure from the [Ce(tstm)]$_n$ polymers and has an extra peak at 1261 cm^{-1} in its IR spectrum (Figure 5), an area of stretching vibrations of phenolic oxygen bonds (Ph–O).[13] Compared to the peak at 1302 cm^{-1}, the stretching vibration of the Ph–O bonds in [Ce(tstm)]$_n$, this extra lower field peak means that some of the Ph–O bonds are weaker than the others in the precipitate. These weaker Ph–O bonds are probably from Ph–O groups with oxygen atoms coordinated to two Ce^{IV} ions at the same time. The same situation was encountered in the Ln$_2$dsp$_3$ compounds, in which coordination

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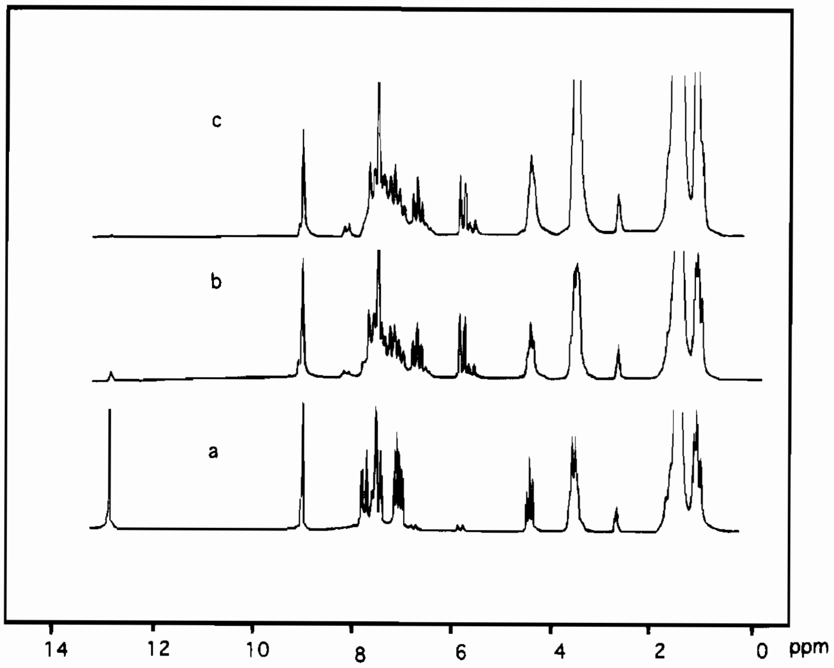

Figure 4. ^{1}H NMR spectra showing the extent of reaction for $Ce(OR)_4$ with premade H_2dsp Schiff base: (a) $Ce(OR)_4$ and H_2dsp in DMSO-d_6 after 1 h at 50 °C; (b) solution a after 1 h at 70 °C; (c) solution a after 3 h at 70 °C.

Table 2. Characterization of $[Ce(tstm)]_n$ and $[Ce(tsts)]_n$ Polymers

		GPC		^{1}H-NMR		
polymer and method	intrinsic viscosity[a]	retention vol[b]	$\overline{M}_n$[c]	rel intens[d]	$\overline{M}_n$[e]	T_g (°C)[f]
$[Ce(tstm)]_n$						
dOR method	18.9	9.42	23 500	52	28 000	157 (143)
cSB method	11.0	9.70	13 500	24	13 000	
dβ method						
trial 1	17.0	9.47	21 000	42	22 800	146 (140)
trial 2	15.0	9.55	18 000	37	20 000	143 (135)
$[Ce(tsts)]_n$						
dOR method	18.5	9.35	26 500	55	31 500	181 (166)
cSB method	12.6	9.65	16 000	36.5	21 000	177 (154)
$[Ce(tsdb)]_n$[g]	19.0	*h*	28 000	57	30 000	184 (169)
$[Zr(tsdb)]_n$[i]	20.0	*h*	30 000	337[j]	33 000	74 (66)
$[Zr(tsb)]_n$[k]	18.0	*h*	49 000			87[i] (77)[i]

[a] Intrinsic viscosity in cm^3/g in NMP at 30.000 ± 0.02 °C. [b] Retention volume (mL) in NMP at room temperature. [c] Polystyrene equivalent number-average molecular weight. [d] Relative intensities of the bridging ligand protons to bsp^{2-} *tert*-butyl protons. [e] $\mathbf{M}_n$ assuming average of one bsp^{2-} (or $dsdt^{2-}$) ligand per chain. [f] Glass transition temperature; onset temperature in parentheses; 20 °C/min heating rate. [g] Reference 13; **dβ** method synthesis. [h] Different column. [i] Reference 32; synthesis by **cSB** method. [j] Relative intensity of aromatic protons to $dsdt^{2-}$ methyl protons. [k] Reference 31; synthesis by **cSB** method.

of oxygen atoms to two Ln^{III} ions at the same time happens to one of the bridging ligands and an extra peak at 1283 cm^{-1} is observed.[34] For Ce^{IV} complexes, a lower stretching vibration frequency at 1261 cm^{-1} is expected because of stronger field exerted by higher 4+ charge on the Ce^{IV} ions. Destruction of some of the tetraamine by oxidation results in a slight excess of Ce^{IV} ions that provides an opportunity for the formation of Ce^{IV} bridges between adjacent polymer chains, which leads to a cross-linked structure in the coordination polymers and yields insoluble products.

Syntheses by Displacement of β-Diketone Ligands (dβ) Method. The **dβ** method, the displacement of the four β-diketone ligands from $Ce(acac)_4$ with the preformed Schiff-base $tstm^{4-}$ ligand works well at ≤55 °C with reflux conditions obtained under reduced pressure. If the reaction temperature is higher than 65 °C, some reduction of Ce^{IV} occurred as denoted by a gradual fading of the dark red color. When dry air or O_2 was introduced into the system, reoxidation of Ce^{III} to Ce^{IV} took place and the color returned to a dark red; however, no precipitate appeared in this reaction. The results (Table 1) also show that products obtained at ≤55 °C by approaching the stoichiometric end-point in either direction (trials 1 and 2) have comparable molecular weights as determined by end-group analysis (Tables 1 and 2). This means that the extent of reaction is not a function of which monomer is held constant during the reactant-ratio adjustment process.

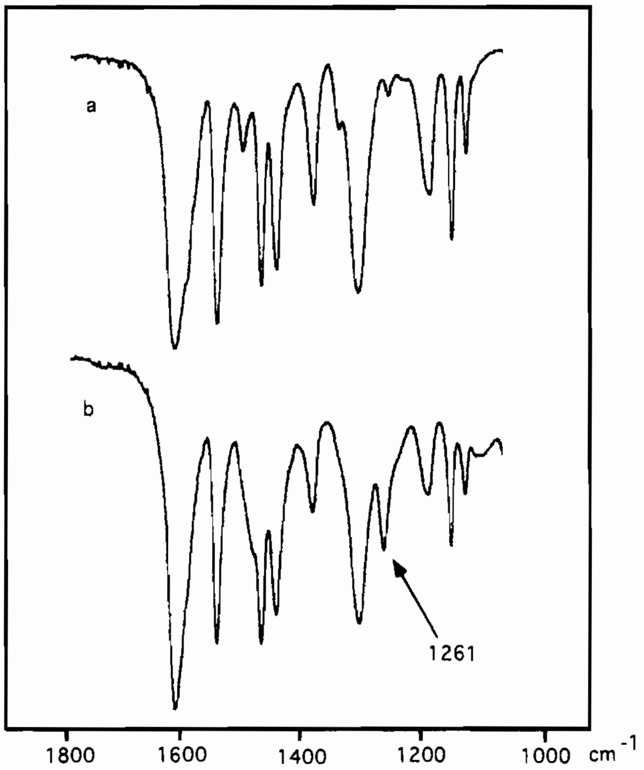

Figure 5. IR spectra (KBr pellet) of (a) the normal $[Ce(tstm)]_n$ polymer, and (b) the insoluble product from the **dSB** method.

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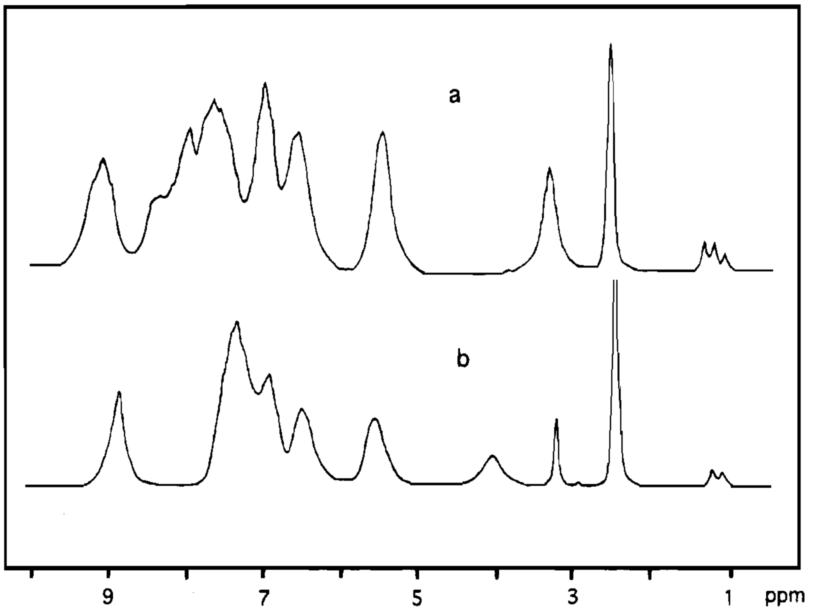

Figure 6. ^{1}H NMR spectra in DMSO-d_6 showing the *tert*-butyl signal of the end capping reagent for (a) an end-capped [Ce(tsts)]$_n$ polymer ($\overline{M}_n$ = 21 000), and (b) an end-capped [Ce(tstm)]$_n$ polymer ($\overline{M}_n$ = 22 800).

Synthesis using this chelation reaction between Ce(acac)$_4$ and a premade Schiff-base had been confirmed to be an effective way to prepare this type of coordination polymer.[13] The extent of reaction studies[13] showed that the displacement of the bidentate actylacetonate ligands by the tetradentate Schiff-base ligands takes place quite rapidly with the reactions proceeding smoothly at temperatures at or below 55 °C. Reflux under reduced pressure accelerates the ligand replacement polymerization reaction of acac$^-$ with tstm^{4-} by taking the advantage of volatility of acetylacetone.

Solubility of Compounds: [Ce(tstm)]$_n$ polymers have excellent solubility in DMSO, NMP, and DMF. The polymers dissolve quite well at room temperature and heating increases the solubility of the high $\overline{M}_n$ fractions. Polymers with number-average molecular weights of about 22 000 exhibit the following solubilities in DMSO at room temperature: ≥15.3, 27.0, and 41.9 g/L for [Ce(tsdb)]$_n$, [Ce(tsts)]$_n$, and [Ce(tstm)]$_n$, respectively. The solubilities of the [Ce(tstm)]$_n$ fractions are strongly affected by their molecular weights. Only a polymer with a low $\overline{M}_n$ can dissolve in THF and dichloromethane. This solubility difference provides another way to fractionate the polymers by removing low $\overline{M}_n$ fractions. On the basis of end group analysis, the $\overline{M}_n$ of the polymer in trial 1 was raised from 22 800 to 26 500 by stirring it in THF. The enhanced solubility of the higher $\overline{M}_n$ [Ce(tstm)]$_n$ fractions in THF and dichloromethane as compared to [Ce(tsdb)]$_n$,[13] are the result of the introduction of a flexible spacer into the each Schiff-base portion of the repeating unit. The introduction of the methylene group in the Schiff-base severs the conjugated system of the ligand and greatly reduces the rigidity of both the parent monomeric ligand and the resulting [Ce(tstm)]$_n$ polymer, and is manifested in the improved solubility of both species.

In contrast to the H$_4$tstm Schiff-base, which is freely soluble in dichlomethane and THF, H$_4$tsts exhibits poor solubility in all organic solvents at room temperature and is only soluble in DMSO at high temperatures (~110 °C). This behavior is similar to that of H$_4$tsdb.[13,32] The reason for this lower solubility may be the result of stronger interactions between the SO$_2$ groups with other Schiff base molecules relative to the CH$_2$ in H$_4$tstm. Again, similar to the H$_4$tsdb analogue, the solubility of the [Ce(tsts)]$_n$ polymers are dramatically higher than the parent Schiff-base. [Ce(tsts)]$_n$ can be dissolved at room temperature in solvents with high dielectric constants, while heating also increases the solubility for the high $\overline{M}_n$ fractions. [Ce(tsts)]$_n$ fractions with low $\overline{M}_n$ values do not dissolve in dichloromethane and THF. These effects on the solubility of the coordination polymers from these small spacing groups are secondary, however, to the reduction of stacking forces associated with the formation of macromolecules with large eight coordination metal centers in each repeating unit.

Films for the polymers that are only soluble in the high-boiling polar organic solvents can be obtained by allowing the solvent to slowly evaporate in air or by using high vacuum to slowly remove solvent at room temperature.

Extent of Reaction. The extent of reaction for the **alkoxide displacement (dOR)** method was investigated between H$_2$dsp and Ce(OR)$_4$ by using NMR spectroscopy with deuterated solvents and at two temperatures in DMSO-d_6. When CDCl$_3$ was used as a solvent, there was minimal reaction between H$_2$dsp and Ce(OR)$_4$ as shown by an NMR spectrum that consisted primarily of uncoordinated H$_2$dsp after 1 h of reaction. Similarly, with DMSO-d$_6$ as the solvent, when the temperature was kept at 50 °C for one hour, only a small percentage of the H$_2$dsp reacted with Ce(OR)$_4$ and is shown by the strong NMR spectral resonance at 12.8 ppm for the phenol protons of the neutral Schiff-base (Figure 4a). When the temperature was raised to 70 °C, the reaction proceeded quickly as shown by the NMR spectrum obtained after one hour of reaction. The spectrum shows a significant reduction in the phenolic resonance at 12.8 ppm and the appearance of peaks assignable to Ce(dsp)$_2$ (Figure 4b). The reaction was almost complete (≥99%) after 3 h at 70 °C; i.e., the NMR spectrum obtained is that of Ce(dsp)$_2$ plus that of *n*-octyl alcohol (Figure 4c). Extents of reaction for the Schiff-base condensation (cSB) and β-diketone displacement (dβ) methods have been investigated previously.[13] Again, the extent of reaction was >99% in each case under the conditions used for reactions in this study.

Polymer Molecular Weights. End-group analyses of the cerium polymers have been obtained by Fourier transform ^{1}H-NMR spectroscopy from the intensity of the *tert*-butyl proton signal (1.1−1.3 ppm) of the end-capping bsp^{2-} vs the signals associated with the Schiff-base protons (Experimental Section and Figure 6). H$_2$bsp has been confirmed to be a good end-capping reagent for these types of polymerization reactions.[13]

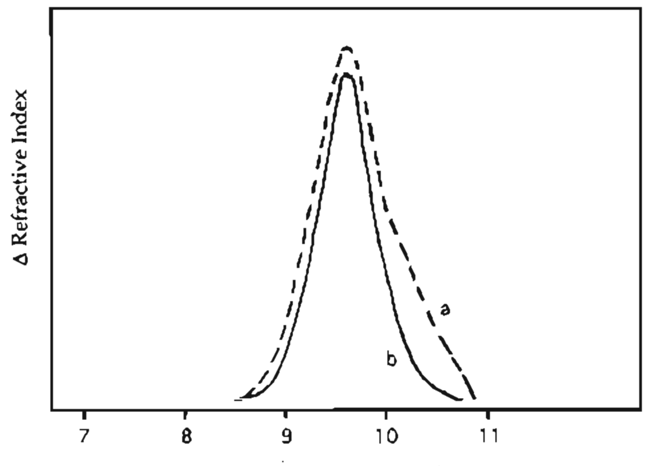

Figure 7. Gel permeation chromatographic results for (a) a $[Ce(tstm)]_n$ polymer ($\overline{M}_n$ = 21 000 based on polystyrene standards) before THF treatment, and (b) the same polymer after THF treatment ($\overline{M}_n$ = 22 700).

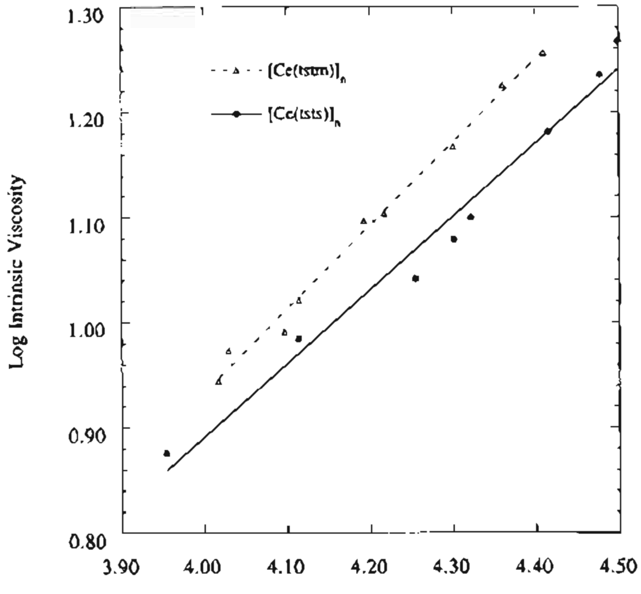

Figure 8. Composite Mark-Houwink plots for the $[Ce(tstm)]_n$ and $[Ce(tsts)]_n$ polymers.

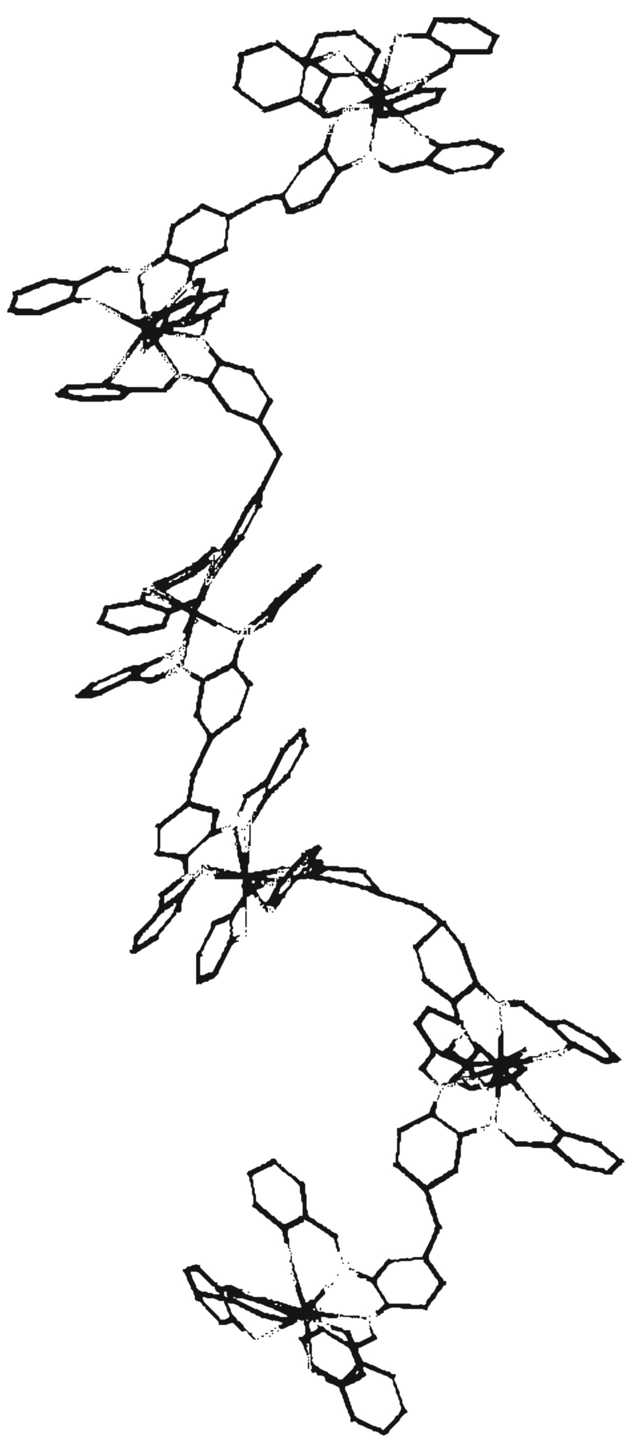

Figure 9. Molecular model representation of a short chain of a $[Ce(tstm)]_n$ polymer based on the known solid-state structure of $[Ce(dsp)_2]$.

The $\overline{M}_n$ values obtained from the NMR end-group analysis after fractionation are provided in Tables 1 and 2. At least one of the multiple peaks in the bsp^{2-} region (1.1−1.3 ppm) could be the result of coprecipitated bsp^{2-}; therefore, the results are conservative estimate of the true number-average molecular weights. (The unsymmetrical coordination of tetradentate ligands in the antiprismatic structure can account for at least two of the peaks in the 1.1−1.3 ppm region.)

Gel permeation chromatographic results for the fractionated $[Ce(tstm)]_n$ and $[Ce(tsts)]_n$ polymers vs polystyrene standards in NMP are noted in Table 2, and a partial set of GPC results for fractionated $[Ce(tstm)]_n$ polymers (synthesized in trial 1 with the β-diketone displacement (dβ) method) are shown in Figure 3. Although polystyrene was used as the reference for estimating the GPC $\overline{M}_n$ values, and an apparent structural difference exists between polystyrene and these coordination polymers, the $\overline{M}_n$ values obtained from GPC are quite comparable to those from NMR end-group analysis (Table 2). The slightly lower $\overline{M}_n$ values from GPC than from the end-group analysis may be the result of the heavier metals in these metal coordination polymers relative to the polystyrene standards. In fact, the density of the analogous zirconium polymers are greater than 1 cm^3/g.[35] After fractionation, the polymer fractions have different retention volumes as shown in Figure 3. As shown in Figure 7, a disappearance of the low molecular weight shoulder of the GPC peak of previously fractionated $[Ce(tstm)]_n$ after the polymer was stirred in THF confirms that THF can be used to remove low molecular weight $[Ce(tstm)]_n$. The results for other eight-coordinate Schiff-base coordination polymers previously prepared in our laboratory are also given in Table 2 for comparison.

The viscosity results for the fractionated $[Ce(tstm)]_n$ and $[Ce(tsts)]_n$ polymers prepared by each method are given in Table 1. The logarithms of the $\overline{M}_n$ values from the NMR end-group analysis of a series of fractionated $[Ce(tstm)]_n$ polymers have

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[35] Cronin, J. A. Unpublished results.

Table 3. Spectral Characterization of Schiff Bases and Corresponding Ce(IV) Polymers

H_4tsts	H_4tstm	H_4tsdb	[Ce(tsts)]$_n$	[Ce(tstm)]$_n$	[Ce(tsdb)]$_n$	assignment
Infrared (cm^{-1})^a						
3429	3450	3450				O−H
1614	1613	1615	1604	1629	1608	C=N
1278	1278	1278	1306	1302	1301	Ph−O
Nuclear Magnetic Resonance (ppm)^b						
12.62 (s, <2)	13.00 (d, 2.2)	12.94 (s, 2.7)				O−H
12.34 (s, <2)						
9.06 (s, 2)	8.95 (s, 4)	9.08 (d, 4)	9.4−8.6 (s, br)	8.95 (s, br)	9.2−8.9 (s, br)	aldimine
8.94 (s, 2)						
6.83−8.17 (m, >22)	7.7−6.8 (m, 22)	7.9−6.9 (m, >22)	8.6−6.0 (m, br)	7.6−6.1 (m, br)	8.7−7.5 (m, br)	aromatic
			5.8−5.0 (s, br)	5.6 (s, br)	6.0−5.3 (s, br)	
	4.11 (s, 2)			4.10 (s, br)		methylene
Ultraviolet−Visible (nm)^c						
364 (4.52, sh)	360 (4.56, sh)	374 (4.70, sh)	375 (4.41, sh)	360 (4.52, sh)	374 (4.89, sh)	n−π^*
342 (4.62)	342 (4.63, sh)	350 (4.73)	321 (4.56, sh)	326 (4.58, sh)	348 (4.98)	$\pi-\pi^*$
285 (4.68)	276 (4.64)	275 (4.64)	298 (4.65)	294 (4.66)	298 (4.90, sh)	$\pi-\pi^*$

[a] KBr pellets; w = weak; sh = shoulder. [b] DMSO-d_6 solvent; s = singlet; d = doublet; m = multiplet; br = broad; ratio of number of protons in parentheses. [c] DMSO solvent; log ϵ (molar extinction coefficient) in parentheses.

been plotted against the logarithms of their intrinsic viscosities (in cm^3/g) in order to determine the constants a and K in the Mark−Houwink equation[25] (Figure 8). The plots give $a = 0.79$ and $K = 5.84 \times 10^{-3}$ cm^3/g with a linear regression with $R^2 = 0.995$ for [Ce(tstm)]$_n$ (Figure 8) and $a = 0.70$ and $K = 1.25 \times 10^{-2}$ cm^{-3}/g with a linear regression with $R^2 = 0.987$ for [Ce(tsts)]$_n$ (Figure 9). Comparing to $a = 0.76$ and $K = 7.36 \times 10^{-3}$ cm^{-3}/g for [Ce(tsdb)]$_n$,[13] the a value decreases from [Ce(tstm)]$_n$ to [Ce(tsdb)]$_n$ and then to [Ce(tsts)]$_n$. The high a value of [Ce(tstm)]$_n$ indicates that NMP is a good solvent for this polymer.

Thermal analyses of the polymers have included thermal gravimetry and differential scanning calorimetry (DSC). When preheated to 230 °C to remove any residual solvent, the polymers show good thermal stability with >98% mass retention at 340 °C for [Ce(tstm)]$_n$ and 350 °C for [Ce(tsts)]$_n$. Polymers with different M_n values still have similar decomposition temperatures. TGA traces are available as supplementary material. The decomposition temperatures are reasonable because metal coordination polymers usually show high thermal stability;[32] however, because of less conjugated structures, these polymers have lower thermal stability than [Ce(tsdb)]$_n$,[13] [Zr(tsdb)]$_n$,[32] or [Zr(tsb)]$_n$,[31] where tsb^{4-} is the anion of the Schiff-base formed between salicylaldehyde and 1,2,4,5-tetraaminobenzene.

The glass transition temperatures (T_g) for [Ce(tstm)]$_n$ and [Ce(tsts)]$_n$ have been calculated from DSC measurements and are provided in Table 2 along with their onset temperatures. DSC scans are available as supplementary material. The glass transition temperatures around 150 °C for [Ce(tstm)]$_n$ is the lowest among the three cerium polymers (Table 2). The T_g values observed for the [Ce(tstm)]$_n$ polymers are logical based on the greater flexibility anticipated because of the methylene groups in the polymer chains. The increased flexibility of the polymer chains reduces their T_g. On the other hand, the higher T_g values of around 180 °C for the [Ce(tsts)]$_n$ polymers suggests more rigidity for this polymer in the solid state, apparently due to some interchain attractions incurred by the presence of the SO_2 groups.

Structural Information of [Ce(tstm)]$_n$ and [Ce(tsts)]$_n$ Polymers. The spectral characterization of the polymers (Table 3) clearly shows that the [Ce(tstm)]$_n$ and [Ce(tsts)]$_n$ polymers have structures around the Ce^{IV} ions similar as to that of [Ce(tsdb)]$_n$, which was prepared previously in our laboratory. The infrared spectra of [Ce(tstm)]$_n$ and [Ce(tsts)]$_n$ show an absence of the PhO−H vibration at 3450 cm^{-1}, that exists in the parent Schiff-bases. A shift in the C=N stretching vibration from 1614 cm^{-1} in H_4tstm to 1629 cm^{-1} in [Ce(tstm)]$_n$ and a shift in the Ph−O stretching vibration from 1278 cm^{-1} in H_4tstm to 1302 cm^{-1} in [Ce(tstm)]$_n$ are observed when the Schiff-base ligands coordinate to Ce^{IV} ions. Similar changes are also found for [Ce(tsts)]$_n$ (Table 3). The totality of these spectral shifts indicate that all of the oxygen and nitrogen atoms in the Schiff-base ligands are coordinated to the metal ions,[13,31,32] consistent with the coordination number of 8 for the cerium ions, as in the Ce(dsp)$_2$ monomer.[36] Results from proton nuclear magnetic resonance further confirm the formation of polymers by the disappearance of resonances assigned to the phenol protons and the bandlike spectra of the polymers (Figure 6) due to high viscosity of the polymer solutions. Furthermore, the similarity of the electronic spectral data of [Ce(tstm)]$_n$ and [Ce(tsts)]$_n$ to that of [Ce(tsdb)]$_n$ can be clearly seen in Table 3.

A molecular model of a short chain [Ce(tstm)]$_n$ polymer is shown in Figure 9, which is based on the known structure of the square antiprismatic Ce(dsp)$_2$ monomer.

In summary, two new soluble linear cerium(IV) Schiff base coordination polymers have been successfully prepared and characterized. The introduction of methyl groups to Schiff-bases and polymers greatly increases their flexibility and solubility; the introduction of sulfonyl groups to Schiff-base and polymers, on the other hand, does not improve the flexibility of the polymers. The best synthetic method for the ceric coordination polymers is the chelation polymerization between ceric complexes such as a cerium(IV) alkoxide or cerium(IV) acetylacetonate and a premade Schiff base.

Acknowledgment. The authors wish to acknowledge the financial support of the Petroleum Research Fund, administered by the American Chemical Society, and the constructive criticism provided by the reviewers.

Supplementary Material Available: TGA and DSC graphs for the new polymers (4 pages). Ordering information is given on any current masthead page.

IC9410811

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