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Synthesis and Characterization of Linear Cerium(IV) Schiff-Base Coordination Polymers

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ABSTRACT: The first soluble linear Schiff-base rare earth coordination polymer, *catena*-poly[cerium(IV)-*μ*-*N,N′,N″,N‴*-tetrasalicylidene(3,3′-diaminobenzidinato)-*O,N,N′,O′,O″,N″,N‴,O‴*] [Ce(tsdb)]$_n$, has been synthesized. The metathetical reaction between tetrakis(acetylacetonato)cerium(IV), [Ce(acac)$_4$], and the premade tetrasalicylidene-3,3′-diaminobenzidine Schiff base, [H$_4$tsdb], and the condensation reaction between the new chelate tetrakis(salicylaldehydato)cerium(IV), [Ce(sal)$_4$], and 3,3′-diaminobenzidine were confirmed to be effective syntheses for the preparation of coordination polymers with stoichiometrically controlled polymerization. The polymers have been characterized by gel permeation (size exclusion) chromatography, viscosity measurements, and ^{1}H nuclear magnetic resonance end-group analyses. On the basis of the results from the end-group analysis, polymers with number-average molecular masses ($\bar{M}_n$) as high as 30 000 have been obtained. The polymers exhibit high thermal stability and high glass-transition temperatures. Mark-Houwink constants of $a = 0.76$ and $K = 7.36 \times 10^{-5}$ have been obtained from the intrinsic viscosities (in dL/g) and the NMR $\bar{M}_n$ values.

Introduction

Soluble linear coordination polymers with lanthanide metal ions in the main chain appear to have been unknown prior to this study. Previously characterized lanthanide polymers containing lanthanide elements can be divided into three groups: (1) polymers as matrixes for lanthanide complexes, especially for organic compounds with low $\bar{M}_n$ values[1–3], (2) polymeric systems in which lanthanide metals are directly bonded to a branch of the polymer chain[4–8], and (3) oligomeric or polymeric compounds in the solid state that either fall apart upon dissolution or remain insoluble precluding $\bar{M}_n$ determination.[9–11]

We have now synthesized and characterized a new coordination polymer, *catena*-poly[cerium(IV)-*μ*-*N,N′,N″,N‴*-tetrasalicylidene(3,3′-diaminobenzidinato)-*O,N,N′,O′,O″,N″,N‴,O‴*], [Ce(tsdb)]$_n$, that is soluble in polar organic solvents even when average degree of polymerization ($\overline{\mathrm{DP}}$) values of about 80 are obtained. Two different methods have been used to prepare polymeric [Ce(tsdb)]$_n$ (Figure 1), and a third method has only produced short oligomers. The reaction of [tetrakis(acetylacetonato)cerium(IV)], [Ce(acac)$_4$], with the premade Schiff base (tetrasalicylidene-3,3′-diaminobenzidine), H$_4$tsdb, and the condensation reaction between [tetrakis(salicylaldehydato)cerium(IV)], [Ce(sal)$_4$], which was prepared for the first time in our laboratory, and 3,3′-diaminobenzidine are confirmed as effective methods for the preparation of polymers with fairly high $\bar{M}_n$ values, especially for *soluble* metal coordination polymers.[12,13]

Characterization methods include Fourier-transform infrared (IR), ultraviolet (UV), and Fourier-transform nuclear magnetic resonance (NMR) spectroscopies, gel permeation chromatography (GPC), viscosity measurements, and thermal analysis. The $\bar{M}_n$ values of the polymers have been firmly determined by NMR end-group analysis with [*N,N′*-bis(5-*tert*-butylsalicylidene)-1,2-phenylenediamine], H$_2$bsp. This Schiff base, being used for the first time as an end-capping group, gives very reliable data because of the 18 protons in the two *tert*-butyl groups of the end-capping ligand (Figure 2). The low solubility of metal coordination polymers (that commonly results from the intermolecular stacking forces that exist in flat unsaturated ligands)[12,13] can be improved in this class of polymers because the polymer chains formed with the Schiff-base ligands and the metal ions are not strictly linear rigid rods, as can be clearly seen from the antiprismatic structure of the related monomeric bis(*N,N′*-disalicyclidine-1,2-phenylenediamino)cerium(IV), [Ce(dsp)$_2$].[14] An analogous situation occurs in the tractable dodecahedral coordination polymers formed by zirconium(IV) with polydentate Schiff-base ligands such as [Zr(tsdb)]$_n$[15] and [Zr(tsb)]$_n$,[16] where tsb = *N,N′,N″,N‴*-tetrakis(salicylidene)-1,2,4,5-tetraaminobenzenato ligand with a 4− charge.

Experimental Section

Syntheses. Reagents. Reagent-grade and HPLC-grade solvents and chemicals were used throughout. Prior to use, dimethyl sulfoxide, DMSO, *N*-methylpyrrolidone, NMP, and *N,N*-dimethylformamide, DMF, were stirred for 2 days with barium oxide and fractionally distilled over calcium hydride under reduced pressure. Salicylaldehyde, Hsal, was distilled under reduced pressure. *o*-Phenylenediamine, pd, was recrystallized from methanol. 3,3′-Diaminobenzidine, db, was purified just prior to use by the method of Vogel and Marvel.[17,18] The compound was kept under an inert atmosphere of N$_2$ or Ar to avoid oxidation of the amine groups.

***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 in a manner similar to earlier procedures.[19–21] The compound was confirmed by its ^{1}H NMR data in CDCl$_3$: [ppm relative to tetramethylsilane (TMS) (multiplicity and relative intensity in parentheses)] 12.4 (s, 2), 8.6 (s, 2), 7.5–7.1 (m, 8), 7.1–6.8 (m, 4).

5-*tert*-Butylsalicylaldehyde, Hbsal. The literature[22] method was used to prepare Hbsal. The compound was confirmed by its ^{1}H NMR data in CDCl$_3$: [ppm relative to TMS (multiplicity and relative intensity in parentheses)] 10.8 (s, 1), 9.9 (s, 1), 7.6 (d, 1), 7.5 (s, 1), 6.9 (d, 1), 1.26 (s, 9).

***N,N′*-Bis(5-*tert*-butylsalicylidene)-1,2-phenylenediamine, H$_2$bsp.** A solution of 5-*tert*-butylsalicylaldehyde (12.0 g, 67.4 mmol) in 30 mL of methanol was slowly added to 70 mL of methanol solution containing 3.7 g (33.7 mmol) of *o*-phenylenediamine. The resulting solution was allowed to react under reflux conditions under N$_2$ for 2 h. The orange Schiff-base crystals precipitate readily. The solution was cooled with dry ice–acetone. The crude product was filtered, washed with methanol, and purified by homogeneous precipitation by adding hexane (1 part by volume) to a solution of the crude material in dichloromethane (2 parts by volume) and allowing preferential evaporation of the

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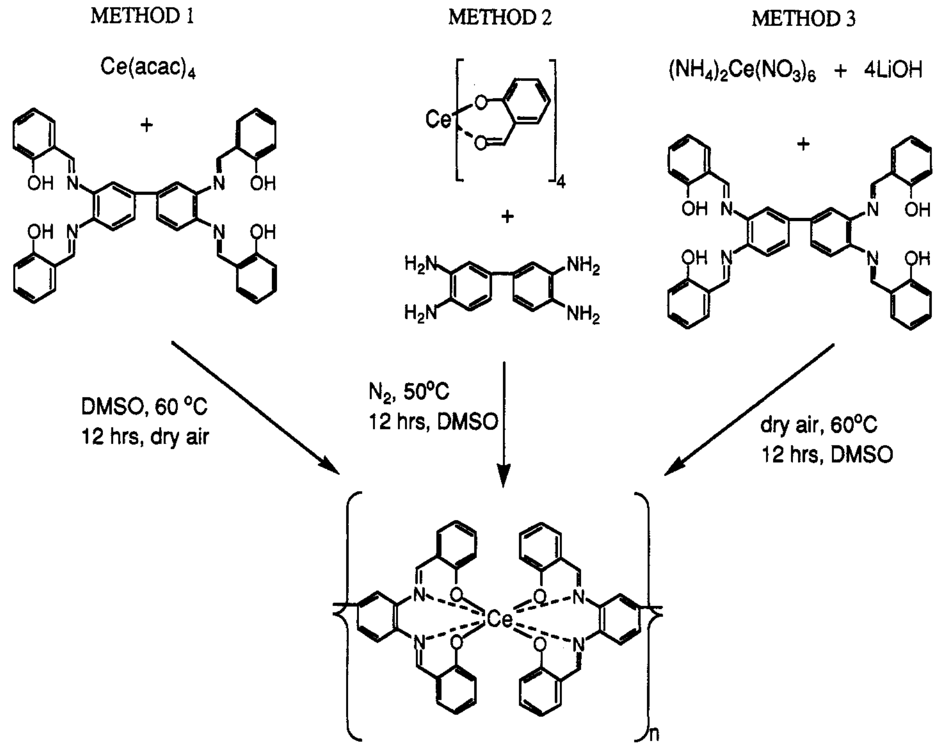

Figure 1. Three methods for synthesizing the [Ce(tsdb)]$_n$ polymers.

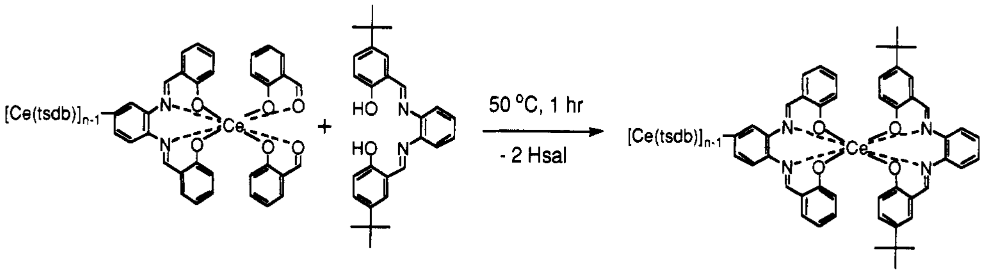

Figure 2. The end-capping reaction for polymers synthesized by method 2. Analogous reaction replace two $acac^-$ ligands from the "cerium" ends of polymers prepared by method 1 and NO_3^- ligands from polymers prepared by method 3.

dichloromethane. Mp: 165–166 °C (uncalibrated). Yield: 10 g, 70%. Anal. Calcd for $C_{28}H_{32}O_2N_2$: C, 78.5; H, 7.48; N, 6.54. Found: C, 78.4; H, 7.56; N, 6.51.

***N,N',N'',N'''*-Tetrasalicylidene-3,3'-diaminobenzidine, H_4tsdb.** Whereas both yellow and orange isomers of H_4tsdb were obtained by solvent variation, only the yellow form was used in this study. The yellow H_4tsdb was prepared by dissolving 3,3'-diaminobenzidine (1.2 g, 5.61 mmol) in 30 mL of DMSO, adding a slight excess of Hsal (3.1 g, 25.5 mmol), heating the solution to 70 °C under N_2 for 2 h, and allowing the resulting deep orange solution to stand overnight. The copious yellow precipitate that formed was filtered, washed with acetone, recrystallized from hot DMSO and dried *in vacuo* at 100 °C. Anal. Calcd for $C_{40}H_{20}N_4O_4$: C, 76.1; H, 4.76; N, 8.89. Found: C, 75.9; H, 4.75; N, 8.86.

Monomers. Ce(acac)$_4$. This compound (where $acac^-$ = the anion of 2,4-pentanedione) was prepared according to the literature[23] (mp: 150–151 °C). The compound was confirmed by its ^1H NMR spectrum in chloroform (ppm): 5.3 (s, 1), 1.9 (s, 6).

Ce(sal)$_4$. Ce(acac)$_4$ (4.1 g, 7.7 mmol) was dissolved in 40 mL of Hsal. The reaction occurred under reduced pressure (2–3 Torr) and elevated temperature (*ca.* 55 °C) for 24 h. The dark brown precipitate that formed was filtered, washed with hexane, and dried *in vacuo* at 65 °C. Yield: 4.4 g, 92%. Anal. Calcd for $CeC_{28}H_{20}O_8$: C, 53.9; H, 3.23. Found: C, 53.8; H, 3.29.

Ce(dsp)$_2$. (a). H_2dsp (2.4 g, 7.4 mmol) was dissolved in 15 mL of DMF, and Ce(acac)$_4$ (2.0 g, 3.7 mmol) in 5 mL DMF was added slowly to the H_2dsp solution. The reaction proceeded at 60 °C for 2 h. Copious amounts of dark brown precipitate appeared, and the mixture was filtered after standing overnight at room temperature. The product was washed with ether and purified in a hexane–dichloromethane solution. Yield: 2.0 g, 70%.

(b). Ce(sal)$_4$ (2.00 g, 3.20 mmol) was dissolved in 15 mL of DMSO, and pd (0.69 g, 6.42 mmol) in 10 mL of DMSO was added dropwise under N_2 at 50 °C with magnetic stirring. The resulting solution was allowed to react for 2 h and then stand overnight at room temperature. The brown precipitate was then filtered, washed with methanol, and purified in a hexane–dichloromethane solution. Yield: 1.5 g, 61%. A literature method[14] was used to prepare Ce(dsp)$_2$ for comparison. The compounds prepared by all three methods have identical melting points (309–310 °C) and IR and NMR spectra.

[Ce(tsdb)]$_n$ Polymer. Method 1. H_4tsdb (1.0000 g, 1.587 mmol) was dissolved in 30 mL of DMSO at 100 °C. The solution was cooled to 60 °C and 0.8506 g (1.587 mmol) of Ce(acac)$_4$ in 15 mL of DMSO was slowly added. The reaction proceeded for 16 h at 60 °C under dry air before 0.2 g (0.5 mmol) of end-capping H_2bsp in 5 mL of DMSO was added, and the solution was stirred for 1 h more. The product obtained by adding about 125 mL of methanol was filtered, washed with methanol, and dried *in vacuo* at 100 °C. Yield: 0.80 g, 65%.

Method 2. Ce(sal)$_4$ (1.0000 g, 1.602 mmol) was dissolved in 30 mL of DMSO, and 3,3'-diaminobenzidine (0.3429 g, 1.602 mmol) in 15 mL of DMSO was added. The resulting solution was stirred at 50 °C under Ar for 16 h. Then 0.2 g (0.5 mmol)

Table 1. Spectral Characterization of H_4tsdb, Ce(sal)$_3$, Ce(sal)$_4$, and [Ce(tsdb)]$_n$

H_4tsdb	Ce(sal)$_4$	Ce(dsp)$_2$	[Ce(tsdb)]$_n$	assignment
		Infrared (cm^{-1})[a]		
3450				O—H
1615	1629	1604	1608	C=O, C=N
1570				C=C
1551 (sh)				
1278	1301	1301	1301	Ph—O
	456		455	Ce—O
		Ultraviolet–Visible (nm)[b]		
374 (4.70, sh)	378 (3.80)		374 (4.89, sh)	
350 (4.73)	326 (4.20)		348 (4.98)	
275 (4.64)	267 (4.14)		298 (4.90, sh)	
		Nuclear Magnetic Resonance (ppm)[c]		
12.94 (s) (2.7)				O—H
9.08 (d) (4)	10.1 (s) (4)	8.69 (s) (4)	9.2–8.9 (b)	aldimine
7.9–7.3 (m) (14)	7.6–7.3 (m) (8)	7.3–7.0 (m) (16)	8.7–7.5 (b)	aromatic
6.9 (m) (9.3)	6.9–6.3 (m) (8)	6.58 (t) (4)	6.0–5.3 (b)	
		5.90 (d) (4)		

[a] KBr pellets; w = weak; 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.

of end-capping H_2bsp in 5 mL of DMSO was added, and the solution was stirred for 1 h more. The product precipitated when 125 mL of methanol was added. The product was filtered, washed with methanol, and dried *in vacuo* at 100 °C. Yield: 0.75 g, 61%.

Method 3. H_4tsdb (1.0000 g, 1.587 mmol) was dissolved in 30 mL of DMSO at 100 °C. The solution was cooled down to 60 °C and neutralized with 0.1524 g (6.349 mmol) of LiOH. $(NH_4)_2Ce(NO_3)_6$ (0.8696 g, 1.587 mmol) in 15 mL of DMSO was slowly added. The reaction proceeded for 16 h at 60 °C under dry air before 0.2 g (0.5 mmol) of the end-capping H_2bsp in 5 mL of DMSO and 0.0224 g (1.0 mmol) of LiOH were added, and the solution was stirred for 1 h more. The product was precipitated with 125 mL of methanol, filtered, washed with methanol, and dried *in vacuo* at 100 °C. Yield: 0.7 g, 57%. Anal. Calcd for $[Ce(C_{40}H_{26}N_4O_4)]_n{\cdot}0.2C_2H_6SO$: C, 61.9; H, 3.48; N, 7.16; S, 0.82. Found: C, 61.8; H, 3.55; N, 7.93; S, 0.83.

The best stoichiometry for each of the three methods was verified by varying the mole ratios of Ce(sal)$_4$:db, Ce(acac)$_4$:H_4tsdb, and $(NH_4)_2Ce(NO_3)_6$:H_4tsdb, respectively, with ratios of 0.990:1.000, 0.995:1.000, 1.000:1.000, 1.000:0.995, and 1.000:0.990 for each. The reactions were conducted under the same conditions as above.

The resulting polymers were fractionated by dissolving them in DMSO and precipitating them with 1:1 dichloromethane–benzene. Yields for the fractionated polymers were about 30–40%.

Extent of Reaction Confirmed with NMR. (a). Ce(acac)$_4$ (0.1473 g, 0.275 mmol) and 0.1738 g (0.550 mmol) of H_2dsp were dissolved in 5 mL of DMSO-d_6 at 60 °C under dry air with stirring, and the mixture was checked by NMR from time to time to follow the extent of the reaction to Ce(dsp)$_2$.

(b). Ce(sal)$_4$ (0.1530 g, 0.245 mmol) and 0.0530 g (0.490 mmol) phenylenediamine were dissolved in 5 mL of DMSO-d_6. The resulting solution was allowed to react at 50 °C under N_2 with stirring and checked by NMR from time to time to follow the extent of the reaction to Ce(dsp)$_2$.

End-Capping Confirmation. H_4tsdb (0.5200 g, 0.825 mmol) in 10 mL of hot DMSO was added dropwise to Ce(acac)$_4$ (0.8844 g, 1.650 mmol) in 10 mL of DMSO. The reaction proceeded at 60 °C under dry air for 1 h. A second reaction was conducted under identical conditions, except that 0.7020 g (1.650 mmol) of the end-capping Schiff base H_2bsp was added to the solution after the 1 h at 60 °C. This solution was then stirred for 1 h more at 60 °C. After cooling to room temperature, methanol was added to both solutions in order to precipitate the products.

Physical Measurements. Proton Fourier-transform nuclear magnetic resonance (FT-NMR) measurements were taken with a Varian Model XL 80. The bsp-end-capped-polymer *tert*-butyl protons (average of 18 per chain) were integrated against the aromatic and aldehydic protons of 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 $\overline{DP} = 2(n_{mer}/n_e)$.[24] More than 10 000 acquisitions were used to obtain reliable results for the high $\bar{M}_n$ polymers.

Gel permeation (size exclusion) chromatography (GPC) measurements were conducted with a Waters Model 6000 A pump, a Model R 401 differential refractometer, and a 10^3-Å ultrastyragel column. NMP was used as the solvent. The column was calibrated with polystyrene standards.

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-4 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 microprocessors.

Results

The H_4tsdb Schiff-Base Ligand. Although the H_4tsdb bis(tetradentate) Schiff-base bridging ligand was prepared earlier,[25] its low solubility in organic solvents thwarted its use in polymerization reactions at the time. We have now shown that it has appreciable solubility in DMSO at elevated temperatures (>50 g/L at 100 °C, and at least 30 g/L stays in solution at 50 °C during polymerization reactions). Spectral characterization of the ligand is provided in Table 1.

Monomeric Metal Reactants. Although several trivalent lanthanide salicylaldehyde complexes formulated as Ln(sal)$_3$ had been prepared in aqueous solution previously,[26] the synthesis of Ce(sal)$_4$ had not been reported. The synthesis of pure Ce(sal)$_4$ depends upon preventing the reduction of Ce^{4+} and cleanly separating the desired product from any remaining starting materials. Several different preparative methods were attempted, but the method of preparing Ce(sal)$_4$ from Ce(acac)$_4$ in neat Hsal has been confirmed to be an effective way to obtain a pure product using the lability of cerium(IV) complexes and the greater volatility of Hacac relative to Hsal. The purity of the Ce(acac)$_4$ starting material and moderate temperatures (<55 °C) during the synthesis are necessary to obtain pure Ce(sal)$_4$. Earlier, the same method had also been used to prepare pure Zr(sal)$_4$.[27] FT-IR, ultraviolet, and FT-^{1}H NMR spectral data of Ce(sal)$_4$ are listed in Table 1.

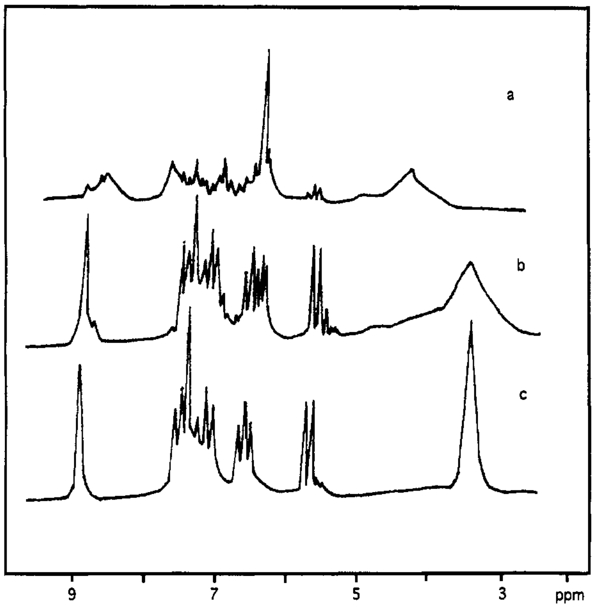

Figure 3. The ^1H NMR spectra for $Ce(sal)_4$ plus *o*-phenylenediamine in DMSO-d_6 at 50 °C after 20 min (a), 2 h (b), and 3 h (c).

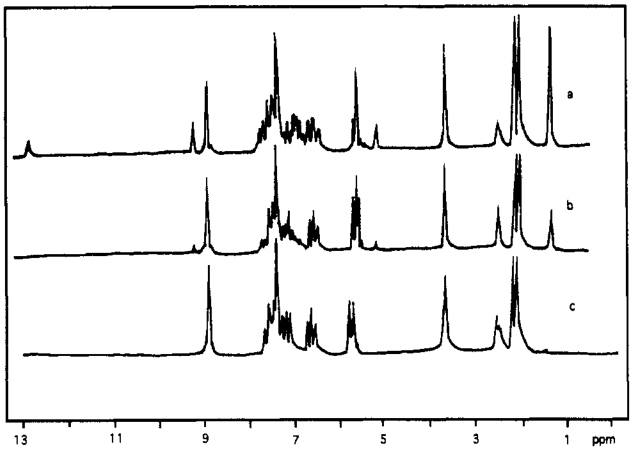

Figure 4. The ^1H NMR spectra for $Ce(acac)_4$ plus H_2dsp in DMSO-d_6 at 60 °C after 5 min (a), 20 min (b), and 40 min (c).

$Ce(acac)_4$ is also an effective starting material for preparing cerium Schiff-base monomers and polymers. For preparing Schiff-base complexes (monomers), when benzene–methanol (1:4) is used as a mixed solvent, products with high yield (95%) and good purity can be obtained.[28]

The results from an investigation on the extent of reaction by NMR show that the reaction between $Ce(sal)_4$ and pd goes to completion (>99%) at 50 °C within 3 h in DMSO-d_6 and gives spectra identical to $Ce(dsp)_2$ plus a large peak at about 3.3 ppm from the H_2O produced in the reaction (Figure 3), and the spectrum obtained after 12 h is identical to that obtained after 3 h. NMR spectra indicate that the reaction between $Ce(acac)_4$ and H_2dsp is almost complete at 60 °C after 20 min, as is evident from the disappearance of the phenolic proton peak of the salicylaldehyde (*ca.* 12.7 ppm) when it coordinates to the Ce(IV) ion. The spectrum obtained after 40 min (Figure 4) is virtually identical to the spectra of $Ce(dsp)_2$ plus Hacac.

Polymers. The highest number-average molecular weights for the $[Ce(tsdb)]_n$ polymers before fractionation (based the NMR end-group analysis) are 16K (for the trial with the ratio of $Ce(sal)_4$:db = 1.000:1.000) for method 1, 14K (for the trial with the ratio of $Ce(acac)_4$:H_4tsdb = 1.005:1.000) for method 2, and 6K (for the trial with the ratio of $(NH_4)_2Ce(NO_3)_6$:H_4tsdb = 1.000:0.995) for method 3. After fractionation, the $\bar{M}_n$ values from the NMR analyses rise to 30K ($[Ce(tsdb)]_n$ method 1) with a 30% yield, 24K ($[Ce(tsdb)]_n$ method 2) with a 35% yield, and 10K ($[Ce(tsdb)]_n$, method 3) with a 40% yield for these highest molecular weight fractions (Table 2).

Table 2. Characterization of Fractionated $[Ce(tsdb)]_n$ Polymers

		GPC		^1H NMR		
polymer (syn method)	intrinsic viscosity[a]	retention volume[b]	$\bar{M}_n$[c]	relative intensity[d]	$\bar{M}_n$[e]	T_g(K)[f]
$[Ce(tsdb)]_n$ (1)	0.19	6.72	28 000	57	30 000	455
$[Ce(tsdb)]_n$ (2)	0.16	7.52	20 000	45	24 000	453
$[Ce(tsdb)]_n$ (3)	0.085	8.08	9 000	19	10 000	393
$[Zr(tsdb)]_n$[g]	0.20		30 000		33 000	347
$[Zr(tsb)]_n$[h]	0.18		49 000			360[g]

[a] Intrinsic viscosity in dL/g in NMP at 30 °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] $\bar{M}_n$ assuming average of one bsp^{2-} ligand per chain. [f] Glass transition temperature. [g] Reference 15. [h] Reference 16.

DMSO solutions of $[Ce(tsdb)]_n$ can be put aside overnight at room temperature without any precipitate forming. However, the $tsdb^{4-}$ ligand has limited solubility and precipitates from solution after cooling to room temperature. The polymers with low $\bar{M}_n$ values dissolve easily in either DMSO or NMP at room temperature. For polymers with high $\bar{M}_n$ values, heating increases their solubility. When the solvent is gradually evaporated under reduced pressure, a film appears on the surface of the solution, and complete evaporation of the solvent gives shiny dark-brown films that are quite fragile.

The end-capping confirmation study for the reaction of 2 mol of $Ce(acac)_4$ with 1 mol of H_4tsdb provides proof that the end-capping reagent virtually completely displaces the acac–ligands. The NMR spectrum of the product without added end-capping ligand shows a signal for the acac–methyl protons at 1.36 ppm and for the $acac^-$ methyne protons at 5.25 ppm. When a stoichiometric amount of H_2bsp end-capping ligand is added, both peaks disappear completely and a signal for the *tert*-butyl protons of coordinated bsp^{2-} appears at 1.16 ppm (Figure 5). This means that the end-capping bsp^{2-} ligand replaces virtually all of the $acac^-$ end groups under these reaction conditions, even at the stoichiometric ratio of one H_2bsp per end to be capped, let alone at the much greater excess of end-capping H_2bsp available when it was used in polymer end-capping. For the polymers prepared with $(NH_4)_2Ce(NO_3)_6$ and $Ce(sal)_4$ as starting materials, the nitrate and sal^- ligands at the ends of the polymer chains should be even easier to replace because of their poorer coordinating ability relative to $acac^-$.

End-group analyses of $[Ce(tsdb)]_n$ have been obtained by FT-NMR spectroscopy from the intensity of the *tert*-butyl proton signal of the end-capping bsp^{2-} at about 1.2 ppm (18 protons per bsp^{2-}) *vs* the signals associated with the Schiff-base protons ranging from 5.5 to 9.2 ppm (26 protons per repeating unit), as shown in Figure 6. The strong signal from the two *tert*-butyl protons in bsp^{2-} gives much more reliable data then the toluene derivative used previously[15] because the toluene derivative has only three protons per end group. The highest $\bar{M}_n$ value obtained from the NMR end-group analysis after fractionation is 30 000 (Table 2).

The inherent viscosities of the $[Ce(tsdb)]_n$ polymers have been determined using Kraemer's approximation:[29] $[\eta]_{inh} = (1/c)\ln(t_{soln}/t_{solv})$, where $[\eta]_{inh}$ is the inherent

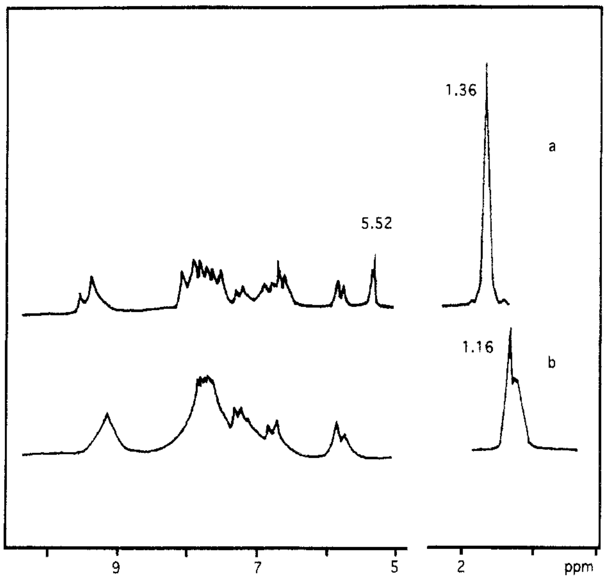

Figure 5. The ^{1}H NMR spectra in DMSO-d_6 for the product obtained from the reaction between 2 mol of Ce(acac)$_4$ plus 1 mol of H$_4$tsdb in DMSO by direct precipitation (a) and after the addition of 2 mol of the H$_2$bsp end capping reagent (b).

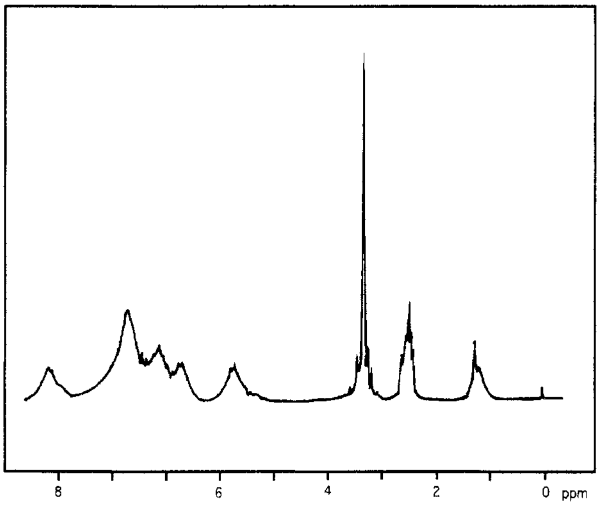

Figure 6. The ^{1}H NMR spectra for a low molecular weight ($\bar{M}_n$ = 6600) end-capped [Ce(tsdb)]$_n$ polymer in DMSO-d_6 showing the *tert*-butyl signal of the end-capping reagent.

viscosity, c is the concentration (g/dL) and t is the time (s) for the solution (soln) or solvent (solv). The intrinsic viscosity has been obtained by extrapolation of the inherent viscosity values to zero concentration. Viscosity results for the fractionated [Ce(tsdb)]$_n$ polymers prepared by each method are given in Table 2.

Gel permeation chromatography of the fractionated [Ce(tsdb)]$_n$ polymers in NMP gives $\bar{M}_n$ values of 28 000 for [Ce(tsdb)]$_n$ by method 1, 20 000 for [Ce(tsdb)]$_n$ by method 2, and 9000 for [Ce(tsdb)]$_n$ by method 3 (Figure 7) relative to polystyrene standards, as noted in Table 2.

Thermal analyses of the polymers have included thermal gravimetry and differential scanning calorimetry (DSC). The [Ce(tsdb)]$_n$ (method 2) polymer shows a high thermal stability with 98% mass retention at 673 K and 82% at 1073 K when preheated to 573 K, at which temperature the 0.2 mol of DMSO that is observed for the polymer as synthesized is lost. The glass-transition temperatures have been calculated from DSC measurements of the fractionated polymers to be 457 K for [Ce(tsdb)]$_n$ (method 1) with an onset temperature of 442 K, 456 K for [Ce(tsdb)]$_n$ (method 2) with an onset temperature of 440 K, and 393 K for [Ce(tsdb)]$_n$ (method 3) with an onset temperature of 347 K (Table 2).

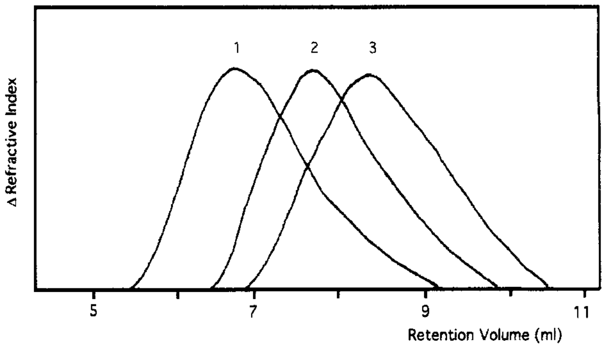

Figure 7. Gel permeation chromatographic results for the [Ce(tsdb)]$_n$ polymers (after fractionation) prepared by the three methods (*cf.* Table 2).

Spectral characterization of [Ce(tsdb)]$_n$ are provided in Table 1.

Discussion

Ce(sal)$_4$. The newly prepared Ce(sal)$_4$ has been synthesized and characterized. The IR spectrum of this compound has a Ph–O stretching vibration at 1301 cm^{-1}, shifted from 1275 cm^{-1} in Hsal. This shift is analogous to other chelates of Hsal and Schiff bases.[19,30,31] The NMR spectrum of Ce(sal)$_4$ (Table 1) exhibits no peaks beyond 9 ppm in the phenolic O–H region; therefore, no OH groups remain. The results from a hydrolysis investigation followed by NMR show that the hydrolysis of Ce(sal)$_4$ is very solvent dependent. In DMSO-d_6, Ce(sal)$_4$ is quite stable at room temperature (the spectrum shows no change after standing for several days) and when a drop of water is added to the deuterated solution, the proton NMR changes only very slightly after 1 h and the Ce(sal)$_4$ appears to be about 50% hydrolyzed after 1 day. But when Ce(sal)$_4$ dissolves in CD$_2$Cl$_2$ hydrolysis takes place almost immediately and NMR peaks for the free Hsal are apparent within a few minutes. These results are consistent with the fact that DMSO is a very efficient H$_2$O scavenger, which makes it a good solvent for these condensation polymerizations. The stability of Ce(sal)$_4$ to hydrolysis in DMSO is greater than that of Zr(sal)$_4$; therefore, Ce(sal)$_4$ is a good starting material for the formation of polymers. One disadvantage of Ce(sal)$_4$ is the ease of reduction of Ce^{4+} at high temperatures. The reduction can be clearly seen from a broadening of the NMR spectra when samples are kept at or above 60 °C for several hours. However, when the temperature is kept at <50 °C no reduction is apparent from the NMR spectra, even overnight. Thermal gravimetric analysis of Ce(sal)$_4$ shows that the compound decomposes quickly above 230 °C, and loses a small amount of mass (4.3%) by 200 °C. This could be the slow decomposition of the compound as happens to Ln^{III}(sal)$_3$.[13] The UV–visible spectrum of Ce(sal)$_4$ shows a shoulder at 381 nm after sal$^-$ coordinates to the Ce(IV) ions. This shoulder is not apparent in either Hsal or Ce(IV) ions. The new transition can be attributed to a ligand-to-metal charge-transfer (LMCT) transition.

Cerium(IV) Schiff-Base Complexes. Although the Schiff base H$_2$bsp and its cerium(IV) complexes were synthesized for the first time, the introduction of electron donating *tert*-butyl groups to H$_2$salen had been done previously.[32] The other Schiff bases and their cerium(IV) complexes had been prepared previously and are well-characterized.[14,33,34] Ce(acac)$_4$ as a starting material for Schiff-base or polymer synthesis had not been reported before. The results show that it is an effective reagent for

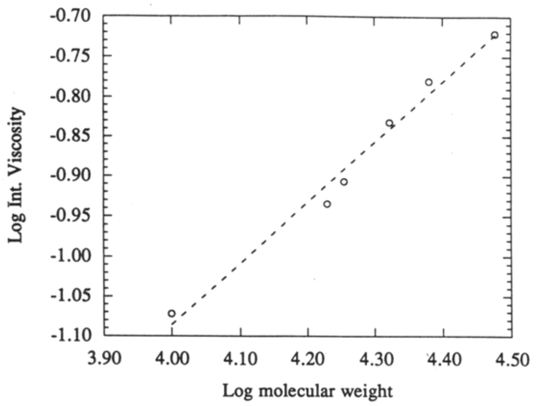

Figure 8. A composite Mark–Houwink plot for the [Ce(tsdb)]$_n$ polymers.

the preparation of Ce(IV) Schiff-base complexes. Syntheses in polar solvents have been used to obtain relevant information for conducting coordinate polymerization reactions. When Schiff-base ligands are coordinated to Ce(IV), the frequency of the C=N stretching vibration decreases about 10 cm^{-1} and C–O stretching frequency increases about 20 cm^{-1} relative to the free Schiff base (Table 1). The NMR spectra of the complexes show the disappearance of the phenolic proton signal when the Schiff bases coordinate to cerium(IV). Among the Schiff-base complexes, Ce(dsp)$_2$ is particularly of interest because of its similarity to [Ce(tsdb)]$_n$ polymer. Experiments have shown that the interactions between Schiff-base ligands and Ce(IV) ions are quite strong;[34] i.e., dsp^{2-} greatly stabilizes Ce(IV) as shown by the much more negative shift in the reduction potential [Ce(dsp)$_2$/Ce(dsp)$_2^-$ = −0.529 V] relative to the aqueous system [Ce(IV)Ce(III) = +1.20 V].[34] The strong coordination between the tetradentate ligand and Ce(IV) makes it possible to form a linear coordination polymer with a high $\bar{M}_n$.

[Ce(tsdb)]$_n$ Polymer. The formation of the [Ce(tsdb)]$_n$ polymer is a linear condensation polymerization. Naturally, the three different methods yield different byproducts, i.e., H_2O, Hacac, and $LiNO_3$ (Figure 1).

The conditions for each a synthetic method were set to maximize polymerization. Dimethyl sulfoxide was chosen as the solvent for the polymerization reactions due to its properties as a good polymer solvent[35,36] and its strong hydrogen bonding with water, which makes it an excellent water scavenger. The infrared spectra of the polymers show that the Ph–O stretch moves from 1278 cm^{-1} in H$_4$tsdb to 1301 cm^{-1} in the polymers and the C=N stretch moves from 1615 to 1608 cm^{-1}; both shifts are analogous to those of the cerium complexes discussed above. The NMR spectra exhibit no phenolic proton peaks, which is consistent with anionic coordination. No attempt was made to interpret the UV–visible spectra. The formation of films upon solvent evaporation gives further evidence for the formation of soluble polymers.

In the present study, polymerization through a reaction between Ce(acac)$_4$ and the Schiff base H$_4$tsdb (method 1) has been found to be a very effective method of preparing the [Ce(tsdb)]$_n$ polymer. H$_4$tsdb dissolves easily in DMSO at 60 °C in the presence of cerium(IV); otherwise, temperatures of at least 80 °C are necessary to dissolve appreciable amounts of the H$_4$tsdb ligand in DMSO. The large increase of entropy (chelate effect) that occurs when a tsdb^{4-} ligand replaces four acac$^-$ ions apparently enhances the polymerization reaction. An NMR investigation of the monomer reaction shows that the reaction is essentially complete after 40 min at 60 °C. The highest $\bar{M}_n$ value obtained from the NMR end-group analysis reaches about 30 000 after fractionation.

Polymers prepared by method 2 exhibit high $\overline{DP}$ values because condensation between sal$^-$ and phenylenediamine goes essentially to completion to yield the polymeric product. The H_2O byproduct is effectively scavenged by DMSO, which has been confirmed in the syntheses of similar coordination polymers with zirconium, [Zr(tsb)]$_n$[16] and [Zr(tsdb)]$_n$.[15] Results from the NMR investigation show that reaction between Ce(sal)$_4$ and *o*-phenylenediamine is essentially complete under the reaction conditions after 2 h. The NMR spectra obtained after 3 and 12 h are virtually identical to the spectrum of Ce(dsp)$_2$. The reaction temperature was kept under 50 °C to prevent reduction of Ce(IV). After fractionation, the highest $\bar{M}_n$ value obtained from the NMR end-group analyses was 24 000. Polymerization of the metal–salicylaldehyde complex and the tetraamine had been previously demonstrated to be an effective method of synthesizing this class of coordination polymers.[15,16]

The results from method 3 indicate less extensive polymerization using this method. Problems come from the low solubility of LiOH in DMSO and/or the difficulty in controlling the stoichiometric ratio. The highest $\bar{M}_n$ value obtained for this method, even after fractionation, is only 10 000, based on the NMR end-group analyses.

According to the Carothers equation, the number-average degree of polymerization ($\overline{DP}$) for a condensation reaction can be expressed as

$$\overline{DP} = (1 + r)/(1 + r - 2rp) \qquad (1)$$

here r is reactant ratio and p is extent of reaction.[24] In order to obtain polymers with high $\bar{M}_n$ values, the stoichiometric ratio of the reactants must be almost exactly 1:1 and the extent of reaction must be very close to unity. Adjustment of the ratio of the starting materials from 0.990:1 to 1:0.990 by 1/2% increments has been used to ensure the reactant ratios are as close to unity as possible. In each case, the maximum $\bar{M}_n$ value was obtained when

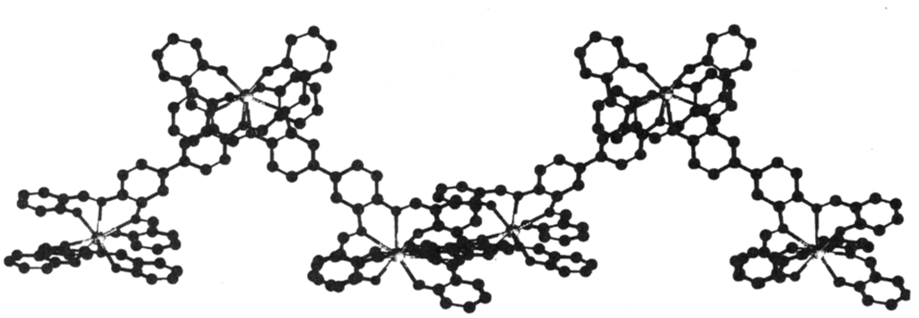

Figure 9. A molecular model representation of a short chain of a [Ce(tsdb)]$_n$ polymer based on the known solid-state structure of [Ce(dsp)$_2$].

the ratio of reactants was within 1/2% of the theoretical value. Because reactant ratios were varied in 1/2% increments, the r value for the highest $\bar{M}_n$ result for each method must be >0.9975; in fact, r is probably ≥0.998 because the viscosities found for the products using adjacent reactant ratios indicate lower $\bar{M}_n$ values by at least 7%.

The highest $\bar{M}_n$ obtained before fractionation is 16 000 ($\overline{DP} \sim 40$). Since the reactant ratio r is ≥0.998, a $\overline{DP}$ of 40 implies an extent of reaction p of 0.976 by eq 1, *if all* of the product were in the isolated material. The actual extent of reaction is undoubtedly a little lower since some low molecular weight material does not precipitate out, even when the methanol:DMSO ratio is 2.5:1 (v/v).

The $\bar{M}_n$ values obtained from the GPC results (shown in the Table 2) are in good agreement with the results from the NMR end-group analysis, although the $\bar{M}_n$ values from the GPC results are based on polystyrene standards.

Logarithms of the $\bar{M}_n$ values from the NMR end-group analysis of a series of fractionated $[Ce(tsdb)]_n$ polymers have been plotted against the logarithms of their intrinsic viscosities (in dL/g) in order to determine the constants a and K in the Mark-Houwink equation[24] (Figure 8). The plot gives $a = 0.76$ and $K = 7.36 \times 10^{-5}$ dL/g after linear regression with $R^2 = 0.991$. The a value shows that NMP is a good solvent for the $[Ce(tsdb)]_n$ polymer. The smaller K and higher a values than those observed for $[Zr(tsdb)]_n$ ($a = 0.68$, $K = 1.53 \times 10^{-4}$ dL/g)[15] means that the chains of the $[Ce(tsdb)]_n$ polymer are more rigid than those of $[Zr(tsdb)]_n$. This conclusion is also consistent with the higher T_g values observed for the cerium polymer (Table 2).

The cerium polymer has high thermal stability with 98% of the weight still intact at 673 K and 82% at 1073 K if the polymer has been preconditioned at 573 K, at which temperature the 0.2 mol of DMSO that is observed on the polymer as synthesized is lost. The glass-transition temperature (T_g) values of 455 K for $[Ce(tsdb)]_n$ (method 1) 453 K for $[Ce(tsdb)]_n$ (method 2) and 399 K for $[Ce(tsdb)]_n$ (method 3) are quite reasonable because the T_g values are related to the flexibility of the polymer in the solid state. Longer chain polymers have higher glass-transition temperatures because more intermolecular interactions must be broken in order to attain the glassy state than for shorter chain polymers. The T_g values for $[Zr(tsdb)]_n$ and $[Zr(tsb)]_n$ are also given in Table 2 for comparison. The much lower T_g values for the Zr(IV) coordination polymers relative to the Ce(IV) species (Table 2) indicate less flexibility for $[Ce(tsdb)]_n$, which may be related to the structural differences of the monomers. The structure of $Zr(dsp)_2$ is dodecahedral,[19] but the structure of $Ce(dsp)_2$ is square antiprismatic.[14] The antiprismatic structure would appear to allow more intermolecular forces to occur. A representation of a segment of a typical $[Ce(tsdb)]_n$ polymer chain based on the monomer structure is shown in Figure 9.

In conclusion, a well-defined coordination or chelate polymer of cerium(IV) has been prepared that is thermally stable and that can be characterized using the methods used for organic polymers.

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