Inorg. Chem. **1990**, *29*, 39–43

Contribution from the Department of Chemistry,
University of Massachusetts, Amherst, Massachusetts 01003

Synthesis and Characterization of the Thermally Stable Copolymer of Tetrakis(salicylaldehydato-*O*,*O*′)zirconium(IV) and 3,3′-Diaminobenzidine[1]

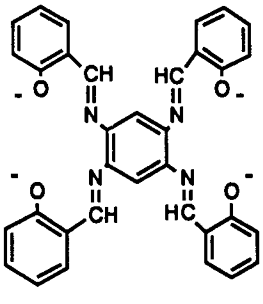
Ronald D. Archer* and Bing Wang[2]

Received June 30, 1989

A new soluble linear Schiff-base coordination polymer *catena*-poly[zirconium(IV)(*μ*-*N*,*N*′,*N*″,*N*‴-tetrasalicylidene-3,3′-diaminobenzidinato-*O*,*N*,*N*′,*O*′:*O*″,*N*″,*N*‴,*O*‴)] has been synthesized via the condensation of 3,3′-diaminobenzidine with tetrakis(salicylaldehydato-*O*,*O*′)zirconium(IV) in dry dimethyl sulfoxide. The copolymer chain length has been evaluated by ^{1}H NMR spectroscopy (end-group analysis), gel permeation (size exclusion) chromatography, and viscosity measurements. A copolymer average degree of polymerization of up to 92 has been obtained by careful stoichiometry control plus fractional precipitation. An electronic charge-transfer transition at about 400 nm has also been observed with a molar extinction coefficient of 3.2×10^4 L (mol of Zr)$^{-1}$ cm^{-1}. The polymer shows high thermal stability to about 770 K as measured by thermal gravimetric analysis and has a glass transition temperature of 347 K as measured by differential scanning calorimetry. The glass transition temperature of the analogous 1,2,4,5-tetraaminobenzene copolymer with tetrakis(salicylaldehydato)zirconium(IV) has also been determined to be 360 K.

Introduction

Soluble (or tractable) thermally stable metal coordination polymers are difficult to synthesize because of the intermolecular stacking forces that exist in the flat unsaturated ligands normally used to obtain thermal stability.[3] For example, attempts to make polymers with planar Schiff bases or similar ligands and divalent metal ions typically yield intractable oligomers, which prevent true polymer formation.[4] However, a soluble linear Schiff-base polymer, *catena*-poly[zirconium(IV)(*μ*-*N*,*N*′,*N*″,*N*‴-tetrasalicylidene-1,2,4,5-tetraaminobenzenato-*O*,*N*,*N*′,*O*′:*O*″,*N*″,*N*‴,*O*‴)], $[Zr(tsb)_4]_n$, had been previously synthesized and partially characterized in our laboratory.[5] Whereas the parent bridging bis-quadridentate Schiff-base ligand (tsb^{4-}, **1**) and its protonated form, H_4tsb, have very low solubility in all organic solvents,[6] the in situ synthesis of the polymer by the Schiff-base condensation of 1,2,4,5-tetraaminobenzene with tetrakis(salicylaldehydato-*O*,*O*′)zirconium(IV), $Zr(sal)_4$, provides a polymer with much greater solubility than the ligand.[5] The X-ray results[7] for the model monomeric compound bis(*N*,*N*′-disalicylidene-1,2-phenylenediamino)zirconium(IV), $Zr(dsp)_2$, show that the two quadridentate ligands around the zirconium are distorted from a strictly linear geometry and provide a relatively random organic sheath around the metal, even though the four oxygen and four nitrogen donors form a regular trigonal-faced dodecahedron about the zirconium in this solid-state environment. Also, in solution, eight-coordinate zirconium is typically nonrigid.[8] The nonregular organic sheath together with the nonrigidity appears to provide less opportunity for extensive interchain stacking, which in turn yields better solubility for the growing polymer chains than has been observed for most linear metal coordination polymers.



1

We have now synthesized a new series of polymers by the condensation of 3,3′-diaminobenzidine, db, with tetrakis(salicylaldehydato-*O*,*O*′)zirconium(IV), $Zr(sal)_4$, as shown in eq 1, and have more firmly established their molecular weights by FT-NMR end-group analysis, in addition to gel permeation (size exclusion) chromatography and viscosity measurements, which only provide approximate molecular weight information. Reaction times, temperatures, and stoichiometry have been varied in order to maximize the molecular weight. The probable structure of this polymer series is depicted in Figure 1. The zirconium-containing end groups have been capped with disalicylidene-3,4-diaminotoluene, H_2dsdt, as shown in eq 2, in order to provide an NMR handle for molecular weight determination, avoid end-group hydrolysis (eq 3), and minimize adhesion of the polymer to glass. One reason for our interest in these polymers is their strong adhesion to silica[9] and aluminum[10] (actually alumina on aluminum) surfaces unless the zirconium polymers are end-capped.

Experimental Section

Solvents. HPLC grade (Aldrich) dimethyl sulfoxide, DMSO, and *N*-methylpyrrolidone, NMP, were used. Both solvents were stirred for 2 days with barium oxide and fractionally distilled over calcium hydride under reduced pressure.

Tetrakis(salicylaldehydato)zirconium(IV). $Zr(sal)_4$ was prepared (91% yield) as previously described[11] and used promptly in a dry atmosphere to avoid hydrolysis of the compound.

Anal. Calcd for $ZrC_{28}H_{20}O_8$: C, 58.4; H, 3.51. Found: C, 58.2; H, 3.66.

3,3′-Diaminobenzidine, db. The method of Marvel and Vogel[12,13] was used to purify db. The compound was kept under an inert atmosphere

---

(1) Taken in part from the Ph.D. dissertation of B. Wang, University of Massachusetts, Amherst, MA, Feb 1989. Presented in part at the National Meeting of the American Chemical Society, Los Angeles, CA, Sept 1988; paper INOR 236. An alternate name for this series of polymers would be poly[(*N*,*N*′,*N*″,*N*‴-tetrasalicylidene-3,3′-diaminobenzidinato)zirconium(IV)]. The nomenclature used in this paper is based on the recommendations of the IUPAC Inorganic Chemistry Division Commission on Nomenclature of Inorganic Chemistry: *Pure Appl. Chem.* **1981**, *53*, 2283.

(2) Current address: Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061.

(3) (a) Archer, R. D.; Wang, B.; Tramontano, V. J.; Lee, A. Y.; Ochaya, V. O. In *Inorganic and Metallic Polymers*; Zeldin, M., Wynne, K. J.; Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society Washington, DC, 1988; p 463. Cf: (b) Foxman, B. M.; Gersten, S. W. *Encycl. Polym. Sci. Eng.* **1985**, *4*, 175. (c) Pittman, C. U., Jr.; Carraher, C. E., Jr.; Reynolds, J. R. *Encycl. Polym. Sci. Eng., 2nd ed.* **1987**, *10*, 541. (d) Sheats, J. E. *Kirk-Othmer Encycl. Chem. Technol., 3rd Ed.* **1981**, *15*, 184. (e) Hagihara, N.; Sonogashira, K.; Takahashi, S. *Adv. Polym. Sci.* **1981**, *41*, 149. (f) Bailar, J. C., Jr. In *Organometallic Polymers*; Carraher, C. E., Jr., Sheats, J. E., Pittman, C. U., Jr., Eds.; Academic Press: New York, 1978; p 313.

(4) (a) Deshpanda, U. G.; Shah, J. R. *J. Macromol. Sci., Chem.* **1983**, *A20*, 355. (b) For earlier citations see ref 5, Introduction.

(5) Archer, R. D.; Illingsworth, M. L.; Rau, D. N.; Hardiman, C. J. *Macromolecules* **1985**, *18*, 1371.

(6) Merrell, P. H.; Osgood, R. A. *Inorg. Chim. Acta* **1975**, *14*, L33.

(7) Archer, R. D.; Day, R. O.; Illingsworth, M. L. *Inorg. Chem.* **1979**, *18*, 2908.

(8) Fay, R. C.; Howie, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 1115.

(9) Wang, B.; Archer, R. D. *Polym. Mater. Sci. Eng.* **1988**, *59*, 120.

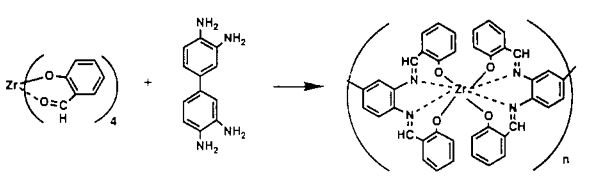
(10) Wang, B.; Archer, R. D. *Polym. Mater. Sci. Eng.* **1989**, *60*, 710.

(11) Archer, R. D.; Illingsworth, M. L. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 661.

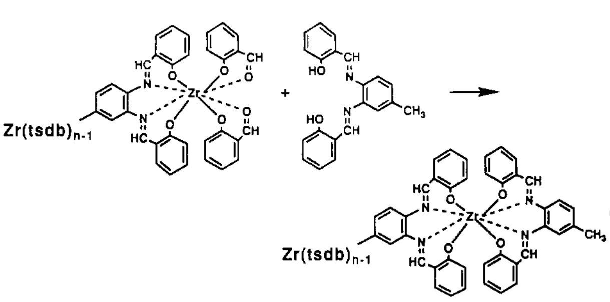
(12) Vogel, H.; Marvel, C. S. *J. Polym. Sci.* **1963**, *A1*, 1531.

(13) Vogel, H.; Marvel, C. S. *J. Polym. Sci.* **1961**, *50*, 511.

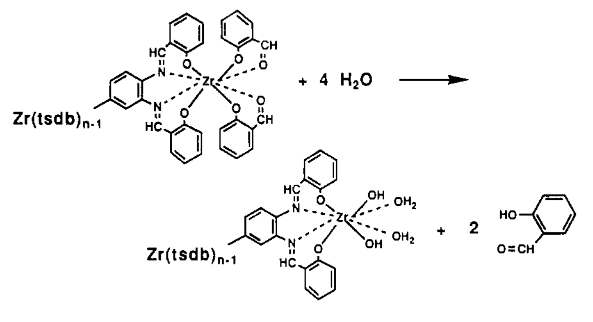
0020-1669/90/1329-0039$02.50/0



(1)



(2)



(3)

to avoid oxidation of the amine groups.

Disalicylidene-3,4-diaminotoluene. H_2dsdt, which was used as the end-capping reagent, was prepared by heating 4.0 g (33 mmol) of 3,4-diaminotoluene, which was previously purified by sublimation at 70–80 °C, and 8.0 g (66 mmol) of salicylaldehyde in 150 mL of toluene under reflux conditions overnight with distillation traps for the removal of water. The solvent was evaporated, and the compound was recrystallized from benzene/hexane mixtures. Yield: 8.2 g, 75%.

Anal. Calcd for $C_{21}H_{18}O_2N_2$: C, 76.4; H, 5.45; N, 8.5. Found: C, 76.1; H, 5.52; N, 8.3.

***catena*-Poly[zirconium(IV)(μ-*N*,*N'*,*N''*,*N'''*-tetrasalicylidene-3,3'-diaminobenzidinato-*O*,*N*,*N'*,*O'*:*O''*,*N''*,*N'''*,*O'''*)], [Zr(tsdb)]$_n$.** In order to study the relationship between reaction times, temperatures, and the degrees of polymerization at an exact 1:1 mole ratio, the reaction was allowed to proceed for 15 min at room temperature, 1 h at room temperature, 5 h at 50 °C, and 9 h at 60 °C.

For the first batch, 2.2405 g (3.895 mmol) of Zr(sal)$_4$ dissolved in 60 mL of DMSO under argon and 0.8335 g (3.895 mmol) of 3,3'-diaminobenzidine in 20 mL of DMSO under argon were mixed together and the solution was stirred for 15 min. Then 1 g (3 mmol) of H_2dsdt in 20 mL of DMSO under argon was added to end-cap the polymer, which was precipitated with methanol, filtered, and washed with methanol. Yield: 1.8 g, 63%.

For the second batch, the reagents were the same as the first batch, except that the Schiff-base condensation reaction was allowed to proceed for 1 h. Then 0.66 g (2 mmol) of H_2dsdt in 20 mL of DMSO was added to the solution and stirred for 30 min more. The product was precipitated with benzene, filtered, and washed with benzene. Yield: 1.5 g, 55%.

For the third batch, the Schiff-base reagents were stirred at 50 °C for 5 h. The end-capping and precipitation were identical to the second batch. Yield: 1.7 g, 61%.

The fourth batch was also very similar except that the Schiff-base reaction was allowed to proceed for 9 h at 60 °C. Then 0.33 g (1 mmol) of H_2dsdt in 10 mL of DMSO was added to end cap the polymer, which was precipitated with benzene, filtered, and washed with benzene. Yield: 1.9 g, 68%. For fractionation, this polymer was dissolved in fresh DMSO and then precipitated with CH_2Cl_2, filtered, and washed with CH_2Cl_2. The product was dried in vacuo for 24 h at 60 °C. Yield: 1.4 g, 47%.

Anal. Calcd for $[(C_{40}H_{26}N_4O_4Zr)\cdot 0.5C_2H_6SO]_n$: C, 65.1; H, 3.86; N, 7.40; S, 2.12; Zr, 12.0. Found: C, 63.0; H, 3.68; N, 7.42; S, 1.99; Zr, 11.3. $n^{20}{}_D = 1.5445 \pm 0.0005$.

The stoichiometry was changed by varying the mole ratios Zr(sal)$_4$:db. Ratios of 0.990:1.000, 0.995:1.000, 1.000:1.000, 1.000:0.995, and 1.000:0.900 were used for reactions conducted under the same conditions as the fourth batch above (9 h at 60 °C).

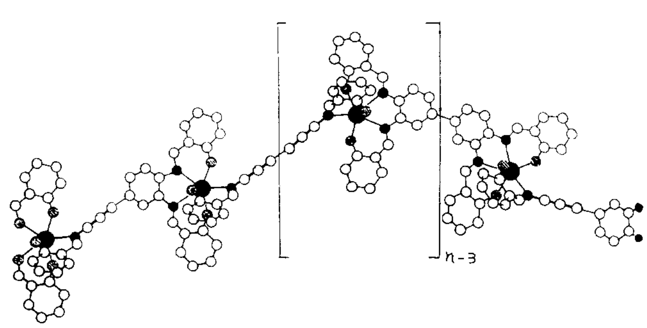


Figure 1. Anticipated structure of a typical [Zr(tsdb)]$_n$ polymer chain. The small black balls represent N, the small shaded balls represent O, the small white balls represent C, and the larger balls represent Zr. The parts of the ligand below the plane and the hydrogen atoms are not shown. For 1:1 stoichiometry, 50% will have the structure shown, 25% will have amines at both ends, and 25% will have zirconium salicylaldehyde groups at both ends. [Zr(tsb)]$_n$ is similar, except that a single aromatic benzene ring replaces the biphenyl rings of [Zr(tsdb)]$_n$.

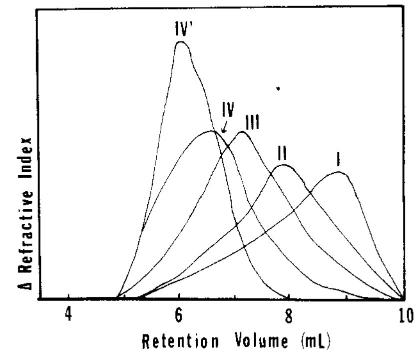


Figure 2. Gel permeation chromatography results for the [Zr(tsdb)]$_n$ polymers; cf. Table I. The molecular weight distributions are typical for such a step-growth polymer.

In another series of reactions, the stoichiometry was changed much more drastically from 1.2:1 to 1:1.2 Zr(sal)$_4$:db for a series of end-group variation studies. The reactions were allowed to proceed for 1 h at room temperature and analyzed spectroscopically.

***catena*-Poly[zirconium(IV)(μ-*N*,*N'*,*N''*,*N'''*-tetrasalicylidene-1,2,4,5-tetraaminobenzenato-*O*,*N*,*N'*,*O'*:*O''*,*N''*,*N'''*,*O'''*)], [Zr(tsb)]$_n$.** Samples of this polymer were available from our previous study.[5]

End-Capping Reaction Confirmation. An experimental determination of the extent of the end-capping reaction was made by allowing 1 mol of Zr(sal)$_4$ to react with an excess (>2 mol) of H_2dsdt. About 95% of the calculated number of moles of salicylaldehyde was collected. A little more undoubtedly remained in the distillation apparatus and/or went into the tubing beyond the distillation system; thus, the reaction goes essentially to completion.

Physical Measurements. Proton Fourier-transform nuclear magnetic resonances (FT-NMR) measurements were taken with a Varian Model XL200 spectrometer. The dsdt-end-capped-polymer methyl protons (average of 3 protons per chain) were integrated against the aromatic protons (22 protons per Schiff-base unit). From the ratio of intensities, the average number of monomeric units ($\bar{n}_{\rm mer}$) vs the average number of dsdt end groups ($\bar{n}_e$) was obtained. The average degree of polymerization was calculated by $\overline{\rm DP} = 2(\bar{n}_{\rm mer}/\bar{n}_e)$.[14] Several thousand aquisitions were necessary to get sufficient signal intensity for the end-group protons on the higher molecular weight polymers. For the highest molecular weight materials, DCl in D_2O was added to break down the chains sufficiently for the FT-NMR experiments.

Gel permeation chromatography measurements were conducted with a Waters Model 6000A pump, a Model R401 differential refractometer, and a 10^3-Å Ultrastyragel column. NMP was used as the solvent, and the column was calibrated with polystyrene standards.

Viscosity measurements were conducted in a Canon–Fenske type viscometer in NMP at 30.00 ± 0.02 °C.

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

---

(14) Elias, H.-G. *Macromolecules. 2. Synthesis, Materials, and Technology*, 2nd ed.; Plenum Press: New York, 1984; p 590. [Zr(tsdb)]$_n$ is an (AB)$_n$ copolymer with the degree of polymerization (DP) being twice the number of repeating units (the subscript *n* in [Zr(tsdb)]$_n$).

Table I. Reaction Conditions and Characterization of $[Zr(tsdb)]_n$

reacn time and temp	GPC			NMR			
	vol[a]	$\bar{M}_n$[b]	$\overline{DP}$	intens[c]	$\overline{DP}$[d]	viscosity[e]	batch
15 min at room temp[f]	8.26	2870	8	36	10[h]	0.046	I
1 h at room temp	7.71	6100	17	84	23[h]	0.065	II
5 h at 50 °C	6.95	10760	30	143	39	0.100	III
9 h at 60 °C	6.62	17930	50	264	72	0.158	IV
9 h at 60 °C[g]	6.29	30000	82	337	92	0.195	IV′

[a] Retention volume (mL) in NMP at 30 °C. [b] $\bar{M}_n$ vs polystyrene standards. [c] Relative intensities of aromatic protons to dsdt methyl protons. [d] $\overline{DP}$ was obtained from $2(\bar{n}_{mer}/n_e)$. [e] Intrinsic viscosity in dL/g. [f] Precipitated with methanol. [g] After fractionation of the preceding sample. [h] $\overline{DP}$ was also verified from the ratios of aldimine (four per unit) to methyl (three per chain) protons.

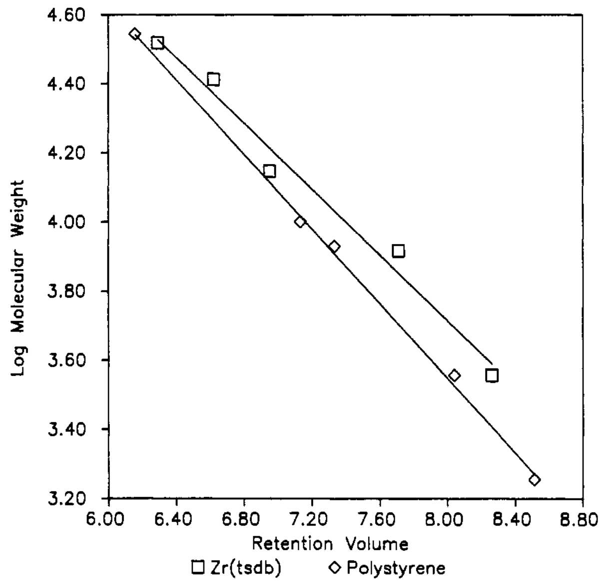


Figure 3. Universal gel permeation chromatographic calibration for $[Zr(tsdb)]_n$ polymers ($\bar{M}_n$ based on NMR) and polystyrene in *N*-methylpyrrolidone on a 10^3-Å Ultrastyragel column.

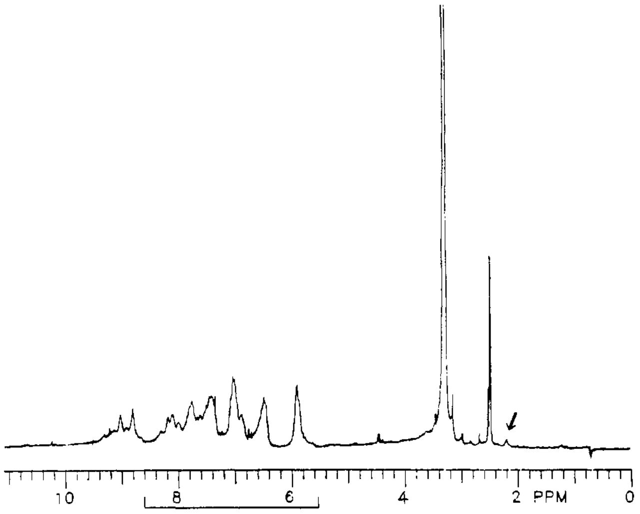


Figure 4. Proton nuclear magnetic resonance spectrum of a moderate-chain-length $[Zr(tsdb)]_n$ polymer.

Table II. Average Degrees of Polymerization of $[Zr(tsdb)]_n$ Polymers vs Stoichiometry[a]

$Zr(sal)_4$:db	NMR intens[b]	% Zr(dsdt)[c]	$\overline{DP}$[d]
0.990:1.000	210	34[d]	39
0.995:1.000	216	40[c]	48
1.000:1.000	266	50	72
1.000:1.000	338	50	92
1.000:0.995	152	59[c]	51
1.000:0.990	107	66[c]	42

[a] Nine hours at 60 °C. [b] Intensity ratios of aromatic protons to dsdt methyl protons. [c] Percent of Zr(tsdt) end groups based on the extent of reaction ($p = 0.99$) and reactant mole ratios. [d] $\overline{DP}$ obtained as 2(intens × 3/22)[% Zr(tsdt) ends]/50%.

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 anlaysis data stations and System 4 microprocessors. For the T_g measurements, the samples were scanned (heated) three times with rapid cooling between scans.

Results

catena-Poly[zirconium(IV)(μ-*N,N′,N″,N‴*-tetrasalicylidene-3,3′-diaminobenzidinato-*O,N,N′,O′:O″,N″,N‴,O‴*)], $[Zr(tsdb)]_n$, has been prepared through the reaction of tetrakis(salicylaldehydato)zirconium(IV) and 3,3′-diaminobenzidine in DMSO under a variety of conditions. The maximum molecular weight was obtained for the exact 1:1 stoichiometry with reaction times of 9 h at 60 °C. Precipitation of insoluble cross-linked materials occurred at higher reaction temperatures with longer reaction times. The polymers were end-capped with disalicylidene-3,4-diaminotoluene, H_2dsdt, to avoid adhesion to glass vessels during subsequent manipulation of the polymers in the characterization studies.

Gel permeation chromatography (GPC) of the $[Zr(tsdb)]_n$ polymer samples in NMP, as shown in Figure 2, indicates number-average molecular weights of up to about 30000 relative to polystyrene standards (Table I). The log (molecular weight) vs retention volume universal calibration curves have been plotted in Figure 3 for polystyrene standards and for the end-capped $[Zr(tsdb)]_n$ polymers. The molecular weights of the $[Zr(tsdb)]_n$ polymers were based on the NMR end-group analyses noted below.

End-group analyses of $[Zr(tsdb)]_n$ have been obtained by FT-NMR spectroscopy from the intensity of the end-cap $dsdt^{2-}$ methyl proton signal, which is at 2.2 ppm, vs the Schiff-base aromatic region, which has 22 protons per repeating unit and ranges from 5.5 to 8.7 ppm as shown in Figure 4 for a short-chain polymer. The highest molecular weight obtained from the NMR end-group analyses is 33000. See Tables I and II.

Comparisons with the four aldimine protons from 8.8 to 9.2 ppm were used to verify these results as noted in Table I, but could not be used in the experiments when DCl was added to enhance solubility because some of the aldimine groups decompose and/or undergo deuterium exchange.

Inherent viscosities of $[Zr(tsdb)]_n$ have been measured by Kraemer's approximation:[15]

$$[\eta]_{inh} = (1/c)\ \ln\ (t_{soln}/t_{solv})$$

Here, $[\eta]_{inh}$ is the inherent viscosity, c is the concentration in g/dL, and t is the time in seconds for the solution or solvent. The intrinsic viscosity has been obtained by extrapolation of the inherent viscosity values to zero concentration. The results are shown in Table I.

Spectral characterization of $[Zr(tsdb)]_n$ (in addition to the FT-NMR results) includes infrared vibrational spectra, which exhibit strong bands at 1610 and 1310 cm^{-1}, which have been

---

(15) Kraemer, E. O. *Ind. Eng. Chem.* **1938**, *30*, 1200.

Table III. Molar Extinction Coefficients of $[Zr(tsdb)]_n$ vs Stoichiometry[a]

			ϵ^e	
$Zr(sal)_4$:db	% Zr[b]	$\overline{DP}$	molar ($\times 10^5$)	per Zr ($\times 10^4$)[f]
1.2:1.0	84	7.6[c]	1.31	3.16
1.1:1.0	75	10.8[c]	1.86	3.29
1.0:1.0	50	23.2[d]	3.30	2.95
1.0:1.1	25	10.8[c]	1.67	3.24
1.0:1.2	16	7.6[c]	1.10	3.19

[a] One hour at room temperature. [b] Percent of Zr end group in the polymer obtained from calculations based on the extent of reaction ($p = 0.96$) and reactant mole ratios. [c] Calculated from degree of polymerization relative to mole ratios and extent of reaction. [d] Based on NMR results. [e] Extinction coefficients. [f] Molar extinction coefficient/Zr atoms per average chain.

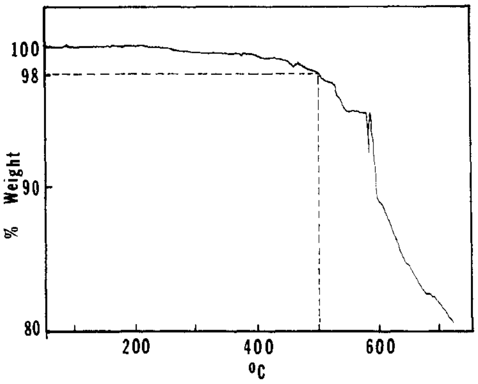


Figure 5. Thermogravimetric analysis of the long-chain $[Zr(tsdb)]_n$ polymer (IV′ of Table I).

assigned as a C=N stretch and a C—O stretch of the Zr–O–phenyl unit, respectively.[5,16] A strong electronic transition is observed at 400 nm with a molar extinction coefficient of about 3.2×10^4 L (mol of Zr)$^{-1}$ cm^{-1} in the various polymers as noted in Table III.

Thermal analyses of $[Zr(tsdb)]_n$ have included thermal gravimetry and differential scanning calorimetry (DSC). The high molecular weight polymer ($\overline{DP} = 92$) shows a high thermal stability with 98% weight retention at 773 K; cf. Figure 5. The glass transition temperature (T_g) has been calculated from the DSC measurements to be 347 K, with an onset temperature of 339 K. The corresponding values for $[Zr(tsb)]_n$ have been determined to be 360 K and 350 K, respectively. The hysteresis of the transitions show that they are T_g transitions.[17]

Discussion

Dimethyl sulfoxide has been used as the reaction medium in the Schiff-base polymerization reaction (eq 1) because of its strong hydrogen bonding with water,[18] its properties as a polymer solvent,[19,20] and its success in our earlier work.[5] Both reagents were separately dissolved in DMSO so that the dissolution rate would not be the rate-determining step in the polymerization reaction. Formation of the deep red color associated with the polymeric product occurs almost instantaneously upon mixing of the solutions at room temperature. The end-capping agent H_2dsdt provides quadridentate coordination and easily replaces the bidentate salicylaldehydato ligands on the zirconium(IV) at the end of the polymer chains (eq 2). At the end of the reactions for obtaining the longest chain polymers, the polymer is precipitated by adding benzene. About one-third of the polymer, undoubtedly lower molecular-weight material, stays in solution as does the excess H_2dsdt, which is soluble in both benzene and DMSO.

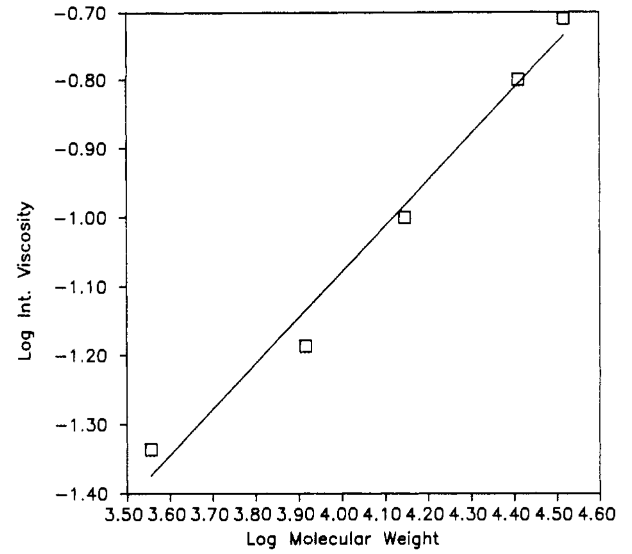


Figure 6. Mark–Houwink plot of the $[Zr(tsdb)]_n$ polymers.

The experimental microanalysis results for C and Zr are a little lower than the calculated values. For polymers with high thermal stability, carbon is typically a few percent lower than it should be,[21] though in the present case it may be because of the formation of some zirconium carbide. Any zirconium carbide formed and not converted to the oxide gives lower microanalysis results for both C and Zr. The Zr values come from the ash, which is assumed to be ZrO_2.

The molecular weights, based on NMR end-group analyses, have been plotted vs the viscosities as a log/log plot to obtain the Mark–Houwink equation[22] ($[\eta] = K'\bar{M}^a$) constants. The plot of log $[\eta]$ vs log $\bar{M}_n$ (Figure 6) gives $a = 0.68$ and $K' = 1.53 \times 10^{-4}$ after linear regression with $R^2 = 0.985$. These values are in the typical ranges found for organic polymers.[23] [Stockmeyer–Fixman equation plots[24] for the same data gave less satisfactory results ($R^2 = 0.936$).]

High thermal stability has been noted for the new $[Zr(tsdb)]_n$ polymer as well as for the $[Zr(tsb)]_n$ polymer.[5] The T_g values of 74 °C for $[Zr(tsdb)]_n$ and 87 °C for $[Zr(tsb)]_n$ are quite reasonable according to their probable geometry, as depicted in Figure 1. As noted in the introduction, the structures of $[Zr(tsdb)]_n$ and $[Zr(tsb)]_n$ provide an irregular organic sheath around the metal ions. This sheath tends to limit the intermolecular forces, which normally prevent the attainment of large decreases of polymerization for metal coordination polymers. The nonrigidity of eight-coordinate zirconium[8] provides further flexibility in these systems relative to the more rigid four- and six-coordinate systems often used to make coordination polymers. The lower T_g value for the $[Zr(tsdb)]_n$ polymer relative to that for $[Zr(tsb)]_n$ is logical considering the fact that benzidene has the possibility of free rotation about the single bond between its two aromatic rings, which provides the $[Zr(tsdb)]_n$ polymer with more flexibility than the relatively rigid $[Zr(tsb)]_n$ single-ring bridge. Lower T_g values are often correlated with greater chain mobility.[25]

As noted in the Introduction, we have also found that these polymers adhere strongly to glass unless they are end-capped or added to glass that has been presilanized. Furthermore, we have

---

(16) (a) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley: New York, 1981; p 130. (b) Calligaris, M.; Randaccio, L. *Compr. Coord. Chem.* **1987**, *2*, 724. (c) Percy, G. C.; Thorton, D. A. *J. Inorg. Nucl. Chem.* **1972**, *34*, 3357, 3369.

(17) Rabek, J. F. *Experimental Methods in Polymer Chemistry. Physical Principles and Applications*; John Wiley: New York, 1980; p 565.

(18) Reynolds, W. L. *Prog. Inorg. Chem.* **1970**, *12*, 1.

(19) Conciatori, A. B.; Chenevey, E. C.; Bohrer, T. C.; Prince, A. E., Jr. *J. Polym. Sci., Part C* **1967**, *19*, 49.

(20) Fachs, O.; Suhr, H. H. *Polymer Handbook*, 2nd ed.; John Wiley: New York, 1975; p 241.

(21) Mulvaney, J. E.; Marvel, C. S. *J. Polym. Sci.* **1961**, *50*, 541.

(22) Rodriguez, F. *Principles of Polymer Systems*; McGraw-Hill: New York, 1970; p 154.

(23) Billmeyer, F. W. *Textbook of Polymer Science*, 2nd ed.; John Wiley: New York, 1984; p 87.

(24) Stockmeyer, W. H.; Fixman, M. *J. Polym. Sci., Part C* **1963**, *1*, 137.

(25) Rosen, S. L. *Fundamental Principles of Polymeric Materials*; John Wiley: New York, 1982; p 92.

found that these polymers also adhere very well to the alumina on aluminum surfaces,[10] and have used the lower oligomers as a component of hybrid polymers, which allows compatibility with a variety of organic polymers from polyesters to polyolefins.[26]

In conclusion, we have found that metal coordination polymers that behave similar to organic polymers can be synthesized by a careful consideration of the intermolecular forces that have typically limited the size of many metal coordination polymers in the past. The additional complication of interface interactions between the ends of metal coordination polymers and oxide surfaces is both a concern for synthesis and characterization and an opportunity for the preparation of improved surface coatings.

Acknowledgment. We acknowledge the partial support of IBM for this research through the University of Massachusetts Institute for Interface Sciences. We also thank Wenyan Tong and Paul West for some computerized spectra retrieval.

---

[26] Archer, R. D.; Wang, B. *Polym. Mater. Sci. Eng.* **1989**, *61*, 101.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, and Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Variable-Temperature ^{1}H NMR Spectra and T_1 Measurements on the Dinuclear Octahydride Complexes $Re_2H_8(PR_3)_4$ (PR_3 = PPh_3, PEt_2Ph, PMe_2Ph, PMe_3) and the Monohydride Complexes Cp_2ReH and $Re_2HCl_3(CO)_2(dppm)_2$ (dppm = $Ph_2PCH_2PPh_2$)

F. Albert Cotton,*[1a] Rudy L. Luck,[1a] Dawn R. Root,[1b] and Richard A. Walton[1b]

Received May 1, 1989

The variable-temperature spectra and T_1 ^{1}H NMR data for the dinuclear complexes $Re_2H_8(PR_3)_4$ (PR_3 = PPh_3, PEt_2Ph, PMe_2Ph, PMe_3) are reported in CD_2Cl_2. The room-temperature spectra consist of a quintet in the hydride region. In all cases, at very low temperatures, it was possible to obtain spectra indicative of a frozen-out species; the quintet for the metal-bonded hydrogen atoms resolved into two distinct resonances of equal intensity. Definitive assignments as to which peak was due to the terminal and which to the bridging hydrogen atoms were made on the basis of an isotopic perturbation of resonance experiment, and thus the peak at higher field was assigned as due to the terminal hydrogen atoms. Furthermore, all of the $Re_2H_8(PR_3)_4$ complexes exhibited minimum T_1 times around ca. 140 ms at 400 MHz. A minimum T_1 value of 280 ms at 400 MHz was found for Cp_2ReH in toluene-d_8. In the case of $Re_2HCl_3(CO)_2(dppm)_2$, the value of ca. 85 ms was obtained at 200 MHz and −80 °C in CD_2Cl_2. These results suggest, at least in the case of $Re_2HCl_3(CO)_2(dppm)_2$, that other relaxation mechanisms, in addition to the H–H dipolar one, can operate in these rhenium complexes.

Introduction

Complexes of the general form $[ReH_x(PR_3)_2]_n$ (PR_3 = tertiary phosphine) were discovered in seminal work by Chatt and Coffey in 1969.[2] However, it remained until there was a neutron diffraction study on $Re_2H_8(PEt_2Ph)_4$ for the exact structural nature of these complexes to be unambiguously established as containing four bridging and four terminal metal-bonded hydrogen atoms.[3] More recently, work in this area has involved protonation and oxidation reactions,[4] auration substitution reactions on these dimers,[5] reactions with *tert*-butyl isocyanide,[6] and studies of different synthetic routes to these complexes.[7]

We were interested in the variable-temperature (VT) ^{1}H NMR spectra and T_1 values for the metal-bonded hydrogen ligands in these complexes as the molecules were completely fluxional down to temperatures of ca. −80 °C.[7b] The VT spectra reported herein reveal that at low enough temperatures it is possible to freeze out the fluxional process responsible for the interconversion of the terminal and bridging hydrogen atoms. Our previous studies on other fluxional rhenium hydride complexes, such as $ReH_3(PMePh_2)_4$ and $ReH_5(PPh_3)_3$, revealed that low T_1 values (<160 ms at 400 MHz) are not always indicative of molecular dihydrogen ligands.[8] In fact, T_1 minimum values for the metal-bonded hydrogen atoms in complexes $Re_2H_8(PR_3)_4$ (PR_3 = PPh_3, (**1**), PEt_2Ph (**2**), PMe_2Ph (**3**), PMe_3 (**4**)) of around 140 ms at 400 MHz were obtained. We have also measured the variable-temperature T_1 values for the monohydride complexes Cp_2ReH (**5**)[9] and $Re_2HCl_3(CO)_2(dppm)_2$ (**6**).[10] A minimum value of 280 ms was obtained for complex **5**, which is consistent with the relaxation of the hydrogen atom by the Re atom via a dipole–dipole mechanism. In the case of the dimer **6**, the data show a decrease in T_1 with temperature to ca. 85 ms at 200 MHz and −50 °C but no increase or decrease as the temperature was lowered further. This result cannot be attributed to a dipole–dipole relaxation mechanism and indicates that some other mechanism, such as scalar coupling, might also contribute to the low T_1 values in this complex and possibly in other rhenium hydrides. Moreover, the T_1 minimum values for the $Re_2H_8(PR_3)_4$ species need not be taken to suggest that η^2-H_2 ligands are present in these complexes. The importance of these results is that they contribute to defining the limits of applicability of the T_1 NMR criterion for detecting η^2-H_2 ligands in rhenium polyhydride complexes.

Experimental Section

The NMR spectra were recorded in CD_2Cl_2 and toluene-d_8 by using Varian XL-200 and XL-400 NMR spectrometers. The inversion-recovery method was used to measure the T_1 values with prior determination of the 180° pulse for some samples. The Carr–Purcell–Meiboom–Gill sequence was employed to evaluate T_2 in $Re_2H_8(PEt_2Ph)_4$ (**2**).[11] Complexes $Re_2H_8(PR_3)_4$ (PR_3 = PEt_2Ph (**2**), PMe_2Ph (**3**), PMe_3 (**4**)) were prepared as described previously,[7b] and $Re_2HCl_3(CO)_2(dppm)_2$ was generously supplied by Professor K. R. Dunbar and S.-J. Chen of Michigan State University. $Re_2H_8(PPh_3)_4$ (**1**) and Cp_2ReH (**5**) were prepared according to procedures in ref 2 and 9, respectively. Complexes of the form $Re_2H_nD_{8-n}(PR_3)_4$ (PR_3 = PEt_2Ph, PMe_2Ph) were prepared by adding mixtures of $LiAlH_4$ and $LiAlD_4$ to the chloride precursors,

---

[1] (a) Texas A&M University. (b) Purdue University.

[2] Chatt, J.; Coffey, R. S. *J. Chem. Soc. A.* **1969**, 1963.

[3] Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872.

[4] Allison, J. D.; Walton, R. A. *J. Chem. Soc., Chem. Commun.* **1983**, 401.

[5] Moehring, G. A.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 1861.

[6] Allison, J. D.; Cotton, F. A.; Powell, G. L.; Walton, R. A. *Inorg. Chem.* **1984**, *23*, 159.

[7] (a) Brant, P.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 2674. (b) Fanwick, P. E.; Root, D. R.; Walton, R. A. *Inorg. Chem.* **1989**, *28*, 395. (c) Roberts, D. A.; Geoffroy, G. L. *J. Organomet. Chem.* **1981**, *214*, 221.

[8] (a) Luck, R. L.; Cotton, F. A. *Inorg. Chem.* **1989**, *28*, 2182. (b) Luck, R. L.; Cotton, F. A. *Inorg. Chem.* **1989**, *28*, 6. (c) Cotton, F. A.; Luck, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 5757.

[9] (a) Wilkinson, G.; Birmingham, J. M. *J. Am. Chem. Soc.* **1955**, *77*, 3421. (b) Green, M. L. H.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1958**, 3916.

[10] Chen, S.-J.; Dunbar, K. R. To be submitted for publication.

[11] (a) Carr, H. Y.; Purcell, E. M. *Phys. Rev.* **1954**, *94*, 630. (b) Meiboom, S.; Gill, D. *Rev. Sci. Instrum.* **1958**, *29*, 688.

0020-1669/90/1329-0043$02.50/0