Macromolecules **1985**, *18*, 1371–1376

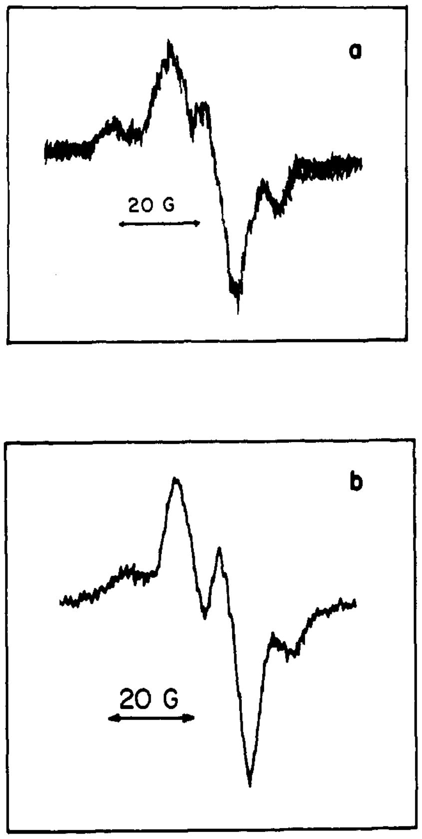

Figure 7. ESR spectra of PVP-1: (a) UV irradiated at 298 K and measured at 77 K; (b) UV irradiated at 77 K, heated to 298 K, and measured at 77 K.

polymers (PVP-2 and PVP-3) produced from electrochemical and photoelectrochemical methods had the characteristics of the polymer (PVP-1) synthesized with Ziegler–Natta catalyst. Visible-light-induced photoelectrochemical polymerization has been reported for the first time at a n-GaAs semiconductor electrode.

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Registry No. Poly(1-vinylpyrene), 25120-43-8; 1-vinylpyrene, 17088-21-0.

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A Soluble Linear Schiff-Base Coordination Polymer Containing Eight-Coordinate Zirconium(IV)

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ABSTRACT: The first soluble linear Schiff-base heavy-metal coordination polymer has been synthesized via the condensation of 1,2,4,5-tetraaminobenzene and tetrakis(salicylaldehydato)zirconium(IV) in dry dimethyl sulfoxide. The (*N*,*N*′,*N*″,*N*‴-tetrasalicylidene-1,2,4,5-tetraaminobenzenato)zirconium(IV) polymer has a number-average molecular weight of up to 4.9×10^4 based on inherent viscosity, gel permeation chromatography, and elemental analysis. Spectral properties of this polymer indicate a structure analogous to the model compound bis(*N*,*N*′-disalicylidene-1,2-phenylenediamino)zirconium(IV). Thermal characterization of the polymer is also discussed.

Introduction

Linear metal chelate polymers with Schiff-base ligands in which the metal is a part of the polymer backbone[1-5] or is added to a polymeric Schiff base[5-10] are typically insoluble materials. The X-ray study of bis(*N*,*N*′-disalicylidene-1,2-phenylenediamino)zirconium(IV)[11] shows that two quadridentate Schiff-base ligands on zirconium(IV) are oriented such that a polymeric extension should be distorted from a strictly linear geometry, which might cause intermolecular stacking and intractability, a serious problem in the attempted polymerizations of divalent ions with Schiff-base (and other) bridging ligands.[12] Further-

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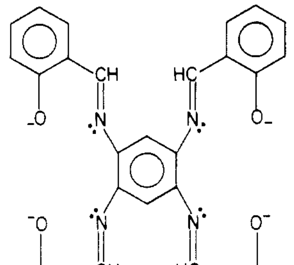
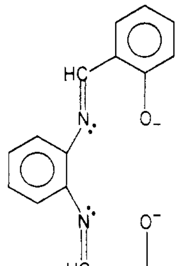
more, the possibility of flexibility for nonrigid metal centers, even with conjugated organic bridging ligands, provided further incentive to use zirconium as the metal for synthesizing a tractable Schiff-base chelate polymer. Zirconium(IV) eight-coordinate chelates are typically nonrigid.[13] The D_{2d} dodecahedron and the D_{4d} square antiprism, which are the two most common geometrical arrangements for eight ligand donor atoms around a central metal ion, are very similar in energy and normally possess a low energy barrier to interconversion; thus, nonrigid behavior is typical, even for chelates.

Zirconium(IV) is a labile metal ion; therefore, we have used a bis(quadridentate) delocalized chelating ligand, *N,N′,N″,N‴*-tetrasalicylidene-1,2,4,5-tetraaminobenzene (H_4tsb, 1), to retard the rate of ligand exchange in solution, to allow extensive polymer chain growth, and to provide good thermal stability.[14] Such Schiff-base ligands are capable of sufficient nonplanarity for the interconversion between the dodecahedron and the antiprism.[15,16] Thus, nonrigidity, suggested above, should still be possible.

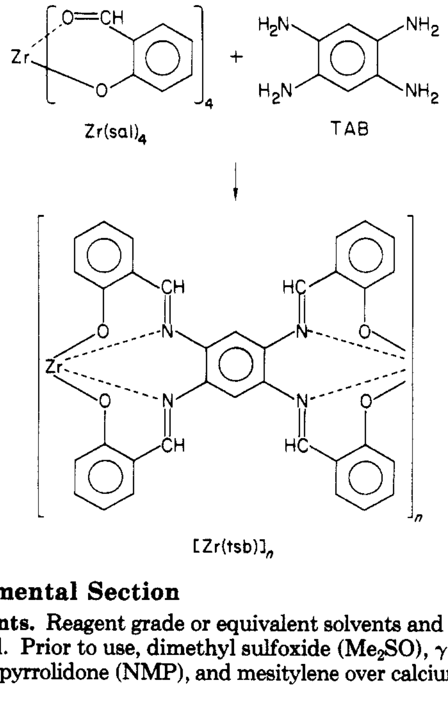


1, tsb^{4-}



2, dsb^{2-}

The soluble red coordination polymer has been obtained through the condensation of tetrakis(salicylaldehydato)zirconium(IV) (Zr(sal)$_4$) with 1,2,4,5-tetraaminobenzene (TAB), analogous to the reaction between Zr(Sal)$_4$ and *o*-phenylenediamine, which we reported previously.[17] The low solubility of H_4tsb in ordinary solvents[18] caused us to investigate this alternative to polymerization through normal ligand-displacement reactions. This ligand-forming condensation reaction (eq 1) proved successful.[19]



(1)

Experimental Section

Reagents. Reagent grade or equivalent solvents and chemicals were used. Prior to use, dimethyl sulfoxide (Me$_2$SO), γ-collidine, *N*-methylpyrrolidone (NMP), and mesitylene over calcium hydride were distilled under reduced pressure; methylene chloride over calcium hydride, and methanol and acetone over anhydrous calcium sulfate, were distilled at atmospheric pressure. A nitrogen atmosphere was used in the presence of free amines, with Zr(sal)$_4$, and during the polymerization reactions.

Tetrakis(salicylaldehydato)zirconium(IV). Zr(sal)$_4$ was prepared as previously described[17] and used promptly.

Poly[(*N,N′,N″,N‴*-tetrasalicylidene-1,2,4,5-tetraaminobenzenato)zirconium(IV)]. 1,2,4,5-Tetraaminobenzene (TAB) tetrahydrochloride (Burdick and Jackson Laboratories) was dehydrohalogenated prior to use, modifying the method of Dudgeon.[20] Twenty-five milliliters of oxygen-free water, 5.0 g (0.017 mol) of TAB·4HCl, and a small amount of Norit A were mixed and heated to boiling under a nitrogen atmosphere. The hot mixture was suction filtered into a dry ice/acetone chilled flask. The clear and nearly colorless filtrate was then quickly transferred with stirring into 25 mL of ice-cold 15% aqueous NaOH solution and the free TAB instantly precipitated as white flakes. The mixture was filtered, ice-water washed, dried in vacuo, and weighed under nitrogen; yield 1.43 g, 58%.

Then 0.816 g (5.92 mmol) of TAB and 3.401 g (5.92 mmol) of freshly prepared Zr(sal)$_4$ were separately dissolved in 100 and 200 mL, respectively, of dry, deoxygenated Me$_2$SO under a nitrogen atmosphere. The pale tan tetraamine solution was added in one portion to the chartreuse-yellow Zr(sal)$_4$ solution in a 500-mL flask. A deep red color developed immediately. With continued magnetic stirring, the Me$_2$SO–water azeotrope was slowly distilled under reduced pressure [41 °C (1.6 torr)], leaving a red glassy solid, which was purified by dissolution in dry Me$_2$SO and precipitated with dry acetone.

Anal. Calcd for $[C_{34}H_{22}N_4O_4Zr]_n$: C, 63.6; H, 3.43; N, 8.73; Zr, 14.2. Calcd for 0.1 mol of Me$_2$SO/Zr(tsb): C, 63.2; H, 3.5; N, 8.6; S, 0.5; Zr, 14.0. Found:[21] C, 62.7; H, 3.8; N, 8.3; S, 0.8; Zr, 14.1.

Analysis of a sample prepared by in vacuo removal of Me$_2$SO solvent without the addition of acetone indicates about 1.7 mol of Me$_2$SO per Zr unit and a Zr:4*N* ratio of 1.018. Calcd for $Zr_{31}(C_{34}H_{22}N_4O_4)_{30}(OH)_4{\cdot}53C_2H_6SO$: C, 57.4; H, 4.2; N, 7.1; S, 7.2; Zr, 12.0. Found: C, 57.1; H, 4.3; N, 7.0; S, 6.9; Zr, 11.6.

Bis(quadridentate) Schiff-Base Ligands. Free TAB (1.20 g, 8.1 mmol) prepared as above was dissolved in 175 mL of dried deoxygenated Me$_2$SO, and a stoichiometry amount (3.95 g, 32.4 mmol) of salicylaldehyde was added. The resulting deep red solution was allowed to stand overnight under nitrogen. The copious red-orange precipitate that formed was filtered under a nitrogen stream, washed several times with dried acetone, and dried in vacuo.

Anal. Calcd for $C_{34}H_{26}N_4O_4$: C, 73.6; H, 4.69; N, 10.1. Found: C, 72.7; H, 4.71; N, 9.7. Less than 0.15 mol of Me$_2$SO gives excellent analytical agreement.

Derivatives of H_4tsb were prepared from the reaction of substituted salicylaldehydes with TAB, using an excess of the aldehyde as a melt solvent. For example, 0.8 g (6 mmol) of TAB and 20 g (130 mmol) of 3-methoxysalicylaldehyde were allowed to react for 20 min at 50 °C. Hot filtration of the excess molten aldehyde from the fine red precipitate was followed by trituration with methanol and ethyl ether to remove any final traces of the aldehyde. The precipitate was dried in vacuo at room temperature for 24 h; yield 1.8 g, 50%; mp 261–262 °C dec.

Anal. Calcd for $C_{38}H_{34}N_4O_8$: C, 67.7; H, 5.04; N, 8.31. Found: C, 67.8; H, 4.99; N, 8.21.

Similarly, an analogous reaction between 1.0 g (7.2 mmol) of TAB and 20 g of molten 5-methoxysalicylaldehyde yielded 3.5 g (70%) of a product with mp 280–280.5 °C dec.

Anal. Calcd for $C_{38}H_{34}N_4O_8$: C, 67.7; H, 5.04; N, 8.31. Found: C, 68.0; H, 5.19; N, 8.17.

Condensation of TAB with excess 5-bromosalicylaldehyde and 2-hydroxy-1-naphthaldehyde gave products of very low solubility in common organic solvents. They were not purified.

Physical Properties. The same instrumentation and physical methods of characterization cited previously[17] were employed. In addition, thermal changes of polymer and model compounds were determined by using a DuPont 900 thermal analyzer with a gas (nitrogen or air) flow of 0.2 L/min, a heating rate of 10 °C/min, a sample size of 10 mg, and aluminum chloride as a reference. Sample weight losses corresponding to these thermal changes were measured on a DuPont 950 thermogravimetric analyzer using samples of similar size under identical conditions. Preliminary thermal decomposition pyrolysis was accomplished with a Chromalytics MP-3 multipurpose thermal analyzer. The products were trapped on glass beads using liquid nitrogen and separated with a Varian Aerograph Series 2700 gas chromatograph using Chromosorb 102 for the low-boiling components and General Electric SE 30 on Chromosorb W support for the high-boiling components.

Viscosity data in triplicate were collected in a Canon-Fenske Model No. 100-2873 viscometer or in an Ubbelohde Model No. 1, 2568 viscometer, equilibrated at 30.0 ± 0.02 °C. The solvent was NMP.

A weight-loss experiment was conducted with a "furnace" consisting of a 6-in. test tube in a Wood metal bath. A smaller 4-in. test tube served as the sample container. The sample container was preconditioned in the furnace for 24 h prior to removal for rapid weighing, followed by addition of 0.1 g of polymer, reweighing, reheating, reweighing, etc. Weighings were to ±0.2 mg.

Gel permeation chromatography of the zirconium polymer was conducted on a 10^3-Å Ultrastyragel column (Waters) with NMP as the solvent.

Results

Whereas H_4tsb and its derivatives have very limited solubility, the reaction between Zr(sal)$_4$ and TAB in Me_2SO produces an oligomer that is orders of magnitude more soluble. Solvent removal in vacuo or the addition of a miscible nonsolvent such as acetone is necessary to isolate a solid product.

Because the isopropyl derivative of H_4tsb had shown improved solubility over the unsubstituted compound,[22] several derivatives were prepared to improve the solubility over the parent ligand while avoiding carbon–carbon single bonds. In dry donor solvents such as Me_2SO and γ-collidine, the 3- and 5-methoxy derivatives, which are reported here, show only modest solubility improvement relative to the parent compounds, while the slightly impure Schiff-base products obtained from condensation of 5-bromosalicylaldehyde or 2-hydroxy-1-naphthaldehyde with TAB show no solubility improvement at all.

These modest improvements are in sharp contrast to the polymer solubility improvement obtained in the chelate preparation between Zr(sal)$_4$ and TAB in Me_2SO. The soluble polymer solutions produce thin, light-diffracting films upon the slow evaporation of the Me_2SO solvent. [Me_2SO solution of the free H_4tsb ligand produce crystalline particles.] The red glassy polymer appears to be amorphous since no X-ray diffraction pattern could be obtained, and under microscopic examination the polymer appears as red, translucent, irregular-shaped particles with black striae.

The **elemental analyses** indicate 0.1–1.7 Me_2SO molecules per zirconium unit; the quantity of Me_2SO is dependent on the solvent mix. After considering the Me_2SO solvation, the excess of oxygen (by difference) is suggestive of OH end groups and/or water in the Me_2SO reaction product. Elemental analyses for N and Zr for a variety of samples indicate 1 ligand to 1 Zr within experimental error.

Inherent viscosities for Zr(dsp)$_2$ and the glassy Zr(tsb) polymer samples were determined by using Kraemer's approximation:[23]

$$[\eta]_{\text{inh}} = (1/c)\ \ln\ (T_{\text{solution}}/T_{\text{solvent}}) \qquad (2)$$

where $[\eta]_{\text{inh}}$ is inherent viscosity, c is concentration in d/dL, and T is time in seconds. Samples of the polymer have been prepared which have inherent viscosity values of up to 0.18 dL/g in NMP as noted in Table I. The inherent viscosities of the polymer samples show negligible concentration dependence for a series of dilute solutions so extrapolation to intrinsic viscosities is straightforward.

Table I
GPC and Viscosity Data for Polymeric Zr(tsb) in NMP

volume[a]	$\bar{M}_n$(PS)[b]	$[\eta]$[c]	$\bar{M}_\eta$[d]
5.65	49 000	0.177 ± 0.015	104 000 ± 9000
5.89	38 000	0.140 ± 0.009	87 000 ± 7000
6.17	28 000	0.117 ± 0.018	64 000 ± 10 000
6.24	26 000	0.091 ± 0.008	72 000 ± 7000
9.54	760[e]	0.02 ± 0.01	1000 ± 500

[a] Retention volume in mL on a 10^3-Å Ultrastyragel GPC column with NMP as the solvent. [b] Polystyrene equivalent number-average molecular weight based on calibration with 11 standards. [c] Intrinsic viscosity in NMP at 30.0 °C in dL/g. [d] Molecular weight based on viscosity/GPC universal calibration curve method. [e] Model monomeric zirconium Schiff-base chelate with a molecular weight of 690.

Table II
Infrared Spectral Results for the New Compounds $[Zr(tsb)]_n$ Polymer, $H_4(3\text{-}OMe)_4$tsb, and $H_4(5\text{-}OMe)_4$tsb (cm^{-1})[a]

assignment	[Zr(tsb)·1.7Me_2SO]$_n$	H_4tsb	H_4[(3-OMe)$_4$tsb]	H_4[(5-OMe)$_4$tsb]
ν(O–H), terminal[c]	3650 sh[c]			
ν(O–H), H-bonded or bridging	3430 br[c]	3500 w, br	3450 br	3450 br
ν(C═N)	1602 s[c]	1610 s	$\left.\begin{matrix}1612\\1605\end{matrix}\right\}$ s	1622 m
				1337 m[d]
ν(M–(OPh))	1310 m[c]			
ν(H(OPh))		1275 ms	1268 sh	1270 s
ν(H_3C(OPh))[b]			1250 s	1252 m
ν(H_3(C–O))			1228 w, sh	1228 w
ν(S–O), Me_2SO	1025 br			

[a] KBr pellets. [b] Tentative assignments. [c] Abbreviations: ν, stretching mode; sh, shoulder; br, broad; s, strong; m medium; w, weak. [d] Unknown assignment.

Gel permeation chromatography of the Zr(tsb) polymer samples in NMP yields number-average molecular weights of as much as 49 000 relative to polystyrene standards as noted in Table I. The data for monomeric Zr(dsp)$_2$ are also included in Table I.

Comparing the Zr(tsb) polymer with the free ligand, the *infrared* frequency shifts are analogous to those observed for Zr(dsp)$_2$ relative to H_2dsp except for the persistence of O–H vibrations in the polymer. See Table II. The phenyl ring-to-oxygen stretch is shifted by 35 cm^{-1} to higher frequencies in both the model chelate and the polymer relative to the respective neutral ligands. The imine C═N stretching vibration, by contrast, is almost unaffected, with frequency decreases of only a few wavenumbers in both cases. The major difference is in the O–H stretching region, which shows no absorption in the model chelate but persists with a peak and a shoulder in the polymer.[24]

The zirconium polymer has an **electronic spectrum** in Me_2SO which is more complex and has lower energy transitions than those of the free ligand in the same solvent. Very similar behavior has been noted in the model Zr(dsp)$_2$ system[11] and in other transition-metal complexes of this ligand.[18,22] See Table III.

Unlike monomeric Zr(dsp)$_2$, which has well-behaved **mass spectra**,[11] the polymer is not sufficiently volatile even at 275 °C to give a meaningful mass spectrum. Only a few very minor peaks are observed at mass-to-charge ratios of less than m/e 300.

Thermal analysis of the polymer and the model compound by differential thermal analysis (DTA), thermogravimetric analysis (TGA), and pyrolysis–gas chroma-

Table III
Electronic Spectral Results (cm^{-1}, {log ϵ})[a]

[Zr(tsb)·1.7Me_2SO]$_n$	H_4tsb	H_4[(3-OMe)$_4$tsb]	H_4[(5-OMe)tsb]
39 000 sh[b]	36 700 {4.40}[c]	34 600 {4.45}	35 500 {4.36}
30 800 {4.45}	29 800 sh[d]	29 200 sh	30 300 sh
	28 300 {4.55}[c]	27 900 {4.62}	27 000 {4.57}
26 500 w, sh	25 600 {4.50}[c]	26 500 {4.61}	25 600 {4.61}
22 400 {4.59}	23 900 sh[d]	24 400 sh	23 500 sh
21 200 sh			

[a] One-centimeter matched cells; Me_2SO as solvent. [b] CH_2Cl_2 as solvent. [c] Reference 18. [d] This work.

tography (P–GC) shows many analogous features as anticipated for compounds of similar structure. The DTA of the [Zr(tsb)]$_n$ polymer has a small endotherm which appears in the 130–190 °C range, probably due to loss of water and Me_2SO,[25] and thus is not observed in the DTA of the model compound. A noticeable weight loss near 160 °C is apparent in the polymer's TGA but not in the TGA of Zr(dsp)$_2$, which is consistent with this interpretation.

The next feature, ascending in temperature, is a small exotherm at 225–250 °C for the polymeric species in either nitrogen or air. While the DTA of freshly recrystallized, vacuum-dried Zr(dsp)$_2$ is featureless at these temperatures, samples that have been allowed to stand at length in air display an exotherm nearly identical with the one described above in either nitrogen or air. In the TGA of one 9-month-old sample of Zr(dsp)$_2$, a corresponding 2% weight loss was observed; the analogous feature in the polymer TGA is masked by the Me_2SO evaporation.

In order to discern if a slow decomposition reaction occurs at room temperature or if a bond-breaking and bond-forming reaction takes place upon heating, infrared spectra of the fresh, aged, and heated (to 270 °C) Zr(dsp)$_2$ samples were recorded. The only difference displayed by the aged samples in comparison to the previously reported infrared spectrum of purified Zr(dsp)$_2$[11] is the presence of a broad absorption at 3350–3600 cm^{-1} due to an O–H stretching mode. The heated sample, however, not only maintains an O–H stretching mode, but three new absorptions at 1627, 1163, and 763 (sh) cm^{-1} indicate that a new organic species is present.

The final thermal gravimetric feature displayed by both zirconium species is a large weight loss due to burning in air. This process begins at a slightly lower temperature for the polymer (380 °C) than for the model compound (400 °C). This chemical change is corroborated by the DTA: In air, the huge corresponding exotherm actually begins at less than 300 °C for the polymer and around 400 °C for Zr(dsp)$_2$. However, a rather dramatic difference occurs under nitrogen: whereas the anaerobic decomposition of the model compound is almost coincident with its combustion temperature, the polymer shows no such decomposition at temperatures below 500 °C.

Pyrolysis–gas chromatographic results, by contrast, are of greatest value as a fingerprint method. As anticipated for compounds of similar chemical structure, the gas chromatograms are consistent with the production of several identical pyrolysis fragments in the polymer and the model monomer. Extended heating of polymer samples in air at temperatures approximating the small exotherm (240 °C) produces considerably larger weight losses than those observed at this temperature during slow TGA scans. Approximately 22% and 46% weight losses were observed after 1 and 7 days, respectively, for the 1.7 Me_2SO solvate polymer. These weight losses are comparable to previous weight loss results for other metal chelate Schiff-base polymers.[6-10,14]

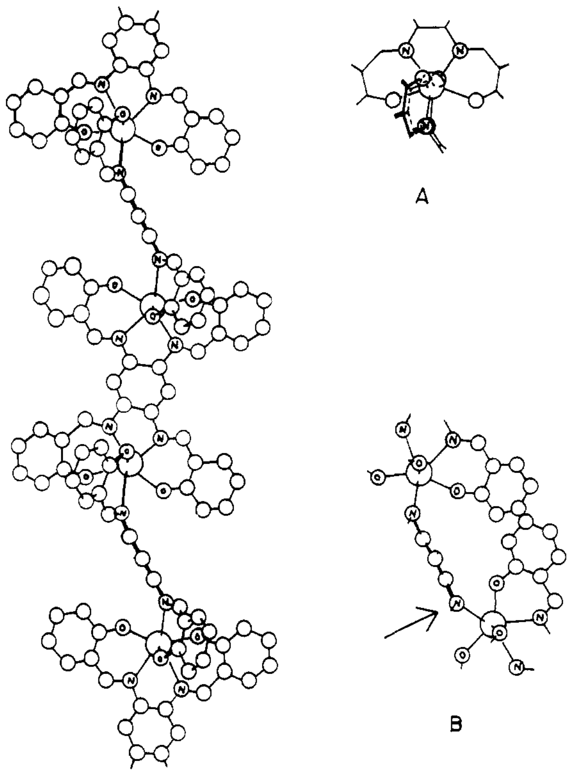


Figure 1. Anticipated structure for a portion of the [Zr(tsb)]$_n$ polymer The larger circles represent the Zr atoms and neither the ring below the plane of the molecule nor the H atoms are shown. The dodecahedral coordination about Zr is shown in inset A. Note that the organic portion of the ligand perpendicular to the plane of inset A is skewed (cf. ref 11) and provides two conformation possibilities, the trans one shown for the chain and the cis one shown in inset B, where the arrow points to the two nitrogens (one is below the one shown) with the changed configuration. Molecular models show that the configuration is possible, but the steric interactions cause us to favor the trans configuration shown at the left.

Discussion

The dramatic difference in the solubility of the Zr(tsb) polymer relative to the free ligand[18] or its derivatives[22] or most other coordination polymers[12] is potentially very significant. Industrially, polymer solubility is very important; e.g., concentrated Me_2SO solutions called dopes are used for spinning certain polymer fibers.[26] Characterization is also more definitive for soluble species. One feature that may in part be responsible for this solubility difference is the puckered, perpendicularly arranged, quadridentate ligands anticipated from the model compound X-ray structure,[11] in which the ligands show no tendency to stack with either benzene solvate molecules or chelate ligands from adjacent molecules. Models of the polymer chains, assuming the described stereochemistry, also depict steric reasons for significantly reduced lattice forces (cf. Figure 1). Nonrigid molecular motion may further hinder packing of the polymer chains. However, average chain length must also be considered as a major factor in comparing solubilities with other coordination polymers. Other ligand-forming polymerizations which allow extended chain lengths are rare.[8]

The Schiff-base polymerization reaction is known to be a high-yield reaction both with and without transition metals.[6-10,27] Also, the method used herein avoids the solubility problem associated with premade H_4tsb ligands. However, the production of water in the presence of hydrolytically reactive Zr(sal)$_4$[17] is of particular concern. Thus, Me_2SO, which is known for its strong hydrogen bonding with water[25] and its properties as a polymer solvent,[26,28] was chosen as the reaction medium. Both reactants were separately dissolved in Me_2SO 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 begins almost instantaneously upon mixing of the solutions at room temperature.

The formation of light-diffracting films upon evaporation of the solvent is a property often shown by, but not limited to, soluble polymers. More concrete evidence is deduced from the GPC, viscosity, and analysis results.

The GPC results for polymers with $\bar{M}_n$ up to 49 000 indicate an average degree of polymerization ($\overline{DP}$) of up to about 80. The results could be underestimating the molecular weight, since the monomeric unit is 643 daltons, and molecular weight models suggest each monomeric unit is about twice the size of a polystyrene unit. Thus, an appreciably higher molecular weight is possible. On the other hand, the large orientation angle between ligands estimated from the X-ray study[11] might give a pseudo-rigid-rod effect. Unfortunately no other heavy-metal chelate polymers are available for comparison. Ferrocene polymers, the closest type, do appear to give results similar to organic polymers.[29]

Consideration of the zirconium:ligand ratio of 1.018 and the elemental analysis corrected for the solvated Me_2SO suggests an average chain length of 20–50 units even if all of the end groups were hydroxides for the lowest molecular weight sample polymer in Table I. Given the equal probability of ligand end groups and of water to be coordinated along the chain or at the ends of the chains, the true degree of polymerization could be appreciably higher. The other samples have ligand:zirconium ratio of 1:1 within experimental error. Naturally, the effect of end groups on the elemental percentages becomes minimal, i.e., within analytical error, when large degrees of polymerization have been attained.

The inherent viscosity values of up to about 0.18 dL/g for the polymer samples in NMP indicate a reasonable degree of polymerization, especially when coupled with the GPC results. The second-order viscosity term in Kraemer's equation is unnecessary. A universal calibration treatment of the data provides an estimate of higher molecular weights as suggested above. The only reference point is the model monomer, which provides an indication that the retention volumes and viscosities are as anticipated. Attempts to estimate the molecular weight from the viscosity with the Mark–Houwink equation[30]

$$[\eta] = KM^a \tag{3}$$

are difficult because no soluble coordination polymers similar to Zr(tsb) exist for which K and a values have been determined. Attempts to measure the absolute molecular weights directly have been frought with insurmountable problems. The fluorescence of the polymer has precluded precise results through light scattering and attempts to use membrane osmometry have been thwarted by the instability of the membranes in NMP. Thus, we are stuck with the "ballpark" figures of between 49 000 based on the direct GPC measurements relative to polystyrene and the 100 000 value from the universal calibration curve, again relative to polystyrene. We have chosen the more conservative number for our claims.

Since the endothermic loss of Me_2SO from the polymer represents desolvation, the 225–250 °C exotherm in the polymer DTA, and similarly for aged samples of $Zr(dsp)_2$, represents the first bond-breaking and bond-forming chemical reaction. The observation that this feature does not occur in freshly recrystallized $Zr(dsp)_2$ necessarily means that samples of the model compound undergo a very slow change upon standing in air at room temperature, but since acquisition of an O–H stretching mode at 3350–3600 cm^{-1} is the only change noted in the infrared absorption spectrum, physical absorption of atmospheric water must be the only process occurring. Only upon heating to 240 °C does a chemical reaction apparently take place between the absorbed water and the Schiff-base complex. New peaks in the infrared at 1627, 1163, and 763 cm^{-1} after heating are consistent with this interpretation. Tentative assignments as a C=O stretch, a 1,2-disubstituted in-plane C–H bend, and a 1,2-disubstituted out-of-plane C–H bend, respectively, are consistent with a product resulting from hydrolysis of one imine bond.

Water produced during Schiff-base condensation presumably accounts for the analogous behavior of the polymer. The broad hydrogen bond O–H stretch in the infrared spectrum of the polymer is consistent with water being present in addition to hydroxy end groups.[24] While the corresponding polymer weight loss also appears small in the TGA, *extended* heating in air at temperatures approximating this exothermic feature produces a much more substantial weight loss, up to 46% after 1 week; accordingly, this could be due to an ongoing reaction with atmospheric moisture, or secondary reactions of hydrolyzed products. Several other Schiff-base polymers, Schiff-base coordination polymers, and chelates show weight loss very near this temperature range.[14]

It should be pointed out that with quadridentate ligands other than Schiff bases, zirconium coordination polymers might not show this feature. In the absence of this hydrolysis exotherm, the only other feature is a major decomposition due to combustion in air, TGA weight loss at 370 °C, with no decomposition occurring in nitrogen up to 500 °C. Other zirconium-containing polymers have shown thermal stabilities in excess of 300 °C.[14]

The close similarities between the polymer spectra and thermal data with those of the model system suggest that the chelation in the Zr(tsb) units is analogous to that observed X-ray diffraction for $Zr(dsp)_2$.[11] Thus, if the chelating part of the tsb^{4-} ligand is as flexible as the corresponding dsp^{2-} ligand,[11,15,16] then some degree of nonrigidity is possible in the polymer.

Condensation polymerizations using the water scavenger 2,2′-dimethoxypropane (DMP)[31] were attempted, but no perceivable increases in the average polymer chain length were obtained. Thus, we conclude either that DMP does not diminish the rate of chain termination or that imprecise stoichiometry limited the chain growth.

Coordination polymerization of premade ligands with reactive zirconium starting materials was also investigated. Stoichiometry (1:2) model reactions between either zirconium tetraalkoxides or tetrakis(acetylacetonato)zirconium(IV) and a quadridentate Schiff-base ligand did not produce clean products in high enough yields to warrant any further attempts at analogous polymerization reactions, although this method has met with some success in the past.[12] Solubility problems limit polymer growth in this system by this method.

In light of the tetrakis(salicylaldehydato)zirconium(IV) chelate hydrolysis and the bis(quadridentate) ligand insolubility, ligand-centered polymerization[32] reactions of preformed eight-coordinate chelates have been considered. The hydrolytic stability of $Zr(dsp)_2$, which can be recrystallized from ordinary reagent grade benzene and petroleum ether without decomposition, is encouraging in this regard. We have initiated studies in this area[33] as we attempt to make long fibers of coordination polymers having unique properties, either alone or as composites. Our aim is to obtain species with improved solubility, flexibility, high thermal stability, and extended conjugation.

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Registry No. 1, 19691-23-7; [Zr(tsb)]$_n$, 77274-52-3; Zr(sal)$_4$, 65531-97-7; TAB, 3204-61-3; Hsal, 90-02-8; H$_4$tsb (3-MeO)$_4$ derivative, 96482-27-8; H$_4$tsb (5-MeO)$_4$ derivative, 96482-26-7; 3-methoxysalicylaldehyde, 148-53-8; 5-methoxysalicylaldehyde, 672-13-9; 5-bromosalicylaldehyde, 1761-61-1; 2-hydroxy-1-naphthaldehyde, 708-06-5.

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Halato-Telechelic Polymers. 11. Viscoelastic Behavior of α,ω-Dicarboxylatopolybutadiene Based on Group 4 Metal Ions

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ABSTRACT: In nonpolar solvents, α,ω-alkaline and -alkaline-earth dicarboxylatopolybutadiene ($\bar{M}_n$ 4600) leads to gel formation at concentrations as low as 1.5 g dL^{-1}. However, any polar additive, i.e., water or alcohol, has a depressive effect on the metal–carboxylate association and the resulting gelation. The use of group 4 metal ions is an efficient way to overcome this drawback. Cross-linking of the carboxy-telechelic polymer is then promoted by a group 4 metal (Ti, Zr, Ce) alkoxide used in excess vs. the acid end groups. When the unreacted alkoxide groups are hydrolyzed into metal oxoalkoxide groupings, the gelation occurs in the presence of the alcohol formed as a byproduct and the required humidity of the medium. Cross-linking efficiency depends on the size of the group 4 cation just like in the series of alkaline and alkaline-earth cations. The deformation mechanism is controlled by the stability of the metal–carboxylate bonds and by the mean number of chain ends attached to the metal oxide aggregates. In this respect, excess alkoxide is a key parameter to impart to the solutions a broader range of rheological properties. Viscous solutions are observed at a metal-to-chain molar ratio of 0.5, whereas increasing excess of metal alkoxide is responsible for a shear-thickening behavior and finally for elastic gels.

Introduction

A few decades ago, macromolecular chemistry enjoyed a new expansion thanks to the development of multiphase polymeric materials. Indeed, the advent of block copolymers and more especially of thermoplastic elastomers opened up bright prospects for both scientists and tech-

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