Coordination Chemistry Reviews, 128 (1993) 49–68

Coordination chemistry from monomers to copolymers*

Ronald D. Archer
Department of Chemistry, University of Massachusetts, Amherst, MA 01003 (USA)

(Received 16 September 1992)

CONTENTS

ABSTRACT

Coordination polymers can often provide the best properties of both their organic and inorganic components, e.g. flexibility coupled with high thermal stability. Some of the coordination polymers that are discussed are stable to 500°C and yet provide sufficient flexibility to be studied like organic polymers. Whereas intractability has been the norm for metal coordination polymers in the past, examples of tractable (organic solvent-soluble) transition metal, inner transition metal, and main group metal ion coordination polymers are now known. Syntheses of linear metal coordination polymers through functionalized metal coordination monomers copolymerized with polymerization reactions on the organic part of

---

* Dedicated to the memory of Professor John C. Bailar, Jr.

Correspondence to: R.D. Archer, Department of Chemistry, University of Massachusetts, Amherst, MA 01003, USA.

0010-8545/93/$24.00

the molecules often provide higher molecular weight species than syntheses using metal salts plus bridging ligands, i.e. a higher extent of reaction often occurs in the polymerization reactions, although examples of virtually complete substitution of bridging ligands for simpler ligands of simple coordination compounds do exist. Also, coordination polymers also provide unique opportunities for end-capping reactions that can provide definitive molecular weight information and/or modify the properties of the polymers.

ABBREVIATIONS

DMSO	dimethyl sulfoxide
FTNMR	Fourier-transform nuclear magnetic resonance
GPC	gel permeation chromatography
Hacac	acetylacetone (or 2,4-pentanedione)
H_2acacen	bis(acetylacetone)ethylenediamine
H_2bbsd	*N*,*N*′-bis(5-*t*-butylsalicylidene-1,2-diaminobenzene)
Hdcq	5,7-dichloro-8-quinolinol
H_2dq	5,8-quinoxalinediol
H_2dsdt	*N*,*N*′-disalicylidene-3,4-diaminotoluene or *N*,*N*′-disalicylidene-1,2-diamino-4-methylbenzene
H_2dsp	*N*,*N*′-disalicylidene-1,2-phenylenediamine
Hleu	L-leucine
H_4tsb	*N*,*N*′,*N*″,*N*‴-tetrasalicylidene-1,2,4,5-tetraminobenzene (derivative of **1** of Fig. 3)
H_4tsdb	*N*,*N*′,*N*″,*N*‴-tetrasalicylidene-3,3′-diaminobenzidine (derivative of **2** of Fig. 3)
H_4tstm	*N*,*N*′,*N*″,*N*‴-tetrasalicylidene-3,3′,4,4′-tetraminodiphenylmethane (derivative of **3** of Fig. 3)
H_4tsts	*N*,*N*′,*N*″,*N*‴-tetrasalicylidene-3,3′,4,4′-tetraminodiphenylsulfone (derivative of **4** of Fig. 3)
M_n	Number-average molecular weight
NMP	*N*-methylpyrrolidone
NMR	nuclear magnetic resonance

1. INTRODUCTION

Coordination polymers can often provide the best properties of both their organic and inorganic components, e.g. the flexibility of organic polymers coupled with the high thermal stability associated with inorganic species. Some of the coordination polymers noted below are stable to 500°C and yet provide sufficient flexibility to be studied by gel permeation chromatography, viscosity, solid-state FTNMR, and transformed into thin films. However, not all metal coordination polymers provide improved thermal stability [1], and the synthesis of metal coordination polymers that possess solubilities that allow for the characterizations noted above is *not* just a matter of mixing a metal salt and a ligand together and allowing them to react. In fact, synthesizing linear metal coordination polymers that have sufficient solubilities and solution stability to be characterizsed by methods analogous to those used for organic polymers has proved to be a formidable challenge to both inorganic and polymer chemists. A survey of linear metal coordination polymer reviews [2] reveals that almost all of the linear polymeric metal coordination polymers that have been prepared are only oligomers, are insoluble, or are dissolved with concurrent decomposition. John C. Bailar, Jr. had a sizable number of short metal coordination polymers produced in his laboratory [3], but his polymeric compounds were typically plagued with either brittleness or insolubility. (In fact, it was John Bailar's comments to the effect that it appeared virtually impossible to prepare soluble long-chain metal coordination polymers that caused the present author to become interested in the challenge of soluble metal coordination polymer synthesis.) An early exception to this insolubility or intractability problem is the linear β-diketone beryllium coordination polymer reported by Kluiber and Lewis in 1960 [4]. Some of the phosphinates of Block [5] also had solubility and are very thermally stable. Other more recent exceptions also exist, as noted below.

The general insolubility or intractability of linear metal coordination polymers is related to either intermolecular forces or to crosslinking. Until recently, the typical inert-metal coordination polymer contained square-planar metal centers coupled with flat, conjugated, organic ligands. The intermolecular "stacking" forces that are also observed in polyaromatics, develop quite rapidly as the oligomeric chain starts to form. In addition to the normal stacking forces observed in planar organic materials, metal coordination polymers can also interact via the extra donor-atom electron pairs from one chain to the metal of the next. Thus, precipitation occurs prior to long-chain polymer formation. In fact, such planar "polymers" are normally only oligomers, even when designed to improve solubility (see, for example, ref. 6). Thus, contrary to normal coordination chemistry synthesis, precipitation is not desired in the synthesis of coordination polymers until after polymerization to long chain polymers has already occurred.

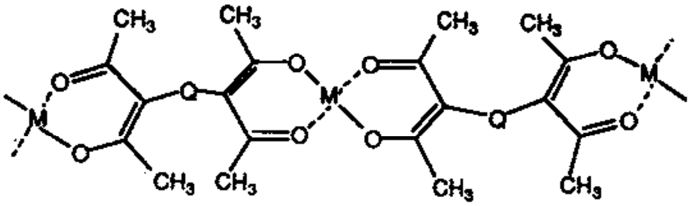
Other challenging problems in the area of the synthesis of metal coordination polymers include (1) the poor solubility of the flat, conjugated ligands needed to provide thermally stable or conducting bridges between the metal centers; (2) the slow substitution reactions of the inert metal ions desired for the synthesis of kinetically stable coordination polymers; and (3) the instability of polymers prepared with labile metal ions. This paper presents a number of ways of overcoming all of these problems, taking advantage of the wealth of knowledge that exists in normal or monomeric coordination chemistry and polymer chemistry.

Linear metal coordination polymers have been synthesized with transition metal, inner transition metal, and main group metal ions. Whereas a sizable number of linear coordination polymers are known in which metal ions are bonded to organic polymers, this paper considers only linear polymers in which the metal ion is an essential part of the backbone (Class I of Fig. 1). Metal ions can also modify the properties of organic polymers (as in the Class II example of Fig. 1) or be anchored to an organic polymer (as in the Class III example of Fig. 1), but these latter categories are of less interest to coordination chemists than those in which the metal is an essential part of the polymer backbone.

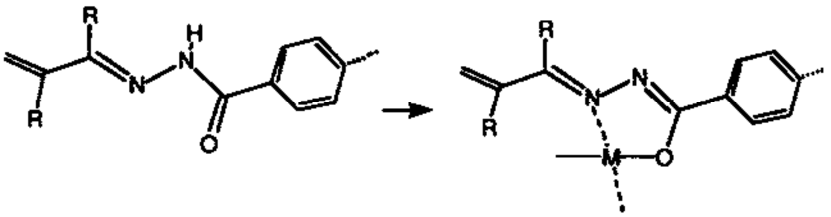
2. SYNTHESIZING ORGANIC SOLVENT-SOLUBLE COORDINATION POLYMERS

How can the intractability (organic-solvent insolubility) of metal coordination polymers be overcome? The following approaches have been found to increase solubility by decreasing intermolecular forces: (i) non-rigid coordination centers; (ii) dioxo metal centers; (iii) strong coordinating solvents; (iv) cis-octahedral complexes with bidentate ligands; (v) unsymmetrical bis-tridentate octahedral coordination;

I. Metal "ions" as part of polymer backbone (schematic)



II. Metal ion modication of polymer backbone (schematic)



III. Anchored coordination polymers (schematic)

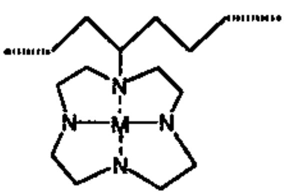


Fig. 1. Linear metal coordination polymers.

(vi) bulky organic groups; and (vii) small tetrahedral centers. Whereas we do not claim to have a monopoly on these methods of improving metal coordination tractability, examples from our laboratory will be used, when appropriate.

2.1 Non-rigid coordination centers

The non-rigid stereochemistry associated with eight-coordinate metal complexes is well known. The energy barrier is very low between the common eight-coordinate structures, the square antiprism (D_{4d}) and the trigonal-faced dodecahedron (D_{2d}) [as well as the intermediate bicapped trigonal prism or C_{2v}-hendecahedron] [7] (Fig. 2). The energies are so similar that species expected to have the same geometry do not. For instance, the structure of the eight-coordinate Ce^{IV} $(dsp)_2$ complex [where dsp = *N,N'*-disalicylidene-1,2-phenylenediamino,*O,N,N',O'*(2-)] is a square antiprism [8], whereas the corresponding zirconium complex is a dodecahedron [9]. The flexibility of the eight-coordinate metal centers, coupled with the organic sheaths about the centers, helps ensure that the polymers continue to grow until the reaction rates diminish, due to the lack of available end groups rather than to precipitation.

2.1.1 Zirconium polymers

A number of zirconium polymers appear to have molecular weights more dependent on stoichiometric control than on a lack of solubility [10]. In fact, the polymers with number-average molecular weights of 30000 or more are soluble in dimethyl sulfoxide (DMSO), *N*-methylpyrrolidone (NMP), and other polar organic solvents. Proof of the high molecular weights is discussed in Sect. 3.

Whereas zirconium(IV) complexes with monodentate and bidentate ligands are known to be quite labile [11], the increasing inertness observed with increasing chelation in normal coordination compounds has been used to provide solution-inert polymers of zirconium(IV). The zirconium polymers all contain bis(tetradentate)

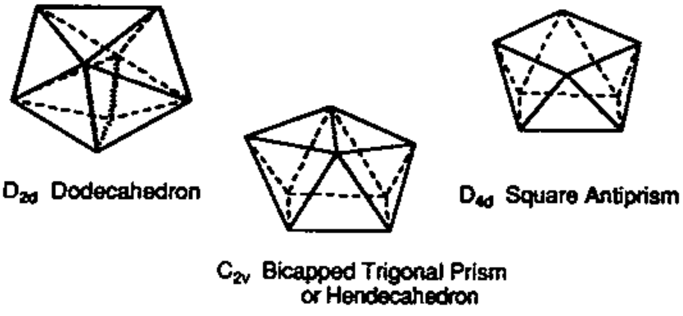
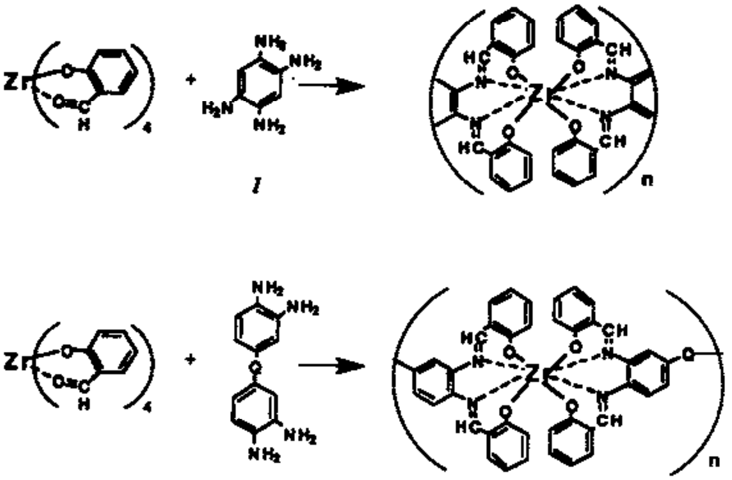


Fig. 2. Eight-coordination polytopes that interconvert rapidly in solution.

Schiff-base ligands and appear to be quite stable in solution for reasonable time periods.

Another problem, the low solubility of multi-ring aromatic ligands, was solved by synthesizing the tetradentate ligands as the polymers are formed, as shown in Fig. 3. Tetrakis(salicylaldehydato)zirconium(IV), synthesized from tetrakis(2,4-pentanedionato)zirconium(IV) [12], was allowed to react with bis(diamines) in order to form the polymeric ligand during the formation of the coordination polymer. The amines have included the simple 1,2,4,5-tetraaminobenzene [10(a)], 3,3′-diaminobenzidine [or 3,3′,4,4′-tetraaminobiphenyl] [10(b)] and the analogous 3,3′,4,4′-tetraamines, in which the two aromatic rings are separated by a methylene group or a sulfone group [10(c)]. DMSO is used as a solvent in order to prevent hydrolysis of the zirconium salicylaldehyde centers as the polymerization proceeds. The thermal stability of the most well-studied of these, the one synthesized from 3,3′-diaminobenzidine, is such that at 500°C only a 2% weight-loss is observed, and most of that loss is due to occluded DMSO. The polymers behave as normal moderate molecular-weight polymers with T_g values below 100°C, intrinsic viscosities between 0.1 and 0.2 dL g^{-1}, and molecular weights of 20 000 to 40 000 for the best samples of each, at least when fractionally precipitated [Table 1].

The end groups of these polymers are zirconium groups with two salicylaldehydes that did not condense with a diamine for steric or kinetics reasons, and diamines that likewise did not condense with a zirconium salicylaldehyde end group as shown in Fig. 4. (Statistically, 50% of the polymer chains have zirconium at one



1

Q = —, CH$_2$, or SO$_2$

2 3 4

Fig. 3. Zirconium(IV) Schiff-base polymer syntheses.

TABLE 1

Zirconium coordination polymers

Coordination polymer	Number (Fig. 3)	Molecular weight, M_n	Method
$[Zr(tsb)]_n$	1	40000	GPC[a]
$[Zr(tsdb)]_n$	2	33000	FTNMR[b]
		30000	GPC[a]
$[Zr(tstm)]_n$	3	10000	FTNMR[c]
		[20000	Viscosity[d]]
$[Zr(tsts)]_n$	4	>30000	FTNMR[b]

[a] GPC results relative to polystyrene standards in NMP on superstyrogel columns; note closeness between GPC and FTNMR results for $[Zr(tsdb)]_n$.
[b] FTNMR results based on H_2dsdt methyl group (3 protons) vs. aromatic protons of the polymer chain (22 aromatic protons including 4 aldimines per repeating unit).
[c] FTNMR results based on H_2bbsd *t*-butyl groups (18 protons) vs. aromatic protons of the polymer chains (as in footnote b).
[d] Separate synthesis. Molecular weight value based on viscosity results in NMP and Mark-Houwink constants ($K' = 1.53 \times 10^{-4}$ and $a = 0.68$) developed for $[Zr(tsdb)]_n$ for which good molecular weight data are available from FTNMR end-group measurements.

end and diamines at the other end, 25% have zirconium at both ends and 25% have diamines at both ends.)

The zirconium Schiff-base polymers have been found to adhere quite strongly to both silica and aluminum (actually to the alumina on the surface) [13]. Evidence that zirconium-containing end-groups are responsible for the adhesion has led to the use of the diamine end groups to form copolymers [14] that are compatible with polyesters and polyolefins as shown in Fig. 5. Lactones can be polymerized by the amine groups at high temperature to form polylactones attached to the zirconium polymers, and stearoyl chloride can be condensed with the amine end groups to provide a C_{18}-hydrocarbon chain. The polylactone copolymer increases the adhesion of polyesters (specifically polylactones and polymethylmethacrylate) to both silica and aluminum. The distearoyl copolymer increases the adhesion of polyethylene and polypropylene to both silica and aluminum. The probable mechanism for this adhesion is the coupling reactions shown as Fig. 6. That is, the dimethyl sulfoxide has a strong affinity for water and the condensation reaction is thereby enhanced. Furthermore, zirconium polymers made with an excess of amine end groups do not adhere so strongly as those made with an excess of zirconium.

A more exotic copolymer of zirconium has also been prepared with bis[2,2'-[[4-[[[(3-isocyanato-4-methylphenyl)amino]carbonyl]amino]-1,2-phenylene]bis-(nitrilomethylidyne)]-bis[phenolato]zirconium(IV) {$Zr(bnuip)_2$} and polytetrahydrofuran [15] as shown in Fig. 7. From a modified stoichiometry experiment, the

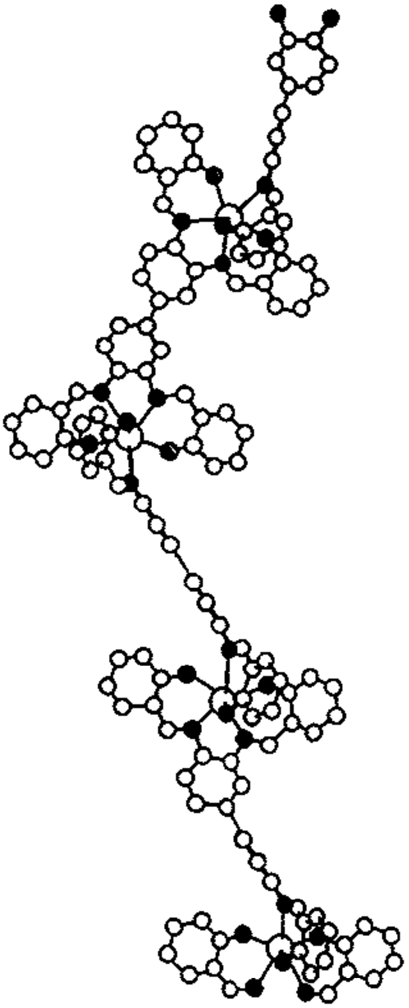


Fig. 4. A typical zirconium(IV) Schiff-base polymer chain where the large circles represent zirconium, black circles nitrogen, hatched circles oxygen and small clear circles carbon atoms. The donor pair below the plane is not shown, nor are the hydrogen atoms.

molecular weights appear to be stoichiometrically controlled, and no attempts to determine a maximum molecular weight were made.

2.1.2 Tungsten(IV) polymer

At least one tungsten(IV) polymer containing low-spin eight-coordinate metal centers has also been synthesized that appears to have a reasonably high molecular weight (based on an inherent viscosity of 0.25 dL g^{-1}) [16]. Because low-spin d^2 eight-coordinate metal centers are inert to substitution reactions [17], the polymer

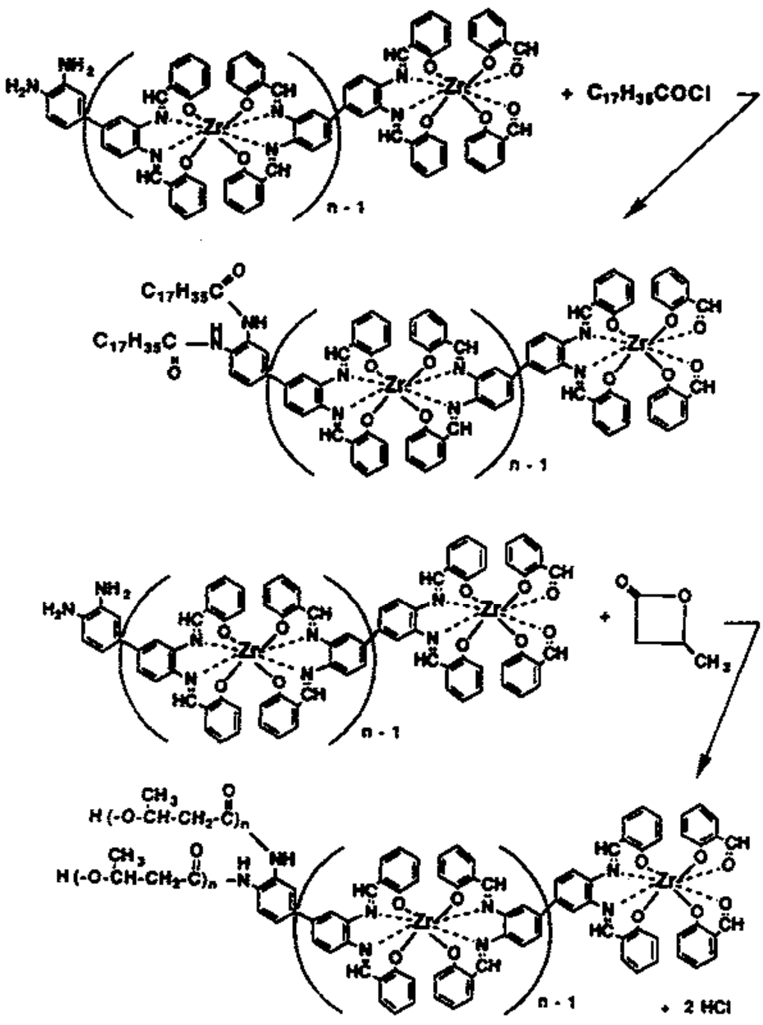


Fig. 5. Zirconium Schiff-base oligomer copolymers with a carbonyl chloride and a polylactone.

was synthesized through a redox reaction between [W(dcq)$_2$(CO)$_2$(PPh$_3$)], where dcq$^-$ is the anion of 5,7-dichloro-8-quinolinol and pH is phenyl, and quinoxaline-5,8-dione (Fig. 8). However, the resulting polymer is not particularly stable. The pyrazine-type nitrogen donors of the quinoxaline ring system apparently do not provide sufficient basicity to bond the tungsten(IV) ions strongly. (In retrospect, this is not too surprising because pK_2 for pyrazine is less than zero. Pyrazine-bridged complexes of ruthenium(II), where six d-electrons are available for π-back-bonding, are well known, but only two d-electrons are available for π-back-bonding in the tungsten(IV) complexes, and all four ligands compete for this weaker back-bonding capability.)

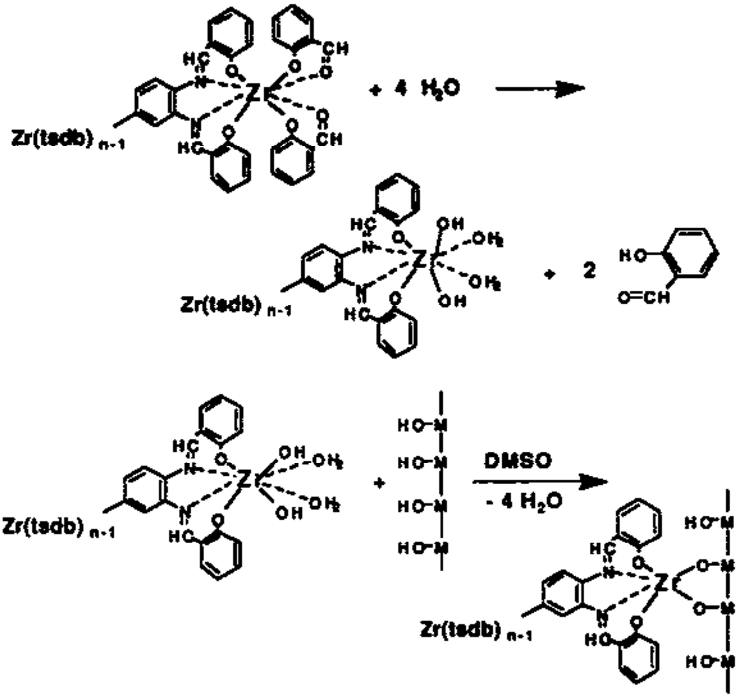


Fig. 6. Postulated zirconium polymer adhesion to silica and alumina.

2.1.3 Cerium(IV) polymer

Extension of the bis(tetradentate) Schiff-base metal coordination polymers to lanthanides has also been initiated. The cerium(IV) polymer between tetrakis (salicylaldehydato)cerium(IV) and 3,3′-diaminobenzidine has been prepared (Fig. 9) [18]. An alternate preparation between tetrakis(2,4-pentanedionato)cerium(IV) and *N,N′,N″,N‴*-tetrasalicylidene-3,3′,4,4′-tetraaminobiphenyl has been found to yield slightly higher molecular weights under comparable conditions (Table 2) [10(c)], but both reactions are apparently stoichiometrically controlled with molecular weights around 30000. A third route, between ammonium hexanitratocerium(IV) and *N,N′,N″,N‴*-tetrasalicylidene-3,3′,4,4′-tetraaminobiphenyl, led to much lower molecular weights (Table 2).

This set of cerium(IV) reactions shows the importance of the extent of reaction on polymer chain length. The average degree of polymerization (DP) can be calculated as follows:

$$\mathrm{DP}=\frac{N_{\mathrm{M}}+N_{\mathrm{L}}}{N_{\mathrm{M}}+N_{\mathrm{L}}-2p} \qquad (1)$$

where N_{M} is the moles of metal, N_{L} is the moles of ligand, and p is the extent of reaction. For exactly 1 : 1 stoichiometry ratios, if $p=0.98$, a DP of 50 is possible, but

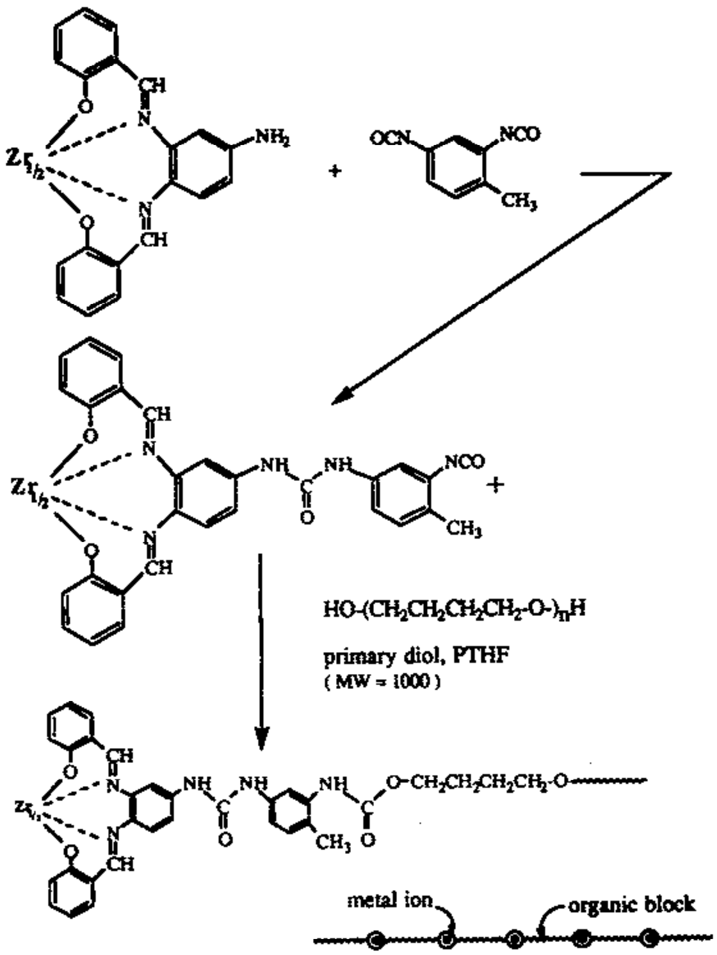


Fig. 7. Zirconium Schiff-base copolymer with poly(tetrahydrofuran).

if $p = 0.90$, DP will not exceed 10 and, since eqn. (1) is based on considering the chain as an AB copolymer, the DP value is twice the average number of repeating units, i.e., a degree of polymerization of 10 is $[ML]_5$. Thus, whereas yields of 90% are often considered acceptable for monomer reactions, it is easy to see that reactions need to proceed to virtual completion if a polymer of more than oligomeric size is to be obtained.

2.2 Dioxo metal centers

Dioxo metal centers, specifically the uranyl {dioxouranium(VI) or $[UO_2]^{2+}$} ion, are also known to form soluble metal complexes with bridging ligands [19].

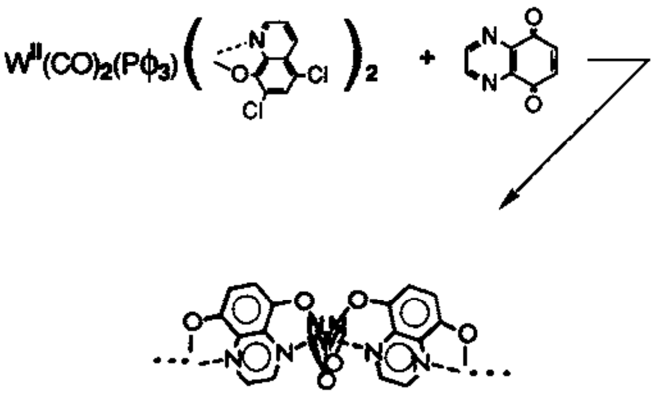


Fig. 8. Synthesis of the tungsten polymer $[W(dcq)_2(dq)]_n$ where dcq^- is deprotonated 5,7-dichloro-8-quinolinol and dq^{2-} is deprotonated 5,8-quinoxalinediol. The dcq^- ligand is represented as $\overset{\frown}{N\,O}$ in the polymeric product.

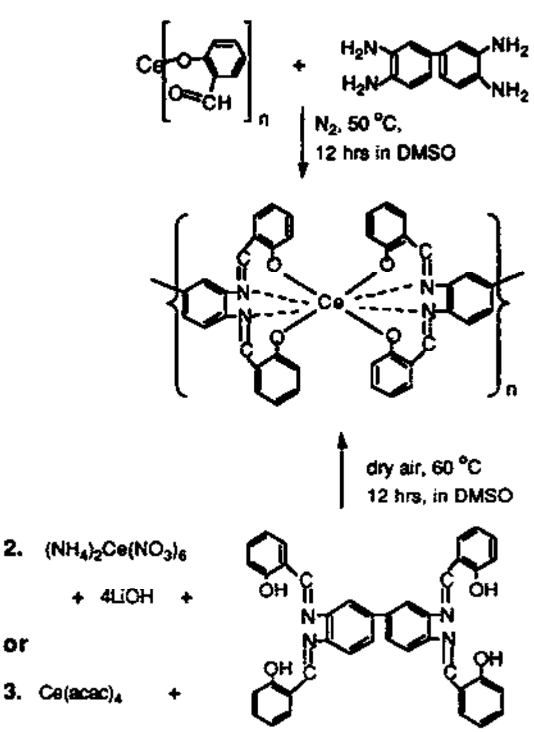


Fig. 9. Syntheses of the cerium(IV) Schiff-base polymer $[Ce(tsdb)]_n$.

TABLE 2

Cerium tetrasalicylidene-3,3′-diaminobenzidine polymers

Method (Fig. 9)[a]	Molecular weight[b]	Viscosity[c] (dL g^{-1})	Glass transition temperature (°C)
1	26000	0.17	182
2	14000	0.10	170
3	32000	0.19	184

[a] Comparably fractionated samples.

[b] Based on FTNMR of H_2bbsd endcapped polymer with two *t*-butyl groups per chain. See footnote c of Table 1.

[c] NMP solvent at 30°C. Results along with 3 other samples gives Mark-Houwink values of ($K' = 2.69 \times 10^{-5}$ and $a = 0.86$).

Carraher's early observations were further quantified and extended by Hardiman and Lee. Details are found in Sect. 2.3 on strong coordinating solvents, which also turn out to be essential for forming soluble metal coordination polymers with the uranyl centers.

2.3 Strong coordinating solvents

Strong coordinating solvents, e.g., dimethyl sulfoxide (DMSO) or *N*-methylpyrrolidone (NMP), can fill in any voids in the metal ion's coordination sphere, in order to minimize interchain attractions. A good example of this is the use of dimethyl sulfoxide with uranyl dicarboxylate polymers.

$$nUO_2(CH_3CO_2)_2 + nHO_2CRCO_2H + (n \times m)C_2H_6SO \rightarrow [UO_2(O_2CRCO_2)(C_2H_6SO)_m]_n + 2nCH_3CO_2H \qquad (2)$$

The fact that the precipitated polymers exhibited different stoichiometries of between one and two molecules of DMSO led us to find that the dicarboxylate polymers of the dioxouranium(VI) ion exist primarily as seven-coordinate centers. In addition to the two oxo donors, five other donors (either a monodentate and a bidentate carboxylate and two DMSO molecules or two bidentate carboxylates and one DMSO molecule) are coordinated to the uranium center [19(d)]. The uranyl polymers with C–S bonds show extreme sensitivity to depolymerization by high-energy radiation (may make good positive resists for computer chips, etc.) [20].

Vanadyl(IV) [oxovanadium(IV)] polymers with bis(β-diketones) have also been synthesized in DMSO [20]. Without a strong coordinating solvent, the VO^{2+} units would stack and become insoluble before polymerization could occur. However, with strong coordinating solvents, a solvent molecule completes the coordination sphere and increases solubility to some extent, but the results were much less satisfactory than in the case of the uranyl ion. For example, with —S—S— bridged bis(β-diketones) of vanadyl(IV), mass spectroscopy results have been interpreted to suggest that solvated trimeric ring compounds are the primary products, rather than the linear chain polymers [21].

2.4 Unsymmetrical octahedral coordination

2.4.1 Three bidentate ligands, but only two active sites

Octahedral complexes of cobalt(III) and chromium(III) that have three bidentate ligands, two of which are reactive to electrophiles, can provide soluble polymers with molecular weights of over 10000 [22]. Three cobalt(III) polymers have been prepared from the electrophilic reactions of sulfur chlorides [SCl_2, S_2Cl_2, and $SOCl_2$] with bis(2,4-pentanedionato)-L-leucinatocobalt(III) as shown in Fig. 10. A fourth polymer, the corresponding sulfone, has been prepared from a hydrogen peroxide oxidation of the sulfoxide polymer. The polymers, with the exception of the sulfoxide polymer, appear to be very susceptible to scission by high-energy radiation, as shown in Table 3. The G_s values are based on Charlesby's equation [23].

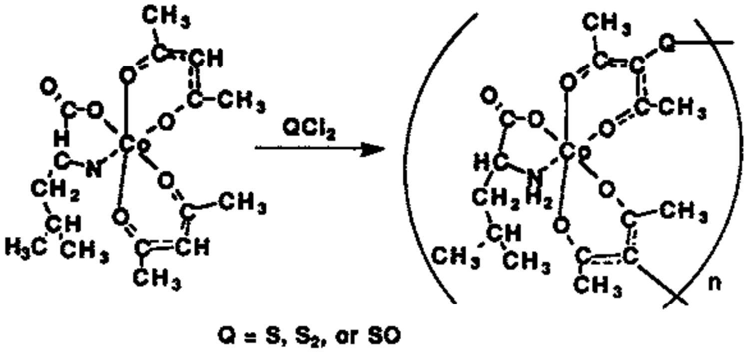


Fig. 10. Syntheses of cobalt(III) polymers containing leucine and 2,4-pentanedione.

TABLE 3

Linear cobalt(III) polymes derived from Co(leucine)(acac)₂

Bridge	M_n (FTNMR)	M_n (GPC)	G_s value[a]
—S—S—	⩾13000	34000	18
—S—	⩾15000	13500	10
—SO—	[⩾10000][b]	[16000][b]	0.4
—SO_2—	⩾10000	17000	60

[a] Approximate values based on changes in GPC M_n values with 662 keV gamma ray irradiation.

[b] Based on sulfone values to which sulfoxide was converted.

Other similar cobalt(III) polymers have been synthesized, but they have not been as well characterized to date [24].

Whereas Jones and Power [25] attempted to synthesize similar polymers in 1970, they chose divalent metal ions that are labile. When the sulfur chlorides were added to the solutions of the divalent β-diketones of these metals (Cu, Ni, Co, Zn), metal sulfides precipitated instead. Undaunted by that experience, they made −S−, −SS−, and −SSS− bridged bis(β-diketones) and allowed them to react with metal salts. Insoluble oligomers resulted, apparently because of the stacking forces noted above.

2.4.2 β-cis-Tetradentate ligand with two active sites plus inactive bidentate ligand

We have preliminary evidence that the cobalt(III) center coordinated with acacen^{2-} (the tetradentate Schiff-base condensation product of two acetylacetonates and ethylenediamine) and 3-methyl-2,4-pentanedionato can be polymerized with S_2Cl_2 [24], although further characterization is still needed.

2.4.3 Two tridentate ligands with one active site each

Further possibilities for octahedral complexes are polymers synthesized from inert octahedral centers with two tridentate ligands, each of which has only one site that is accessible for reaction with electrophiles. If the site is off-center, then the linear chain will have enough non-linearity to provide for enhanced solubility. Although we have projected several such systems in recent research proposals, none has been synthesized in our laboratory to date.

2.5 Bulky organic groups

Bulky organic groups, even on flat ligands such as porphyrins, can enhance the solubility of metal coordination polymers. Orthmann and Wegner [26] have shown that octyl substitution on porphyrins provides solubility for polymeric porphyrins in organic solvents. However, the coordination polymer characteristics could be quite minimal by the time several octyl groups are added to each unit of the polymer.

2.6 Small tetrahedral centers

Small tetrahedral centers should be ideal for the preparation of organic solvent-soluble metal coordination polymers. However, beryllium(II) is the only metal ion with an even number of charges that is small enough to preclude some interchain attractions when bonded tetrahedrally. Whereas beryllium(II) polymers were reported in 1960 [4], the recognition that the beryllium species used to prepare such polymers are *very* toxic has led to the decision that beryllium polymers are not a practical solution to the intractability problem.

2.7 *Overcoming large-conjugated-ligand intractability*

The same stacking forces that preclude long soluble polymers with square-planar metal centers also limit the ligand solubility of flat, conjugated ligands. For example, 1,2,4,5-tetraaminobenzene has such low solubility in organic solvents that polymer formation with the ligand is difficult. However, as noted above (Sect. 2.1.1), the preparation of the ligand during the polymerization reactions avoids that problem and allows polymers with approximately 40 000 molecular weight to be prepared.

2.8 *Overcoming inertness in coordination-polymer synthesis*

Inert metal ions are logically the best source for stable metal coordination polymers. However, ligand replacement reactions with such ions are too slow to allow sizable polymer formation in a reasonable time. Syntheses of linear metal coordination polymers through functionalized metal coordination monomers, polymerized by using standard polymerization reactions, avoids this problem and typically provide higher molecular weight species than syntheses using metal salts plus bridging ligands, i.e. a greater extent of reaction typically occurs in the polymerization reactions. The cobalt(III) reactions noted above (Sect. 2.4) take advantage of this approach. Naturally, other possibilities exist, such as using a small amount of a reducing agent with chromium(III). Another approach, the use of elevated temperatures, runs into the problem of entropy. Lower temperatures provide higher molecular weight polymers, other things being equal.

Not all such analogies are as straightforward as one would hope. For example, attempts to extend the cobalt results to chromium have met with only limited success [24]. Hindsight is obtained by reviewing the earlier electrophilic substitution reactions by Collman [27], who observed more difficulty in getting in all three centers of a tris(bidentate) complex to undergo substitution when the metal center is chromium(III) than when it is cobalt(III).

2.9 *Making labile metal centers into inert polymers*

Normally, it is desirable to have metal coordination polymers that have solution and thermal stability. Therefore, labile metal ions are typically less desirable than inert metal ions for synthesizing useful polymers. On the other hand, increasing the dentate number of the ligands increases the inertness of metal ions substantially. We have taken advantage of that in several of our syntheses. Some examples have been noted above and include the synthesis of tetradentate ligands during the reactions of zirconium(IV) salicylaldehyde with tetraamines (Sect. 2.1.1), the analogous reaction with cerium(IV) (Sect. 2.1.3), and the displacement of acetylacetone by the tetradentate Schiff-base ligation of the tetrasalicylidene-3,3′-diaminobenzidine bridge with cerium(IV) (Sect. 2.1.3).

3. END-CAPPING REAGENTS

Coordination polymers also provide unique opportunities for end-capping reactions. In some of our studies with zirconium polymers, we used the 4-methyl derivative of *N,N'*-disalicylidene-1,2-diaminobenzene (or *N,N'*-disalicylidene-3,4-diaminotoluene (H_2dsdt)) as an end-capping reagent to avoid the strong adhesion of the polymers to glass and metal oxide surfaces and to provide a proton NMR handle on molecule weight. That is, the average polymer chain of the polymer depicted in Fig. 4 can react with one H_2dsdt and reactions with monomers showed it was 95% complete without any excess ligand. However, a large excess is used in the end-capping reactions to ensure complete conversion. (As noted earlier, 50% have one, 25% have two, and 25% have none of these endgroups in actuality.) By the time the molecular weights are over 30000, the accuracy of observing a single methyl group per chain carrying of the order of 20 aromatics per repeating unit becomes very questionable, even with sophisticated FTNMR with several thousand transients. Therefore, end groups with more aliphatic protons have been developed. Presently, we are using bis(4-*t*-butylsalicylidene)-1,2-diaminobenzene [H_2bbsd], which provides 18 aliphatic protons per end group (Fig. 11).

4. CONCLUSIONS

Coordination polymers can often provide the best properties of both their organic and inorganic components, e.g. flexibility coupled with higher thermal sta-

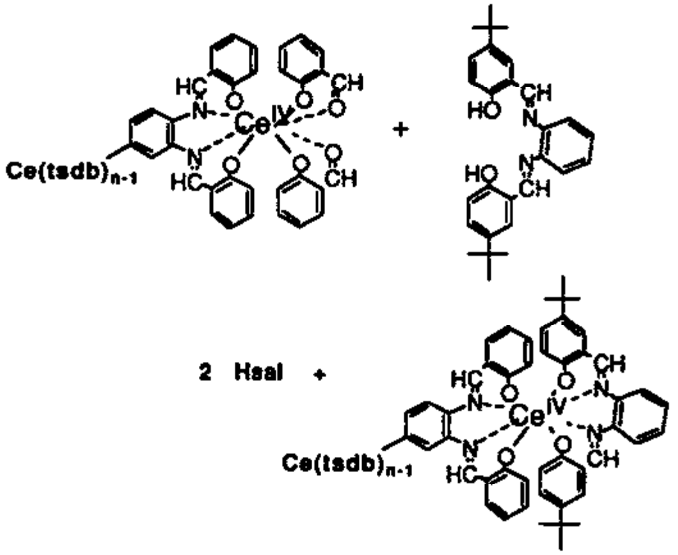


Fig. 11. End-capping reaction for cerium(IV) polymer.

bility. Coordination polymers that are stable to 500°C with sufficient flexibility to be similar to organic polymers can be prepared. Whereas intractability has been the norm for metal coordination polymers in the past, examples of tractable (organic solvent-soluble) transition metal, inner transition metal, and main group metal ion coordination polymers are now known. Syntheses of linear metal coordination polymers through functionalized metal coordination monomers, copolymerized using polymerization reactions on the organic part of the molecules, often provide higher molecular weight species than syntheses using metal salts plus bridging ligands, i.e. a larger extent of reaction often observed in the polymerization reactions, although examples of virtually complete substitution of bridging ligands for simpler ligands of simple coordination compounds do exist. Also, coordination polymers also provide unique opportunities for end-capping reactions that can provide definitive molecular weight information and/or modify the properties of the polymers.

ACKNOWLEDGMENTS

The author acknowledges the debt that he owes the late John C. Bailar, Jr., who kindled his interest in coordination chemistry in general and who, through a statement that indicated the difficulty in preparing linear flexible metal coordination polymers, kindled an interest to prove his mentor wrong. The author also acknowledges a large debt to his many students, a sizable number of whom have contributed to the chemistry discussed herein. Finally, the financial sponsors of much of this research, the National Science Foundation Materials Research Laboratory at the University of Massachusetts, the Army Research Office (Durham), the Office of Naval Research, the Center of University of Massachusetts and Industry Research in Polymers, and IBM, spanning a period of over a decade, are gratefully acknowledged.

REFERENCES

1 C.E. Carraher, Jr., J. Macromol. Sci., Chem., A17 (1982) 1293.

2 (a) J.E. Sheats, C.E. Carraher, Jr., M. Zeldin, ?.?. Currell and C.U. Pittman, Jr., (Eds.), Inorganic and Metal-Containing Polymeric Materials, Plenum, New York, 1991, especially Chap. 1.

(b) C.U. Pittman, Jr., C.E. Carraher, Jr. and J.R. Reynolds, in J.I. Kroschwitz (Ed.), Encyclopaedia of Polymer Science and Engineering, Vol. 10, Wiley, New York, 2nd edn., 1987, pp. 541–594.

(c) B.M. Foxman and S.W. Gersten, in J.I. Kroschwitz (Ed.), Encyclopaedia of Polymer Science and Engineering, Vol. 4, Wiley, New York, 2nd edn., 1985, pp. 175–191.

(d) N. Hagihar, K. Sonogashira and S. Takahashi, Adv. Polym. Sci., 41 (1981) 149.

(e) J.E. Sheats, in M. Grayson and D. Eckroth (Eds.), Kirk-Othmer Encyclopaedia of Chemical Technology, Vol. 15, Wiley, New York, 3rd edn., 1981, pp. 184–220.

3 (a) J.C. Bailar, Jr., in W.L. Jolley (Ed.), Preparative Inorganic Reactions, Vol. 1, Interscience, New York, 1964, pp. 1–27.

(b) R.M. Klein and J.C. Bailar, Jr., Inorg. Chem., 2 (1963) 1187, 1190.
(c) J.S. Oh and J.C. Bailar, Jr., J. Inorg. Nucl. Chem., 24 (1962) 1225.
(d) H.A. Goodwin and J.C. Bailar, Jr., J. Am. Chem. Soc., 83 (1961) 2467.
(e) W.C. Drinkard and J.C. Bailar, Jr., J. Am. Chem. Soc., 81 (1959) 4795.
(f) J.C. Bailar, Jr. and co-workers, W.A.D.C. Tech. Rep. 57-391 (1957), 57-391 II (1958), 58-51 (1958), 58-51 II (1959), 58-51 III (1960), and 59-427 (1960). Co-workers include W.C. Drinkard, M.L. Judd, J.A. McLean, Jr., H.A. Goodwin, M. Moraghan, C. Fujikawa, and L.-C. Chen.
4 R.W. Kluiber and J.W. Lewis, J. Am Chem Soc., 82 (1960) 5777.
5 B.P. Block, Inorg. Macromol. Rev., 1 (1970) 115.
6 F. Wang and J.R. Reynolds, Macromolecules, 23 (1990) 3219.
7 (a) A.F. Wells, Structural Inorganic Chemistry, Clarendon Press, Oxford, 5th edn., 1984, pp. 941, 942.
(b) R.C. Fay and J.K. Howie, J. Am. Chem. Soc., 101 (1979) 1115.
(c) J.K. Burdett, R. Hoffmann and R.C. Fay, Inorg. Chem., 17 (1978) 2553.
(d) D. Kepert, Prog. Inorg. Chem., 24 (1978) 179.
(e) M.G.B. Drew, Coord. Chem. Rev., 24 (1977) 179.
(f) S.J. Lippard, Coord. Chem. Rev., 21 (1975) 91.
(g) S.J. Lippard, Coord. Chem. Rev., 8 (1967) 109.
(h) J.L. Hoard and J.V. Silverton, Inorg. Chem., 2 (1963) 243.
(i) L.E. Orgel, J. Inorg. Nucl. Chem., 14 (1960) 136.
8 A. Terzis, D. Mentzafos and H.A. Tajmir-Riahi, Inorg. Chim. Acta, 84 (1984) 187.
9 R.D. Archer, R.O. Day and M.L. Illingsworth, Inorg. Chem., 18 (1979) 2908.
10 (a) R.D. Archer, M.L. Illingsworth, D.N. Rau and C.J. Hardiman, Macromolecules, 18 (1985) 1371.
(b) R.D. Archer and B. Wang, Inorg. Chem., 29 (1990) 39.
(c) R.D. Archer, H. Chen, J. Cronin and W. Tong, XXIX Intl. Conf. Coord. Chem., Lausanne, Switzerland, 1992, Abstr. 119.
11 (a) H. Taube, Chem. Rev., 50 (1952) 69, especially pp. 83 and 97.
(b) R.C. Fay, in G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, Vol. 3, Pergamon Press, Oxford, 1987, pp. 363–453, especially pp. 364 and 390.
12 R.D. Archer and M.L. Illingsworth, Inorg. Nucl. Chem. Lett., 13 (1977) 661.
13 B. Wang and R.D. Archer, Polym. Mater. Sci. Engr., 59 (1988) 120; 60 (1988) 710.
14 R.D. Archer and B. Wang, Polym. Mater. Sci. Engr., 61 (1989) 101.
15 W. Tong and R.D. Archer, Inorg. Chem., 31 (1992) 3332.
16 R.D. Archer, W.H. Batschelet and M.L. Illingsworth, J. Macromol. Sci., Chem., A16 (1981) 261.
17 (a) A.W. Adamson, J.P. Welker and M. Volpe, J. Am. Chem. Soc., 72 (1950) 4030.
(b) H. Taube, Chem. Rev., 50 (1952) 69.
(c) W.D. Bonds, Jr. and R.D. Archer, Inorg. Chem., 10 (1971) 2057.
(d) C.H. Chang and R.D. Archer, Taehan Hwahakhoe Chi, (J. Korean Chem. Soc.), 34 (1990) 85.
18 R.D. Archer and H. Chen, Am. Chem. Soc. Natl. Meeting, Atlanta, 1991, Abstr. INOR 281.
19 (a) C.E. Carraher, Jr. and J.A. Schroeder, J. Polym. Sci. Polym. Lett. Ed., 13 (1975) 215.
(b) C.J. Hardiman and R.D. Archer, Macromolecules, 20 (1987) 1527.
(c) R.D. Archer, C.J. Hardiman and A. Lee, in H. Yersin and A. Vogler (Eds.), Photochemistry and Photophysics of Coordination Compounds, Springer Verlag, Berlin, 1987, pp. 285–290.
(d) R.D. Archer, B. Wang, V.J. Tramontano, A.Y. Lee and V.O. Ochaya, in M. Zeldin,

K.J. Wynne and H.R. Allcock (Eds.), Inorganic and Organometallic Polymers, American Chemical Society, Washington, DC, 1987, pp. 463–468.
20 R.D. Archer, C.J. Hardiman, R. Grybos and J.C.W. Chien, U.S. Pat. No. 4,693,957, September 15, 1987.
21 R. Grybos and W. Paw, Polyhedron, 9 (1990) 397.
22 (a) R.D. Archer, V.J. Tramontano, V.O. Ochaya, P.V. West and W.G. Cumming, in C.E. Carraher, Jr., C.U. Pittman, Jr., J.E. Sheats, M. Zeldin and B. Currell (Eds.), Inorganic and Metal-Containing Polymeric Materials, Plenum, New York, 1991, pp. 161–171.
23 M. Dole, The Radiation Chemistry of Macromolecules, Vol. 2, Academic Press, New York, 1973, p. 101.
24 V.O. Ochaya, personal communication, 1992.
25 R.D.G. Jones and L.F. Power, Aust. J. Chem., 24 (1970) 735.
26 E. Orthmann and G. Wegner, Macromol. Chem. Rapid Commun., 7 (1986) 243.
27 J.P. Collman, Angew. Chem., 77 (1965) 154.