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Organometallic Polymers with Transition Metals in the Main Chain

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I. Introduction

Since the early 1950s, the rapid development of the organometallic chemistry of the transition elements has resulted in a tremendous variety of new and often remarkable molecular structures and a range of novel catalytic species.[1] More recently, interest in organotransition metal compounds has been extended to the materials science interface. For example, in the past decade or so, organometallic materials with novel magnetic, electrical, and liquid crystalline properties have attracted considerable attention.[2] As it is well-known that the properties of polymers can be modified dramatically by seemingly subtle changes in chemical structure, the possibility of using organometallic structural moieties to prepare macromolecular materials with interesting and possibly useful characteristics is a very attractive one. This article provides an overview of current knowledge of the synthesis, characterization, and properties of organometallic polymers with transition elements in the main chain. (From the standpoint of the article, we define a main chain organometallic polymer as one that possesses M−C σ or π bonds in the backbone.) These materials offer the possibility of making integral use of the metal in accessing either a conjugated pathway along the main chain of the polymer or novel characteristics where the metal atoms interact with one another or function as independent units. As a result of such structures access to new, processable materials with intriguing conductive, magnetic, optical, or redox properties might be envisaged.

On the basis of these considerations, since the 1950s, the incorporation of organometallic groups into polymer structures has attracted growing attention. However, unlike the situation in organic polymer chemistry where many different synthetic approaches are effective, the development of main chain metal-containing polymers offers a considerable synthetic challenge.[3] To access the favorable characteristics of macromolecular materials (e.g., mechanical strength, film and fiber formation, etc.) appreciable molecular weights ($M_n > $ ca. 10 000) with the consequent chain entanglement are necessary. Chain growth polymerizations such as addition polymerization, which tend to yield high molecular weight polymers very easily, are virtually unexplored for organometallic polymers mainly because of the lack of suitable monomers with multiple bonds involving transition elements. Most attention has been directed at the use of step growth, polycondensation approaches involving the reaction of difunctional monomers. Providing that the monomers are pure so that exact stoichiometries of reactants are possible and the reactions proceed to high conversion, high molecular weights can be achieved. However, this is rarely the case with difunctional organometallic species, and it is only comparatively recently that such reactions have been used successfully.[3]

Although many claims concerning the synthesis of main chain organometallic polymers were made in the 1960s, the first soluble, well-characterized transition metal based polymers of appreciable molecular weight were ferrocene-containing materials with organosiloxane spacers (e.g., **1**) which were reported

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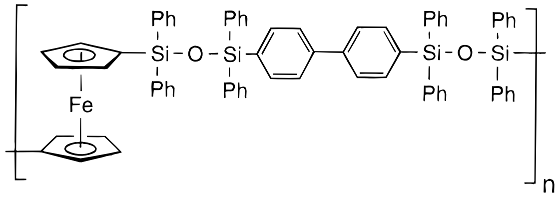
Paul Nguyen (left) was born in Saigon, Vietnam, in 1965 and received a B.Sc. degree in chemistry from the University of Toronto, Canada, in 1990 and a Ph.D. in chemistry from the University of Waterloo, Canada, in 1995. His doctoral research under the supervision of Prof. Todd Marder focused on homogeneous catalysis of cross-coupling reactions and diboration of alkenes. From 1995 to 1997 he was an NSERC postdoctoral fellow in Prof. Ian Manners' group at the University of Toronto studying ring-opening polymerization of strained cobaltocenophanes and ferrocenophanes by thermal- and metal-catalyzed processes. His research interests include metal-containing polymers and new materials for nonlinear optics and liquid crystal applications. He is currently a senior research chemist at Bayer Rubber Inc. in Sarnia, Canada.

Paloma Gómez-Elipe (right) was born in Madrid, Spain, in 1965. After she graduated in chemistry at the University of Valladolid in 1990, she worked on "Polyphosphazenes as Ligands for Transition Metal Complexes" with Profs. Gabino A. Carriedo and Francisco J. Garcia-Alonso in Oviedo, obtaining her Ph.D. in this field of inorganic polymer chemistry in 1994. She obtained a fellowship from the Ministry of Education and Culture (Spain) and joined Prof. Ian Manners' group at the University of Toronto, Canada, in January 1995 where she studied different aspects of the ring-opening polymerization of [1]ferrocenophanes catalyzed by transition metal complexes. Her main scientific interests focus on polymers with metals in either the main chain or side group structure.

Ian Manners (center) was born in London, England, in 1961 and received his B.Sc. and Ph.D. (with Professor Neil Connelly) from the University of Bristol in 1982 and 1985, respectively. From 1986 to 1987 he was a Royal Society European Postdoctoral Fellow at the RWTH, Aachen, Germany (with Professor Peter Paetzold) and from 1988 to 1990 he worked as a Research Associate with Professor Harry R. Allcock at Pennsylvania State University, U.S.A. He joined the Department of Chemistry, University of Toronto, Canada, in July 1990 where he is now Professor of Chemistry. Manners' research interests focus on both the fundamental and applied aspects of the chemistry of rings, chains, and macromolecules based on main group or transition elements. He has received a range of awards, including an E.W.R. Steacie Fellowship from Canada (1997–99), a Corday-Morgan Medal from the United Kingdom (1997), and an Alfred P. Sloan Fellowship from the United States (1994–98). In addition to his scientific interests, he particularly enjoys the music of Beethoven, musical theater, the Simpsons, monster trucks, and walking in the countryside, bird-watching, or travelling with his wife, Deborah.

by Pittman and co-workers in 1974. A few years later, in 1977, the first high molecular weight rigid-rod metal polyyne materials (e.g., **2**) were described by Hagihara et al. In each case, well-defined polycondensation strategies were successfully used. Despite the fact that these initial developments occurred around 25 years ago, until very recently, well-characterized high molecular weight metal-based polymers were still extremely rare. However, with the development, in the past 5−10 years, of creative, well thought out polycondensation strategies to linear and dendritic materials and the discovery of novel ring-opening polymerization (ROP) approaches,[4] the future of transition metal based polymer science appears very bright.



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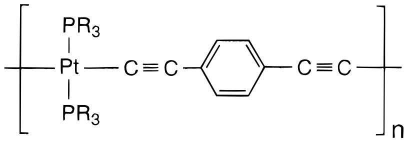


2

At present, two major classes of organometallic polymers exist with transition metals in the main chain. The first, poly(metallocenes), were targeted in the early 1960s, but, as described below, the materials generated were of low molecular weight and often possessed very poorly defined structures. However, high molecular weight examples are now well-known and have been found to possess a range of interesting properties. The second major class, rigid-rod polymers such as metal-acetylide or poly-yne materials, are also now well-known and are quite stable, presumably due to lack of a β-hydride elimination decomposition pathway, which is inherent to many metal alkyl complexes. In addition, the M(dπ)-acetylide(pπ) interaction, which can effectively strengthen the M−C bonds, and the rigid structure of these materials can generate very interesting physical properties. Overviews of the current knowledge of these two classes of polymers are provided in the next two sections (II and III). Another much less studied but very intriguing class of organometallic polymers possesses metal−metal bonds in the main chain and these materials are discussed in the final section (IV).

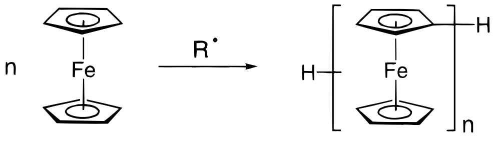
It should be noted that other important classes of transition metal-based polymers exist such as materials with organometallic moieties in the side group structure, and coordination polymers. The latter include the exciting materials derived from the coordination of metals to conjugated polymeric organic frameworks.[5] These materials are not covered in this article which focuses on organometallic polymers with metal−carbon bonds in the main chain.

II. Poly(metallocenes)

II.1. Main Chain Poly(metallocenes) with Short Spacers

II.1.1 Poly(metallocenylenes) and Poly(metallocenes) with Short Spacers via Condensation Routes

a. Poly(metallocenylenes). The earliest routes to poly(ferrocenylene) involved poorly defined free-radical processes (eq 1). Korshak[6] and Nesmeyanov[7] first reported in 1960 the polyrecombination reaction of ferrocene at 200 °C in the presence of *tert*-butyl peroxide as the radical source. The yields obtained were low (5−16%), and the molecular weight (M_n) was <7000. This work was critically reviewed in 1970.[8] After a reinvestigation of the original work, it was found that the soluble polymer was composed of a mixture of short poly(ferrocenylene) segments, with a mixed substitution (represented by **3**) on the ferrocene of homoannular (1,2- and 1,3-) and heteroannular (1,1′-) units, linked by methylene and oxygen-containing hydrocarbon units.[9,10]



(1)

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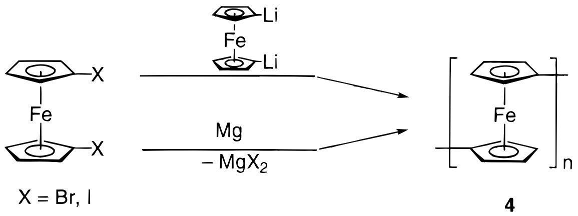
Subsequently, different radical reactions have been reported such as mixed Ullmann reactions of halo- and 1,1′-dihaloferrocene with copper bronze,[11,12] coupling reactions of lithio- and 1,1′-dilithioferrocene with cobalt chloride in the presence of organic halides,[13−15] treatment of poly(mercuriferrocenylene) with metallic silver[16] or in molten ferrocene,[17] or glow discharge polymerization.[18] All led to oligomers with molecular weights in the range $M_n = 1000−3500$, with poorly defined structures, low conductivity ($\sigma = 10^{-7}$ to 10^{-9} S cm^{-1}), and paramagnetic behavior. This may be due to the presence of impurities or oxidized iron sites within the oligomer chain.[8] In the case of glow discharge polymerization, cross-linked poly(ferrocenylene) is produced.

Other reported methods, like polyrecombination from chloromercuriferrocene and bis(chloromercuri)ferrocene assisted by palladium salts[19] or the reaction of dilithioferrocene·TMEDA with cobalt chloride,[20] resulted in the formation of paramagnetic oligomers in low yields together with biferrocenylene resulting from internal cyclization.

Pittman et al.[21−23] studied the conductivity of unoxidized oligo(1,1′-ferrocenylene) prepared by radical recombination of ferrocene[10] and concluded that the material was an insulator. However, upon partial oxidation, the mixed valence states induced increased conductivity values from 10^{-14} S cm^{-1} to a maximum of 10^{-6} to 10^{-8} S cm^{-1} at room temperature. Similar values have been observed for biferrocenylene[24,25] and biferrocene[26] salts.

The most impressive early results on poly(ferrocenylenes) (in terms of yield, molecular weight, and purity) were obtained by Neuse et al.[27] in 1979 using the step growth polycoupling reaction of equimolecular amounts of dilithioferrocene·TMEDA with diiodoferrocene at temperatures not exceeding 25 °C (eq 2). Thus, a total yield of 85% of light tan, soluble, spectroscopically well-defined (all heteroannular), amorphous, and diamagnetic poly(ferrocenylene) (**4**) was produced with M_n < 4000 (determined by VPO), from which subfractions in the range $M_n = 1000−10\,000$ were obtained.



(2)

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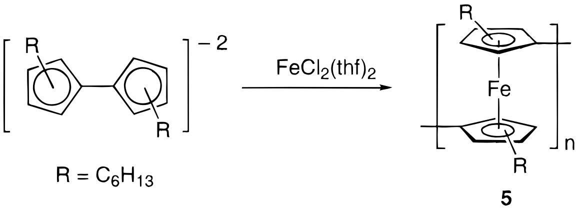
More recently, dehalogenation of dihaloferrocenes with magnesium produced semicrystalline poly(ferrocenylene) in 45−77% yield (eq 2).[28,29] Soluble fractions of this product ($M_n = 4600$), when partially oxidized with TCNQ, showed a higher degree of crystallinity and, presumably as a consequence,[30] higher electrical conductivity ($\sigma = 10^{-2}$ S cm^{-1}) than found previously. Rapid electron transfer between Fe^{II} and Fe^{III} sites was also observed for these TCNQ-doped materials on the Mössbauer spectroscopic time scale (10^{-7} s) at room temperature. This observation was supported by electrochemical studies of poly(ferrocenylene)-modified electrodes which indicated hole delocalization among iron atoms.[31] Further studies on the electronic structure by UV photoelectron spectroscopy suggested that the moderate conductivity for these polymers is a consequence of limited hole mobility, and this led to their description as systems with intermediate delocalization between that of delocalized, π-conjugated conducting polymers such as polyacetylene and localized polymers such as polyethylene.[32]

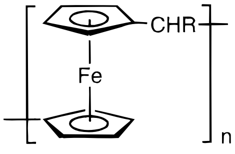
Nishihara et al. have recently developed a methodology that permits the synthesis of more soluble substituted poly(ferrocenylenes) by reaction of the dihexylfulvalene dianion with [FeCl$_2$(thf)$_2$] (eq 3).[33] The presence of the hexyl group increased the solubility of the products. Although this polycondensation method is not appropriate for the preparation of high molecular weight materials, a fraction of poly(1,1′-dihexylferrocenylene) (**5**) with M_n > 4000 was formed in low yield. In addition, when oxidized with TCNQ or TCNE, this material exhibited photoconductivity and acted as a p-type semiconductor, as was previously noted for nonsubstituted poly(ferrocenylenes).[31]



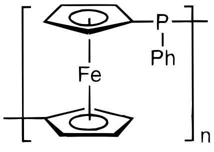
(3)

5

b. Poly(metallocenes). Poly(metallocenes) with single carbon bridges (i.e., **6**) have been the focus of numerous investigations.[8] Condensation routes have involved the reaction of aldehydes with the corresponding metallocene (M = Fe, Ru), as well as the cationic polymerization of carbinols. Both methods were carried out using Lewis acid or protic acid catalysts and yielded similar products. The materials obtained were oligomeric in nature and consisted of a mixture of heteroannular (1,1′-) and homoannular (1,2- and 1,3-) substituted metallocene units. Cross-linking was noticed at high temperatures, resulting in an increase in the number of methylene bridges per repeat unit.



6
R = H, CH_3, C_6H_5



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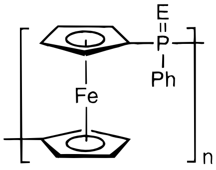
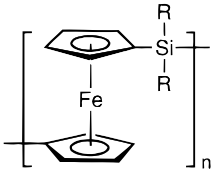


8
E = O, S

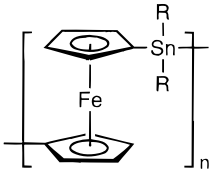
A similar route was reported by Neuse[34] and Pittman[35] for the synthesis of phosphorus-bridged poly(ferrocenes) (**7**, **8**). Reaction of ferrocene with $PPhCl_2$, $P(O)PhCl_2$, or $P(S)PhCl_2$ in the presence of a Lewis acid catalyst in the melt or in solution at 80−170 °C yielded low molecular weight materials ($M_n < 6000$, by VPO), the composition of which depended on the reaction conditions. Again, in these materials a mixture of different ferrocenylene linkages was present. The polymers were characterized by ^1H NMR and IR spectroscopy and elemental analysis.

Well-defined materials were obtained by Seyferth[36] from the reported polycondensation reaction of 1,1′-dilithioferrocene·TMEDA with $PPhCl_2$. The molecular weights of the poly(ferrocenylphosphine) products were found to depend on the reaction conditions. For example, the authors reported products with $M_w = 8900$ (by light scattering) when the reaction was performed in dimethoxyethane at 25 °C, while high molecular weights ($M_w = 131\,000-161\,000$) were obtained in ether at 25 °C or DME at −40 °C. The molecular weight in the latter case is highly unexpected when dilithioferrocene, which is highly reactive and difficult to purify, is used in condensation reactions, because exact stoichiometries are required to achieve high molecular weight materials. Recent work has shown that these high molecular weight products probably arise from a chain growth reaction rather than a polycondensation (see section II.1.2d). This involves the anionic ring-opening polymerization of an in situ generated [1]phosphaferrocenophane. The air and thermally stable ($T_{dec} > 350$ °C) poly(ferrocenylphosphines) were shown to react with low concentrations of $Co_2(CO)_8$, to chelate cobalt in a tridentate fashion.[37] According to IR and ^{31}P NMR, three Co−P bonds are formed and the cobalt centers possess a pseudotrigonal bipyramidal geometry. The catalytic potential of the materials in the hydroformylation of 1-hexene was studied and was shown to be similar to the complex $HCo(CO)_3PPh_3$.

Poly(ferrocenylsilanes) (**9**) were first described in two patents by Rosenberg in the 1960s.[38,39] Low molecular weight polymers were prepared from dilithioferrocene by a reported polycondensation reaction with the appropiate dihaloorganosilanes (Me_2SiCl_2 or Ph_2SiCl_2) in polar solvent mixtures at 0−25 °C. The resulting partially soluble and reasonably thermally stable ($T_{dec} > 250$ °C) polymers were characterized by elemental analysis, although their dark color indicated that they were impure. VPO gave molecular weights (M_n) of 1700 (R = Me) and 4000−7000 (R = Ph) which corresponded to 5−20 repeating units.



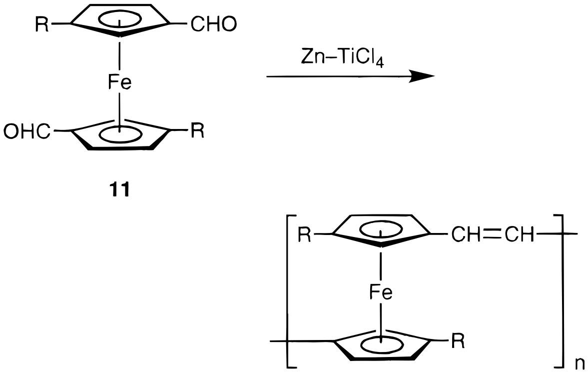
9
R = Me, Ph



10
R = Me, Et, n–Bu, Ph

This work was preceded by an alternative route that involved the condensation of $FeCl_2$ with $Li_2[Cp_2SiMe_2]$[38] and afforded very low molecular weight oligo(ferrocenyldimethylsilane). Very recently, slightly higher molecular weight material with M_n up to 4100 has been reported by Park, Chang, et al. using this route.[40] However, the low values for M_n are expected for condensation processes involving dilithio reagents which are difficult to obtain in a high degree of purity. Following a similar reaction pathway, Osborne[41] and Seyferth[42] have reported the synthesis of low molecular weight poly(ferrocenylstannanes) (**10**). Only when R = Me was soluble material (with $M_w = 4600$) obtained.

Poly(ferrocenylenevinylene) derivatives (**12**) with GPC-derived M_n values of 3000−10 000 and polydispersities of ca. 2.2−2.8 have recently been synthesized[43] in high yields via the titanium-induced McMurry coupling reaction of the corresponding alkylferrocenyl carbaldehyde monomers **11** (eq 4). These soluble polymers were characterized by NMR and IR which revealed the presence of *trans*-vinylene units. The UV−vis spectra of the polymers are similar to those of the monomers, indicating a fairly localized electronic structure. This is also reflected in the electrical and optical properties with values for doped-conductivity ($\sigma = 10^{-2}$ S cm^{-1}) and nonlinear third-order optical susceptibility ($\chi^{(3)} = 1-4 \times 10^{-12}$ esu) lower than those of linear conjugated polymers such as poly(1,4-phenylenevinylene) ($\sigma = 2.5 \times 10^3$ S cm^{-1}, $\chi^{(3)} = 8 \times 10^{-12}$ esu).

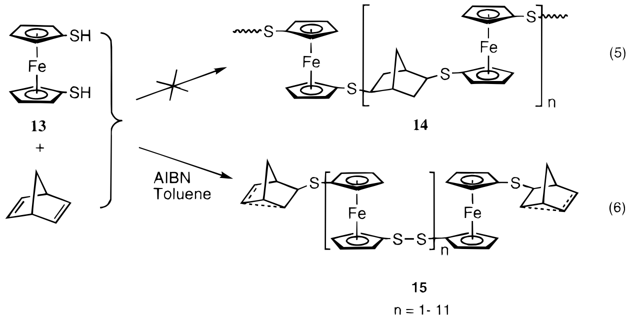


11

12
R = C_2H_5, C_6H_{13}, $C_{12}H_{25}$

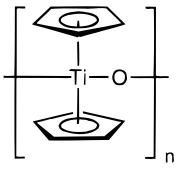
(4)

Disulfide-bridged oligoferrocenes (M_w < 3500) were prepared in an attempt to copolymerize ferrocenedithiol (**13**) with norbornadiene in the presence of AIBN in toluene.[44,45] Rather than the expected radical-induced polyaddition[46] to give **14** (eq 5), condensation of the ferrocene monomer was observed with norbornene and nortricyclane units as end-groups (eq 6). The isolated oligomers (**15**) were characterized by NMR spectroscopy and field-desorption mass spectrometry and have a chain length of 2–12 repeat units as determined by GPC.



Another group of polymers to consider are poly(metalloxanes) where metallocene fragments are connected through the metal via oxygen or other elements. Most of the work done in this area has involved titanium derivatives and was carried out with the aim of exploiting the catalytic properties that the $TiCp_2$ unit can introduce to the polymer.

Several attempts have been made to synthesize polytitanoxane (**16**). Thus, Giddings[47] claimed the synthesis of polytitanoxane by sequential reduction (zinc)-oxidation (oxygen) of titanocene dichloride in organic solvents, because the use of aqueous basic conditions lead to metal ring bond cleavage. The yellow polymer obtained, however, was an insoluble cross-linked material with poor thermal and hydrolytic stability in which some of the cyclopentadienyl substituents had been eliminated. The characterization was poor, and the structure (**17**) was postulated mainly on the basis of elemental analysis. A linear polymer product was postulated when $[Cp_2Ti]_2$ or $Cp_2Ti(CO)_2$ was reacted with oxygen, but in this case an insoluble material was also obtained with a suggested peroxo-bridged structure based on its diamagnetic behavior.[48]



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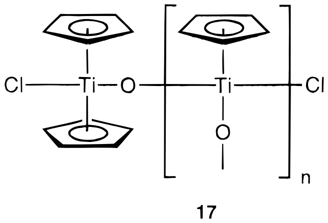


17

II.1.2 Ring-Opening Polymerization (ROP) of Strained Metallocenophanes

a. Introduction. ROP reactions generally occur via a chain growth mechanism and therefore represent a particularly desirable route for the preparation of high molecular weight poly(ferrocenes). As is clear from the polymers described above, such materials are very rare, particularly if the ferrocene groups are in close proximity to one another so as to permit metal–metal interactions. The first syntheses of poly(metallocenes) via ROP were reported in early 1992. The atom abstraction induced ROP process discovered by Rauchfuss and co-workers was described early in that year and is discussed in section II.1.3. Thermal ROP of strained metallocenophanes, which is discussed in this section, was reported by Manners et al. a few months thereafter.

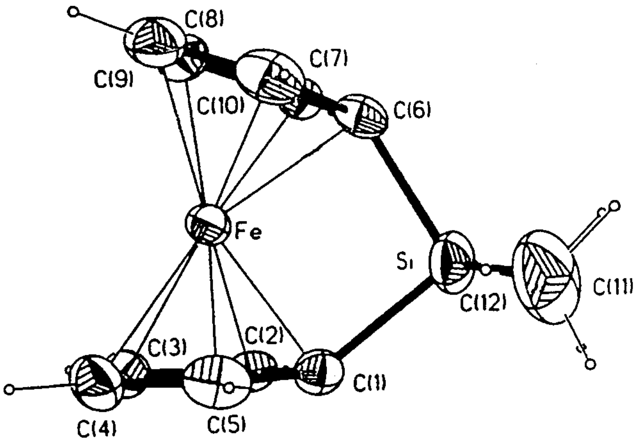
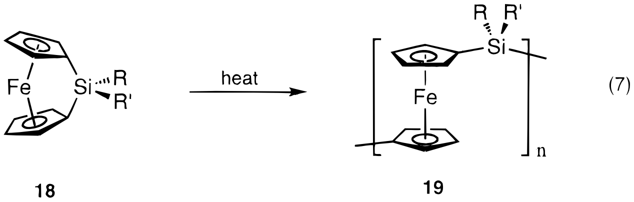


Figure 1. X-ray structure of [1]silaferrocenophane **18** (R = R′ = Me).

A key requirement for a classical ROP process is a strained cyclic monomer. Metallocenophanes in which a single atom bridges the two cyclopentadienyl ligands (i.e., [1]metallocenophanes) possess strained ring-tilted structures and have been known since 1975. Such species possess tilt-angles between the planes of the Cp ligands of 6–32°, but no successful ROP reactions for these species had been reported until very recently. However, in the early 1980s Seyferth et al. showed that phosphorus-bridged [1]ferrocenophanes undergo anionic ring-opening oligomerization to yield mainly dimeric and trimeric oligo(ferrocenylphosphines) (**7**) with traces of the tetramer and pentamer.[36] Although anionic ROP was also attempted by these researchers using small quantities of anionic initiator, these reactions were unsuccessful and a similar distribution of oligomers (mainly dimer and trimer) was isolated.[36]

b. Thermal Ring-Opening Polymerization of Silicon-Bridged [1]Ferrocenophanes. The first examples of the use of ROP of strained metallocenophanes to prepare high molecular weight poly(metallocenes) (M_n > 10^5) involved organosilane spacers.[49,50] Specifically, poly(ferrocenylsilanes) such as **19** (R = R′ = Me) were prepared via the thermal ring-opening polymerization of strained, ring-tilted [1]ferrocenophanes (**18**) (Figure 1). These high polymeric materials were prepared by heating the silicon-bridged [1]ferrocenophanes in the melt, at 130–220 °C in evacuated tubes (eq 7).[49–51]



18 19

The thermal ROP route is very general, and a wide range of semicrystalline, glassy, or elastomeric poly-

Table 1. Thermal Transition and GPC Molecular Weight Data for Selected Poly(ferrocenylsilanes) 19[60,68,74,75b]

R	R′	T_g (T_m) °C[b]	M_n[a]	PDI[c]
H	H	16 (165)	—[e]	—[e]
Me	Me	33 (122−145)	3.4×10^5	1.5
Et	Et	22 (108)	4.8×10^5	1.5
n-Pr	*n*-Pr	24 (98)	8.5×10^4	2.7
n-Bu	*n*-Bu	3 (116, 129)	3.4×10^5	2.6
n-Pen	*n*-Pen	−11 (80−105)	3.0×10^5	1.6
n-Hex	*n*-Hex	−26	7.6×10^4	1.6
Me	H	9 (87, 102)	4.2×10^5	2.0
Me	$CH_2CH_2CF_3$	59	8.1×10^5	3.3
Me	$CH{=}CH_2$	28	7.7×10^4	2.1
Me	*n*-$C_{18}H_{37}$	1 (16)	5.6×10^5	2.5
Me	Ph	54	1.5×10^5	2.0
Me	Fc[d]	99	7.1×10^4	2.3
Me	5-norbornyl	81	1.1×10^5	1.5
OMe	OMe	19	1.5×10^5	2.0
OEt	OEt	0	3.8×10^5	2.1
OCH_2CF_3	OCH_2CF_3	16	2.2×10^5	1.2
OBu	OBu	−43	3.9×10^5	2.1
OHex	OHex	−51	0.9×10^5	2.6
$O(CH_2)_{11}CH_3$	$O(CH_2)_{11}CH_3$	(−30)	1.9×10^5	2.5
$O(CH_2)_{17}CH_3$	$O(CH_2)_{17}CH_3$	(32)	2.3×10^5	2.1
OC_6H_5	OC_6H_5	54	2.3×10^5	2.0
OC_6H_4-*p*-^{t}Bu	OC_6H_4-*p*-^{t}Bu	89	1.9×10^5	1.9
OC_6H_4-*p*-Ph	OC_6H_4-*p*-Ph	97	5.4×10^4	2.0
Me[f]	Me[f]	93	2.8×10^5	1.5
Me[g]	Me[g]	116	2.3×10^5	1.4

[a] Obtained from analysis of THF polymer solutions which contained 0.1% $[Bu_4N][Br]$ and estimated vs polystyrene standards. [b] DSC data collected at a heating rate of 10 °C/min. [c] PDI = M_w/M_n. [d] Fc = $(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$. [e] Insoluble polymer. [f] One Me group on each Cp ligand. [g] One C_5Me_4 ligand and one C_5H_4 ligand.

(ferrocenylsilanes) have been prepared from silicon-bridged [1]ferrocenophanes with a range of different substituents at silicon or the cyclopentadienyl rings (Table 1).[52−60] These polymers have been fully characterized using a range of spectroscopic and analytical methods, and their molecular weights (M_w), which have been established by absolute methods such as low angle laser light scattering, lie in the 10^5−10^6 range with polydispersity indices of ca. 2. It has recently been shown that spirocyclic [1]ferrocenophanes function as cross-linking agents, allowing access to poly(ferrocenylsilanes) with controlled cross-link densities.[61] A key feature that was initially noted concerning these polymers was the presence of two reversible oxidation waves in their cyclic voltammograms (e.g., Figure 2).[49] The proposed explanation invoked initial oxidation at alternating iron sites as a consequence of interactions between the iron atoms. Thus, as one iron center is oxidized, the neighboring sites become more difficult to oxidize and therefore do so at a higher potential, and so two oxidation waves result. Recent studies on model oligo(ferrocenylsilanes) fully support this theory.[62,63] The peak separations for the different polymers, which provide a useful estimate of the degree of interaction between the metal centers, are generally in the range $\Delta E_{1/2}$ = 0.16−0.29 V in CH_2Cl_2, depending on the substituents present.[49,55,56,58] When oxidized, poly(ferrocenylsilanes) undergo a color change from amber to blue. The interesting electrochromic behavior has been studied in some detail for several polymers.[64,65]

Pristine high molecular weight poly(ferrocenylsilanes) are insulating ($\sigma = 10^{-14}$ S cm^{-1}), and when amorphous samples are partially oxidized by I_2, the conductivities ($\sigma = 10^{-8}$ to 10^{-7} S cm^{-1}) lie in the weak semiconductor range and show electron localization on the Mössbauer spectroscopic time scale.

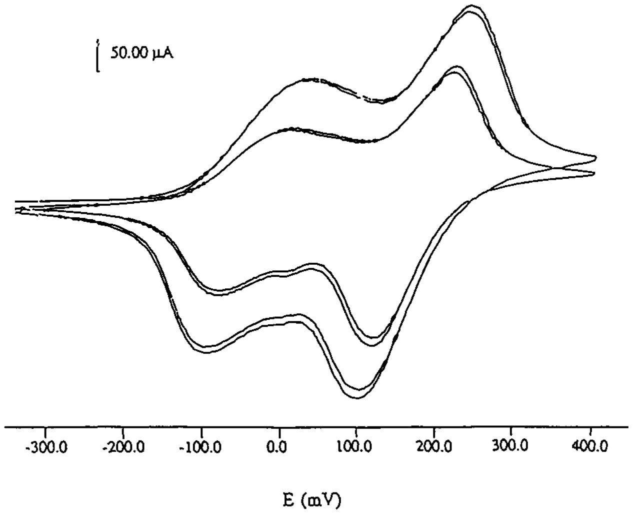


Figure 2. Cyclic voltammogram (in CH_2Cl_2) of poly(ferrocenylsilane) **19** (R = R′ = Me).

Recent studies of oriented, crystalline samples of poly(ferrocenyldi(*n*-butyl)silane), **19** (R = R′ = *n*-Bu), have indicated conductivities in the respectable semiconductor range (up to ca. 2×10^{-4} S cm^{-1}) on doping with I_2.[55] In addition, amorphous poly(ferrocenylsilanes) such as **19** (R = Me, R′ = Ph) possess appreciable hole mobilities.[55] Intriguingly, studies on TCNE-oxidized oligo(ferrocenylsilanes) (M_w = ca. 1500) reported by Garnier et al. indicated the presence of electron delocalization and in some cases the presence of ferromagnetic ordering at low temperature.[66] However, attempts to reproduce this behavior with high molecular weight samples were unsuccessful.[74] Poly(ferrocenylsilanes) such as **19** (R = R′ = Me) are thermally stable up to 350−400 °C with a weight retention of 35−40% at 1000 °C, yielding ferromagnetic Fe−Si−C ceramic composites.[67] The insoluble, semicrystalline poly(ferrocenyldihydrosilane) **19** (R = R′ = H) gave the highest ceramic yield with a weight retention of 90% at 600 °C and 63% at 1000 °C.[68] Pyrolysis of **19** (R = R′ = Me) can also be performed within the hexagonal pores of the mesoporous silica material MCM-41. Following thermal ROP of the monomer **18** (R = R′ = Me) within the channels, nanoscale cylinders of the poly(ferrocenylsilane) are formed and subsequent pyrolysis yields superparamagnetic nanostructures.[69]

Glass transitions for poly(ferrocenylalkyl/arylsilanes) **19**, as observed by DSC, cover a wide range of temperatures (−26 to 116 °C). Symmetrically substituted derivatives often show a propensity to crystallize and have been studied by DSC, WAXS, and atomic force microscopy.[60,70] The morphology of many of the materials shows thermal history dependence with an increase in crystallinity over time. Modeling studies on oligo(ferrocenylsilanes) by O'Hare and coworkers using molecular mechanics have also been performed, and these provide excellent insight into the conformational preferences of macromolecules in the solid state.[71,72] These studies provided results which are interesting to compare with those from single crystal X-ray diffraction work performed on species such as the linear pentamer which possesses a trans planar zigzag conformation (Figure 3).[62,63]

Another recently studied feature of poly(ferrocenylsilanes) is their tunability. Thus, functional ma-

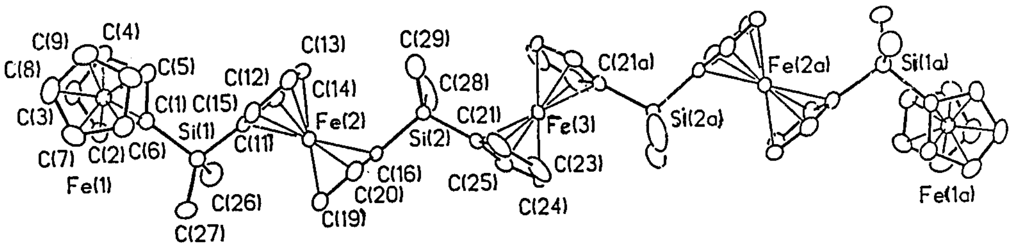
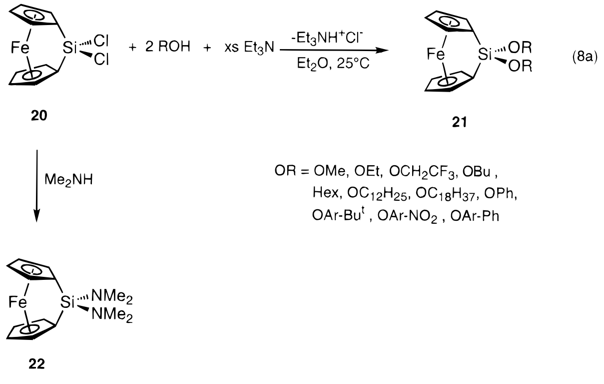


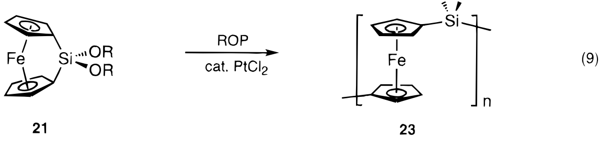
Figure 3. X-ray structure of linear pentamer (Fc-SiMe$_2$-fc-SiMe$_2$-fc-SiMe$_2$-fc-SiMe$_2$-Fc).

terials can be prepared via substitution reactions on polymers with Si−Cl bonds, including water-soluble materials.[73] A related convenient and versatile synthetic route has been developed very recently for the preparation of new alkoxy, aryloxy, and amino-substituted silicon-bridged [1]ferrocenophanes **21** and **22** via an unexpectedly facile chlorine substitution reaction at the bridging atom of a readily available SiCl$_2$-bridged [1]ferrocenophane precursor **20** (eq 8a,b).[75] The corresponding high molecular weight polymers **23** ($M_w = 1-8 \times 10^5$ vs polystyrene standards) were obtained via metal-catalyzed ROP (vide infra) of **21** (eq 9), whereas polymer **24** was obtained via thermal ROP of **22** (eq 10). Poly(ferrocenylsilanes) **23** exhibit a wide range of T_g values from −51 to 98 °C.[75] Side-chain crystallization was observed when long chain alkoxy substituents were present such as in the case of **23** (OR = OC$_{18}$H$_{37}$). This material possesses a lamellar structure with interdigitated side groups according to WAXS studies.[75] In addition, hydrosilylation reactions have been used with polymers containing Si−H functionalities to attach mesogenic groups, which allows access to thermotropic side chain liquid crystalline materials.[76]



OR = OMe, OEt, OCH$_2$CF$_3$, OBu, Hex, OC$_{12}$H$_{25}$, OC$_{18}$H$_{37}$, OPh, OAr-Bu^t, OAr-NO$_2$, OAr-Ph

(8b)



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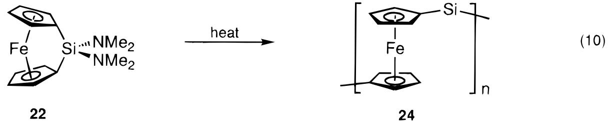
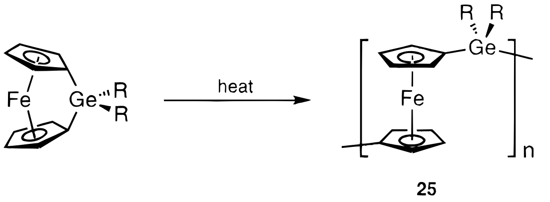


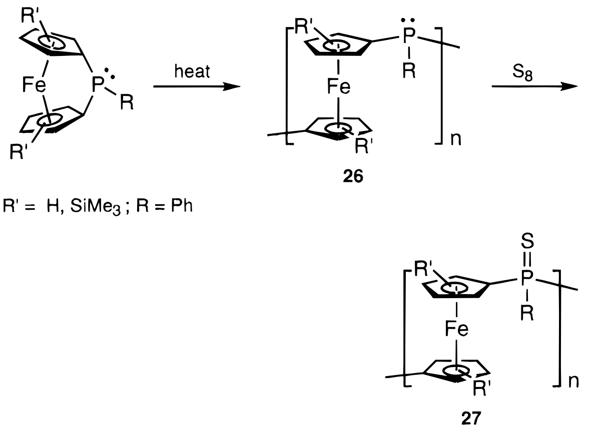
(10)

c. Thermal Ring-Opening Polymerization of Other Strained Metallocenophanes. This thermal ROP methodology has been extended to other strained metallocenophanes. Thus, poly(ferrocenylgermanes) (**25**) have been reported as high molecular weight ($M_w = 10^5$ to 10^6) materials from the ROP of the corresponding germanium-bridged [1]ferrocenophanes at 90 °C and above (eq 11).[77] The resulting golden-yellow polymers exhibit electrochemical and thermal behavior similar to poly(ferrocenylsilanes) with slightly lower T_g values.[64,77−80]



(11)

Poly(ferrocenylphosphines) (**26**), similar to those previously claimed by condensation routes,[36] have also been prepared via thermal ROP (eq 12).[81] Solubility increased when one of the cyclopentadienyl rings was substituted with an *n*-butyl group. Sulfurization of the unsubstituted and *n*-butyl-substituted polymers was carried out to facilitate their characterization by GPC, as the poly(ferrocenylphosphine) precursors were found to be adsorbed to the GPC column material (styragel). Polymers with trimethylsilyl substituents on the cyclopentadienyl rings, however, could be analyzed by GPC without sulfurization. A comparison between unsulfurized (**26**, R′ = SiMe$_3$, R = Ph) and sulfurized (**27**, R′ = SiMe$_3$, R = Ph) samples of this polymer revealed that these materials possess essentially the same molecular weight, indicating that chain cleavage does not occur during the sulfurization step.

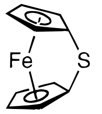


R′ = H, SiMe$_3$; R = Ph

(12)

Ring-opening polymerization of the sulfur-bridged [1]ferrocenophane (**28**) produces the poly(ferrocenylsulfide) (**29**).[82,83] This material is insoluble, but random methylation of the Cp rings affords soluble materials which possess more substantial metal–metal interactions ($\Delta E_{1/2} > 0.31$ V) than analogous poly(ferrocenylsilanes), according to electrochemical measurements.

Very recently, a (to date) unique first-row element bridged [1]boraferrocenophane (**30** R = $N(SiMe_3)_2$) was reported[84] with the largest tilt angle to date (ca. 32°),[85] which also undergoes ROP to give an insoluble poly(ferrocenylborane) (**31** R = $N(SiMe_3)_2$). The recent synthesis of a [1]stannaferrocenophane has led, upon heating at 150 °C, to the first high molecular weight poly(ferrocenylstannane) ($M_w = 1.3 \times 10^5$, PDI = 1.6). The polymer **32** also possesses significant interactions between iron atoms as shown by cyclic voltammetry ($\Delta E_{1/2} = 0.24$ V).[86]



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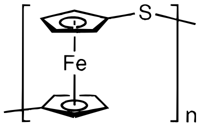

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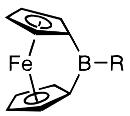

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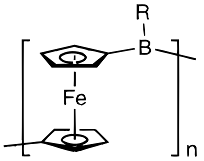

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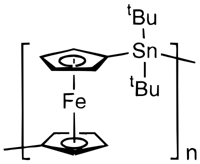
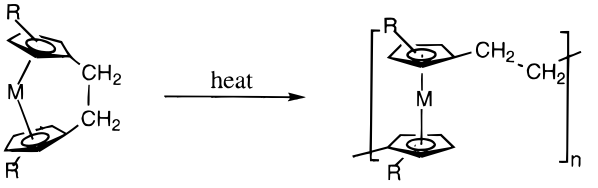


32

Hydrocarbon-bridged [2]ferrocenophanes (**33**, M = Fe) were found to undergo ROP at 300 °C, providing access to poly(ferrocenylethylenes) (**34a**) (eq 13).[87] The polymers were insoluble if R = H but readily soluble when R = Me. In the latter case, a bimodal weight distribution was found, with an oligomeric fraction ($M_w = 4800$) and a high molecular weight fraction ($M_w = 9.6 \times 10^4$). Because of the more insulating hydrocarbon bridge, only slight electronic communication is observed by cyclic voltammetry (peak separation of $\Delta E_{1/2} = 90$ mV). Nevertheless, cooperative magnetic behavior has been observed in TCNE-oxidized materials at low temperature.[88] The analogous [2]ruthenocenophanes, which possess greater ring-tilt angles, undergo ROP at lower temperatures (220 °C) to yield poly(ruthenocenylethylenes) (**34b**) although their electrochemistry is significantly different.[89]

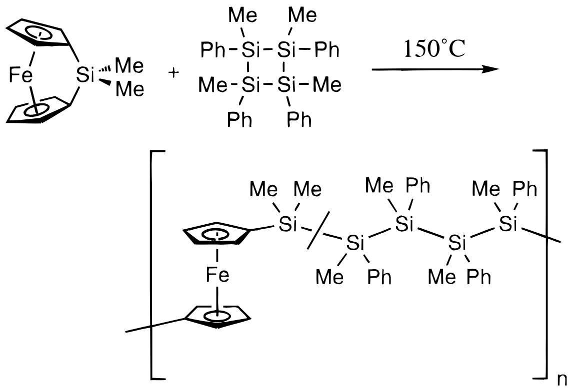


(13)

33
R = H, Me

(**34a**) M = Fe
(**34b**) M = Ru

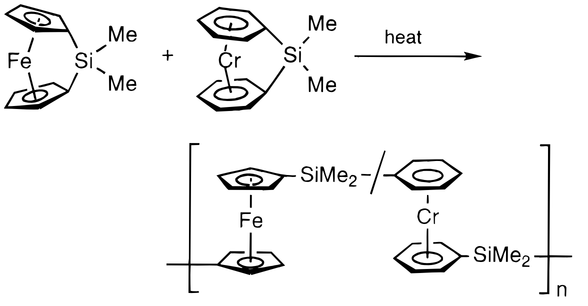
The use of thermal ROP also allows access to novel random copolymers. The first examples, poly(ferrocenylsilane)-*co*-poly(silane) materials (**35**) (eq 14), were reported in early 1995.[90] These copolymers are particularly interesting because they contain ferrocene moieties linked by σ-delocalized oligosilane segments, and these are inaccessible via thermal ROP of ferrocenophanes with oligosilane bridges, as they are insufficiently strained.[53] The polymers are photosensitive, and the polysilane segments can be cleaved with UV radiation. Interesting charge transport properties have been demonstrated for these materials.[55]



(14)

35

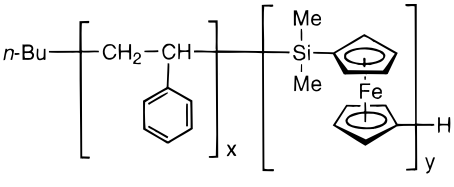
Subsequently, a range of other copolymers derived from different [1]ferrocenophanes[68] as well as [1]-ferrocenophanes and silicon-bridged bis(benzene)-chromium complexes[91] (**36**) (eq 15) have been reported.



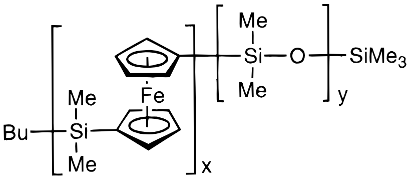
(15)

36

d. Anionic Ring-Opening Polymerization of Strained Metallocenophanes. In 1994, the first anionic ROP reactions for metallocenophanes were reported. Silicon-bridged [1]ferrocenophanes such as **18** (R = R′ = Me) were initially shown to oligomerize with lithioferrocene as initiator.[62,63] By decreasing the initiator concentration further, poly(ferrocenylsilanes) were produced. Moreover, using extremely pure monomer and stringent reaction conditions, the anionic ROP of **18** (R = R′ = Me) was shown to be living.[92] Poly(ferrocenylsilanes) **19** (R = R′ = Me) with controlled molecular weights (M_w) up to ca. 120 000 and with very narrow polydispersities (PDI = 1.05–1.10) were formed depending on the monomer-to-initiator ratio. As the anionic ROP is living, functionalization of polymer chain-ends is facile, and the synthesis of diblock and multiblock copolymers (e.g., **37a**,**b**) using [1]silaferrocenophanes and styrene or hexamethylcyclotrisiloxane has been possible.[93] Triblock and pentablock copolymers have also been synthesized and characterized.[93] Very recently, water-soluble block copolymers with N-methylated vinylpyridine and poly(ethylene oxide) segments have also been prepared by anionic methods.

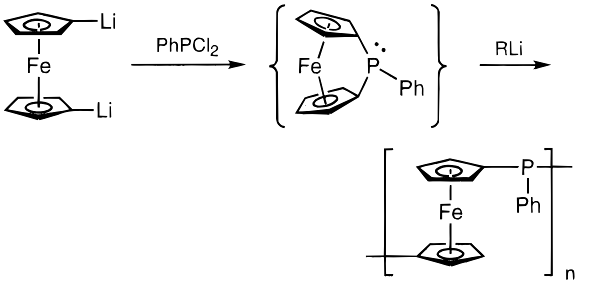


37a



37b

As mentioned above, oligomeric ferrocenylphosphines (mainly the dimer and trimer) have been prepared from the reaction of [1]phenylphosphaferrocenophane with approximately equimolar amounts of lithio(diphenylphosphino)ferrocene.[36] However, previous attempts to prepare polymers by reducing the initiator concentration were reported to be unsuccessful.[36] Recently, it has been demonstrated that anionic ROP of phosphorus-bridged [1]ferrocenophanes does indeed occur.[94] Poly(ferrocenylphosphines) with controlled molecular weights (up to M_w = ca. 36 000) and narrow polydispersities (PDI = 1.08–1.25) were prepared together with block copolymers. The demonstration that anionic ROP of phosphorus-bridged [1]ferrocenophanes is possible suggests that the high molecular weight poly(ferrocenylphosphines) (**7**) generated under certain conditions during the condensation polymerization of dilithioferrocene·TMEDA and $PhPCl_2$ reported by Seyferth in the early 1980s almost certainly occurs via a chain growth route, namely the anionic ROP of a [1]ferrocenophane which is generated in situ under the reaction conditions used (eq 16).[94] It is plausible that similar types of anionic ROP reactions occur at least to some extent in the original condensation routes to poly(ferrocenylsilanes) described in the 1960s by Rosenberg.[38,39,95]



(16)

7

The novel poly(ferrocene) block copolymer materials accessible via the living ROP of [1]ferrocenophanes are of interest as they provide access to periodic phase-separated, redox-active organometallic domains in the solid state (spheres, cylinders or their antistructures, lamellae, etc., depending on the block ratio and molecular weight) and to novel micellar aggregates in selective solvents for one of the blocks.[93,96–98] For example, annealed (150 °C) films of polystyrene-poly(ferrocenylsilane) block copolymers **37a** with approximately equal block lengths afford ordered lamellar structures that can be observed by TEM (Figure 4a).[96] In contrast, thin films of poly(ferrocenylsilane)-poly(dimethylsiloxane) block copolymers **37b** (block ratio x:y = 1.0:6.0) possessing a cylindrical morphology in the solid state and dissolution in hexanes, a selective solvent for the siloxane block, cylindrical micelles with an organometallic, potentially semiconducting poly(ferrocene) core, and an insulating polysiloxane corona are formed (Figure 4b).[97] Ideas concerning the possible utilization of

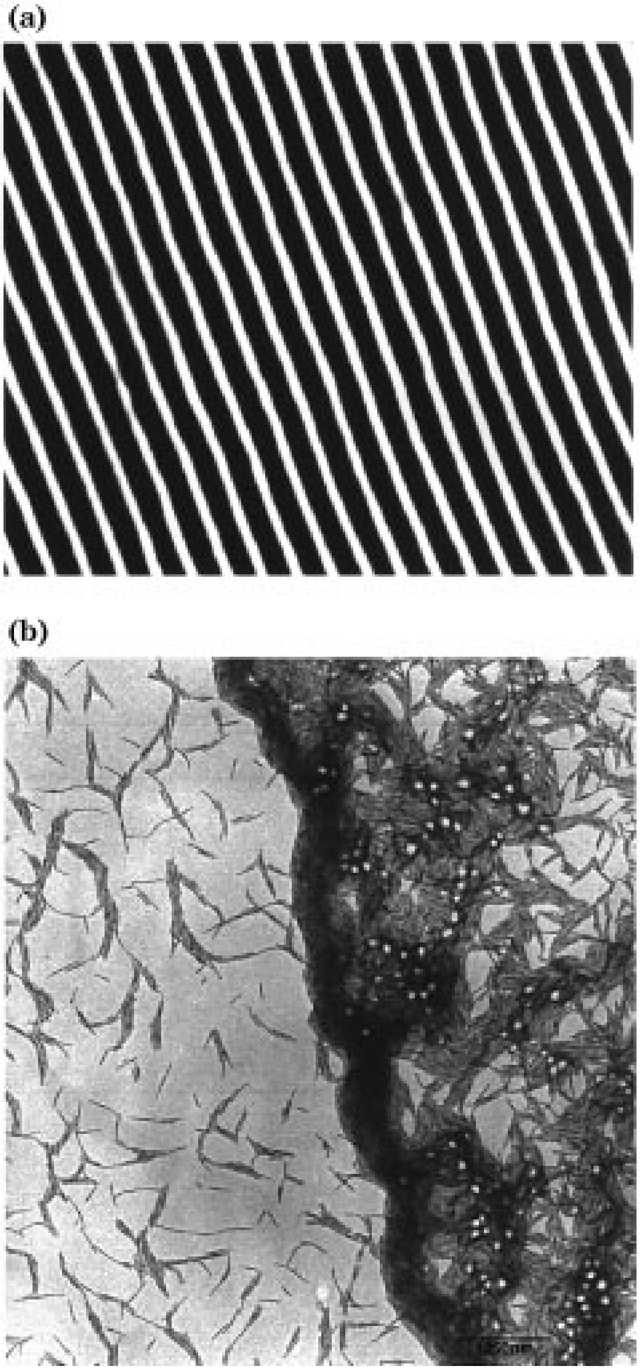
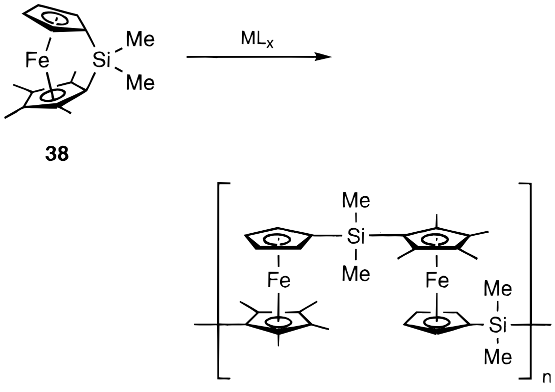


Figure 4. (a) TEM of poly(styrene)–poly(ferrocenylsilane) block copolymer and (b) TEM of cylindrical micelles and film of poly(ferrocenylsilane)–polysiloxane block copolymer.

highly ordered examples of these phase-separated structures as precursors to materials with selectively oxidized domains (using scanning electrochemical microscopy, for example), as novel charge transport materials, as precursors to magnetic nanostructures via pyrolysis (in a manner similar to that demonstrated for the poly(ferrocenylsilane)/MCM-41 composites[69]) and the potential behavior of the cylindrical micelles as semiconducting nanowires have have been outlined.[96,98]

e. Transition Metal Catalyzed Ring-Opening Polymerization of Metallocenophanes. A very convenient transition metal catalyzed ROP route to poly(metallocenes) from metallocenophanes was reported in 1995. Manners et al. reported that a series of Rh^{I}, Pd^{II}, and Pt^{II} complexes catalyzed the ROP of [1]silaferrocenophanes at room temperature to yield high molecular weight poly(ferrocenylsilanes) ($M_n =$ ca. 10^5).[99a] A few months later, Tanaka et al. independently reported transition metal catalyzed ROP reactions using mainly Pd^0 and Pt^0 catalysts.[99b] A major advantage of these transition metal catalyzed processes is that, unlike anionic polymerization, ambient temperature polymerization is possible without the need for a monomer of extremely high purity. Copolymerization of silicon- and germanium-bridged [1]ferrocenophanes is possible and affords random copolymers.[78,99b] Random copolymerization of silicon-bridged [1]ferrocenophanes with cyclocarbosilanes is also possible to yield novel poly(ferrocenylsilane)-poly(carbosilane) random copolymers.[99c] Ambient temperature, transition metal-catalyzed ROP is especially advantageous in the case of [1]ferrocenophanes with halogen substituents at silicon where thermal ROP proceeds at temperatures higher than normal (>250 °C).[73]

Moreover, recent work[100] has shown that unsymmetrically Cp-methylated species such as **38** yield regioregular poly(ferrocenylsilanes) (**39**) via transition metal catalyzed ROP as a result of exclusive $Cp^{H}-Si$ bond cleavage (eq 17). In contrast, thermal ROP yields more random structures arising from cleavage of both $Cp^{H}-Si$ and $Cp^{Me}-Si$ bonds.[52,74]



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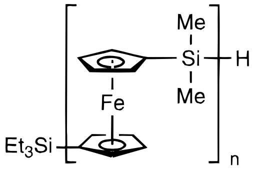
(17)

39

Furthermore, molecular weight control in the range ($M_n = 10^3$ to 10^5) is also possible by the addition of Et_3SiH which leads to the isolation of end-capped polymers **40**. The use of poly(methylhydrosiloxane) as the source of Si−H bonds allows access to novel graft copolymers **41**.[100] This methodology can also be extended to the preparation of star and block structures, including water-soluble materials.[100]



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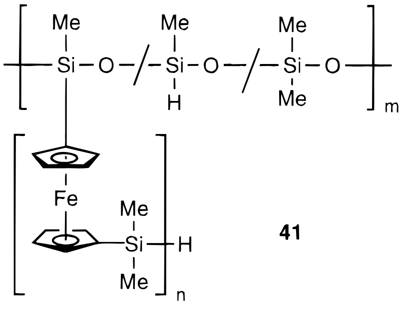
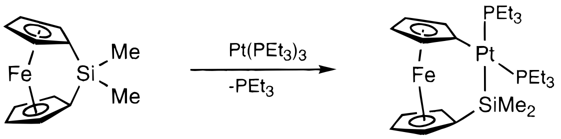


41

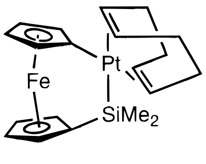
Recent work has also focused on understanding the mechanism of the transition metal catalyzed ROP reactions. A logical first step in the polymerization is insertion of the transition metal into the strained Cp−carbon bridging element bond in the ferrocenophane. Very recently, the first examples of this type of insertion reaction were reported (eq 18).[101]



(18)

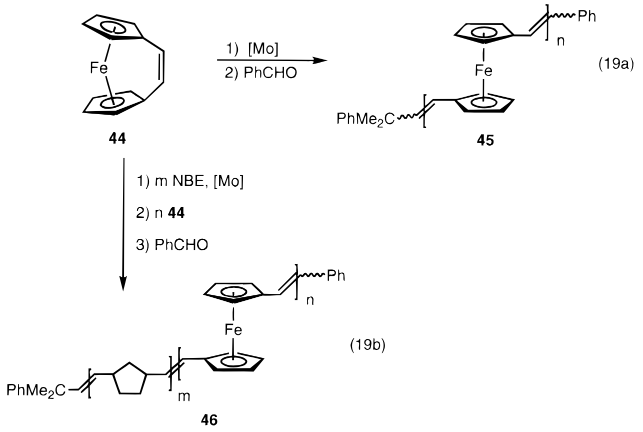
42

The [2]platinasilaferrocenophane **42** does not react further with [1]silaferrocenophane **18** (R = R′ = Me). However, if the phosphine groups are replaced by more weakly bound ligands as in **43**, synthesized via the reaction of **18** (R = R′ = Me) with Pt(1,5-cod)$_2$, the species does function as a ROP precatalyst.[101b] Moreover, the ROP is inhibited by the presence of added 1,5-cod supporting cycloolefin dissociation from **43** as a key step in the ROP mechanism.



43

Very recently, Buretea and Tilley reported the synthesis of poly(ferrocenylenevinylene) via ring-opening metathesis polymerization (ROMP) of a vinylene-bridged [2]ferrocenophane (**44**)[102a,102d] which was obtained from the McMurry coupling of 1,1-ferrocenedicarbaldehyde.[102a] In the presence of the molybdenum ROMP catalyst, **44** was found to undergo polymerization (eq 19a) to give an insoluble orange powder which exhibited doped-conductivity of 10^{-3} S cm^{-1}. Partially soluble block copolymers of **44** with norbornene (NBE) were also obtained by ROMP route (eq 19b). The material with a catalyst:NBE:**44** ratio of 1:10:10 gave a thick red gel with M_w of 1710 by GPC analysis (vs polystyrene standards) and a slightly higher M_w of 3000 by end-group analysis. Similar material with a catalyst:NBE:**44** ratio of 1:50:10 gave considerably higher M_w of 21 000 by GPC. The cyclic voltammograms of these materials showed two reversible redox waves with a separation of 250 mV, indicating significant interaction between the Fe centers.



44

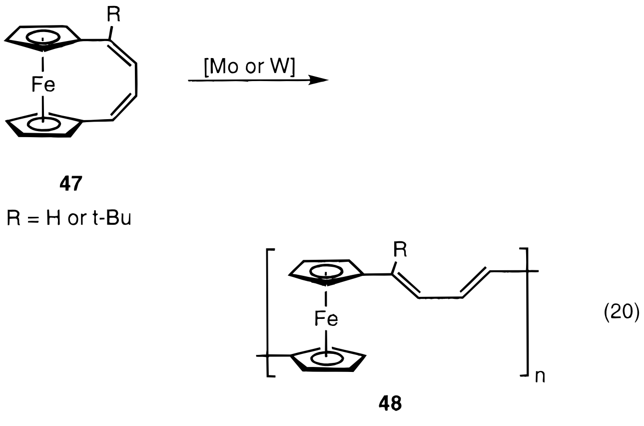
45

(19a)

46

(19b)

ROMP of [4]ferrocenophanes **47** (R = H) with unsaturated —C═C—C═C— bridges (eq 20) has also been used by Grubbs, Lewis, and co-workers to obtain related ferrocene polymers, poly(ferrocenylenedivinylene)s **48** (R = H), with a π-conjugated structure.[102b] These materials are rather insoluble, but copolymerization with *sec*-butylcyclooctatetraene yields more soluble materials with molecular weights up to $M_w = 24\,400$ (PDI = 2.1). Very recently, Lee and co-workers have described the first soluble, very high molecular weight materials **48** (R = *t*-Bu) ($M_n > 300\,000$) via the ROMP of *tert*-butyl-substituted [4]-ferrocenophane monomers.[102c] Further studies of these polymers are of considerable interest.



47

R = H or t-Bu

48

(20)

II.1.3 Atom Abstraction Induced Ring-Opening Polymerization of Chalcogenido-Bridged Metallocenophanes

In early 1992, a novel atom abstraction induced ROP process was reported by Rauchfuss and co-workers.[103] The synthesis of well-defined poly(ferrocenylene persulfides) (**50**) was achieved via the desulfurization of [3]trithiaferrocenophane (**49**) with PBu_3 (eq 21), and this led to yellow materials that were soluble only when ferrocene was substituted with alkyl groups. The molecular weights (M_w) have been determined to be in the range 12 000−359 000 for **50** (R = *n*-Bu, R′ = H) and 25 000 in the case of a less soluble copolymer between monomers **49** (R′ = H) with R = H and *n*-Bu in a 53:47 ratio. These polymers have been fully characterized by NMR and elemental analysis and they exhibited very interesting properties.[103,104] The materials are air-stable in the solid state but are photosensitive in solution. The persulfide bond can be reductively cleaved with Li[BEt_3H] and subsequently regenerated upon reoxidation with I_2. Electrochemical studies showed two reversible oxidation waves, as observed for poly(ferrocenylsilanes), that can be attributed to oxidation of alternating iron sites along the polymer chain. A wave separation of 0.32 V suggests that the interaction between iron sites is greater than that observed in diferrocenyl disulfide[105] (Fc—S—S—Fc) or poly(ferrocenylsilanes) (Figure 5). More recently, mono-substituted and disubstituted *t*-Bu derivatives have been reported.[106] The polymerization was slower and solvent dependent yielding highly soluble polymers **50** with M_w values of 26 000 (R = *t*-Bu, R′ = H) and as high as 250 000 (R = R′ = *t*-Bu), with high polydispersities.

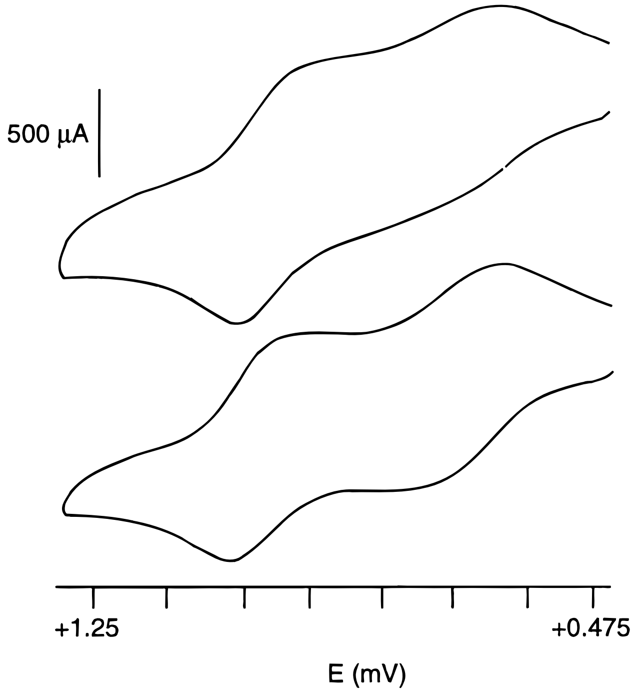
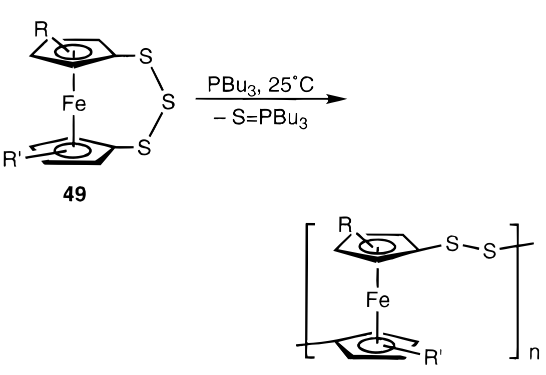


Figure 5. Cyclic voltammogram (in CH_2Cl_2) of poly(ferrocenyldisulfide) **50** (R = R′ = *t*-Bu) (top) and **50** (R = *t*-Bu, R′ = H) (bottom).

This atom abstraction route was also used by the same authors for the preparation of soluble polymeric networks from alkylated [3,3′]bis(trithia)ferrocenophanes.[103b] A bimodal molecular weight distribution, with maxima at $M_n \approx 5000$ and 5×10^5, was obtained by GPC for the material from which a polymer fraction was isolated ($M_n = 8.5 \times 10^5$).

Low molecular weight poly(ferrocenylene perselenides) have also been prepared from the selenium analogue of **49**.[104b] These materials also undergo photodegradation upon exposure to UV light in air.



49

50

R = R' = H, *t*-Bu
R = *n*-Bu, *t*-Bu R' = H

(21)

II.1.4 Face-to-Face Poly(metallocenes)

Multidecker sandwich structures, apart from those in which the stacking takes place upon crystallization, can be classified in the forms shown in Figure 6. Several attempts have been made to synthesize these types of polymeric structures, but in most cases dimer complexes or double- or triple-decker structures were produced. Rosenblum et al. have developed the synthesis of novel polymeric metallocenes (type b) held face-to-face by naphthalene or binaphthyl spacer groups. The condensation route involved palladium-catalyzed cross-coupling of chlorozinc ferrocenes or ruthenocenes with 1,8-diiodonaphthalene.[107,108] Because the ferrocene reagent is very reactive and cannot be prepared in pure form, it is difficult to achieve the exact stoichiometry of reactants required for a high degree of polymerization. Also, the rigidity of the polymer framework makes these materials relatively insoluble, and, consequently, with this methodology only materials up to $M_n = 4000$ have been prepared.[109] Crystallographic studies on a trimetal oligomer as a model for a segment of the polymer showed a cisoid arrangement for the naphthalene rings. Extrapolation would suggest a helical structure for the polymer.[110]

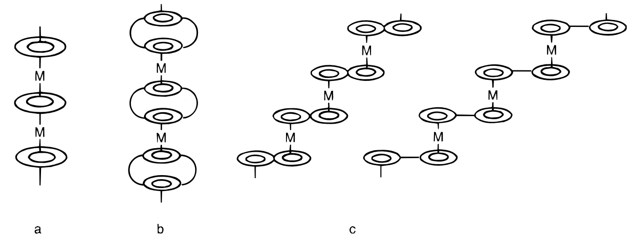
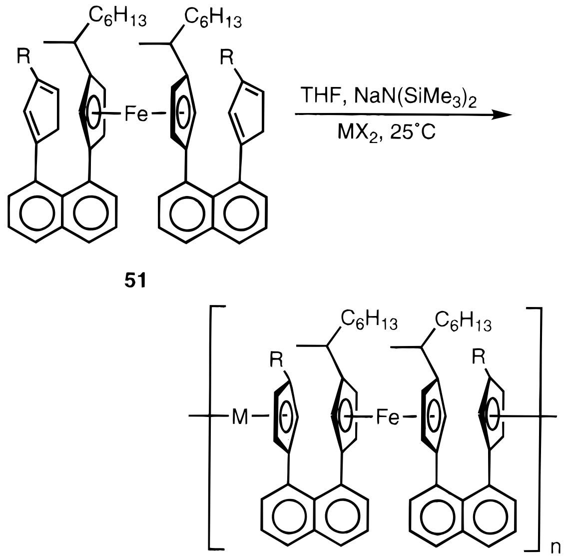


Figure 6. Different types of multidecker sandwich polymers.

An alternative, more successful route, in which a ferrocene monomer (**51**) is polymerized by treatment with sodium bis(trimethylsilyl)amide and $FeCl_2$ at room temperature (eq 22), has been recently reported by the same group.[111] The introduction of long hydrocarbon chains as substituents in the monomer unit clearly improves the solubility; thus, polymers **52** with values of M_n up to 18 000 can be easily prepared, and in some cases components of higher molecular weight were also detected.



51

52

(22)

M = Fe, Co X = Cl
M = Ni, X = CH_3COO
R = H, 2–octyl

This is a more general route to these materials and allows access to not only processable high molecular weight iron derivatives but also to nickel and mixed nickel– or cobalt–iron structures. However, to date, only low molecular weight products ($M_n < 4000$ for homometallic and < 2000 for heterometallic materials) have been described.[112]

The electrical and magnetic properties for these polymers were investigated.[112] When the iron-based polymers were partially oxidized with iodine, an increase in the electrical conductivity from less than 10^{-12} S cm^{-1} to 6.7×10^{-3} S cm^{-1} was detected, reflecting semiconductor behavior. This value is almost 2 orders of magnitude lower than that for the analogous crystalline poly(1,1′-ferrocenylene).[28,29] The electrochemistry of oligomers reflects some degree of electronic interaction and charge delocalization between the metal centers of the partially oxidized species ($\Delta E_{1/2} = 100-200$ mV at 50 mV s^{-1}).[107] The corresponding I_2-doped polymers appear to be weakly interacting mixed-valent systems by Mössbauer spectroscopy.[112] The bulk magnetic susceptibility was determined for the paramagnetic nickel polymer and heterometallic copolymers. In all of the polymers, the values were greater than those for the corresponding nickelocene or cobaltocene which was interpretated in terms of cooperative magnetic behavior.

Tetradecker sandwich oligomeric complexes containing carborane C_2B_3 rings have been synthesized by Grimes and co-workers via successive deprotonation of the reactive C_2B_3 end rings followed by metathesis reactions with the appropriate metal salts (Figure 7).[113] Oligomers having 5–17 metal atoms have been synthesized via this route. Cyclic voltammetry studies of these compounds suggested little intersandwich electronic communication with good evidence for electronic delocalization within the individual tetradecker stacks.[114]

Among recent attempts to obtain polymers of type c, where the successive metal–ring bonding is laterally displaced, is the interesting contribution by Katz

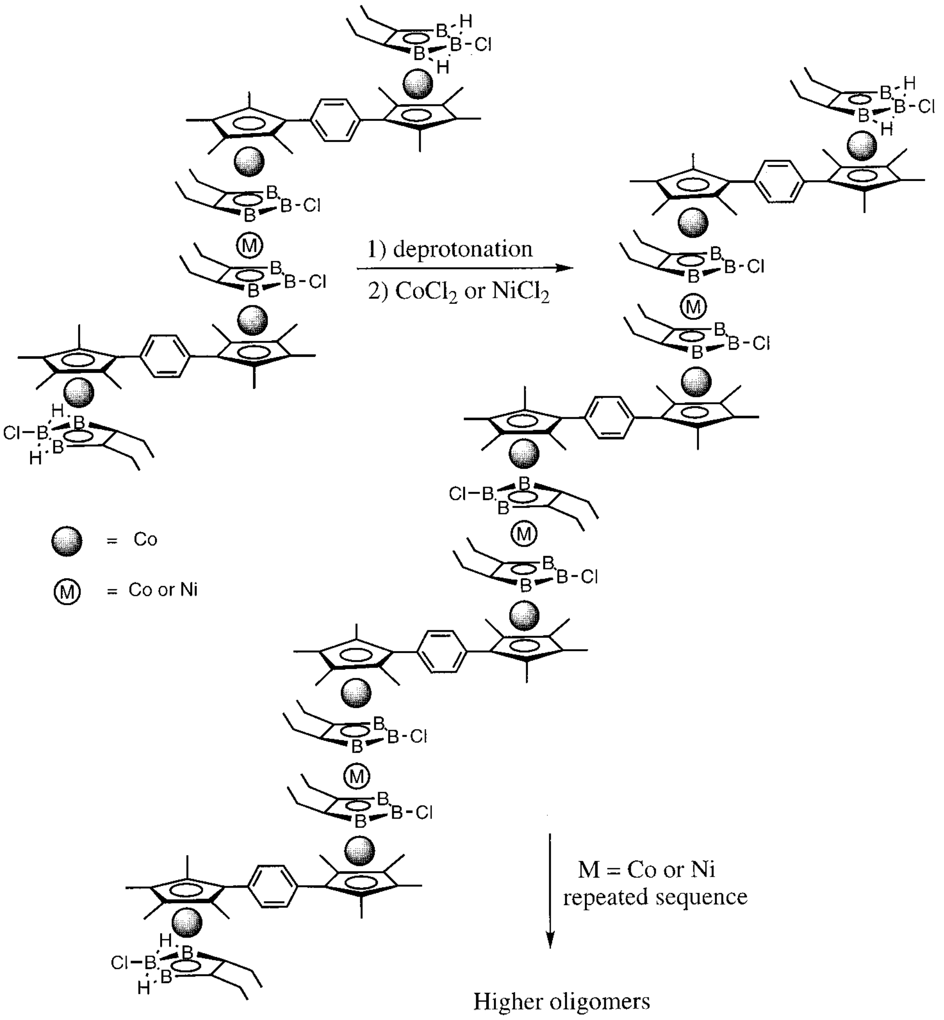
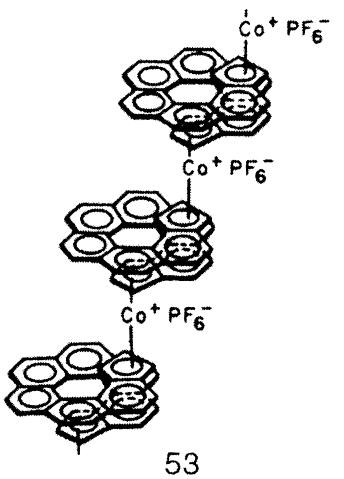


Figure 7. Structures of tetradecker sandwich complexes.

et al.[115] From the elaborate synthesis of [9]helicene hydrocarbon dianions, they achieved, after treatment with $CoBr_2$·DME and anion metathesis, the synthesis of soluble helical cobaltocenium oligomers (**53**, up to 6 units) in high yields. These are the first examples in which metallocenes are joined by fused conjugated systems of multiple bonds. Studies on their properties showed a weak interaction between metals via electrochemistry ($\Delta E_{1/2} = 130$ mV), similar to the face-to-face polymers described above, and a high optical activity.



53

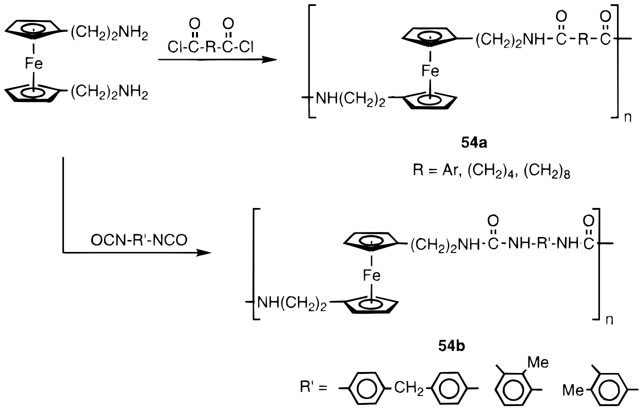
II.2. Main Chain Poly(metallocenes) with Long Spacers

II.2.1 Insulating Spacers

a. Hydrocarbon Spacers. The thermal stability and interesting physical properties of ferrocene provided the initial motivation for the inclusion of ferrocene moieties into polymer chains. Thus, in the 1960s, a large number of attempts to produce ferrocene-containing organic polymers, including polyalkenes, polyketones, polyesters, polyamines, polyamides, polyurethanes, polyureas, etc., were reported. This work has been excellently reviewed by Neuse and Rosenberg in 1970.[8] In general, these polymers were very poorly characterized and were of low molecular weight. Often, no analytical data or structural characterization was given. The conditions used followed classic condensation methods at high temperatures and frequently involved side reactions which led to impure materials or cross-linking and, when successful, the molecular weights for soluble materials were very low ($M_n < 6000$).[116]

Interfacial polycondensation routes at room temperature were considered as a convenient alternative to the classic condensations. They were first reported in the early 1960s by Knobloch and Rauscher[117] for the preparation of polyamides and polyesters from the reaction of 1,1′-ferrocenyldicarbonyl chloride with several diamines and diols. Okawara,[118] reported the synthesis of polyurethanes from the condensation of 1,1′-ferrocenedimethanol and 1,1′-bis(hydroxyethyl)ferrocene with diisocyanates, although the polymers possessed low molecular weights.

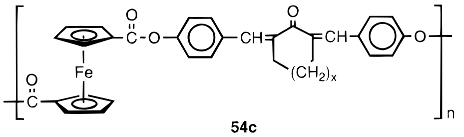
In 1984 Rausch et al.[119] briefly reported the synthesis of elastomeric polyamides (**54a**, $M_n = 10\,000-18\,000$) in high yields from 1,1′-bis(β-aminoethyl)ferrocene and diacid chlorides. Also, polyureas (**54b**) were prepared when starting from the same ferrocene monomer and diisocyanates, and polyesters and polyurethanes, when starting from 1,1′-bis(β-hydroxyethyl)ferrocene. However, these materials had much lower molecular weights and were characterized by scanning electron microscopy, X-ray, and IR analyses. The employment of ferrocenes in which the active center is separated by at least two methylene units was crucial in order to reduce steric effects and the instability found previously in polymers of α-functionalized ferrocene due to the α-ferrocenyl carbonium ion stability.[120]



54a

R = Ar, $(CH_2)_4$, $(CH_2)_8$

54b

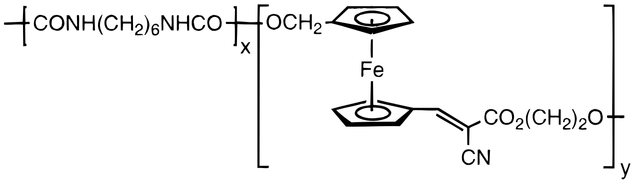


54c

X = 0, 1, 2

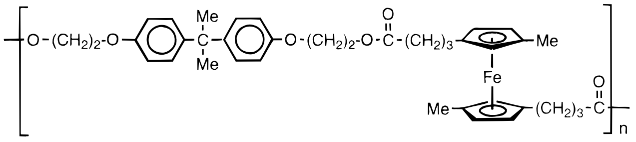
This technique was also used to prepare ferrocene-containing arylidene polyesters (**54c**) in good yields, from dicarboxyl ferrocenes and organic diols. The products were characterized by elemental analysis, IR spectroscopy, viscometry, and WAXS.[121] These polymers were semicrystalline and soluble in polar solvents, and conductivity studies showed an n-type semiconductor behavior ($\sigma = 3 \times 10^{-10}$ S cm^{-1} at room temperature) that followed a one-term Arrhenius-type equation with increasing conductivity over the range 300−500 K.

Wright et al.[122] have utilized Knoevenagel condensations to prepare new nonlinear optical (NLO) ferrocene-containing polymers for second harmonic generation (SHG) applications. The recent use of ferrocenes in this area is based on their large hyperpolarizability values[123] combined with their thermal and photochemical stability which make them desirable candidates for NLO materials. Thus, they synthesized a polyurethane copolymer (**55**) in moderate yields from a ferrocene derivative in which side reactions are minimized. The polymer was fully characterized and possessed a value of $M_n = 7600$, although no T_g was found using DSC.[122] Contrary to previous results with perfectly chromophore oriented organometallic polymers,[124] because of the random chromophore orientation in a head-to-tail sense, this material displays SHG activity after corona poling at 150 °C with reasonable stability for the SHG signal.



55

Zentel et al.[125] synthesized several ferrocene-containing copolyesters, such as **56**, via Ti(O-iPr)$_4$-catalyzed melt polycondensation. The polymers had molecular weights in the range 9000−30 000 (by capillary viscometry) and they were characterized by NMR, IR, and DSC. When ferrocene diols are incorporated into polyesters there is an increase of the oxidation potential of ≈40−50 mV, presumably because of a charge transfer through space interaction between the electron poor ester group and ferrocene, since the ester group is separated from the ferrocene moiety by 4 to 6 σ-bonds. The authors carried out dynamical mechanical analysis which showed a strong influence of the ferrocene unit on the rheological properties, with an unusual, rubber-like behavior.

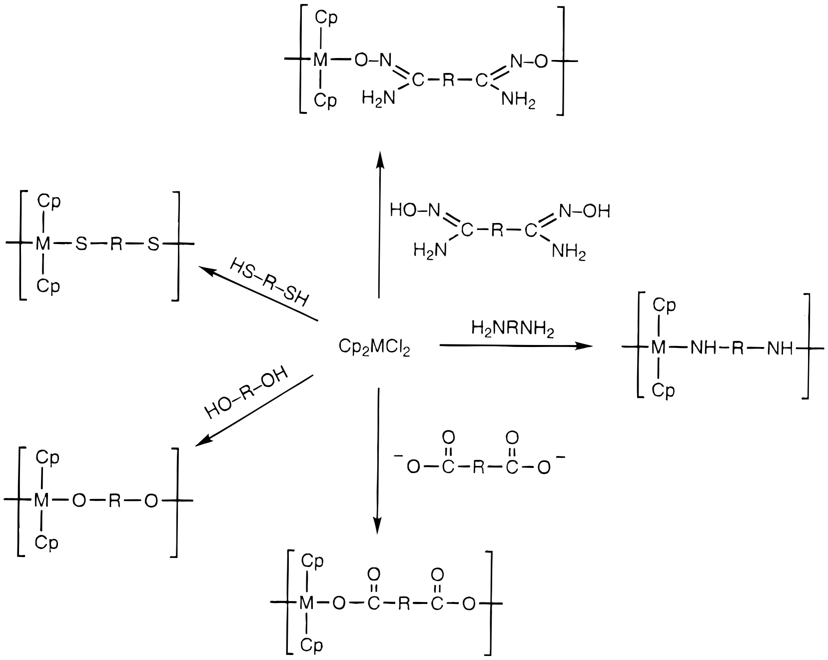


56

A large variety of group 4 (Ti, Zr, Hf) metallocene-containing polyethers, polythioethers, polyesters, polyamines, polyoximes, and polyamidoximes have also been reported.[126,127] Their synthesis, based on the reaction of Cp_2MCl_2 with Lewis bases (diol, dithiol, etc.) (Scheme 1), was carried out either in aqueous solution or using interfacial condensation techniques, depending on the solubility of the base. In 1977, Carraher[116] reviewed the preparation of these polymers; the materials are yellow to orange for titanium and white to light gray for zirconium and hafnium. Molecular weights ranged from oligomers to 10^6 although their solubility was limited. Some, such as the titanium polyethers, were insoluble and were characterized by IR, which showed characteristic bands for both metallocene and organic fragments. This allowed a determination of metal content,[128] since in most cases elemental analyses for carbon were not consistent with expected values, possibly because of the high stability of thermal degradation products.[129]

An interesting condensation reaction, in terms of applications of the resulting polymers, is that in which dyes were utilized as Lewis bases.[130,131] Thus,

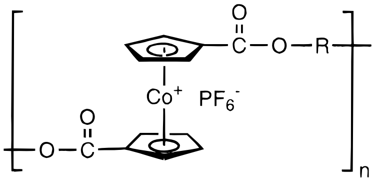
Scheme 1



soluble, high molecular weight (e.g., $M_w = 5.3 \times 10^5$ for bromophenol blue) titanium polydyes were synthesized in yields depending on the reaction conditions and the dye used. Their claimed advantage was their potential permanent, nonleaching nature in comparison with monomeric dyes. These polydyes are fluorescent, and, when used as coloring or doping agents in paper, cloth, paint, and plastic, materials with this property were obtained.

The synthesis of polymers containing cobaltocenium salts has also been studied, since this organometallic moiety is isoelectronic with ferrocene and is resistant to strong oxidizing agents. Pittman reported the synthesis of polyesters (**57**; R = $(CH_2)_4$, CH_2ArCH_2)[132] by solution polymerization techniques yielding low molecular weight (M_n = ca. 3000) products in which exchange of PF_6^- by Cl^- was observed complicating the characterization, as well as polyamides,[133] which led to insoluble materials that were difficult to characterize.

Later, Sheats[134] summarized the attempts to achieve soluble high molecular weight polymers by copolymerization of cobaltocenium 1,1′-dicarboxylic acid with organometallic monomers, such as titanocene or zirconocene (**57**; R = Cp_2Ti, Cp_2Zr). These materials were characterized by IR, TGA, and DSC. The presence of charges along the chain was expected to increase the solubility in polar solvents, but the products showed limited solubility although molecular weights (by intrinsic viscosity in 2-chloroethanol) of approximately 80 000 were reported.[135,136]



57

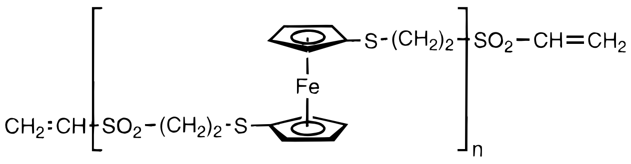
R = $(CH_2)_4$, CH_2ArCH_2, Cp_2Ti, Cp_2Zr

Polyamides, on the other hand, were prepared by Neuse[137] by reacting aromatic diamines with 1,1′-dicarboxylcobaltocenium chloride species in molten antimony trichloride at 150−175 °C. The products were isolated as PF_6^- salts upon treatment with NH_4PF_6 and characterized by IR, NMR, and elemental analysis, which confirmed the linear polyamide structure. Unfortunately, viscosity and VPO measurements proved inconclusive because of polydissociation in solution, and the authors based the claim concerning their polymeric nature on their film forming properties and the low concentration of the carboxyl end group with respect to the amide.

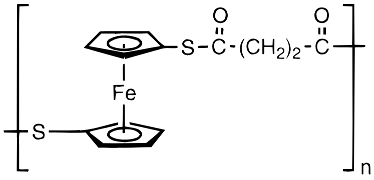
Well-characterized polymers with ferrocenes joined by sulfur-containing moeities, other than disulfide (see section II.1.3), have been reported by Nuyken et al.[138] by introducing an alkylthio spacer between the ferrocene and the thiol groups. Thus, polyaddition of 1,1′-bis(2-mercaptopropylthio)ferrocene to divinyl sulfone afforded a soluble, orange, low molecular weight (M_n = ca. 3000) material in 90% yield that was characterized by NMR and elemental analysis.

These workers also reported recently a series of sulfur-containing ferrocene polymers[138] that were prepared from either 1,1′-bis(2-mercaptoethyl)ferrocene or 1,1′-dimercaptoferrocene by base-catalyzed polyaddition to activated diolefins containing electron-withdrawing substituents (e.g., **58a**) and by interfacial condensation with acid dichlorides for the synthesis of poly(thioesters) (e.g., **58b**). This afforded yellow, soluble polymers with low molecular weights (M_n < 5000 by GPC; PDI = 1.6−5) which were characterized by several analytical and spectroscopic methods.

b. Organosilicon Spacers. Modification of poly(siloxanes) (silicones) has also been an important area of interest, and ferrocene has been introduced into organosilicon polymers including siloxanes and carbosilanes. The first approaches to siloxanes were made in the 1960s by Schaaf and Greber's groups. They applied the principle of controlled hydrolysis of



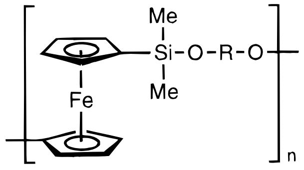
58a



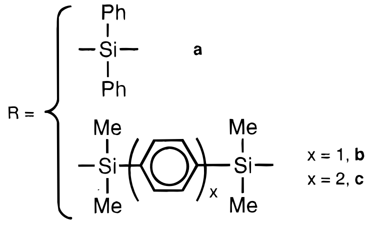
58b

diethoxysilyl-[139] or chlorosiloxanylsilyl-ferrocene[140] derivatives, but the products were oils with low molecular weights due in part (in the former case) to intramolecular condensation side reactions.[8]

Pittman described the first examples of well-characterized, high molecular weight poly(ferrocenylsiloxanes) (**59**) from the condensation reaction in melt or solution, at 100−110 °C, of 1,1′-bis(dimethylaminodimethylsilyl)ferrocene with three different disilanols.[141] Molecular weights (M_n) were in the range 9000−20 000 (by GPC) with melt polymerization giving the highest molecular weights and narrowest distributions. Intramolecular cyclization is favored over intermolecular condensation when using diphenylsilanediol as noticed previously by Schaaf. DSC studies revealed for these soluble, fibrous polymers, sharp melt transitions between 40 and 80 °C. The polymer **59b** appeared to be as thermally stable (up to 400 °C) and as stable to hydrolysis (in THF/H_2O) as the corresponding arylene polysiloxane without ferrocene moieties in the backbone.

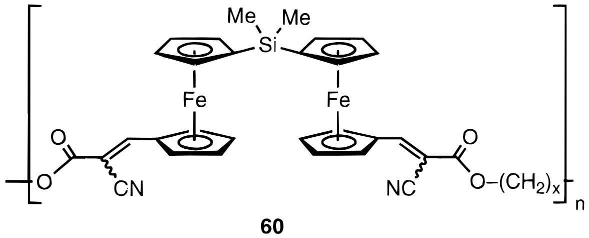


59



Greber and Hallensleben have reported the use of Diels−Alder[142] and platinum-catalyzed[142,143] polyaddition reactions of vinyl ferrocene derivatives to prepare ferrocene-containing poly(carbosilanes). These reactions were also used to prepare materials with additional functional groups leading to ferrocene and silicon-containing polyesters, polyamides, and polyurethanes.[140] Molecular weights varied in the range of 3800−6000, and products were liquids or elastomers. The authors carried out only comparative studies in terms of thermal stability with respect to one another.

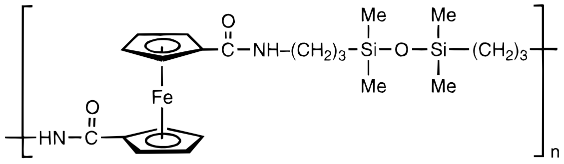
Novel organometallic accordion-type[144] copolymers were prepared by Wright and Sigman in 1992 through the Knoevenagel polycondensation of a bis(ferrocene aldehyde)silane with several bis(cyanoacetates).[145] The reaction produced soluble copolymers (**60**), consisting of biferrocenylsilane units with long organic spacers in isomeric (*E*/*Z*) mixtures. They were fully characterized by spectroscopic and analytical methods and possessed significantly high molecular weights (M_n = 9100−26 600).



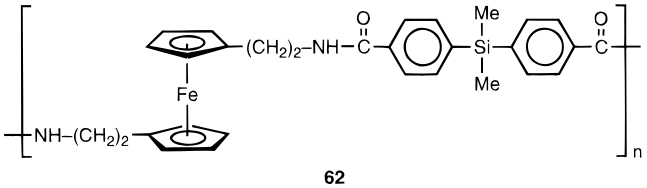
60

x = 4, 6, 8

Recently a new approach toward ferrocene-silicon-containing polyamides such as **61** and **62** has been developed.[146] Solution or interfacial polycondensation reactions at room temperature or low temperature yielded well-defined solid materials for which molecular weights (M_n) of 10 600−12 500 were determined by VPO. The iron centers were found to be noninteracting, as shown by a single reversible oxidation wave by cyclic voltammetry, and no oxidative precipitation of the polymers was observed. Thus, they can be used for chemical modification of electrodes because vapor-deposited films on different electrodes exhibited the characteristic behavior of surface confined redox couples.

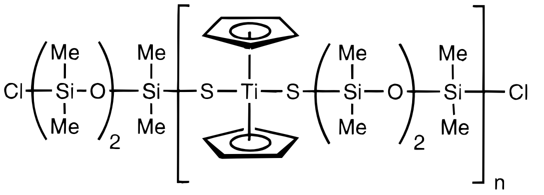


61



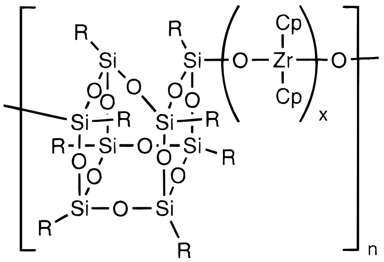
62

c. Poly(metallosiloxanes). The synthesis of poly(metallosiloxanes) by controlled condensation of Cp_2MR_2 (M = Ti, Zr, Hf) with silanes or siloxanes has been investigated on the basis of the improvements in heat resistance that might be realized with the introduction of the metal moiety into the polysiloxane backbone. The results obtained in the area were critically reviewed by Neuse and Rosenberg[8] since partial cleavage of the metal−ring bond occurred in all of the cases and the products were poorly characterized with no data provided. Only when $Cp_2Ti(SH)_2$ and siloxanes were used as reagents in the presence of triethylamine were linear oligomers (**63**, $n = 6$) described, although these were hydrolytically sensitive.



63

A new approach in this area has been reported by Lichtenhan and Haddad with the synthesis of novel polymeric zirconocene–silsesquioxanes (**64**).[147,148] The condensation of zirconocene derivatives with polyhedral silsesquioxanes led to amorphous polymers in high yields (≈90%) that were characterized by NMR spectroscopy and elemental analysis. These high molecular weight ($M_n = 14\,000$) materials exhibited high thermal stability ($T_{dec} = 474–515$ °C), and surprisingly **64a** is stable to both air and hydrolysis.

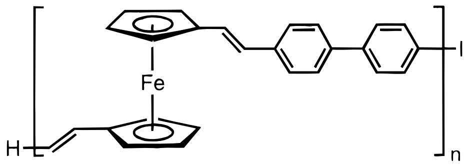


64a x = 1
64b x = 2

II.2.2 Conjugated Spacers

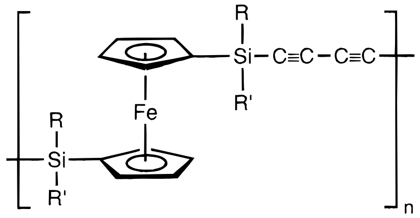
As poly(1,1′-ferrocenylene) exhibits significant electrical conductivity when doped, the introduction of ferrocene units into the main chain of polymers with σ, σ-π, or π-conjugation along the backbone is an interesting research objective.

Conjugated organic polymers such as polyacetylene, poly(*p*-phenylene) or poly(*p*-phenylene vinylene) are typically insoluble and rigid materials that are difficult to process. Several attempts have been made to introduce skeletal ferrocene units into the main chain of these materials[149–155] which has been shown to increase the flexibility and solubility of the chains.[156] Unfortunately, virtually all of the materials reported (e.g., **65**) have low molecular weights ($M_w < 5000$) or poor solubility, and electrochemical studies showed only weak interactions ($\Delta E_{1/2} = 70–120$ mV) between the iron centers, which are widely spaced.[154] However, in an important recent development, Rehahn and co-workers have successfully used a Pd-catalyzed coupling procedure to prepare high molecular weight, soluble poly(ferrocenes) with *p*-oligophenylene spacers with molecular weights (M_w) up to 35 500 as determined by light scattering.[155] This discovery paves the way for detailed studies of these very interesting materials.



65

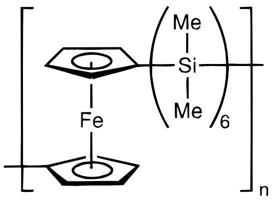
Interesting carbosilanes containing organometallic moieties (e.g., **66**) are illustrated by the oligomeric diacetylenes ($M_w < 3000$) isolated by Corriu et al.[157] They were prepared in high yields following condensation routes from the di-Grignard reagent of diacetylene and 1,1′-bis(chloro-diorganosilyl)ferrocenes, and were characterized by NMR spectroscopy, IR, and elemental analysis.



66

R = R′ = Me, Ph
R = Me, R′ = Ph

Also, poly(ferrocenylhexasilane) (**67**) has been synthesized in an attempt to obtain polymers where ferrocenes are joined to σ-delocalized polysilane segments in a regular alternating structure.[158] The condensation of dilithioferrocene and 1,6-dichlorodecamethylhexasilane gave a soluble, well-characterized polymer showing a monomodal molecular weight distribution by GPC with maximum at $M_w \approx 3500$. After doping, conductivity values ($\sigma = 3 \times 10^{-5}$ S cm^{-1}) were 3 orders of magnitude higher than octadecasilane which suggested that conjugation between ferrocenediyl and hexasilanediyl contributes to the conductivity, although the values are much lower than for the corresponding poly(1,1′-ferrocenylenes).[28]

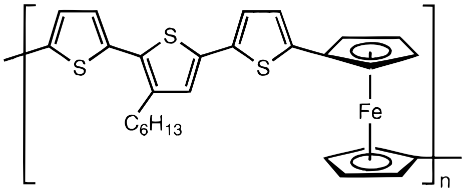


67

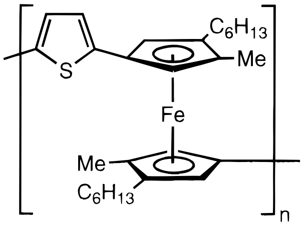
Thiophene units have also been employed for bridging ferrocenes in order to obtain conjugated polymers.[66] The reaction of a di-zinc ferrocene derivative with a dibromothiophene afforded a poly(ferrocenylene thienylene) (**68a**) with moderate molecular weight ($M_n \approx 4500$) which was characterized by NMR spectrometry and elemental analysis. Studies on doped materials with $SbCl_6^-$, BF_4^-, and $TCNQ^-$

counteranions showed the presence of weak antiferromagnetic interactions.

Very recently, Curtis and co-workers have briefly reported condensation routes to well-defined poly(ferrocenes) with arene and thiophene spacers (e.g., **68b**).[159] These materials are soluble with molecular weights $M_w = 42\,000-52\,000$ with broad polydispersities (PDI = 10−15). The magnetic properties of oxidized materials have been studied and were interpreted in terms of the temperature dependence of the magnetic moment of ferrocene units.



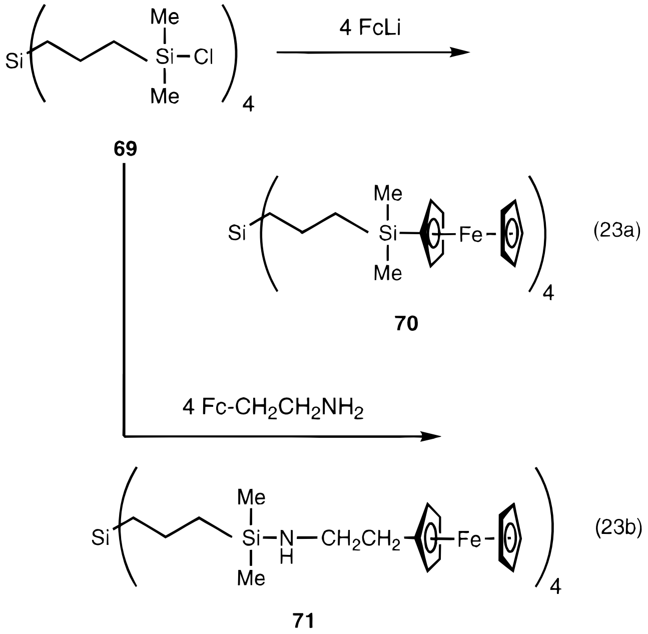
68a



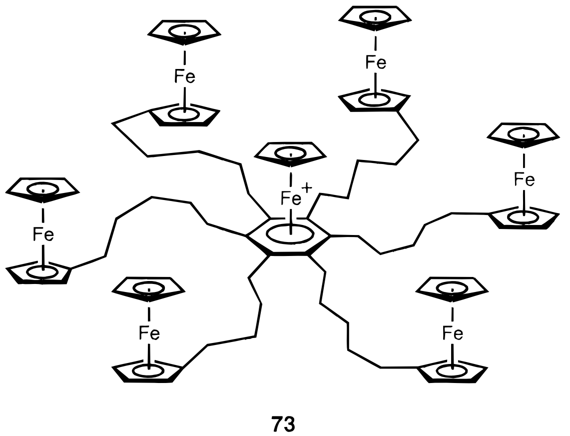
68b

II.3. Star and Dendritic Poly(metallocenes)

A particularly novel class of organometallic ferrocene-containing polymers are the dendrimers reported by Cuadrado and co-workers.[160a] From tetraallylsilane as the initiator core, the researchers constructed novel silane dendrimers (e.g., **69**) in which reactive SiCl end groups are present. The reaction with lithioferrocene or β-aminoethylferrocene afforded the corresponding tetraferrocenyl dendrimers (**70**) and (**71**) that represent the first examples of well-defined and well-characterized, redox-active macromolecules of this type (eq 23a,b). A similar synthetic approach has also been used to synthesize the corresponding octaferrocenyl derivatives. Very recently, the same research group has reported a series of new ferrocenyl dendritic macromolecules (**72a**−**e**) (see Figure 8) based on flexible poly(propylenimine) dendrimer cores containing 4, 8, 16, 32, and 64 peripheral ferrocenyl moieties via condensation reactions of 1-(chlorocarbonyl)ferrocene with the first-, second-, third-, fourth-, and fifth-generation of diaminobutane-based poly(propylenimine) dendrimers functionalized with terminal NH_2 groups.[160] Cyclic voltammetric studies of these compounds[160b] showed one reversible oxidation wave characteristic of independent, noninteracting redox centers. Also, the use of these materials for modification of electrode surfaces was explored. The researchers found that platinum, glass, and carbon-disk electrodes modified by electrodeposited films of these dendrimers are extremely durable and reproducible with no loss of electroactivity or material with their use in different electrolyte solutions or after standing for long periods in air. Recent studies on thermodynamics and kinetics of adsorption of these redox-active dendrimers onto Pt electrodes using electrochemical and electrochemical quartz crystal microbalance techniques showed adsorption processes to be activation-controlled rather than diffusion-controlled. Moreover, they are dependent on the nature of the dendrimer but not the concentration, and the adsorption free energies were found to decrease in order **72e** > **72d** > **72b**.[162] Dendrimers **72a**−**c** have also been explored as guest systems for inclusion complexation by cyclodextrin (β-CD) hosts.[163]



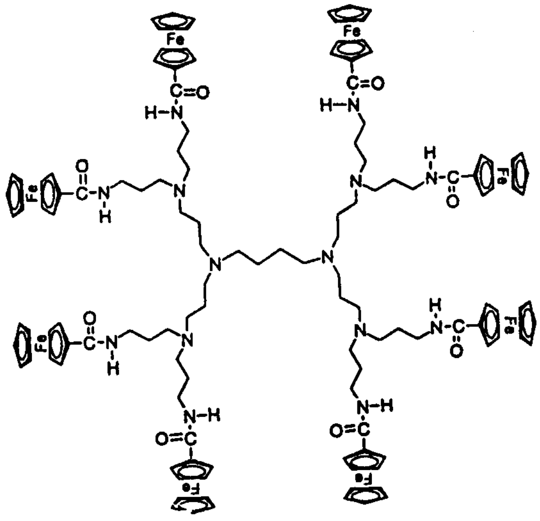
Astruc et al.[164] have reported the synthesis of star-shaped macromolecules with $[FeCp(C_6Me_6)]^+$ as the starting core. The hexaferrocenylalkylation of the C_6Me_6 ligand yielded an heptanuclear complex (**73**) in which the ferrocene moieties are electrochemically equivalent with no influence of the central cationic unit on the oxidation process, leading to a fully reversible six-electron redox system.



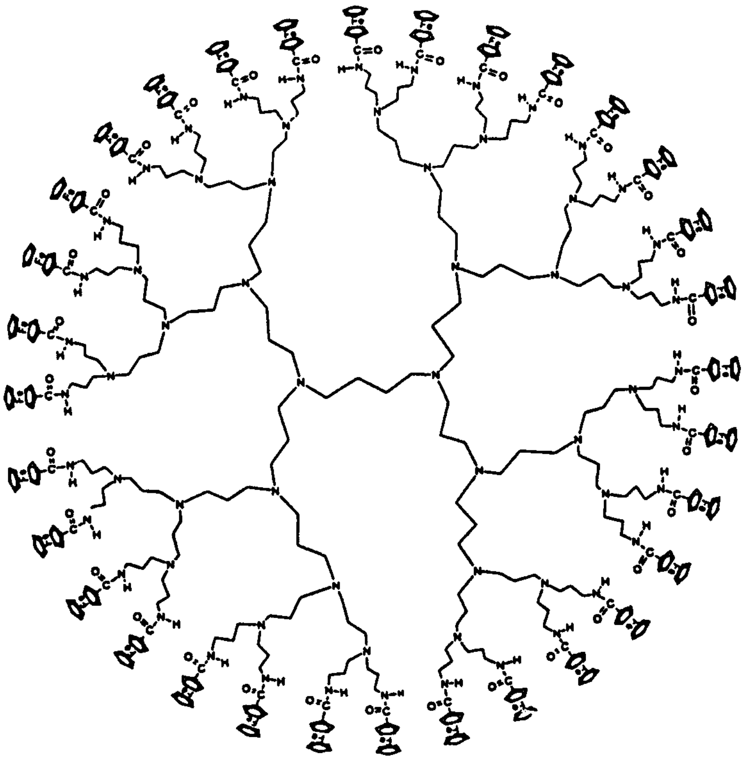
73

Related to this system is the decaferrocenyl ferrocene derivative synthesized recently by Jutzi et al.[165] by hydrosilylation of a decaallylferrocene with dimethylsilylferrocene. In these materials, the outer ferrocenyl moieties are also noninteracting.

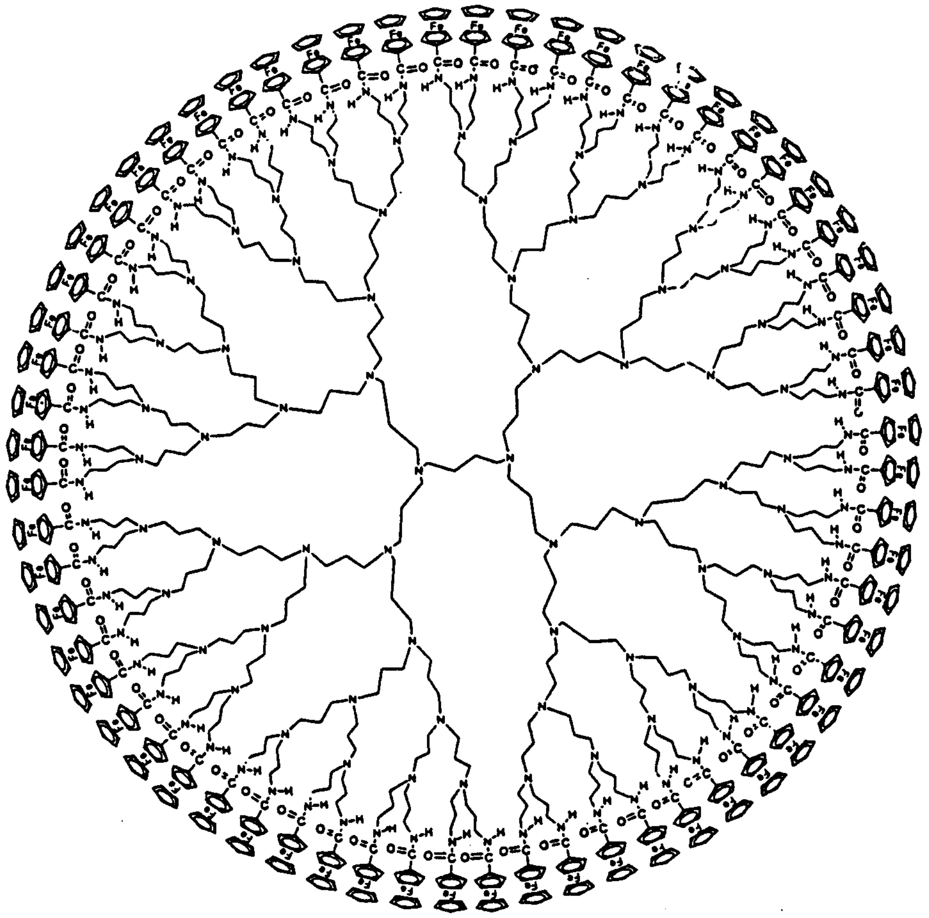
Recently, Astruc et al. reported the synthesis of the amido-ferrocene dendrimers containing 3, 9, and 18 ferrocene moieties (**74a**−**c**) from the reaction of ferrocenylacyl chloride and the corresponding poly-



72b

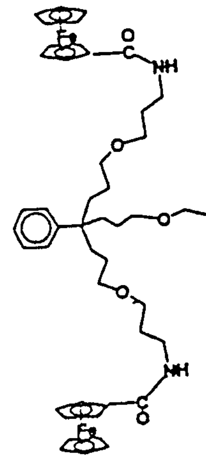


72d

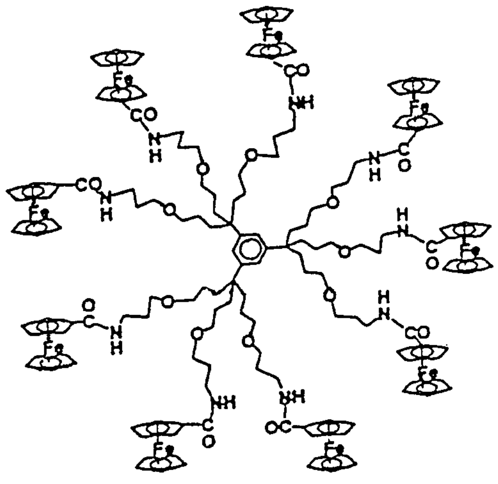


72e

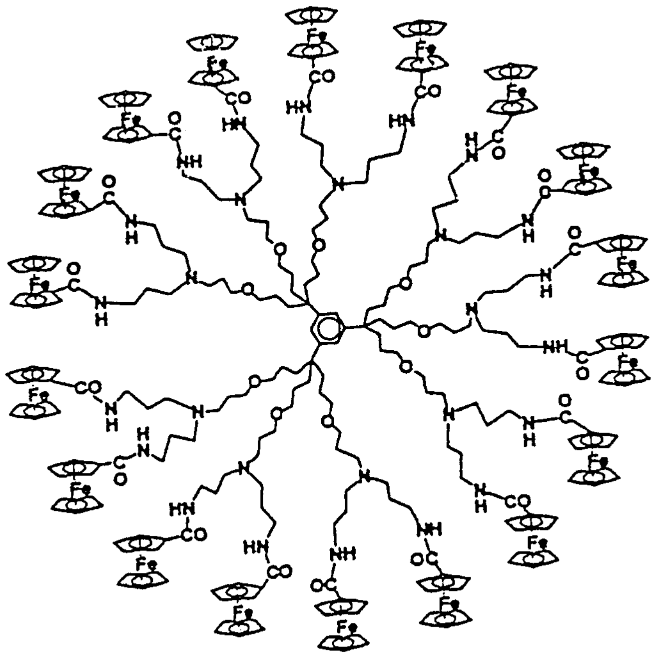
Figure 8. Structures of ferrocenyl dendrimers **72b**, **72d**, and **72e**.



74a



74b

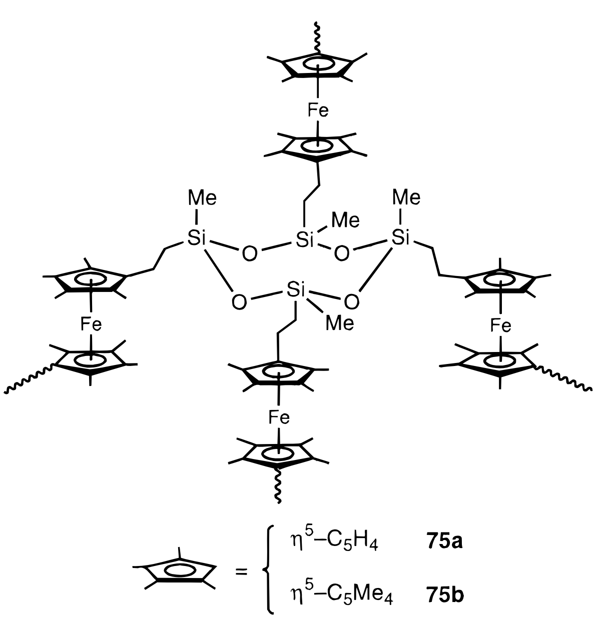


74c

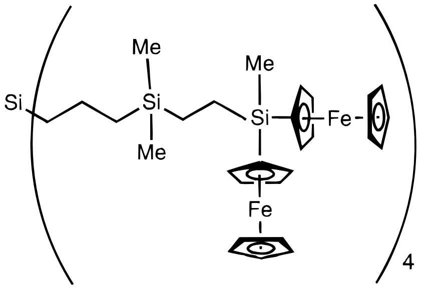
Figure 9. Structures of ferrocenyl dendrimers **74a**–**c**.

NH_2 dendrimers (Figure 9).[166] These materials were found to bind small inorganic anions ($H_2PO_4^{2-}$, HSO_4^-, Cl^-, Br^-, NO_3^-) as monitored by cyclic voltammetry.

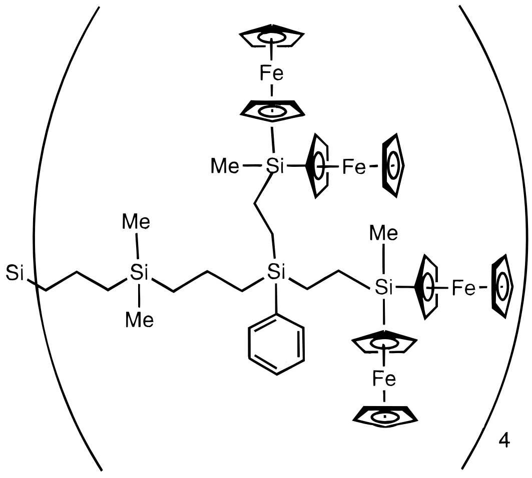
Cuadrado et al. have also reported ferrocenyl and permethylferrocenyl star polymers **75** containing a cyclotetrasiloxane as the core.[167] Their synthesis was achieved via hydrosilylation reactions using vinylferrocene monomers and tetramethylcyclotetrasiloxane. Soluble polymers with $M_n = 1.9-2.3 \times 10^4$ (by VPO) were obtained in high yields and were characterized by NMR, elemental analysis, TGA, and cyclic voltammetry. As with the ferrocenyl-dendritic structures, these materials exhibited only one oxidation wave and modification of platinum electrodes showed that, while the nonmethylated ferrocenyl polymer behaved as a surface-confined redox couple, the permethylated material possessed diffusional features that limit the charge transport through the film.



Cuadrado and co-workers have recently reported a convergent synthesis of novel dendrimers **76** and **77** possessing interacting ferrocenyl units via hydrosilylation reactions of the Si−H polyfunctionalized cores.[168] Electrochemical studies showed that these dendrimers exhibit two distinct oxidation waves separated by 190 and ca. 160 mV for **76** and **77**, respectively.[168] This electrochemical behavior is consistent with the existence of significant communication between two ferrocenyl moieties linked together by the bridging Si atom.



76



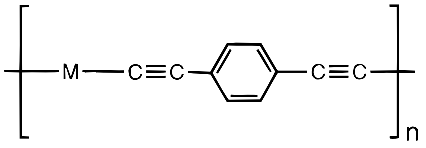
77

III. Rigid-Rod Organometallic Polymers

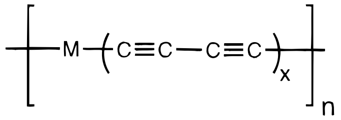
III.1. Transition Metal−Acetylide Polymers

III.1.1 Polymer Synthesis

Polymeric Cu and Hg acetylides **78a** (M = Cu or Hg) were reported as early as 1960 and were proposed to have a linear geometry.[169,170] However, these materials were found to be intractable which precluded their purification and characterization. In the late 1970s, Hagihara and co-workers reported the first soluble poly-ynes containing Pt and Pd metal atoms in the main chain [e.g., **78a** (M = Pt(PBu$_3$)$_2$) and **78b** (M = Pd(PBu$_3$)$_2$, $x = 2$)]. Subsequent work in this group had resulted in general synthetic routes to group 10 metal containing poly-ynes. Recently, the groups of Lewis and Marder and others have developed new routes to incorporate group 8, 9, and 10 metals into the polymer backbone.



78a

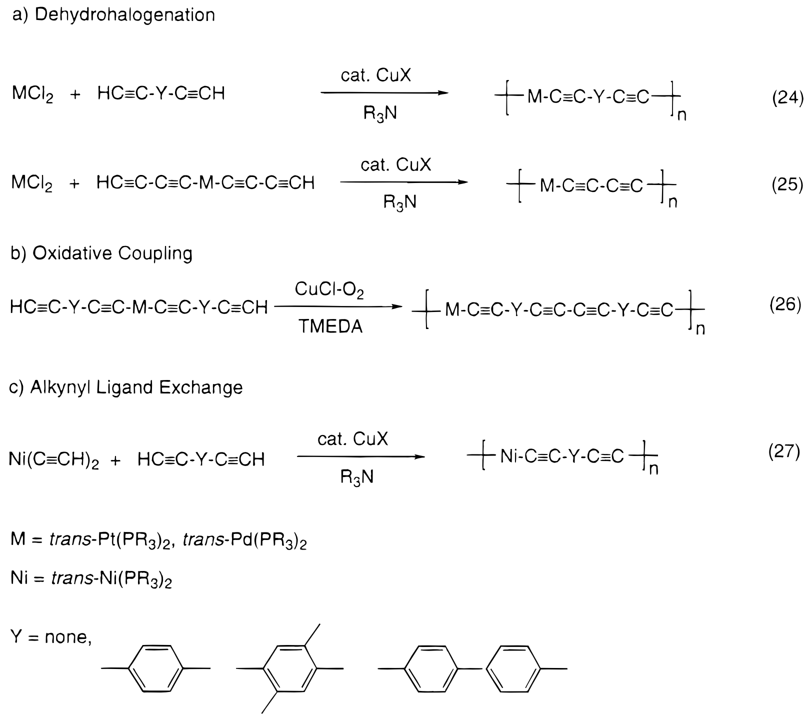


78b

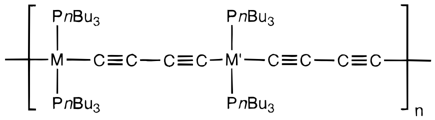
The first soluble metal poly-yne oligomers were reported in 1975 by Hagihara et al. consisting of Pd(P^{n}Bu$_3$)$_2$ and Pt(P^{n}Bu$_3$)$_2$ moieties in the main chain connected by butadiyne and diethynylbenzene bridging units as air-stable, orange-yellow solids with average molecular weights determined by vapor pressure osmometry to be M_n = 5700 and 7300, respectively.[171a] Subsequent work by these researchers reported in 1977 showed that group 10 metal acetylide polymers with much improved molecular weights ($M_w > 10^5$) can be prepared using three main approaches: dehydrohalogenation, oxidative coupling, and alkynyl ligand exchange (see Scheme 2).[171b,172]

The first method involves a polycondensation reaction between metal halides and diterminal alkynes via a cuprous halide catalyzed dehydrohalogenation process.[171,173−176] The reactions are typically performed in amine solvents such as diethylamine or piperidine under reflux conditions to afford high molecular weight polymers. In the cases of gaseous alkynes such as acetylene or butadiyne, the polymers are most conveniently obtained via condensation of the corresponding mononuclear metal bis(alkynyl) complexes and metal halides. The second method involves oxidative homocoupling of the bis(terminal alkynyl) complexes in the presence of a catalytic amount of cuprous halides and O$_2$ as the oxidizing agent.[177] This catalyst system has been used extensively in organic synthesis and is better known as Hay's coupling reaction.[178] Extension of this methodology to organometallic synthesis was demonstrated by Hagihara et al. in the conversion of *trans*-bis-acetylide monomers to polymeric materials. It is worth noting that this method is dependent only on one monomer type, thus high degrees of polymerization are usually obtained. On the other hand, the degree of polymerization employing the dehydrohalogenation approach is dependent upon the exact ratio of the reacting monomer pairs. The above two methods work well for a majority of cases, particularly for platinum, affording high molecular weight macromolecules as determined by gel permeation chromatography with M_w = 60 000−122 000 depending on the nature of the bridging alkynes. However, in the case of palladium much lower molecular weights (M_w = up to 23 000) were obtained. Significantly, neither of these methods is applicable to nickel because of the inherent instability of dihalo nickel complexes in amine solvents and dialkynylnickel complexes in oxidizing media.[177] Thus, the analogous Ni-containing acetylide polymers were prepared using a third method, an alkynyl ligand exchange process, which is catalyzed by CuI in amine solvents.[179]

Scheme 2

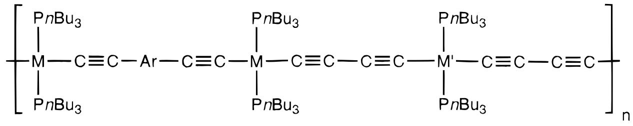


Similar synthetic routes have also been used to prepare the analogous polymeric species **78c** and **78d** containing mixed alkynyl ligands[175] and/or mixed metals[173] in the main chain.



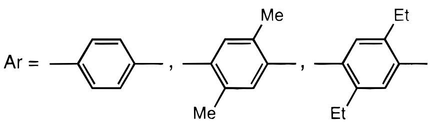
78c

M = Pd, M' = Pt
Ni Pt
Pd Ni

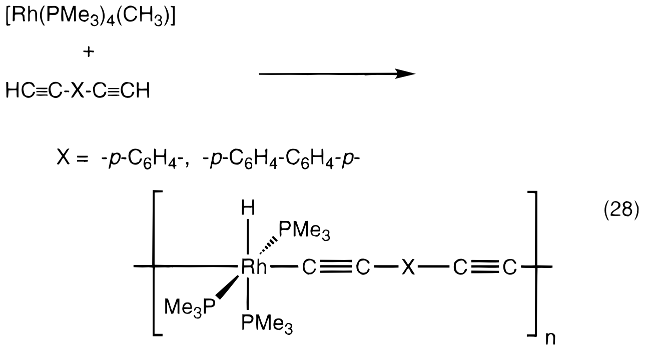


78d

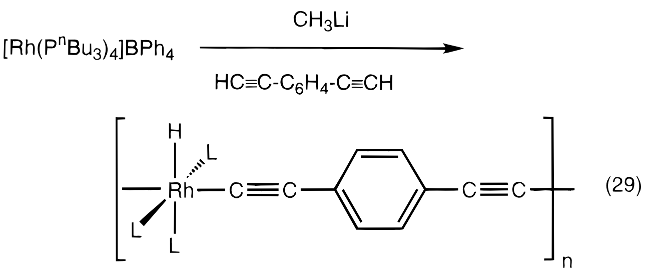
M = Pd, M' = Pt
Pt Pd
Pd Ni



Although Hagihara's methods are generally applicable for the incorporation of group 10 metals into metal acetylide polymers, these approaches could not be extended to group 8 and 9 metals because of the instability of the starting complexes in amine solvents. Research efforts by Marder et al. on the molecular chemistry of hydrido-acetylide complexes of rhodium have resulted in a facile route to group 9 polymers **79a** and **79b**.[180-183] This method involves direct oxidative addition of terminal alkynes to L_4-RhMe with loss of methane (eqs 28 and 29). The reaction, which resembles an earlier report by Klein and co-workers on the synthesis of $Co(PMe_3)_4$-(CCPh),[184] proceeds rapidly at ambient temperature to produce soluble polymers when L = P^nBu_3, and an insoluble white solid was obtained when L = PMe_3. The authors did not report the molecular weight for the resulting polymer. However, the formation of free-standing films of the material upon evaporation of THF solvent suggested that the material was macromolecular in nature.



79a

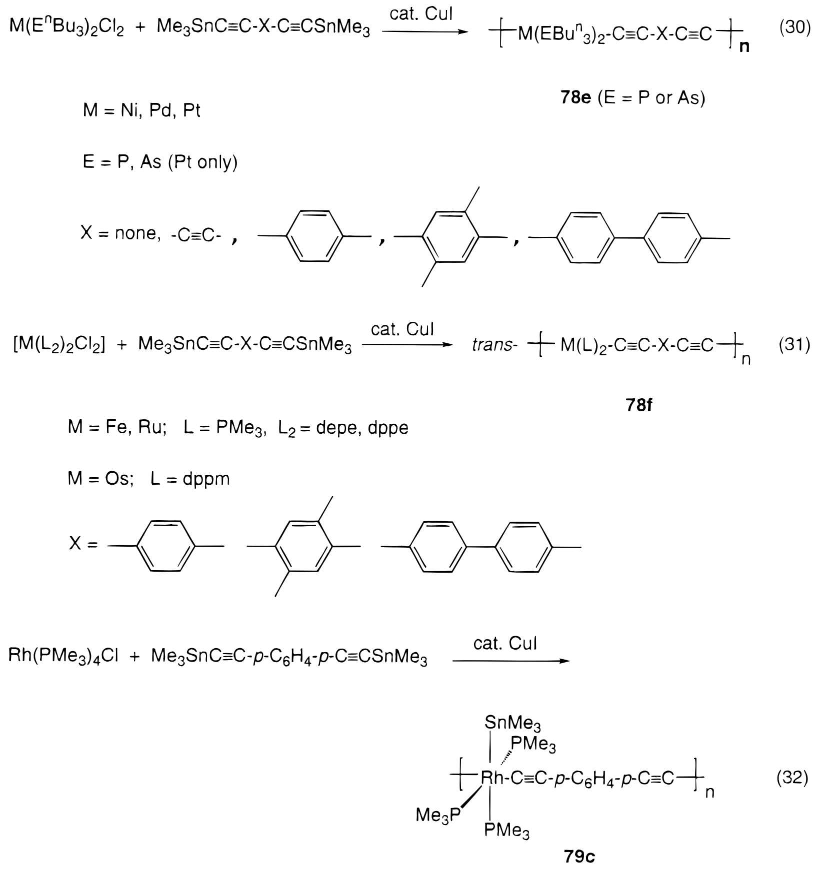


79b

L= P^nBu_3

More recently, Lewis et al. have utilized a convenient metathesis reaction involving trimethyl tin

Scheme 3



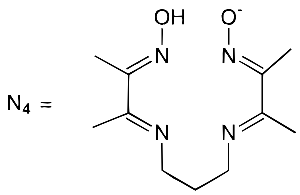
reagents, reported earlier by Lappert and co-workers,[185] to yield poly-ynes containing group 8,[186−189] 9,[190,191] and 10[190−193] metals. The polymers were prepared by reacting an equimolar amount of bis-trimethylstannyl acetylides and the appropiate metal halide complexes in the presence of CuI as a catalyst (Scheme 3). This method is quite general and is reported to produce platinum polymers **78f** (M = Pt, L = EBu$_3$, E = P or As) with slightly higher GPC (vs polystyrene standards) determined average molecular weights (M_w = 82 000−210 000) than those prepared by Hagihara. The analogous Ni and Pd polymeric complexes were obtained with much lower molecular weights (M_w = 20 000−30 000). For rhodium, the polymer **79c** was found to be a white, insoluble solid similar to that (**79a**) observed by Marder et al. Insoluble polymeric materials were also reported for Ru coordinated with trimethylphosphine (PMe$_3$) and for Os with diphenylphosphinomethane (dppm) and bis(ethynyl)biphenyl ligands.

A nonphosphine containing Co-acetylide polymer has also been prepared using this methodology. Thus, air-stable, yellow *trans*-[−CoN$_4$C≡C−*p*-C$_6$H$_4$−C≡C−]$_n$ (N$_4$ = 3,9-dimethyl-4,8-diazaundecane-2,10-dione dioxime) (**80**) with M_w = 16 000 was obtained by reacting *trans*-N$_4$CoCl$_2$ with an equimolar amount of Me$_3$Sn−C≡C−*p*-C$_6$H$_4$−C≡C−SnMe$_3$ in the presence of a catalytic amount of CuI in refluxing CH$_2$Cl$_2$.[194]

Recently, Dixneuf et al. reported an extension of the dehydrohalogenation process to the synthesis of a new class of heterobimetallic poly-yne oligomers (**81**) (eq 33) containing mixed metals with alternating Ru(dppe)$_2$ and Pd(P^{n}Bu$_3$)$_2$ moieties in the polymer backbone with M_w = 14 000 (by GPC measurements).[195] The incorporation of ferrocene units into

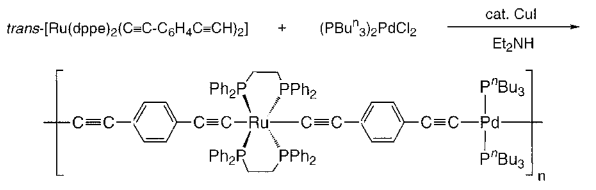
trans- [CoN$_4$-C≡C-*p*-C$_6$H$_4$-C≡C]$_n$

80



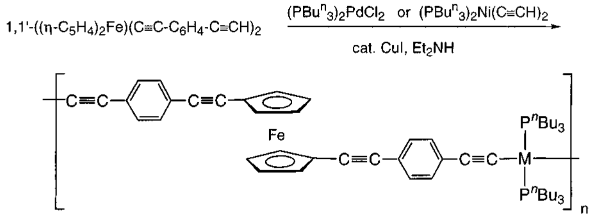
the polymer main chain alternating between either Ni(PBu$_3$)$_2$ (**82a**) or Pd(PBu$_3$)$_2$ (**82b**) moieties has also been achieved (eq 34), and the molecular weights of the resulting polymers were M_w = 26 100 and 21 400, respectively.[195]

Polycondensation between diiodoferrocenes and diethynyl arenes to give poly(aryleneethynylene)s (**83**−**87**) (eq 35) containing ferrocene units in the π-conjugated backbone were recently reported by Yamamoto and co-workers.[196] While polymer **83** was found to be partly soluble, the alkyl-substituted analogues **86** and **87** and the thiophene containing polymer **85** were reported to be completely soluble in common organic solvents. The pyridine-based polymer **84** was found to be partly soluble in organic solvents; however, it dissolved completely in formic acid. Light scattering analysis of **85** and the soluble fraction of **83** in CHCl$_3$ gave an average M_w of 3.4 × 10^4 and 2.1 × 10^4, respectively. UV−vis studies for these polymers showed a strong absorption at 307−351 nm and a weak band at 415−465 nm attributed to π−π* and d−d transitions, respectively. The cor-



81

(33)

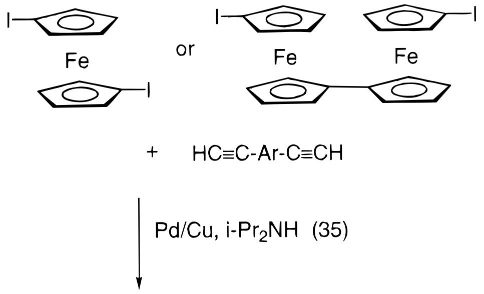


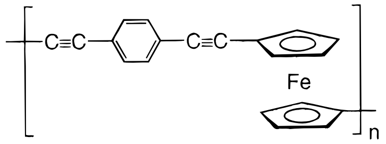
(34)

M = Ni **82a**

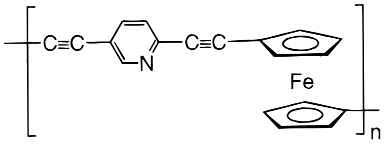
M = Pd **82b**

responding bands for polymer **84** in formic acid were reported at 368 and 526 nm.

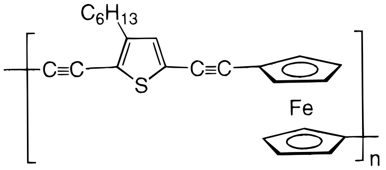




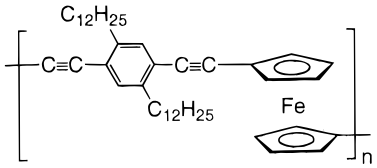
83



84



85



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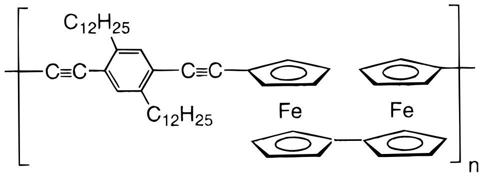
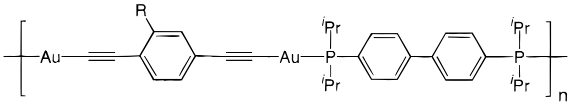


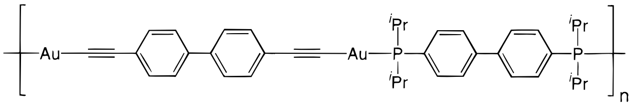
87

Gold(I) containing oligomeric complexes **88a**−**c** bridged by diphosphines and diacetylides have been prepared by Puddephatt and co-workers by either reacting $[AuC{\equiv}CArC{\equiv}CAu]_x$ with the correponding diphosphines or from the reactions of gold phosphine halide dimers with the appropriate diethynylarene in the presence of a base.[197] The resulting oligomers were found to be insoluble in most organic solvents but were partially soluble in THF, dichloromethane, and chloroform with average molecular weights as determined by GPC (versus polystyrene standards) of 15 000−18 000.



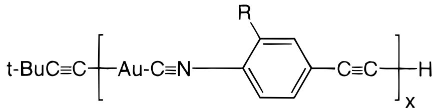
R = H **88a**

R = Me **88b**



88c

These researchers have also reported the synthesis of rigid-rod oligomeric Au(I) complexes (**89a**,**b**) with (isocyanoaryl)acetylide bridging ligands via elimination of *t*-BuC≡CH from the precursor, *t*-BuC≡C−Au−C≡N−Ar−C−Ar−C≡CH.[198,199] However, direct molecular weight determinations of the resulting oligomers were not possible because of insolubility. Similarly, these authors have also reported the synthesis of the insoluble polymeric materials (**90**) with Au(I) centers bridged by diisocyanides and diacetylides.[200]



R = H **89a**

R = Me **89b**

$$\left[\text{Au-C}{\equiv}\text{C-R-C}{\equiv}\text{C-Au-CN-R'-NC}\right]_n$$

90

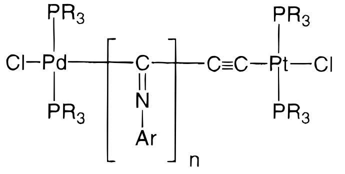
R = C_6H_4, C_6H_4-C_6H_4, $C_6H_2Me_2$, CH_2O-C_6H_4-CMe_2-C_6H_4-OCH_2,

R' = C_6H_4, C_6H_3Me,$C_6H_2Me_2$, C_6Me_4, $C_6H_2Bu^t_2$, $C_6H_2Me_2$-$C_6H_2Me_2$,

A recent investigation of the photophysical properties of these materials showed that the rigid-rod, conjugated Au(I) oligomeric complexes do exhibit weak luminescence in the solid state at ca. 585 or 600 nm.[201]

Takahashi et al. reported a novel route to polymer chains (**91**) containing metal moieties as terminal groups via multiple (up to 100) insertions of arylisocyanides into the Pd−C bond of the heterodinuclear μ-acetylide complex, $[Cl{-}(PR_3)_2Pd{-}\ C{\equiv}C{-}Pt(PR_3)_2{-}Cl]$.[202]

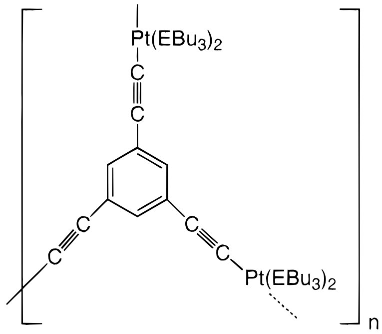
Cross-linked Pt-containing polymers were obtained by Lewis et al. by reacting 1,3,5-triethynylbenzene with the dihalo complexes via the dehydrohalogena-



91

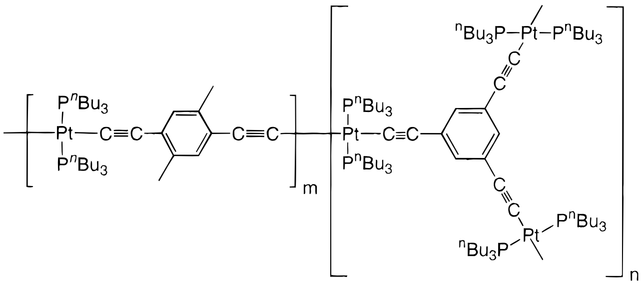
R = Et, ^{n}Bu
Ar = C_6H_4
C_6H_4-C_4H_9-*p*
C_6H_4-C_8H_{17}-*p*
C_6H_4-NO_2-*p*
C_6H_4-CH_3-*p*

tion route. The 2-D poly-hexagonal graphite-like polymers (**92**) were found to have low solubility.[203]



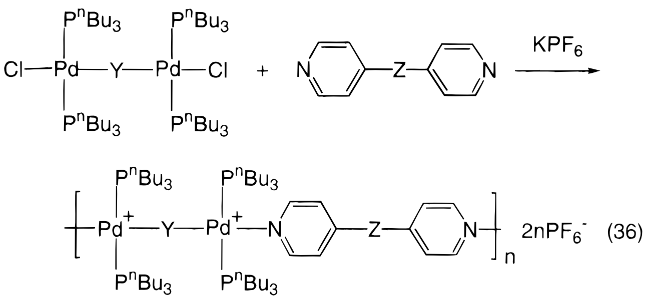
E = P **92a**
E = As **92b**

Improved solubility was achieved for polymer **93** by using comonomer mixtures of 1,3,5-triethynylbenzene and 2,5-diethynyl-*p*-xylene in various molar ratios (1:10, 1:50, 1:100) with *trans*-dichloro(tri-*n*-butylphosphine)platinum. The high degree of cross-linking for the 1:10 mixture resulted in an insoluble material, whereas soluble copolymers were obtained for the other two mixtures with $M_w = 58\,000$ and 27 000 (relative to polystyrene) for the 1:50 and 1:100 molar ratios, respectively.[203]



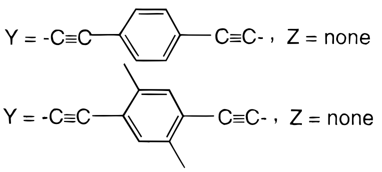
93

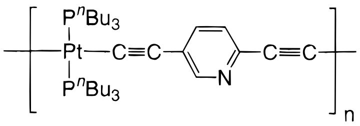
An interesting class of cationic polyyne polymers (**94**) was prepared by Takahashi et al. by reacting the bimetallic complex, *μ*-butadiynediyl-bis[*trans*-chlorobis(tri-*n*-butylphosphine)palladium] with an equimolar amount of 4,4′-bipyridyl in the presence of excess K[PF$_6$] to give an ionic organo-polynuclear complex with alternating butadiyne and pyridyl bridging units in the main chain (eq 36). Other analogous ionomeric polymers were obtained similarly using the appropriate dihalide complex and bypyridyl derivatives.[204a]



94

Y = -C≡C-C≡C-, Z = none
Y = -C≡C-C≡C-, Z = CH_2CH_2
Y = -C≡C-C≡C-, Z = CH=CH





95

Kakkar et al. have reported the synthesis and study of another interesting type of platinum polyyne (**95**) with skeletal pyridyl units using the dehydrohalogenation method (i.e., method (a) in Scheme 2) or using an Me_3SnCl elimination procedure analogous to that in eq 31. The resulting polymers could be quaternized with methyl iodide and triflate.[204b]

III.1.2 Structural Studies and Bonding in the M–C≡C Fragment

Retention of trans configuration around the metal centers in the aforementioned Pt-polymers was evident by spectroscopic analysis of model compounds up to hexanuclear complexes,[205] as well as single-crystal X-ray diffraction studies[206] of representative molecules. For instance, Marder et al. have reported a detailed study on the molecular structure and crystal packing arrangement of a series of symmetric and unsymmetric bis(acetylide) complexes, [Pt(PMe$_2$Ph)$_2$(C≡CC$_6$H$_4$–*p*-R)(C≡CC$_6$H$_4$–*p*-R′)] (R, R′ = MeO, MeS, NH$_2$, NMe$_2$, CN, NO$_2$), and the analogous bis(butadiyne) complex.[183] X-ray diffraction provided conclusive proof of the trans configuration at the Pt center.[183] The trans disposition of the acetylide units has also been established for Ni and Pd analogues, as well as for group 8 and 9 complexes[206] such as octahedral *trans*-[Ru(dppe)$_2$(C≡CC$_6$H$_5$)$_2$][207] and *mer*, *trans*-[Rh(PMe$_3$)$_3$(H)(C≡CC$_6$H$_5$)$_2$],[208] respectively. The binuclear Rh(I) complex [Rh(PMe$_3$)$_4$(C≡C–C$_6$H$_4$–C≡C)Rh(PMe$_3$)$_4$] has also been characterized crystallographically (Figure 10).[181] In addition, ^{31}P NMR spectral data has provided an exceptional tool for determining the configuration at the metal centers.[171–174,177] For example, the trans configuration of phosphine ligands in Pt-bis-acetylide complexes gives rise to a

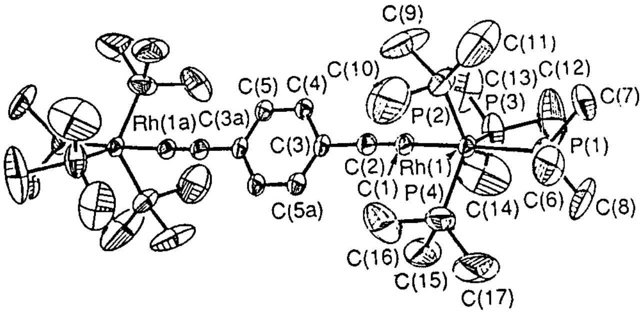


Figure 10. X-ray structure of the binuclear Rh complex $[Rh(PMe_3)_4C\equiv C-C_6H_4-C\equiv CRh(PMe_3)_4]$.

^{31}P signal at 3.0 to 5.0 ppm, whereas the cis configuration gives rise to a signal at −2.0 to −4.0 ppm (referenced to 85% phosphoric acid standard). In all of the Pt-containing polymers prepared by Hagihara et al., as well as the Pd and Ni analogues, no resonances were detected in the region assigned to the cis configuration. Thus, these polymers are believed to possess a rodlike structure with an all-trans configuration at the square-planar metal centers. Additional IR spectral analysis was also consistent with the above assignment.[172]

A multinuclear solid-state NMR study has also been carried out on the platinum complex, *trans*-$[ClPt(P^nBu_3)_2-C\equiv C-p\text{-}C_6H_4-C\equiv C-Pt(P^nBu_3)_2Cl]$, and the corresponding polymers, **78f** ($M = Pt$, $L = E^nBu_3$, $E = P$ or As, $X = C_6H_4$); strong evidence for a trans geometry at the Pt metal centers was provided by a ^{31}P NMR study which gave a chemical shift of 4.5 ppm and ^{31}P-^{195}Pt coupling constants of 2440 Hz (dimer) and 2450 Hz (polymer) for the P^nBu_3 ligand.[209]

Electron diffraction and low-dose, high-resolution imaging techniques have also been employed to obtain structural information for the Pt poly-yne, $[-Pt(AsBu_3)_2-C\equiv C-p\text{-}C_6H_4-C\equiv C-]_n$.[210,211] The results show detailed arrangement of the molecular chains into crystallites (ca. 50 nm in diameter) with grain and dislocation defects. The proposed monoclinic unit cell has measured parameters, $a = 2.08$ nm, $c = 1.20$ nm, $90° \le \beta \le 93°$, and calculated $b = 1.9$ nm.[210,211] The authors attributed the variation in β to arise from the openess of the packing and the tendency of the polymer to align on stretching.

Recent studies of the bonding in metal alkynyl, butadiynyl, and bis(alkynyl) complexes, based on photoelectron spectroscopic studies and/or molecular orbital calculations,[188,212−214] support previous calculational findings[215] which indicate that there is considerable mixing of the filled metal d orbitals with the filled π-system of the alkynyl moiety. The energy mismatch between the metal d-levels and alkynyl π^*-levels, at least in cases in which there are no strong π-acceptor substituents in conjugation with the alkynyl moiety, leads to a lack of significant π-backbonding. However, the perturbation of the filled metal d-levels by the π-donor character of the alkynyl groups leads to low-lying metal−ligand charge transfer (MLCT) absorptions. An in-depth compilation and analysis of data obtained primarily from X-ray diffraction, electronic, and vibrational studies aimed at probing the nature of bonding in metal-alkynyl complexes have been reported by Hopkins and coworkers.[206] Recently reported extended Hückel band calculations[216] on metal poly-yne polymers indicated that in $[-L_nM-C\equiv C-R-C\equiv C-]_x$ systems, the highest occupied crystal orbital (HOCO, which is roughly analogous to the HOMO in a molecular system) is predominantly metal-d character and is delocalized along the chain through the ML_n groups for $n = 2$ (square planar) and $n = 4$ (octahedral) geometries. The calculations indicated that the lowest unoccupied crystal orbital (LUCO) is predominantly alkynyl-π^* character. It was suggested that the electrical conductivity of poly-yne polymers can be improved by altering the character of the HOCO and the LUCO. The nature of the metal is expected to play a significant role in affecting the HOCO energy level such that the higher the energy and more diffuse the d orbitals, the higher the HOCO level. In contrast, extending the π-conjugation length in the alkynyl linker groups would lower the optical gap in such metal poly-yne systems predominantly by lowering the energy of the LUCO. These calculations indicated that electrical conductivity is favored for poly-ynes containing 4-coordinate d^8 square-planar metals over that of the 6-coordinate d^6 octahedral metals, mainly because of the greater conduction bandwith in the former case (ca. 0.4 eV). Bredas et al. have also reported similar extended Hückel calculations on Pt-containing polymers and concluded that the Pt centers do contribute to some electronic delocalization along the polymer chain.[217]

III.1.3 Polymer Properties

a. Stability. Group 10 metal poly-yne polymers generally show good stability in air in the solid state, but slow decomposition tends to occur in solution.[172] The thermal stability of these materials was investigated by Hagihara et al. using TGA, and the results indicated that the platinum-containing polymers are considerably more stable that the palladium and nickel-analogues (Table 2). In air, these compounds decomposed explosively with significant weight loss of ca. 35−60%.[172]

b. Solution Properties. The high solubility of many metal−poly-yne polymers in common organic solvents such as benzene, toluene, tetrahydrofuran, and methylene chloride is attributed to the alkyl substituents on phosphorus which promote good solvent−polymer chain segment interactions and

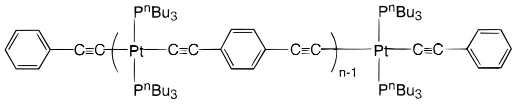
Table 2. Thermal Stability of Group 10 Metal Poly-yne Polymers (Measured by TGA at Heating Rate of 5 °C/min)

polymer	$M_w \times 10^3$	decomposition temp (°C) in air	decomposition temp (°C) in N_2
$[-Pt(P^nBu_3)_2-C\equiv C-C\equiv C-]_n$	120	270	350
$[-Pd(P^nBu_3)_2-C\equiv C-C\equiv C-]_n$	24	150	200
$[-Ni(P^nBu_3)_2-C\equiv C-C\equiv C-]_n$	10	150	165
$[-Pt(P^nBu_3)_2-C\equiv C-C_6H_4-C\equiv C-]_n$	72	230	300
$[-Pd(P^nBu_3)_2-C\equiv C-C_6H_4-C\equiv C-]_n$	25	145	170
$[-Ni(P^nBu_3)_2-C\equiv C-C_6H_4-C\equiv C-]_n$	13	135	140
$[-Pt(P^nBu_3)_2(-C\equiv C-C\equiv C-)_2]_n$	30	210	210
$[-Pd(P^nBu_3)_2(-C\equiv C-C_6H_4-C\equiv C-)_2]_n$	120	250	250
$[-Pt(P^nBu_3)_2(-C\equiv C-C\equiv C-)\text{-}Pt(P^nBu_3)_2(-C\equiv C-C_6H_4-C\equiv C-)]_n$	34	−	330

decrease interchain interactions. Molecular weight measurements have generally involved GPC. This relative technique usually provides only approximate estimates of the molecular weight as it assumes that the hydrodynamic size of the polymers under study is similar to that of the calibration standard, generally polystyrene, of the same molecular weight. This is clearly unrealistic for rigid chain materials. However, the sedimentation equilibrium method has been used by Hagihara et al. to provide absolute measurements of the molecular weight of several platinum poly-ynes, and these clearly established the macromolecular nature of these materials.[171] For example, samples of the representative polymer, **78b** ($M = Pt(P^nBu_3)_2$, $x = 2$), were found to have a value of M ($\approx M_w$) $> 10^5$ by the sedimentation equilibrium method.[171] The intrinsic viscosities of this and related polymers, $[\eta] = 1.19-1.25$, were found to be independent of the nature of the solvent, and the solubility parameter δ was found to be in the range of 6.6−9.7 (cal/mL)$^{1/2}$.[172,174] In addition, the α-value in the Mark−Houwink equation (ca. 1.7) was also determined and indicates that this type of polymer has a stiff rodlike structure in solution.[172,174] However, it is worth noting that subsequent studies on the same polymer by Fujita[218] and Tabata[219] and their co-workers suggested that the polymer chain is more flexible and can be best represented by a wormlike model.

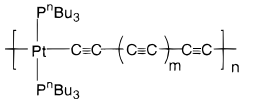
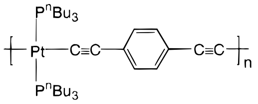
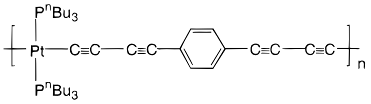
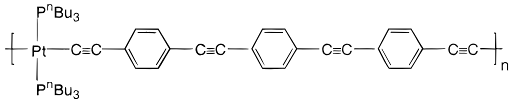
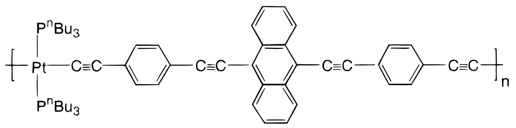
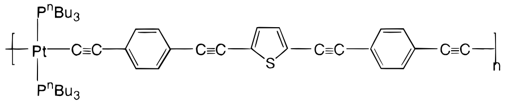
The rigid, extended nature of metal poly-yne polymers is also evident in their tendency to form lyotropic liquid crystal phases.[172,220,221] Homometallic polymers as well as mixed metal systems containing Pt, Ni, and Pd have all been shown to exhibit liquid-crystalline phases in trichloroethylene.[220,221] The formation of a nematic phase observed between crossed polarizers was reported for the platinum poly-yne **78b** ($M = Pt(P^nBu_3)_2$, $x = 2$).[220] The lyotropic liquid crystalline phases formed by these polymers have also been detected by high-resolution ^{31}P NMR spectroscopy.[222,223] The orientation of the polymer chain exhibits a strong response to magnetic and electric perturbations, leading to either parallel or perpendicular alignment with respect to to the applied magnetic field. It was established that the preferred direction of the liquid crystal molecule with respect to the magnetic field is determined by the magnetic anisotropy of the polymer and its structure.[222,223]

Table 3. λ_{max} **(nm) (in CH_2Cl_2) for the Lowest Optical Absorption Band for**



n	λ_{max} (nm)
2	363
3	371
4	376
5	378
131	380

Table 4. Lowest Optical Transition Measurements as a Function of Alkynyl Ligands

Compound	Eg/eV
	3.23 (m =0) 3.12 (m =1)
	3.26
	3.13
	3.11
	2.48
	2.70

c. Optical Spectroscopy. Metal to alkyne ligand charge transfer (MLCT) transitions are a common spectral feature in all of the linear rigid-rod metal poly-yne polymers. Their optical absorption and emission properties have been examined in some detail.[210,224−227] The optical band gap corresponding to the lowest energy transition varies depending on the metal centers and their coordination geometry, the ancillary ligands, and the nature of the alkyne bridging units.[224−227] The optical transition was investigated as a function of chain length for a series of $[R-(Pt(P^nBu_3)_2-C\equiv C-p\text{-}C_6H_4-C\equiv C-)_{n-1}-Pt(P^nBu_3)_2-R]$ ($n = 2-5$, $R = C\equiv CC_6H_5$).[205] It was found that the optical transition undergoes a red shift as n increases, but the magnitude of the shifts rapidly decreases with increasing n value (Table 3). However, no further significant bathochromic shift was observed in going from the pentamer (λ_{max}= 378 nm) to the long-chain polymer (λ_{max}= 380 nm).[172,205] It was also found that the optical transitions for the polymers occur at lower energies than for the free alkyne ligands which suggests that there is π-conjugation through the metal centers.[227] Further extension of the π-conjugation in the alkyne ligands has a significant effect on the optical transitions as illustrated in Table 4. It is apparent that the triacetylenic bridge ($m = 1$) exhibits a lower optical gap than the diacetylenic analogue ($m = 0$) ($E_g = 3.12$ eV vs 3.23 eV),[225] and likewise, the band gap excitation for the more extended arylenetetraethynylbenzene,[227] is red shifted in comparison with the diethynylbenzene analog[225,226] ($E_g = 3.13$ eV vs 3.26 eV). The more extended anthracene spacer containing three-fused benzene rings is most effective in the delocalization of π-electrons along the polymer backbone.[227] Thio-

Table 5. Second Hyperpolarizabilities for Some Pt-poly-ynes[232]

polymer	n	γ' (10^{-36} esu)	γ'' (10^{-36} esu)
$[-Pt(P^nBu_3)_2-C{\equiv}C-C_6H_4-C{\equiv}C-]_n$	112	102	3401
$[-Pt(P^nBu_3)_2-C{\equiv}C-C_6H_4-C{\equiv}C-C{\equiv}C-C_6H_4-C{\equiv}C-]_n$	>144	856	3570
$[-Pt(P^nBu_3)_2-C{\equiv}C-C_6H_2(Me_2)-C{\equiv}C-]_n$	26	56	1199
$[-Pt(P^nBu_3)_2-C{\equiv}C-C_6H_2(Me_2)-C{\equiv}C-C{\equiv}C-C_6H_2(Me_2)-C{\equiv}C-]_n$	52	181	4366

phene bridging units were also found to be more effective than arene spacers.[227] All compounds shown in Table 4 exhibit photoluminescence and, for the lower three polymers in the table, the emission quantum yields were found to be ca. one-tenth of those for the free ligands.[227] This was attributed to quenching of the long-lived triplet state by the metal. It is worth mentioning that a recent report by Butler et al. of the solid-state vibrational spectroscopic study of these Pt-poly-ynes showed that the backbone units still possess essentially acetylenic character and that π-conjugation is reduced in the presence of phenylene ring in the polymer main chain.[228]

d. Nonlinear Optical Properties. It is well-known that extended π-electron delocalized systems such as conjugated polymers exhibit appreciable nonlinear optical susceptibilities. Thus, metal poly-yne polymers consisting of low oxidation state transition metals with highly polarizable d electrons in the conjugated backbone should enhance the hyperpolarizability. Indeed, third-order nonlinear optical studies[229−235] on the platinum poly-ynes have shown that these polymers exhibit large hyperpolarizabilities comparable to inorganic semiconductors such as InSb (1700×10^{-36} esu) and Ge (2300×10^{-36} esu).[232] Table 5 lists the second hyperpolarizabilities measured by the optical Kerr gate technique for some platinum poly-ynes along with the corresponding chain lengths.[232] The large values of γ' (real component) and γ'' (imaginary component), in which the former refers to nonlinear refraction and the latter results in nonlinear absorption, suggested that these materials are potentially of interest for the construction of nonlinear optical devices.

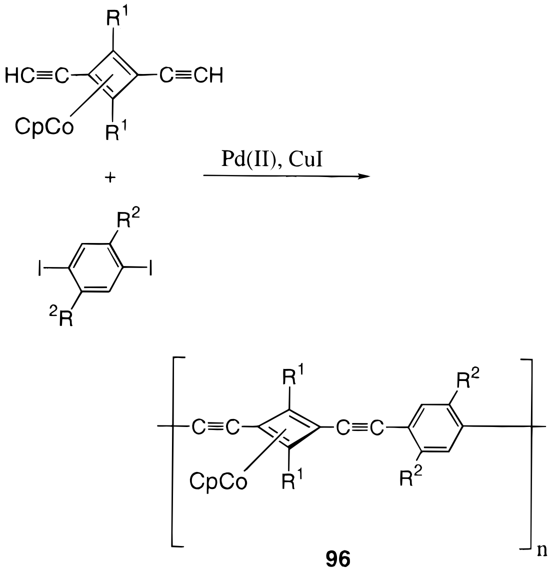
e. Electrochemical and Electrical Properties. The electrochemical properties and electrical conductivity of metal poly-ynes have not yet been investigated in detail, and only a few studies have been reported in the literature.[236] For instance, Matsuda et al. reported that in the unoxidized state **78b** (M = Cu, $x = 1$) is an insulator ($\sigma = 10^{-9}$ S cm^{-1}) and, upon doping with I_2, the conductivity is increased to 10^2 S cm^{-1}.[237] Lewis et al. showed that poly-ynes such as **78a** (M = Ni, Pd, Pt, L = E^nBu_3, E = P or As) can either be oxidized with nitric acid or doped with I_2.[210] Conductivity measurements on undoped films showed poor conduction with conductivity values of ca. 10^{-7} S cm^{-1}, which improved to ca. 10^{-6} S cm^{-1} in the I_2-doped samples.[210]

Cyclic voltammetry studies for the ferrocene-arylene-ethynylene polymers **83**, **86**, and **87** showed a single, broad oxidation wave at 0.25−0.27 V (cf. 0.02 V for ferrocene). The authors attributed the broadening of the CV peak to an exchange of electrons (ca. 1 s on the CV time scale) between metal centers through the π-conjugated chain. However, Mössbauer spectra of an I_2-oxidized sample of polymer **83** showed no coalescence of the Fe(II) and Fe(III) signals at 273.4 K, indicating slow exchange of electrons on the time scale of this experiment (10^{-7} s). The unoxidized samples of polymers **83**−**85** were found to be insulating ($\sigma = 1.0 \times 10^{-12}$ S cm^{-1}); however, upon oxidation with I_2 the electrical conductivity increased to 1.3×10^{-4}, 1.3×10^{-6}, and 6.0×10^{-7} S cm^{-1}, for **83**, **84**, and **85**, respectively. Interestingly, a Na-doped sample of **84** showed electrical conductivity of 1.2×10^{-5} S cm^{-1}.[196]

The pyridine-acetylide polymers **95** reported by Kakkar et al. show conductivities of 2.5×10^{-3} S cm^{-1} on doping with iodine. Quaternization followed by iodine doping gave a similar value (3.4×10^{-3} S cm^{-1}). These values appear to be the highest reported to date for soluble poly(metallaynes).[204b]

III.2. Polymers Containing π-Complexed Hydrocarbon Units in the Main Chain

Recent work by Bunz and Altmann includes the synthesis of rigid-rod organocobalt polymers with complexed cyclobutadiene units in the main chain (eq 37).[238] Polymers **96** (M_w = 7400−65 000 by GPC) were found to exhibit interesting thermotropic liquid crystal behavior.[238] Analogous materials containing thiophene in the main chain have also been prepared, and these form smectic lyotropic liquid crystalline phases.[239]

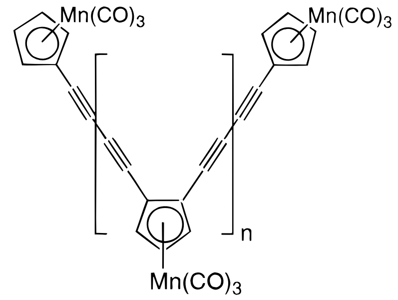


96

(37)

R^1 = H, SiMe$_3$; R^2 = H, hexyl, dodecyl

The same authors have also prepared similar materials (**97**−**99**) with butadiyne bridging units in the main chain using Hay's oxidative coupling of the starting monomers containing diterminal alkynes.[240,241]



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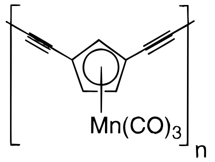

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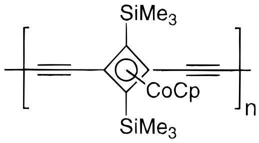
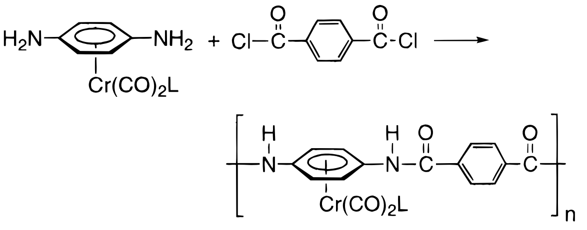


99

The authors have also reported the synthesis of linear oligomers **99** ($n = 2-9$) and have investigated their spectroscopic properties. The effects of increasing the conjugation length generally resulted in a bathochromic shift in the UV−vis absorption with a concomitant increase in peak intensity. The effective conjugation length appeared to have been reached for $n = 7$ (heptamer), because its UV−vis spectrum is almost superimposable with that of the polymer **99**.[242]

Dembek et al. reported the soluble π-complexed aromatic polyamide (**100a**) via polycondensation of (*p*-phenylenediamine)Cr(CO)$_3$ with terephthaloyl chloride in *N*,*N*-dimethylacetamide (eq 38). The highly viscous solution of **100a** exhibited lyotropic liquid crystalline behavior with nematic texture under polarizing optical microscopy. The intrinsic viscosity for **100a** in *N*,*N*-dimethylacetamide was determined to be 4.52 dL/g, and gel permeation chromatography analysis using a viscosity detector gave an absolute molecular weight (M_w) of 78 000 (polydispersity = 1.7). The analogous polymer in which only half of the diamines are complexed to Cr(CO)$_3$ was also reported. The trimethylphosphine derivative **100b** was prepared similarly via polycondensation of (*p*-phenylenediamine)Cr(CO)$_2$PMe$_3$ with terephthaloyl chloride.[243a]

The materials are of importance as the coordination solubilizes poly(*p*-phenyleneteraphthalamide) (used for making Kevlar fibers) in common organic solvents but still allows the formation of ordered, liquid crystalline solutions.



(38)

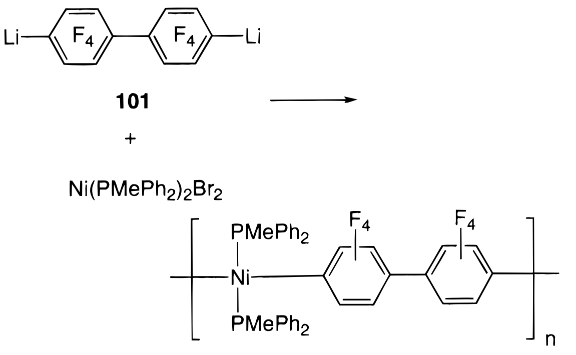
100a L = CO

100b L = PMe$_3$

Dembek and co-workers have also reported that soluble π-complexed aromatic polyamides have also been prepared with (η-C$_5$Me$_5$)Ru moieties.[243b] In addition, Abd-El-Aziz has reported routes to organic polymers in which aromatic groups are π-complexed by (η-C$_5$H$_5$)Fe groups.[243c,d]

III.3. Polymers with Skeletal Transition Metal−Arene Bonds

Hunter and co-workers have devised condensation routes to the novel arene-bridged organonickel polymers **102** via polycondensation of the fluorinated dilithiated species **101** and a Ni(II) complex (eq 39).[244] The rodlike structure of these polymers was established by dilute-solution viscosity measurements which are similar to those reported by Hagihara et al. for the related platinum poly-yne polymers.



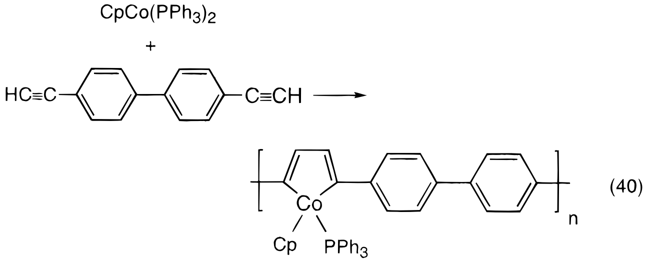
(39)

102

The absolute molecular weights of these materials have been established using GPC by way of the universal calibration technique which involves the acquisition of intrinsic viscosity data. As with the aforementioned platinum poly-yne polymers, the intrinsic viscosities were found to be independent of the nature of the solvent, and a Mark−Houwink α-value of 1.5 was determined, which is indicative of a rodlike structure. Interestingly, it was found that GPC using polystyrene standards underestimates the true molecular weight. Absolute values of M_w up to ca. 1×10^5 were determined for the polymer samples.[245]

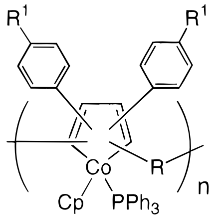
III.4. Polymers with Skeletal Metallocyclopentadiene Units

A new class of organometallic π-conjugated polymers (**103**) containing cobaltcyclopentadiene units along the main chain was synthesized by Nishihara et al. by employing double addition of acetylenes to CpCo(PPh$_3$)$_2$ (eq 40). These polymers were found to be intractable in common organic solvents.[246]

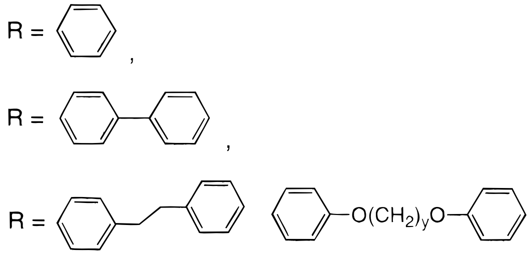


103

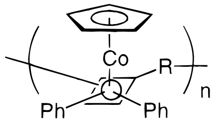
Endo and co-workers have also reported a similar synthetic approach to polymers **104** with improved solubility by incorporating flexible aliphatic spacers in the main chain.[247] These polymers undergo thermal rearrangement to the more stable (η^4-cyclobutadiene)cobalt derivatives (**105**) in quantitative yields.[248−250] Reaction with isocyanates afforded new polymers containing 2-pyridone moieties in the polymer backbone (**106**).[248]



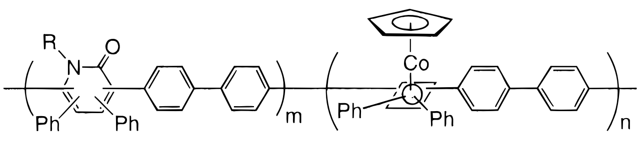
104



R^1 = H, n-O(CH$_2$)$_x$CH$_3$
x = 6, 10, 14
y = 6, 9, 10

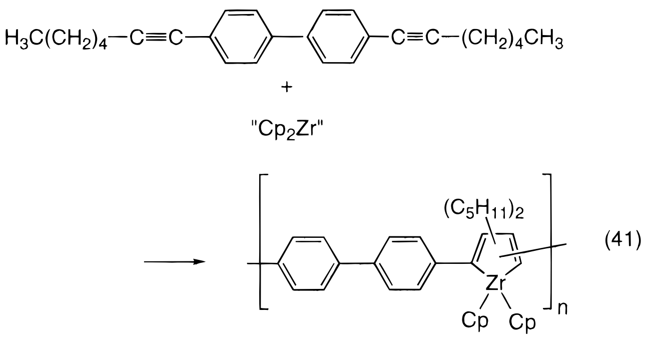


105



106

Recently, Mao and Tilley have reported a novel extension of the metal-induced coupling of diynes to prepare zirconocene containing polymers **107** (eq 41) with M_w = 37 000 by GPC (relative to polystyrene). The same authors have also reported the related organosilicon polymers and macrocycles derived from the zirconocene coupling of $CH_3C\equiv CSiMe_2C_6H_4SiMe_2C\equiv CCH_3$.[251] These polymers are not only of intrinsic interest, but they also permit chemical modification reactions in which the Zr atom is replaced.[252] This allows the introduction of diene, thiophene, phosphole, and aromatic functionalities to yield novel conjugated polymers with controlled structures and electronic properties.



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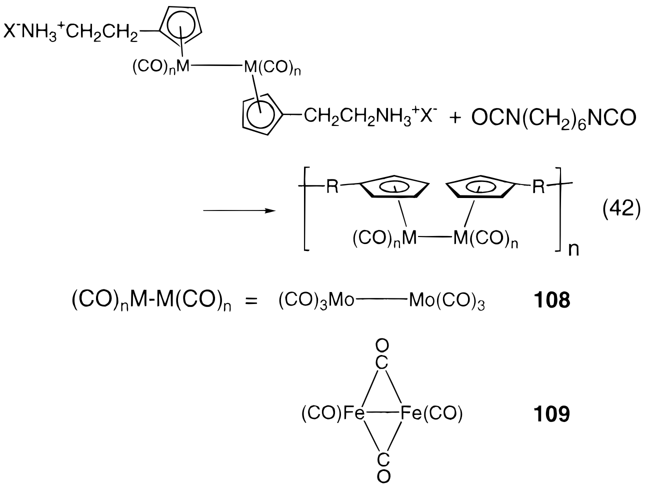
IV. Organometallic Polymers with Metal−Metal Bonds in the Main Chain

Polymers containing metal−metal bonds in the polymer backbone might be expected to possess novel conductive and photochemical properties. This is an area in which considerable synthetic challenges must be overcome if progress is to be made. In general, little work has been carried out so far, but that the area is so intriguing makes the efforts so far of particular note.

In 1989, Tyler and co-workers reported polycondensation routes to polyurethanes that contain Mo−Mo bonds **108** (R = urethane linkage) or Fe(μ-CO)$_2$Fe units **109** in the polymer backbone (eq 42).[253,254] These polymers possessed M_n values between 5000−20 000 and are of interest as photoreactive materials as the metal−metal bonds could be cleaved photochemically by visible light. In contrast, existing polymers generally require ultraviolet light for photodegradation. The quantum yields for the degradation of the polymers were found to decrease with increasing molecular weight. Poly(ether urethane) copolymers with Mo−Mo and Fe−Fe bonds in the polymer backbone were also reported by the same group.[252,253]

Morán, Cuadrado, and Mosada and co-workers have also reported the synthesis of a further class of polymers of structure **109** where R is an oligosiloxane linkage, and these materials display interesting electrochemical properties.[255] A future area of considerable interest concerns soluble polymers containing metal−metal multiple bonds in the backbone.[256]



(42)

108

109

V. Summary

The idea of incorporating organometallic moieties into polymer structures has been around for almost 50 years. Despite early pioneering efforts in the 1960s and 1970s, until recently, well-characterized, soluble, and high molecular weight materials have been exceedingly rare. As illustrated by much of the recent literature cited in this review, because of synthetic breakthroughs, the area of metal-containing polymers is currently undergoing a resurgence. Synthetic organometallic chemistry, which has provided access to many remarkable molecular compounds with fascinating structures and properties, has now permitted routes to polymeric materials with a variety of novel architectures and characteristics. Polymer science, which has traditionally been dominated by organic polymers, should benefit from the discovery of the new metal-containing macromolecular structures in a fundamental sense, and if some of the polymers possess properties which fulfill the requirements of niche-markets, in a technological sense as well.

VI. Abbreviations

The following abbreviations are used throughout the text.

DSC	differential scanning calorimetry
T_g	glass transition temperature
GPC	gel permeation chromatography
M_w	weight average molecular weight
M_n	number average molecular weight
PDI	polydispersity index
VPO	vapor pressure osmometry
WAXS	wide-angle X-ray scattering
TEM	transmission electron microscopy
AFM	atomic force microscopy
ROP	ring-opening polymerization
ROMP	ring-opening metathesis polymerization
Fc	$(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)Fe$
fc	$(\eta^5\text{-}C_5H_4)_2Fe$
Cp, Cp^H	$\eta^5\text{-}C_5H_4$
Cp^{Me}	$\eta^5\text{-}C_5Me_4$
AIBN	azobisisobutyronitrile
cod	cyclooctadiene
DME	1,2-dimethoxyethane
TMEDA	*N*,*N*,*N*,*N'*-tetramethylethylenediamine
TGA	thermogravimetric analysis
TCNE	tetracyanoethylene
TCNQ	7,7,8,8-tetracyanoquinodimethane

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