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Organoiron polymers

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Contents

Abstract

Organoiron polymers are one of the most well-examined classes of metal-containing polymers in light of their diverse structures, properties and applications. In this review, organoiron polymers are classified according to their structural make-up. The synthesis and characterization of oligomers and polymers containing dienes and cyclobutadiene rings coordinated to iron tricarbonyl moieties are described. This is followed by a thorough investigation of ferrocene-based polymers. The ferrocenyl units are found in the polymer main and side chains, and a wide variety of these organoiron polymers and their properties is reviewed. Polymers containing cyclopentadienyliron tricarbonyl complexes in their backbones and side chains are also described. Cationic η^6-arene-η^5-cyclopentadienyliron complexes have been incorporated into polymeric materials where the iron moieties are pendent to the main or side chains. The final class of organoiron polymers includes the iron-acetylides; these polymers are unique amongst the other examples described in this review since the iron complexes are σ-bonded to the organic backbones of the polymers.

Keywords: Organoiron polymers; Ferrocene; Iron carbonyl complexes; Arene cyclopentadienyliron complexes; Iron polyynes

1. Introduction

Iron is the second most abundant metal and the fourth most abundant element found in the Earth's crust [1]. Iron is easy to extract from its ore and is easily molded into different shapes, and consequently, it has been used since prehistoric times in the production of weapons, tools, etc. Currently, iron is the most commonly used metal, which is a reflection of its excellent properties and its low cost in comparison to other metals. Iron is a very reactive metal and forms a number of alloys and complexes. The most important complexes of iron possess oxidation states of II and III.

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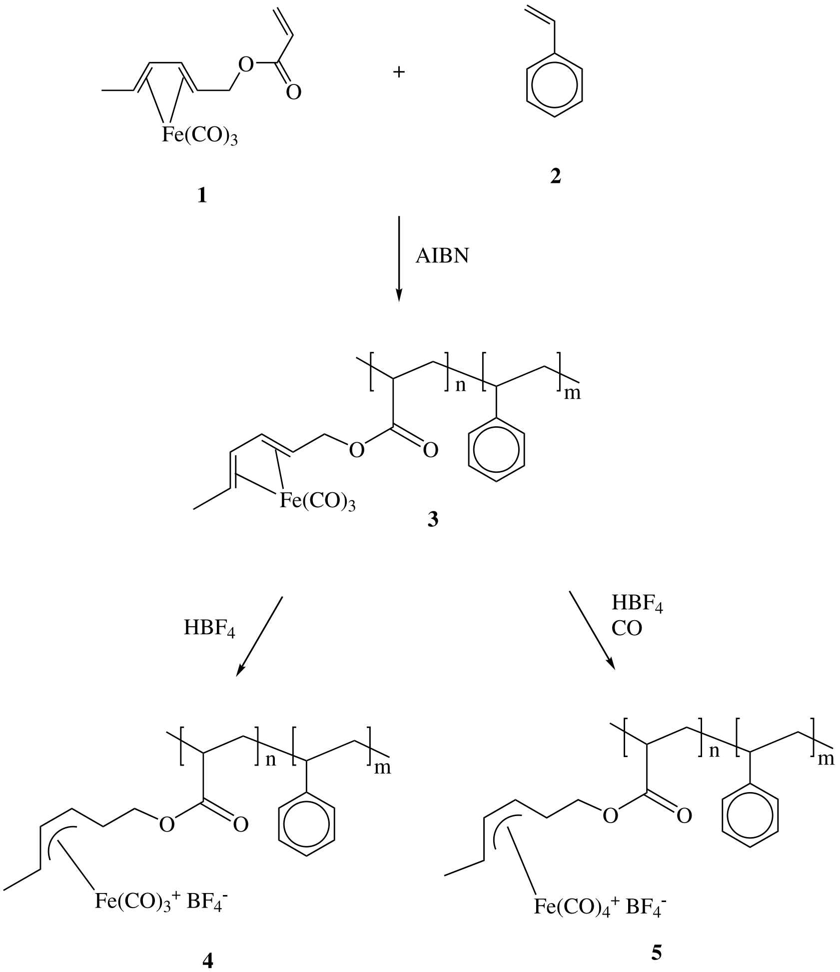
Coordination complexes of iron are also essential for life and our bodies are composed of 0.0004% iron. Hemoglobin transports oxygen through our bodies, and during this process, the iron atoms convert between the II and III oxidation states [1,2].

Organometallic chemistry was developing rather slowly until the discovery of ferrocene in 1951 [3]. Kealy and Pauson were attempting to prepare fulvalene from the Grignard reagent of cyclopentadienylbromide using ferric chloride, and instead isolated the orange organoiron complex bis(cyclopentadienyl)iron. At about the same time, Miller et al. [4] reported the synthesis of $Fe(C_5H_5)_2$ from the reaction of C_5H_6 with freshly reduced Fe at 300 °C. Soon after, a number of articles appeared by the research groups of Woodward and coworkers [5–8] describing the properties and possible structure of this complex. The name ferrocene was given to this molecule because the cyclopentadienyl rings had aromatic character similar to benzene [6]. X-ray diffraction studies determined that the ferrocene molecule had a sandwich-type structure [9,10]. In 1973, Ernst Fisher and Geoffrey Wilkinson were awarded a Nobel Prize for their contributions to this field. Ferrocene is a very stable complex and its synthesis sparked interest in the development of other organometallic sandwich-type complexes. A vast number of organoiron complexes have since been prepared using a number of organic ligands, however, cyclopentadienyl and carbonyl complexes are the most common. Other important organoiron complexes are the cyclopentadienyliron-coordinated arenes. Coffield et al. [11] first reported this class of cationic organoiron sandwich complex in 1957.

In 1955, Arimoto and Haven [12] reported the synthesis of vinylferrocene, and its subsequent polymerization to produce the first ferrocene-containing polymer. Since that time, there have been tremendous developments in the synthesis of organoiron polymers. While ferrocene-based systems have received the greatest attention, there are also numerous studies outlining the synthesis and characterization of iron carbonyl, arene cyclopentadienyliron and iron-acetylide-containing polymers [13–21]. There are now examples of iron-containing polymers prepared by all conventional organic polymerization techniques as well as via metal-coordination reactions. This review will describe the synthesis, characterization and applications of the various classes of organoiron polymers.



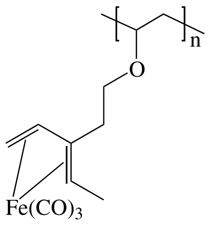
Scheme 1.

2. Polymers coordinated to iron tricarbonyl

2.1. Butadiene complexes

In 1973, Pittman et al. [22] reported the AIBN-initiated homo- and co-polymerizations of π-(2,4-hexadien-1-yl acrylate)tricarbonyliron. The relative reactivity ratios for the copolymerization reactions of **1** with styrene (**2**), methyl acrylate, acrylonitrile and vinyl acetate were determined. It was reported that the η^4-diene groups in these polymers (**3**) could be protonated to produce the π-allyliron tricarbonyl (**4**) and tetracarbonyl (**5**) derivatives [23]. Reaction of polymer **5** with the anion of ethyl acetoacetate resulted in loss of the iron moieties and the production of a mixture of two keto esters. The homopolymerization reaction of **1** using 1 wt.% AIBN resulted in a polymer with a weight average molecular weight (M_w) of 17,800, whereas the addition of 0.05 wt.% of AIBN initially, and again after 4 h, resulted in a high molecular weight polymer that was partially branched. While a glass transition temperature (T_g) was not observed for the homopolymer of **1**, the glass transition temperatures of the copolymers were much higher than those of their organic analogues. When the homo- and co-polymers of **1** were heated in air for 15 min, cross-linking reactions occurred and ferric oxide was deposited within the polymer networks. Thermal cross-linking in the presence of nitrogen did not result in the formation of Fe_2O_3 (see Scheme 1).

Nakamura and coworkers [24] have also reported the synthesis and conductivity of polymers containing iron-tricarbonyl fragments coordinated to dienes in their side chains (**6** and **7**). Polymer **6** ($M_n = 21{,}000$) had a conductivity of less than 1×10^{-10} S cm^{-1}, however, upon doping with iodine, its conductivity increased to 3.2×10^{-3} S cm^{-1}. It was noted that the carbonyl stretches in the IR spectrum of polymer **6** shifted to higher wavenumbers upon addition of one equivalent of iodine. This result indicates that the 1,3-pentadiene groups coordinated to iron tricarbonyl were converted to η^3-allyl groups upon doping. The iodine-doped polymer **7** had a conductivity of 1.3×10^{-4} S cm^{-1}, while its copolymers with polymethylmethacrylate had conductivities between 1.3×10^{-5} and 1.4×10^{-5} S cm^{-1}.



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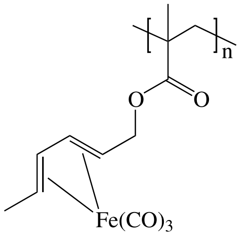

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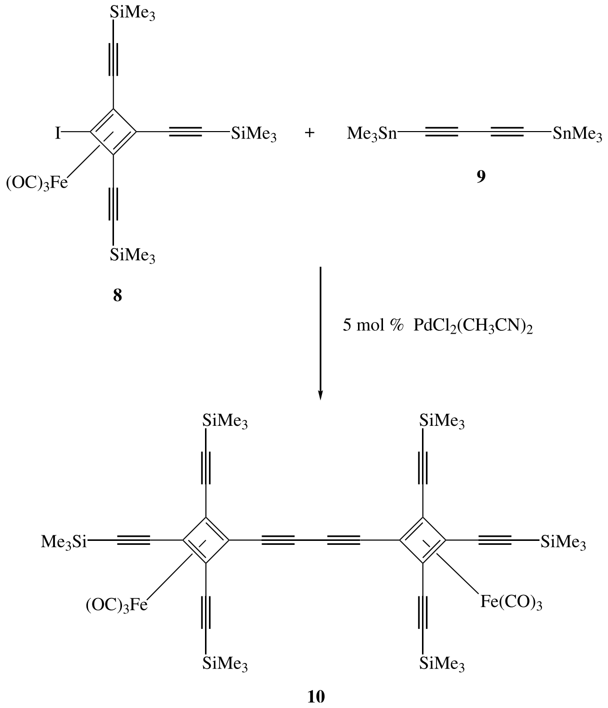
2.2. Cyclobutadiene complexes

Wiegelmann-Kreiter and Bunz [25,26] have reported the synthesis of oligomeric complexes containing iron tricarbonyl moieties coordinated to cyclobutadiene rings. For example, the reaction of complex **8** with bis(trimethylstannyl) butadiyne (**9**) using a palladium catalyst resulted in the production of the dimeric complex **10**. A complex containing three iron tricarbonyl moieties pendent to cyclobutadiene rings was also synthesized [26] (see Scheme 2).

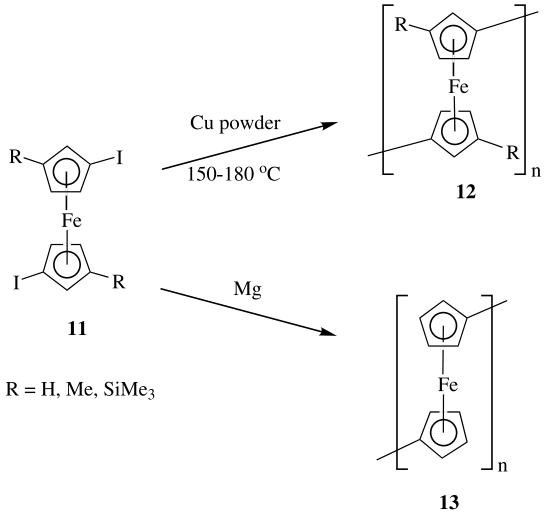


Scheme 2.

3. Polymers containing 5-membered rings coordinated to iron moieties

3.1. Bis(cyclopentadienyliron) in the backbone

Early efforts in the synthesis of polymers containing ferrocenyl moieties in the main chain centered on the synthesis of poly(ferrocenylenes). Poly(ferrocenylenes) are polymers in which the ferrocene rings have direct linkages between one another. Some of the early work dealing with the synthesis of this class of polymer was pioneered by the research groups of Korshak and Nesmeyanov [27,28]. The reaction of ferrocene with *tert*-butyl hydroperoxide resulted in the formation of largely insoluble polymers consisting of ferrocene units in the backbone. A re-examination of this reaction revealed that in addition to ferrocene-linked polymers, there were also ether-substituted cyclopentadienyl rings and the ferrocene rings were 1,1′- and 1,3-substituted [29]. In 1963, Rausch reported the synthesis of a poly(mercuriferrocenylene) via condensation of 1,1’-dichloromercuriferrocene with ethanolic sodium iodide or aqueous sodium thiosulfate [30]. It was found that heating



Scheme 3.

this polymer in molten ferrocene resulted in the production of low molecular weight poly(ferrocenylene) [31].

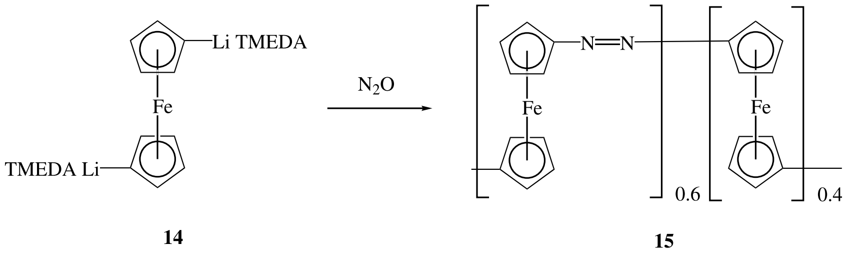
Low molecular weight poly(ferrocenylenes) were also synthesized by reaction of ferrocenyllithium with cobaltous chloride [32,33], and by reaction of haloferrocenes with copper salts [34]. Neuse and Bednarik [35] reported that poly(ferrocenylenes) with molecular weights up to 10,000 were isolated by reaction of 1,1′-dilithio- and 1,1′-diiodoferrocene with catalytic amounts of Cu(II) or Pd(II) salts. Dehalogenation polymerization of dihaloferrocenes with magnesium was reported by Yamamoto and coworkers [36,37] to produce poly(ferrocenylenes) with conductivities ranging from 10^{-2} to 10^{-4} S cm^{-1}. Recently, Foucher and coworkers [38] reported similar results utilizing magnesium- and copper-catalyzed coupling polymerization reactions (Scheme 3). Poly(ferrocenylenes) containing methyl and trimethylsilyl groups on the cyclopentadienyl rings were also synthesized and the methyl-substituted polymers were reported to possess weight average molecular weights as high as 8600 [38].

Nishihara's group has described the synthesis of soluble 1,1′-dihexylferrocene-based oligomers by reaction of a dihexylfulvalene dianion with $[FeCl_2(THF)_2]$ [39]. Degrees of polymerization greater than 10 were obtained, and the charge-transfer complexes of these materials were p-type semiconductors. Reaction of the dilithioferrocene complex **14** with N_2O under high pressure resulted in the production of the azo-substituted poly(ferrocenylene) (**15**) shown in Scheme 4 [40]. The soluble portion of **15** had an M_w of 87,000 and an M_n of 13,000. The UV–Vis spectrum of this polymer had an MLCT band at 535 nm, and the π–π^* transition of this polymer was shifted to a longer wavelength than the oligomeric analogs.

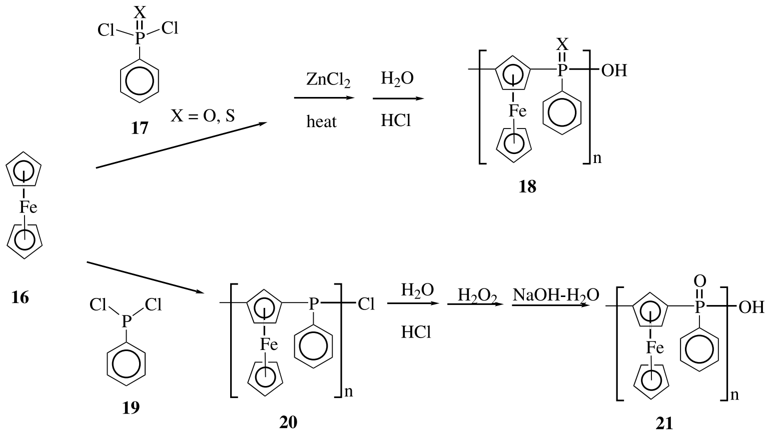
The reaction of ferrocene with phosphine oxide and sulfide compounds results in the production of homoannularly substituted polymers as shown in Scheme 5 [41]. Pittman described the synthesis of ferrocene-based polymers such as **18** containing phosphine oxide or sulfide linkages using zinc chloride as a catalyst. These polymers possessed relatively low molecular weights, but exhibited good thermal stability. When the polymerization of **16** with **17** was conducted at temperatures greater than 140 °C, cyclopentane-bridged polymers were produced following cleavage of some of the cyclopentadienyl rings from iron. Heteroannularly substituted polymers were also observed at high reaction temperatures and after long polymerization times. Around the same time, Neuse utilized a similar approach in the production of phosphorus-bridged poly(ferrocenes) [42].

High molecular weight poly(ferrocenylphosphines) (**22**) were described by Seyferth and coworkers [43] by reaction of 1,1′-dilithioferrocene-tetramethylenediamine (**14**) with phenyldichlorophosphine (**19**) as shown in Scheme 6. While a ferrocenophane (**23**) could be isolated by reaction of **14** with **19** at −78 °C [44], slow addition of **14** to **19** resulted in polymers with weight average molecular weights as high as 161,000, as determined by low-angle laser light scattering [43]. Attempts were also made to ring-open ferrocenophane **23** using catalytic amounts of phenyllithium; however, low molecular weight species were obtained.

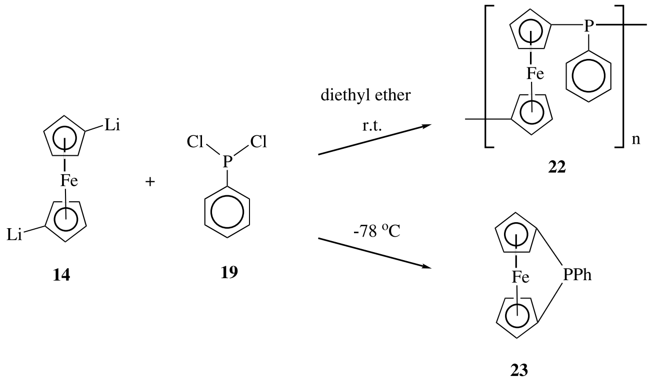
In 1995, Manners and coworkers [45] reported the thermal ring-opening polymerization (ROP) of a number of phosphorus-bridged ferrocenophanes, which produced polymers with phosphorus(III) and phosphorus(V) centers. Reaction of ferrocenophanes **23**–**25** at temperatures between 120 and 250 °C resulted in the ring-opened polymers **26**–**28** shown in Scheme 7. While polymers **26** and **27** could not be analyzed by GPC due to interactions with the column, polymer **28** had a weight average molecular weight of 66,000 and a PDI of 1.98. Poly(ferrocenylphosphines) **26**–**28** could also be reacted with elemental sulfur to produce the corresponding poly(ferrocenylphosphine sulfides)



Scheme 4.



Scheme 5.

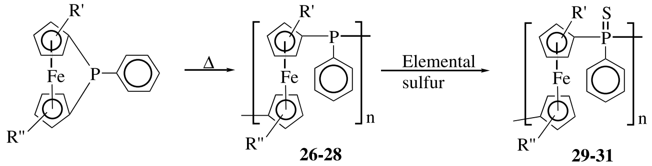


Scheme 6.

29–**31**, with M_w values of 18,000, 19,000 and 65,000, respectively. Direct thermal ROP of a phosphine sulfide-bridged ferrocenophane resulted in partial decomposition of the products and the generation of insoluble materials. The living anionic polymerization of ferrocenophane **23** has also been achieved using *n*-BuLi [46]. The resulting polymer was reacted with sulfur in order to determine that its number average molecular weight ranged from 3600 to 32,000 going from a monomer to catalyst ratio of 11:1 to 100:1.

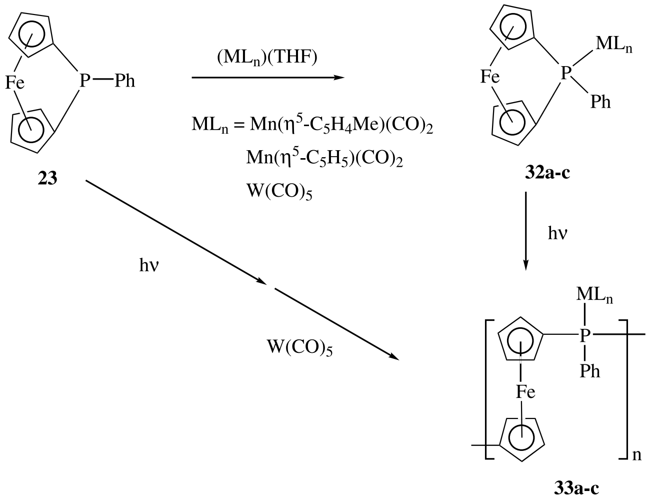
The phosphorus(III) centers in homo- and co-polymers have been functionalized with a number of different reagents. For example, a copolymer prepared by living anionic ROP of **23** with hexamethylcyclotrisiloxane was reacted with either $PdCl_2$ or $Fe(CO)_4$ to produce polymers with ca. 20% of the phosphine groups coordinated to palladium and iron, respectively [46]. Scheme 8 shows the approach taken by Miyoshi and coworkers [47] to prepare poly(ferrocenylphosphines) with transition metal-coordinated phosphine groups in the backbone. Reaction of monomer **23** with three different metal complexes allowed for the production of the corresponding manganese- and tungsten-coordinated monomers **32a**–**32c**. UV irradiation of these monomers in THF resulted in their polymerization and produced the high molecular weight polymers **33a**–**33c**. Monomer **23** was also irradiated directly with UV light in THF, and subsequently reacted with $[W(CO)_5(THF)]$. While this reaction was also successful, ^{31}P-NMR indicated that there was more than one type of phosphorus environment in this polymer's spectrum due to the phosphine's ability to act as mono-, bi-, tri- and multi-dentate centers [47].

[1]Ferrocenophanes with phosphorus bridges have also been shown to undergo transition metal-catalyzed ROP [48,49]. However, phosphorus(III) systems do not undergo ROP under these conditions due to interactions of the lone pair on phosphorus with the catalyst. Reaction of a

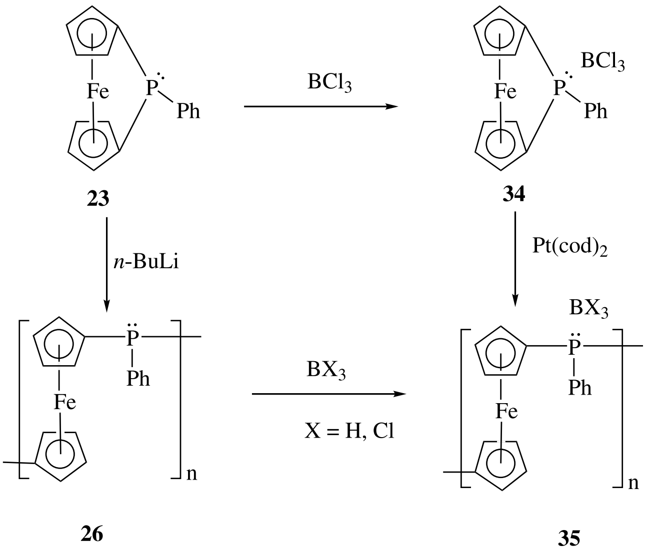


23; R' = R'' = H
24; R' = H, R'' = n-butyl
25; R' = R'' = $SiMe_3$

Scheme 7.



Scheme 8.

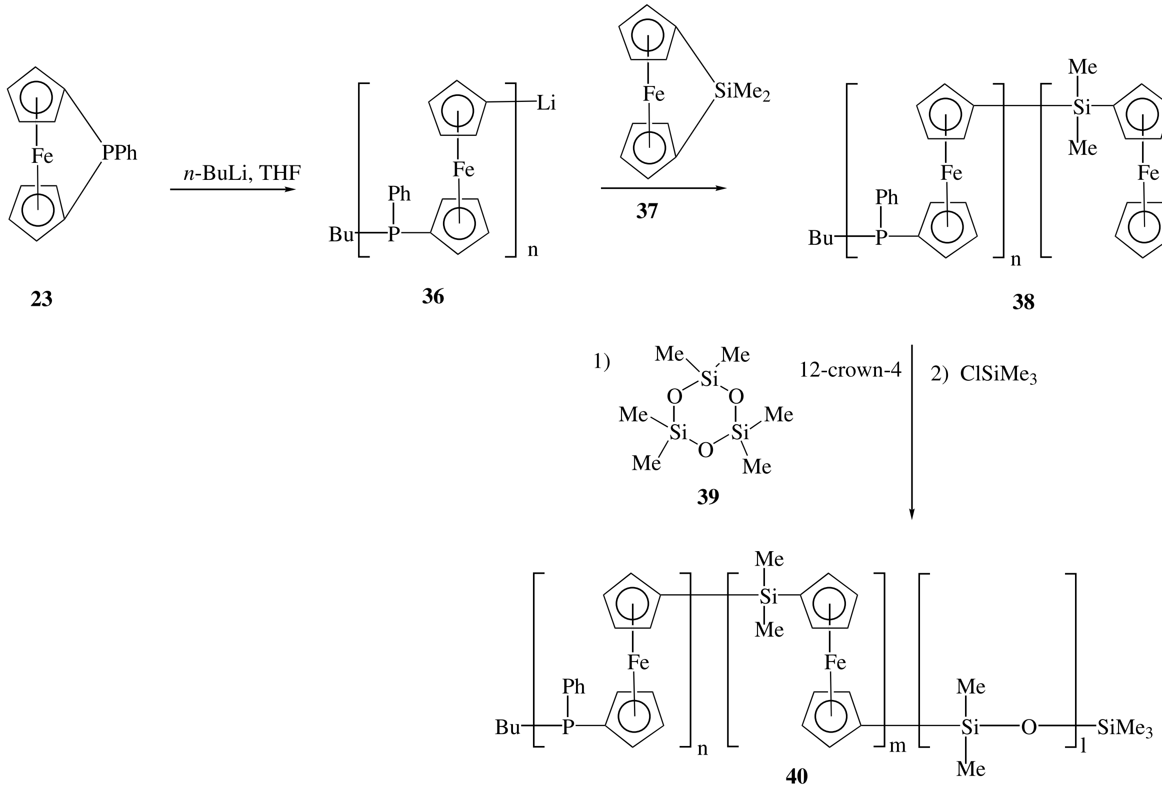


Scheme 9.

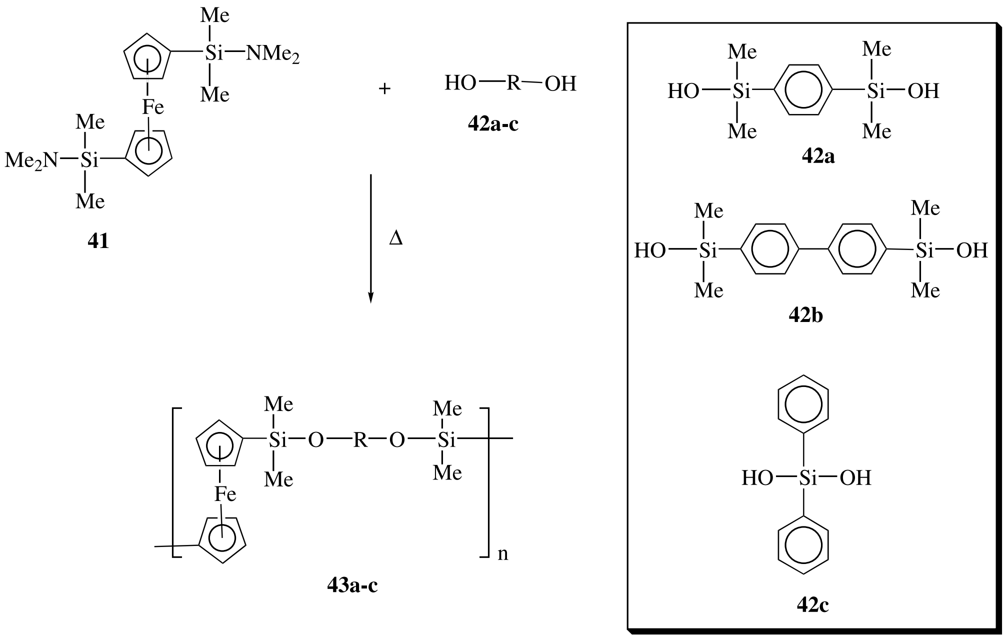
phosphorus-bridged [1]ferrocenophane with methyl triflate led to a phosphonium-bridged ferrocenophane that successfully underwent transition metal-catalyzed ROP [48]. Reaction of monomer **23** with boron trichloride gave rise to adduct **34** as shown in Scheme 9 [49]. This adduct could undergo thermal or transition metal-catalyzed ROP with a platinum catalyst. It is also important to note that reaction of polymer **26** with BCl_3 or BH_3 gave the corresponding adducts **35** [49].

Poly(isoprene-*b*-ferrocenylphosphine) has been synthesized by living anionic polymerization [50]. This polymer formed star-shaped spherical micelles in hexanes with the organometallic blocks at the core and the organic polyisoprene segments at the periphery. The phosphorus centers were reacted with Au(CO)Cl to produce the corresponding gold-coordinated polymers. The polyisoprene portions of the polymers could be cross-linked by UV irradiation in the presence of the radical initiator AIBN. The synthesis of an ABC triblock copolymer containing ferrocenylphenylphosphine, ferrocenyldimethylsilane and dimethylsiloxane blocks (**40**) is shown in Scheme 10 [51]. When six or less poly(ferrocenylphenylphosphine) blocks were incorporated into this polymer, it self-assembled into cylindrical micelles with the organometallic blocks at the core and the poly(dimethylsiloxane) blocks at the corona. When the degree of polymerization for the poly(ferrocenylphenylphosphine) block was 11, star-shaped spherical micelles were formed. While the ferrocenylphosphine blocks are amorphous due to their atacticity, the ferrocenylsilane blocks are crystalline at room temperature. The cylindrical micelles did not exhibit any crystallinity, however, the WAXS spectrum of the spherical micelles indicated that the ferrocenylsilane blocks were crystalline [51].

Polyferrocenes containing silicon bridges have also been investigated since the 1960s, however these polymers were often of low molecular weight and difficult to characterize [52,53]. In 1974, the synthesis and characterization of ferrocene-based polymers with siloxane bridges was ac-



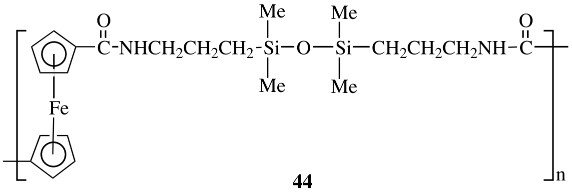
Scheme 10.



Scheme 11.

complished according to the strategy shown in Scheme 11 [54]. Reaction of bis(dimethylaminodimethylsilyl)ferrocene (**41**) with disilanols **42a–42c** either in toluene or in the melt at 100–110 °C resulted in the production of polymers **43a–43c**. Polymers were also prepared by reaction of bis(dimethylamino)silanes with 1,1′-bis(hydroxymethyl)ferrocene [55]. It was found that when a CH_2–O–Si group was present in the polymer backbone, the polymers were susceptible to nucleophilic attack by water, whereas polymers **43a–43c** exhibited hydrolytic stability.

Cuadrado and coworkers [56] prepared polyferrocenes with dimethylsiloxane (**44**) and dimethyldiphenylsilyl (**45**) units in their backbones by polycondensation reactions of diamine monomers with diacid chlorides. The ferrocene monomers used to prepare **44** and **45** were 1,1′-bis(chlorocarbonyl)ferrocene and 1,1′-bis(β-aminoethyl)ferrocene, respectively. The advantage of using 1,1′-bis(β-aminoethyl)ferrocene is that α-functionalized ferrocenes form stable ferrocenyl carbonium ions which lead to polymer instability. The number average molecular weights of these ferrocene-based polymers were measured by vapor-pressure osmometry to be 10,600 and 12,500, respectively [56].



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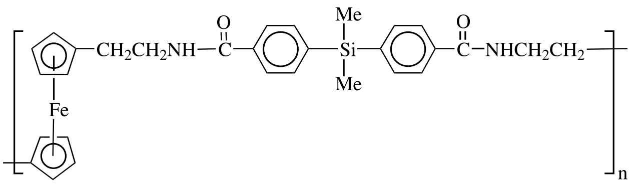

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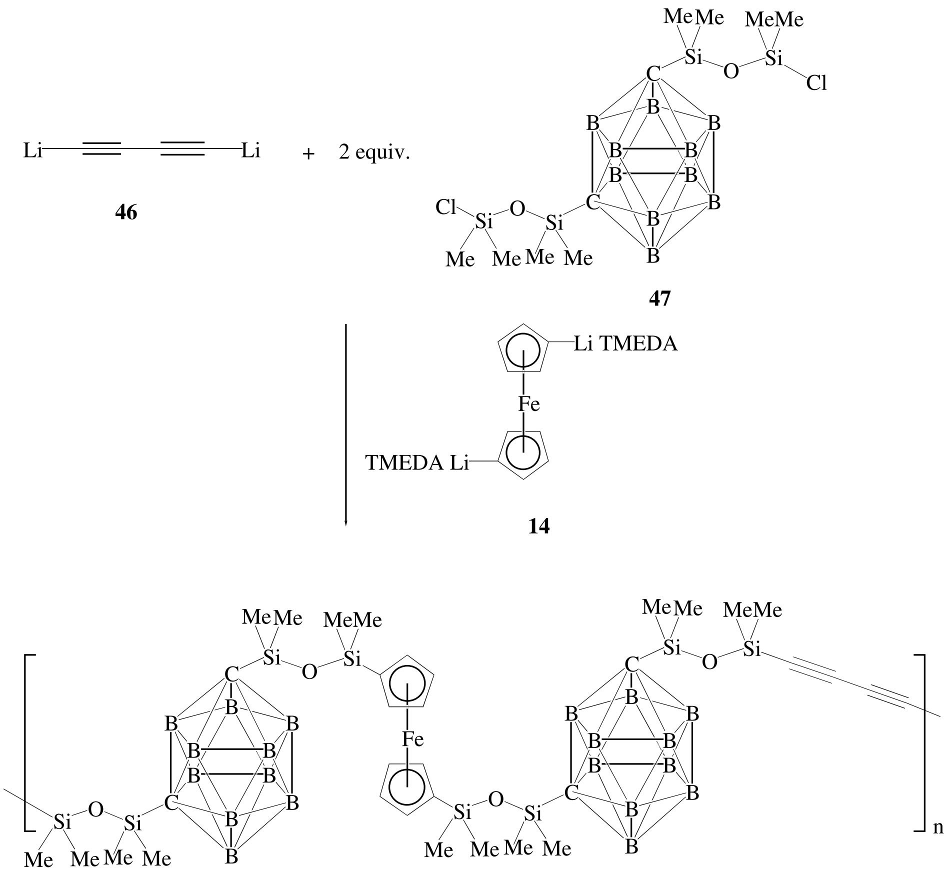
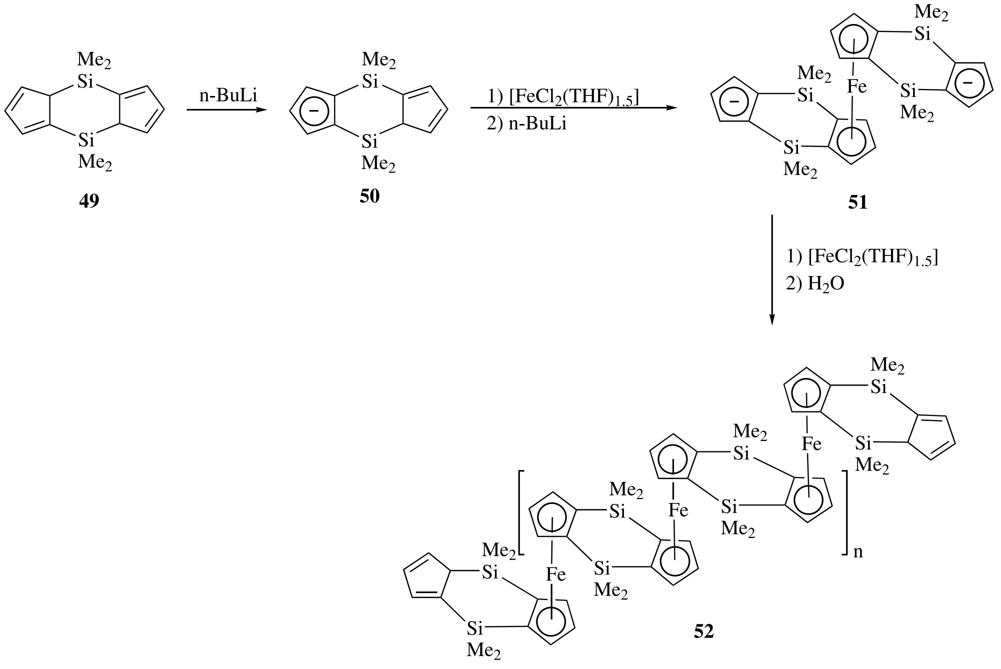
The incorporation of carborane units into the backbones of ferrocene polymers was described by Houser and Keller [57]. Reaction of dilithiobutadiyne (**46**) with two equivalents of 1,7-bis(chlorotetramethyldisiloxyl)-*m*-carborane (**47**) followed by the addition of complex **14** produced a polyferrocene (**48**) with a molecular weight of ca. 10,000. When the siloxane-diacetylene ferrocene polymer was heated to 350 °C under an inert atmosphere, a black elastomeric thermoset was obtained in 98% yield. Thermogravimetric analysis showed that polymer **48** experienced a weight loss at ca. 380 °C. Differential scanning calorimetry and infrared spectroscopy indicated that cross-linking of the butadiyne groups occurred at this temperature. When this polymer was heated to 1000 °C under a nitrogen atmosphere, a hard ceramic that displayed ferromagnetic properties was produced in 78% yield. This ceramic material exhibited excellent oxidative stability due to the presence of boron in its structure. Reaction of 1,1′-bis(chlorodiorganosilyl)ferrocenes with the Grignard reagents of diacetylene resulted in the production of oligomeric materials with degrees of polymerization between 3 and 8 [58](see Scheme 12).

Kohler and coworkers [59] have recently reported the synthesis of linear and cyclic polyferrocenes with bridging dimethylsilyl groups (Scheme 13). Cycles containing between 6 and 18 ferrocene groups in the backbone were isolated and separated by chromatography. Decreasing the reaction temperature from 25 to −20 °C resulted in an in-



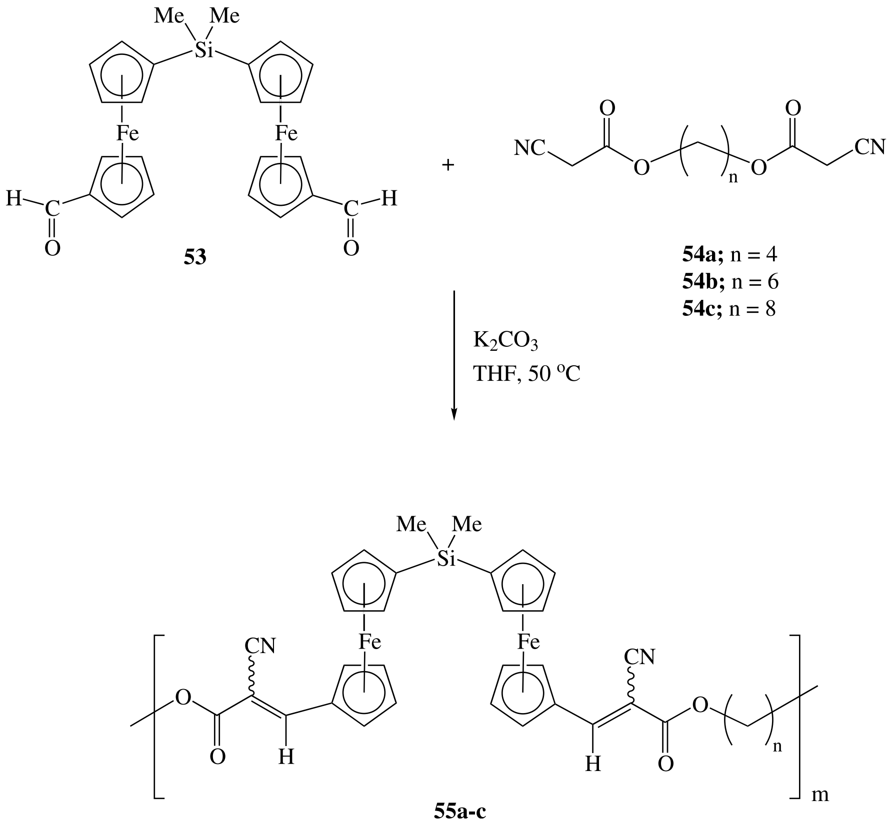
46 47 14 48

Scheme 12.



49 50 51 52

Scheme 13.



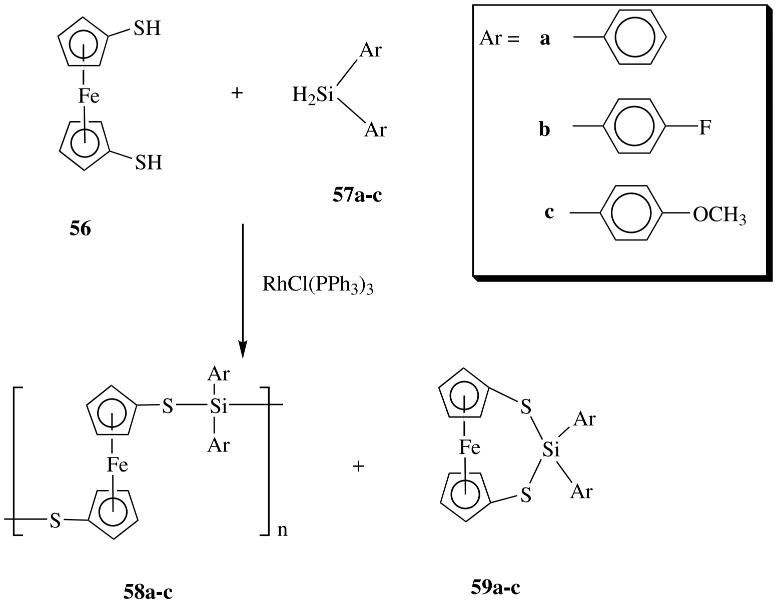
Scheme 14.

crease in the mean ring size from 8.1 to 10.8. Polycondensation of complex **51** with $FeCl_2$ resulted in the formation of low molecular weight polymers with only odd numbers of ferrocene units in their backbones. A similar approach was taken by Park et al. [60] in the synthesis of poly(ferrocenylsilanes). Polycondensation of the dilithium salts of an isomeric mixture of dicyclopentadienyldimethylsilanes with $FeCl_2$ resulted in the formation of low molecular weight polymers ($M_w = 4900$ and $M_n = 4100$) as determined by GPC. Cyclic voltammetry of the polymer showed the presence of two reversible oxidation steps at −0.02 and 0.21 V versus ferrocene, indicating significant electronic interactions between the iron centers.

The synthesis of ferrocene-based polymers (**55a**–**55c**) has also been accomplished via Knoevenagel polycondensation reactions between the dialdehyde complex **53** and the bis(cyanoacetate) monomers **54a**–**54c** [61]. Scheme 14 shows the synthesis of these organoiron polymers (**55a**–**55c**), which were isolated as a mixture of *E* and *Z* isomers, although, purification through precipitation into methanol resulted in an isomerically enriched polymer with 98% of the sample being the *E* isomer. This precipitation procedure lowered the number average molecular weights of the polymers by ca. 30%. Polymers **55a**–**55c** exhibited good solubilities in most organic solvents, and their M_n values were 9200, 9100 and 26,600, respectively. A film of polymer **55c**, with the longest aliphatic spacer in its backbone, displayed elastomeric properties and could be stretched to ca. twice its original length [61].

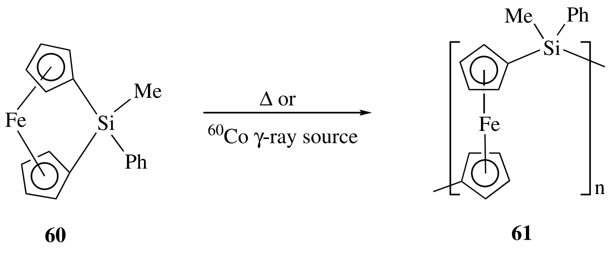
1,1′-Ferrocenedithiol (**56**) undergoes reaction with diarylsilanes (**57a**–**57c**) in the presence of $RhCl(PPh_3)_3$ to produce a mixture of polymers (**58a**–**58c**) and ferrocenophanes (**59a**–**59c**) as shown in Scheme 15 [62]. The polymers were isolated in 37–51% yields as toluene-soluble fractions, whereas the ferrocenophanes precipitated in toluene and were isolated in 22–41% yields. Polymers **58a**–**58c** had number average molecular weights ranging from 2700 to 4600. Toluene solutions of the ferrocenophanes did not undergo ROP, and thus it was concluded that **58a**–**58c** and **59a**–**59c** were produced via inter- and intramolecular dehydrogenation reactions, respectively [62]. In 1960s, Rosenberg [63,64] reported that polycondensation of 1,1′-dilithioferrocene with dichlorosilanes produced low molecular weight poly(ferrocenylsilanes). In 1997, Pannell and Sharma [65] studied these reactions, and determined that ferrocenophanes were produced under the reaction conditions described, and that polymers probably formed via ROP of the strained silaferrocenophanes rather than via polycondensation reactions.

A number of reviews have recently outlined the synthesis and properties of poly(ferrocenylsilanes) [66–68]. In 1992, Manners and coworkers [69] reported the thermal ROP of [1]silaferrocenophanes to produce high molecular weight poly(ferrocenylsilanes). This was an important development



Scheme 15.

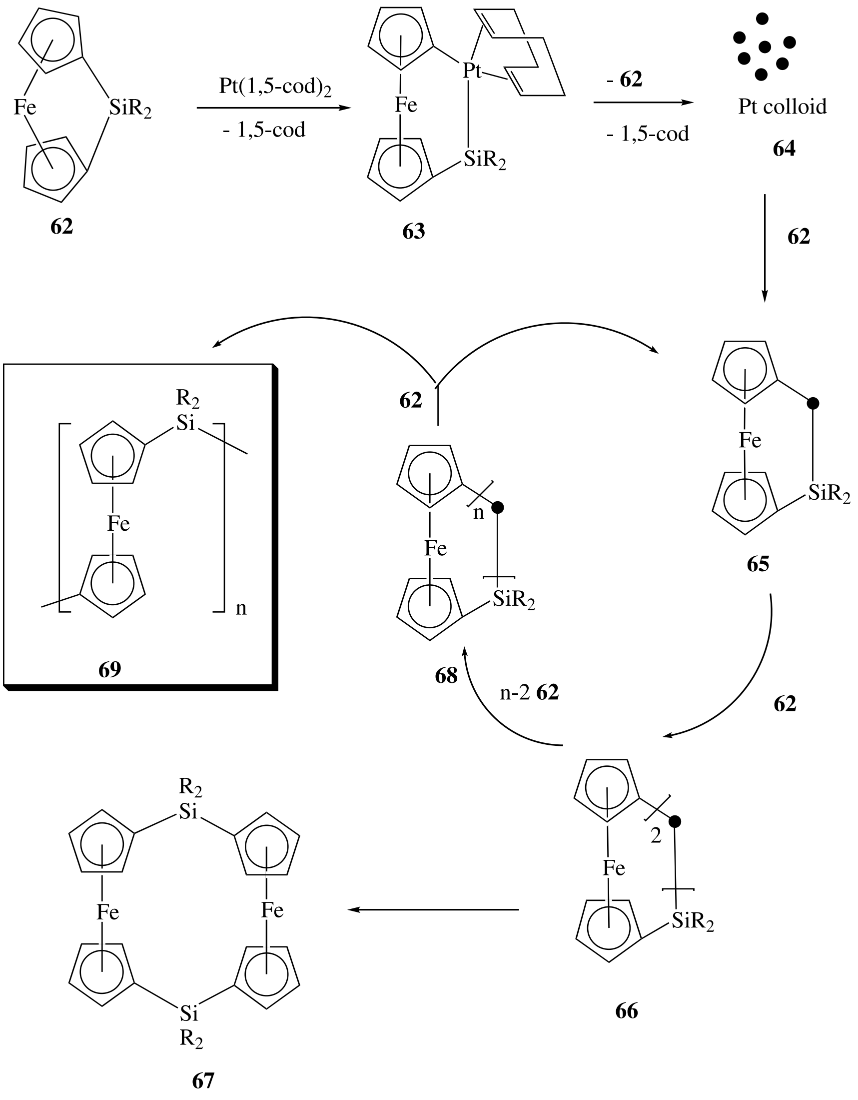
in the field of ferrocene-based polymers because of the well-defined structures and high molecular weights that these materials possessed. Since that time, the polymerization of [1]silaferrocenophanes has been achieved not only thermally, but using anionic [70] and transition metal catalysts [71,72]. It has also been reported that the polymerization of [1]silaferrocenophanes can be achieved in the solid-state by γ-irradiation [73,74]. The degree of polymerization could be controlled by altering the initial radiation dose [73]. For example, weight average molecular weights of 220,000 and 260,000 were obtained when 2.5 and 10 Mrad doses of radiation were used, respectively. AFM images of poly(ferrocenyldimethylsilane) prepared via solid-state polymerization indicated that it had a spherulitic morphology. It is interesting to note that when an unsymmetrical ferrocenophane was polymerized in the solid state, a stereoregular polymer was obtained. For example, when polymer **61** was synthesized by thermal ROP, an amorphous material was obtained [75], whereas γ-irradiation resulted in a polymer whose WAXS spectrum indicated the presence of crystallites (Scheme 16) [74]. The crystallinity of this polymer indicates that there is stereoregularity in the polymer backbone, however, its actual tacticity was not determined.



Scheme 16.

Transition metal-catalyzed ROP has proven to be a quite versatile method to prepare poly(ferrocenylsilanes) because the polymers are prepared using relatively mild reaction conditions and these reactions do not require the monomers to be as pure as they are required to be for anionic-initiated ROP [67]. The mechanism of transition metal-catalyzed ROP was initially proposed to proceed via a homogenous mechanism [76]. However, Manners and coworkers [77] recently proposed that the ROP of [1]silaferrocenophanes (**62**) followed a heterogeneous catalytic cycle with a metal colloid (**64**) as the active catalyst. Scheme 17 shows a possible mechanism in which Pt(1,5-cod)$_2$ is thought to initially form a [2]platinasilaferrocenophane (**63**) via oxidative-addition to the zero-valent Pt complex with elimination of a 1,5-cod ligand. Platinum colloids (**64**) resulted from subsequent elimination of a second 1,5-cod ligand. Oxidative-addition and reductive-elimination at the colloid surface eventually allowed for the production of polymers such as **69**. The mechanism of thermal ROP has also been examined and it was proposed that polymerization proceeds following heterolytic cleavage of the silicon-cyclopentadienyl bonds, which may be initiated by trace impurities such as water or other nucleophilic species [78].

Recent studies have focused on the incorporation of saturated and unsaturated carbon chains, chloroalkyl, chloro and alkoxy substituents into poly(ferrocenylsilanes) using a variety of synthetic methodologies [79–86]. Polymers with acetylenic groups attached to the silicon atoms were recently reported to produce magnetic ceramics in high yields upon pyrolysis [79]. Thermal ROP of monomer **70** resulted in the production of polymer **71**, whose M_w and M_n were 210,000 and 96,000, respectively (Scheme 18) [87]. Hydrosilation of polymer **71** with the azobenzene-containing acrylates (**72a** and **72b**) in the presence of Karstedt's cat-



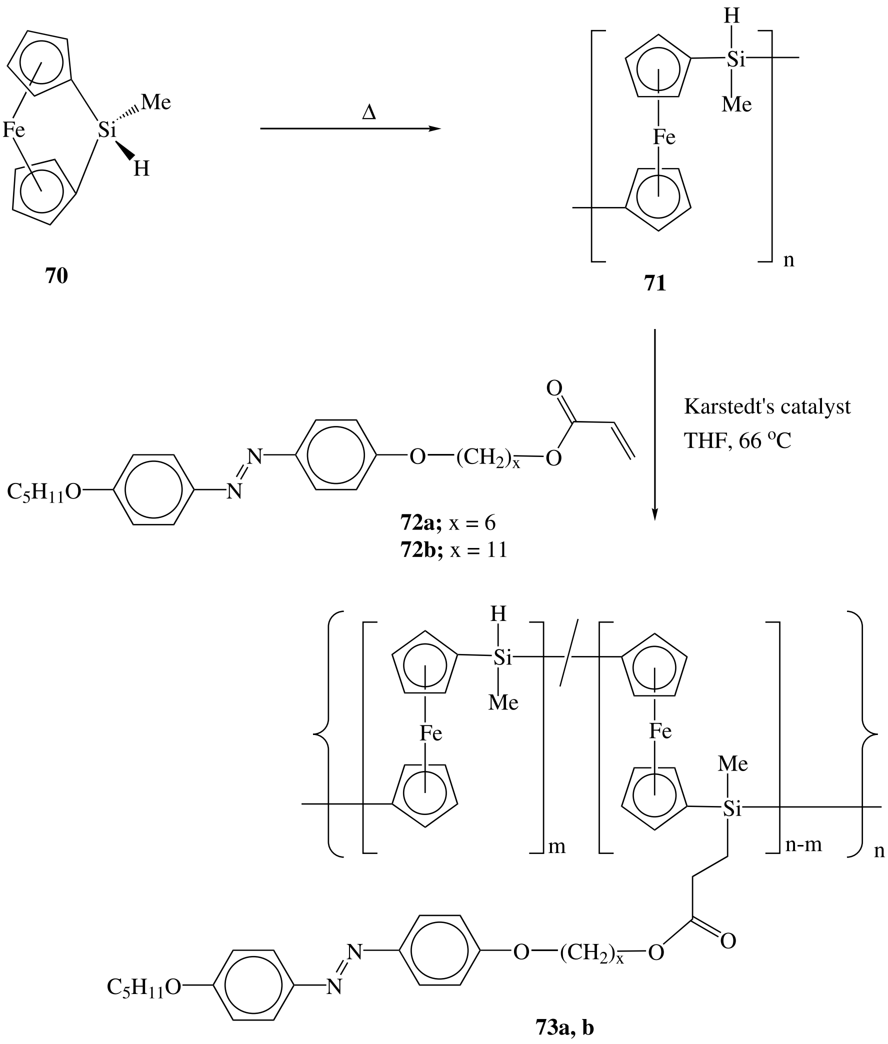
Scheme 17.

alyst resulted in the formation of polymers **73a** and **73b**, in which 83 and 81% of the silane groups were functionalized with the azobenzene mesogens. Differential scanning calorimetry and polarized optical microscopy both indicated that polymers **73a** and **73b** possessed liquid crystalline properties. These polymers exhibited nematic phases from about 35 and 53 °C, respectively, to ca. 250 °C, at which point decomposition occurred [87].

Thermal ROP of a trimetallic [1]ferrocenophane has also been studied, however, a mixture of soluble cyclic and linear polymers were isolated [88]. While thermal ROP of **74** at 200 °C yielded soluble oligomers, polymerization at 250 °C produced an insoluble polymeric material (**75**) as shown in Scheme 19. Monomer **74** was resistant to polymerization using a number of transition metal catalysts. Copolymerization of the trimetallic monomer **74** with the dimethylsilaferrocenophane monomer (**37**) at 150 °C for 36 h resulted in soluble polymers (**76**) with relatively high molecular weights and monomodal distributions. However, due to the lower solubility and reactivity of the sterically crowded trimetallic monomer (**74**), the amount of this monomer incorporated into the copolymers could not be controlled [88].

Functionalization of poly(ferrocenylsilanes) has recently led to the production of water-soluble cationic and anionic polyelectrolytes [84–86,89–93]. The approach taken by Manners and coworkers [84–86,89,90] involved the quaternization of amine groups to produce cationic polymers, or substitution of amines with sulfonate groups to yield anionic poly(ferrocenylsilanes). Scheme 20 shows the synthesis of water-soluble cationic (**80**) and anionic (**82**) poly(ferrocenylsilane) polyelectrolytes utilizing this strategy [86]. Polymers **79** and **81** with the acetylide groups in their structures could also be reduced with hydrazine to yield unsaturated carbon chains attached to silicon.

Vancso and coworkers [91–93] have recently reported the synthesis and self-assembly of anionic and cationic poly(ferrocenylsilanes). The ionic interactions in polyelectrolytes allow these materials to self-assemble into

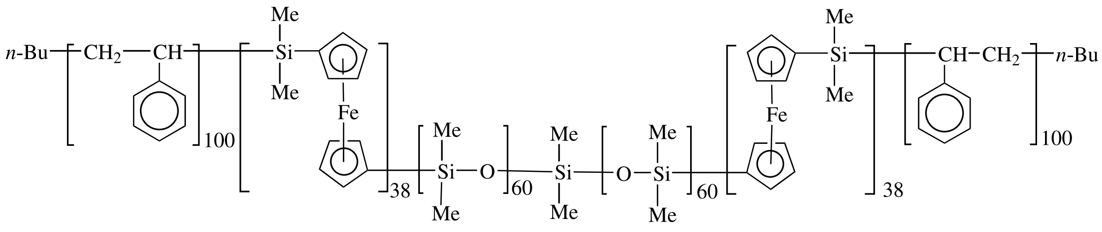


Scheme 18.

supramolecular multilayer films. The anionic polymer **85**, shown in Scheme 21, was very soluble in water above pH 6, and concentrations greater than 100 mg ml^{-1} could be achieved [91]. Solutions of this polymer exhibited polyelectrolyte effects as determined by viscometry measurements. GPC of polymer **83** in THF showed that it had a degree of polymerization of about 80 with a polydispersity of 1.9. GPC measurements of **85** in water showed only one peak, although a measurement of this polymer's molecular weight was not obtained. The cationic polymer, poly(ferrocenyl(3-ammoniumpropyl)methylsilane), was utilized to prepare organoiron multilayer films with **85** by electrostatically depositing the polyions onto various substrates [93].

Copolymerization reactions of [1]ferrocenophanes has resulted in the production of polymers with interesting properties and morphologies [94–110]. One of the aims of these studies has been to incorporate segments with different solubilities into polymers, which allows for their self-assembly into different structures. Poly(dimethylsiloxane) and poly(ferrocenylsilane) have been incorporated into a number of copolymers prepared by thermal, anionic and transition metal initiations [94–103]. Recently, it was reported that certain cationic rhodium(I) complexes are highly active catalysts in the ROP of [1]silaferrocenophanes [108]. However, while high molecular weight ($M_n = 10^5$) polymers were isolated, these materials experienced decreasing molecular weights when they remained in solutions containing the catalysts. Polymer **86** is an example of a pentablock copolymer incorporating polystyrene (PS), poly(ferrocenyldimethylsilane) (PFS) and poly(dimethylsiloxane) (PDMS) blocks in its structure [94]. This polymer, prepared via living anionic polymerization, had three glass transition temperatures at −127, 32 and 103 °C for the PDMS, PFS and PS blocks, respectively.

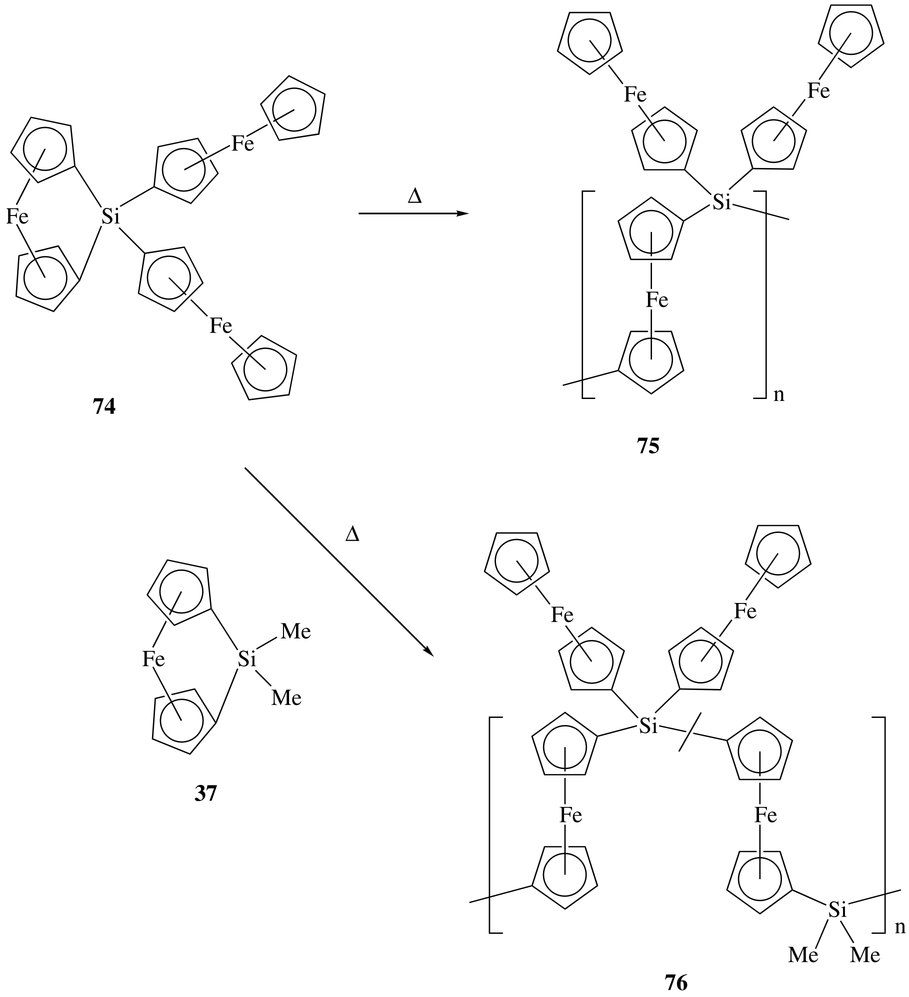
Water-soluble block copolymers have also been synthesized by incorporating poly(ethylene oxide) segments in between organoiron blocks in the polymer backbone [109,110]. This class of polymer formed micelles in water solutions in which the ferrocenylsilane blocks made up the hydrophobic core and the periphery consisted of the hydrophilic poly(ethylene oxide) portions. Scheme 22 shows the synthesis of a water-soluble block copolymer prepared



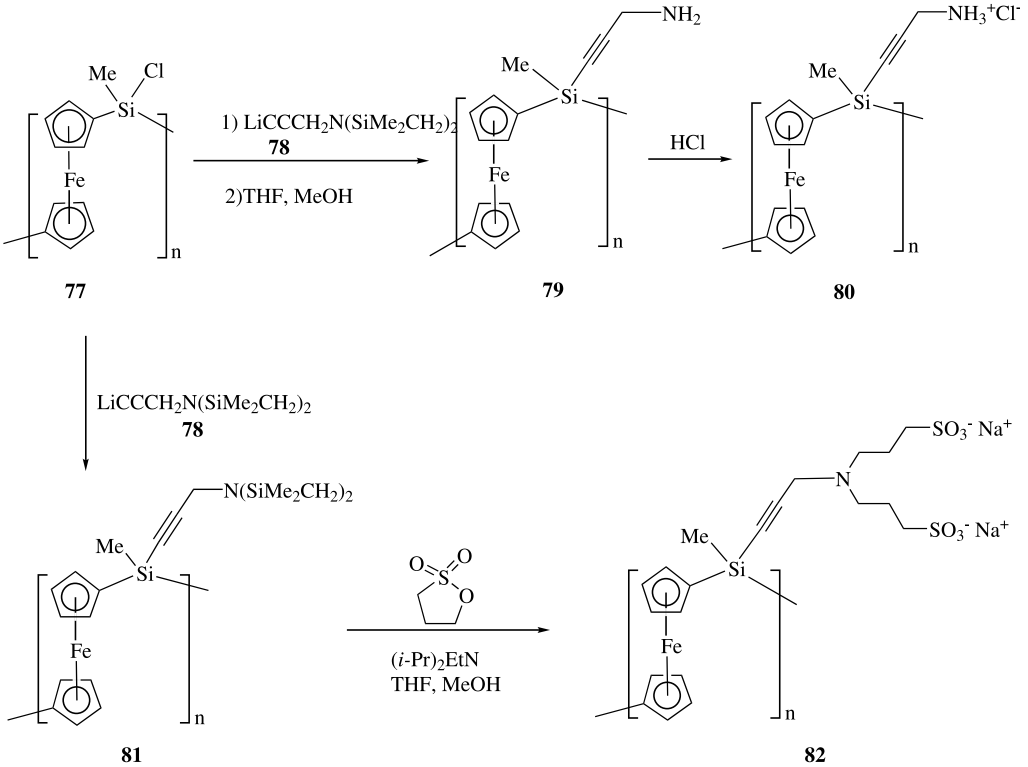
86

by anionic polymerization [110]. Following formation of **88**, potassium hydride was utilized to initiate the living oxyanionic polymerization of 2-(*N*,*N*-dimethylamino)ethyl methacrylate. Eleven organometallic units and fifty-five methacrylate units were incorporated into polymer **90**. Polymer **90** was added to water and stirred for 20 days, which resulted in the formation of a colloid dispersion. A film of this material was analyzed by transmission electron microscopy and it was determined that cylindrical micelles formed.

The synthesis and ROP of a number of [1]germaferrocenophanes has also been achieved [72,111–115]. These ferrocenophanes (**91**) undergo facile thermal ROP to produce high molecular weight polymers (**92**) ($M_w = 10^6$), using milder reaction conditions than required for their silicon analogs [112]. For example, poly(ferrocenyldimethylgermane) was prepared by thermal ROP at temperatures as low as 90 °C, and polymer formation was observed within 5 min. Strained [1]germaferrocenophanes were moisture-sensitive and decomposed to produce bis(ferrocenyl)germoxanes (**93**) as shown in Scheme 23. The copolymerization of [1]silaferrocenophanes with [1]germaferrocenophanes has also been achieved thermally and with transition metal catalysts [72,113]. Pannell and coworkers [115] have recently reported that germanium-bridged polyferrocenes are insula-



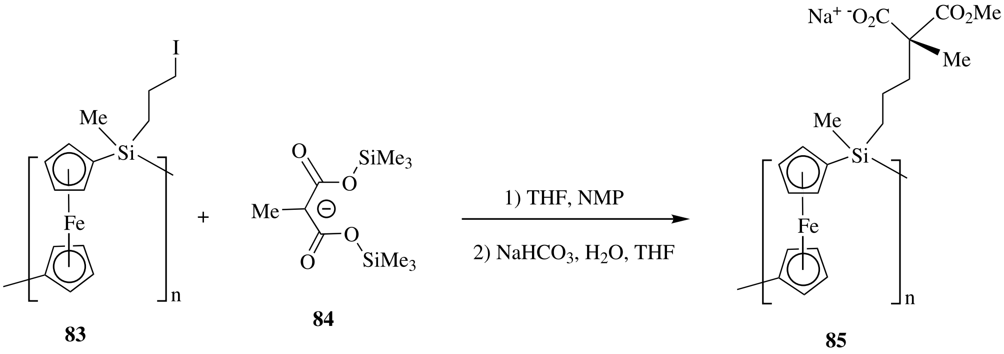
Scheme 19.



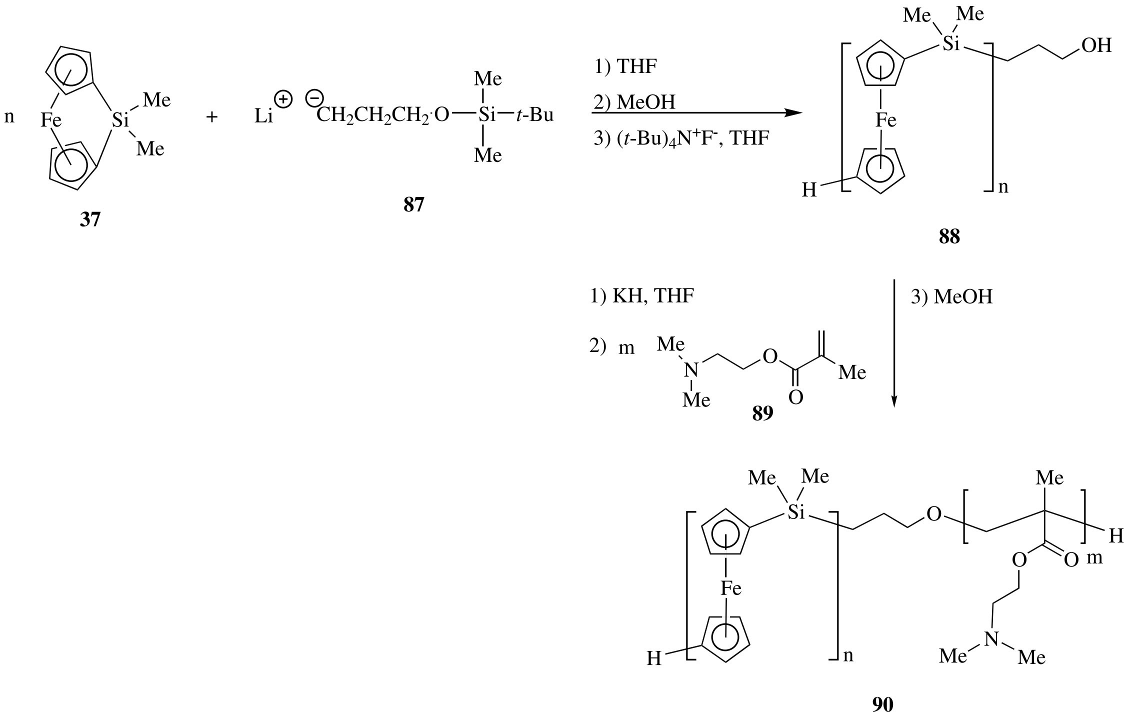
Scheme 20.

tors with conductivities around 10^{-14} Ω^{-1} cm^{-1}, but that they become conducting upon doping with iodine. The conductivities of the germanium-bridged polymers ranged from 10^{-6} to 10^{-4} Ω^{-1} cm^{-1}. An interesting example of a poly(ferrocenylgermane) with a ferrocenyl group as a substituent on germanium was produced by thermal ROP of the corresponding ferrocenophane, $Fe(\eta^5\text{-}C_5H_4)_2FcPhGe$ [116]. Polymerization in toluene or in the melt resulted in the isolation of polymers with weight average molecular weights of 11,000 and 26,000, respectively.

In 1970s, Carraher et al. [117,118] reported the synthesis of silicon-, germanium- and tin-containing polyesters of ferrocene. These organoiron polymers with tin-containing backbones were prepared by reaction of organotin dihalides with disodium ferrocene dicarboxylate [118]. These polymerization reactions were very rapid, yielding insoluble materials within a few minutes. In 1996, Manners and coworkers [119] reported that ROP of tin-bridged ferrocenophanes occurred thermally to produce high molecular weight polymers, and that solutions of the ferrocenophanes at room temperature produced low molecular weight polymers. Further investigation into this reaction revealed that polymerization of [1]stannaferrocenophanes occurs in the presence of trace amounts of nucleophilic species [120–122]. The addition of nucleophilic reagents to ferrocenophanes containing silicon and germanium bridges was also explored. The tin and germanium monomers displayed good reactivity, while the silicon-bridged ferrocenophanes were much more resistant to polymerization under these conditions [121]. The mechanism of the nucleophilically assisted ROP of [1]stan-



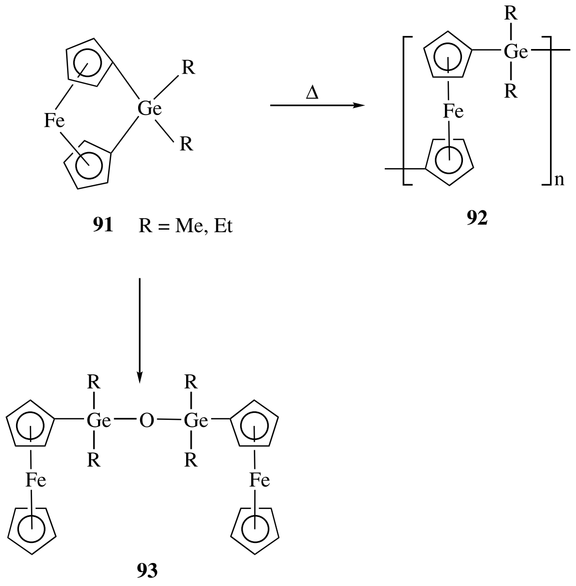
Scheme 21.



Scheme 22.

naferrocenophanes has recently been proposed (Scheme 24) [122]. It was also discovered that cationic ROP occurred in the presence of electrophilic initiators [122]. Pannell and coworkers [123] have reported that thermal ROP of tin-bridged ferrocenophanes occurs in the solid state to produce polymers that are soluble prior to precipitation into hexane.

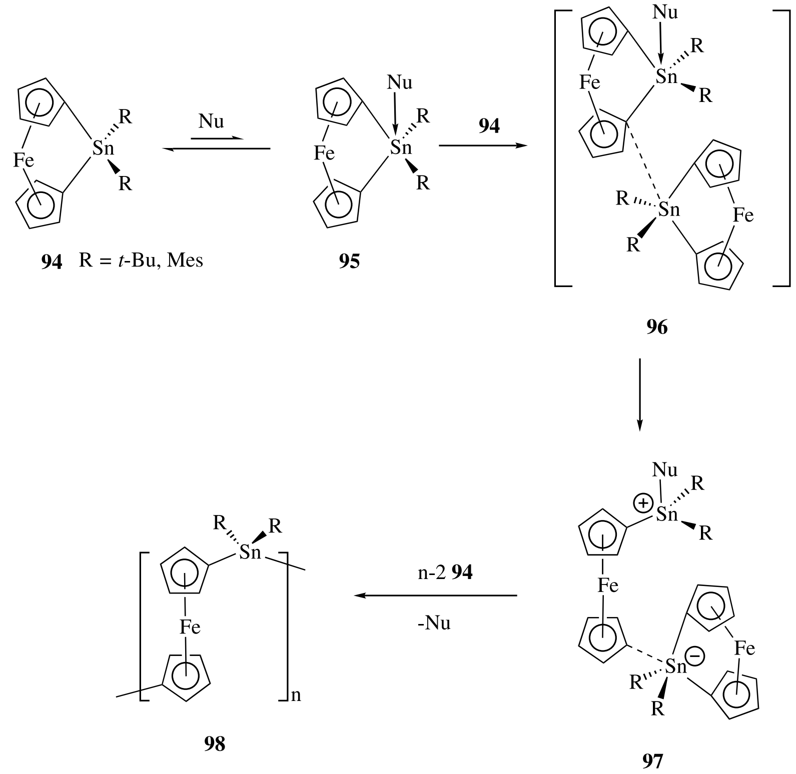
The incorporation of boron into a main chain ferrocene-based polymer was reported by Marvel and coworkers in 1962 [124]. This polymer was prepared by reaction of 1,1′-ferrocenylenediboronic acid or tetra-*n*-butyl 1,1′-ferrocenylenediboronate with 3,3′-diaminobenzidine. The resulting polymer was soluble in polar organic solvents and sulfuric acid. The synthesis of polymers with boron bridges in their backbones has also been achieved by thermal ROP of highly strained [1]ferrocenophanes [125,126]. Scheme 25 shows the ring opening of monomers **99a**–**99c**, which occurred between 170 and 220 °C to produce polymers **100a**–**100c**. Polymers **100a** and **100c** were insoluble, while the soluble polymer **100b** was determined to consist of a mixture of low molecular weight linear and cyclic oligomers [126]. Polyferrocenes containing boron bridges in their backbones have also been isolated by ROP of [1]ferrocenophanes using boron halides as initiators [127]. The resulting materials contain Lewis acidic boron centers in their backbones. Ferrocenylboranes could also be used as capping reagents in the polymerization of poly(ferrocenylsilanes), resulting in the boron-functionalized segment as the polymer end-group [127].



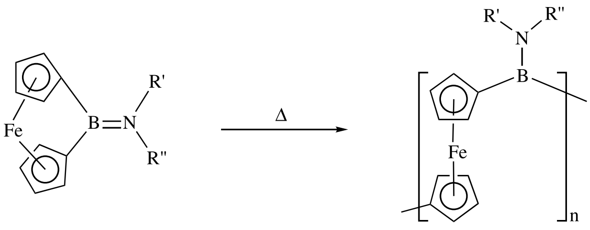
Scheme 23.

Another class of boron-containing polyferrocene (shown in Scheme 26) was prepared by the reaction of the Lewis acidic complex **101** with bipyridine (**102**) [128]. This coordination-type polymer (**103**) was isolated as a crystalline solid that was insoluble in non-coordinating solvents. The polymerization reaction could be reversed by addition of an excess of picoline, which resulted in the formation of the picoline adduct of **101**. Polymer **103** was stable in the solid state up to 240 °C, however, decomposition occurred at about 85 °C in toluene.

Interesting examples involving the synthesis of gallium-bridged ferrocene-based polymers were recently reported by Jutzi et al. [129,130]. Scheme 27 shows the reaction of



Scheme 24.

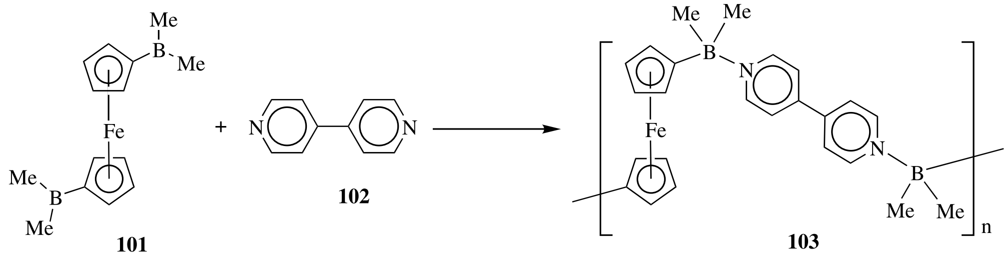


99a; R' = R'' = $SiMe_3$
99b; R' = R'' = *i*-Pr
99c; R' = *t*-Bu , R'' = $SiMe_3$

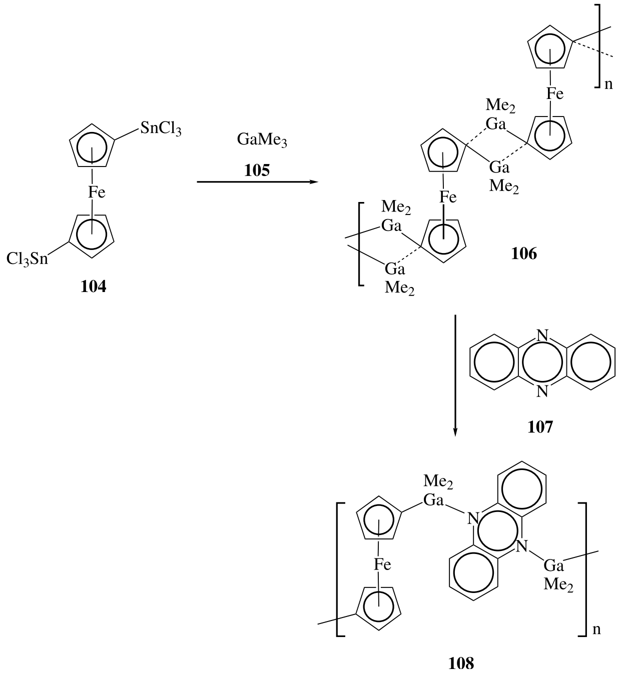
Scheme 25.

1,1′-bis(trichlorostannyl)ferrocene (**104**) with an excess of trimethylgallium (**105**). This reaction resulted in the formation of a polymer (**106**) consisting of ferrocenediyl groups with bridging dimethylgallyl units. The structure of polymer **106** was elucidated from its crystal structure. When the polymeric 1,1′-bis(dimethylgallyl)ferrocene (**106**) was reacted with a stoichiometric amount of phenazine (**107**) in toluene, the coordination polymer **108** was produced [130]. Crystallographic analysis of **108** revealed that each polymer chain was surrounded by four other chains. Ferrocenyl units surrounded the phenazine units in the polymer backbone such that π-stacking interactions between phenazine rings were not possible.

In 1992, Brandt and Rauchfuss [131] reported the desulfurization-induced ROP of [3]trithiaferrocenes. Reaction of [3]trithiaferrocenes with 0.9 to 1 equivalent of PBu_3 produced insoluble polymers when the ferrocenyl rings were unsubstituted and high molecular weight soluble polymers when one or both of the cyclopentadienyl rings were functionalized with butyl groups [131–133]. A copolymer prepared by reaction of $Fe(C_5H_4)_2S_3$ with $Fe(C_5H_4)(n\text{-}Bu\text{–}C_5H_3)S_3$ had a weight average molecular weight of 25,000 [131]. Scheme 28 shows the polymerization of **109** to produce the corresponding poly(ferrocenylene persul-

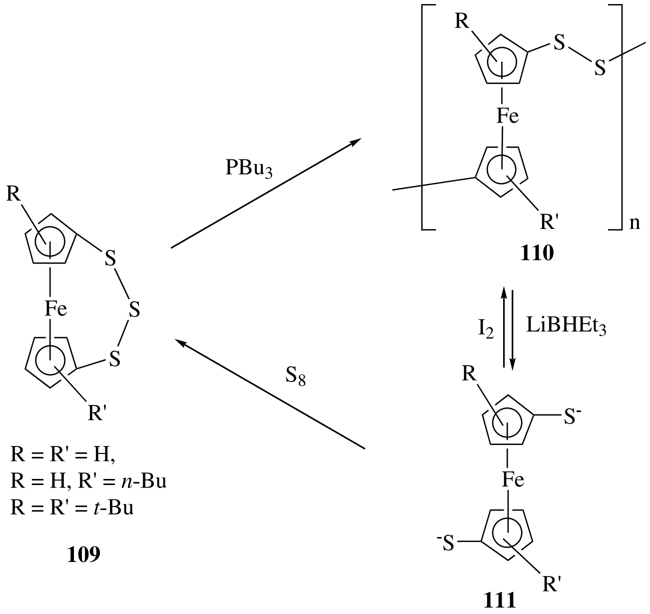


Scheme 26.



Scheme 27.

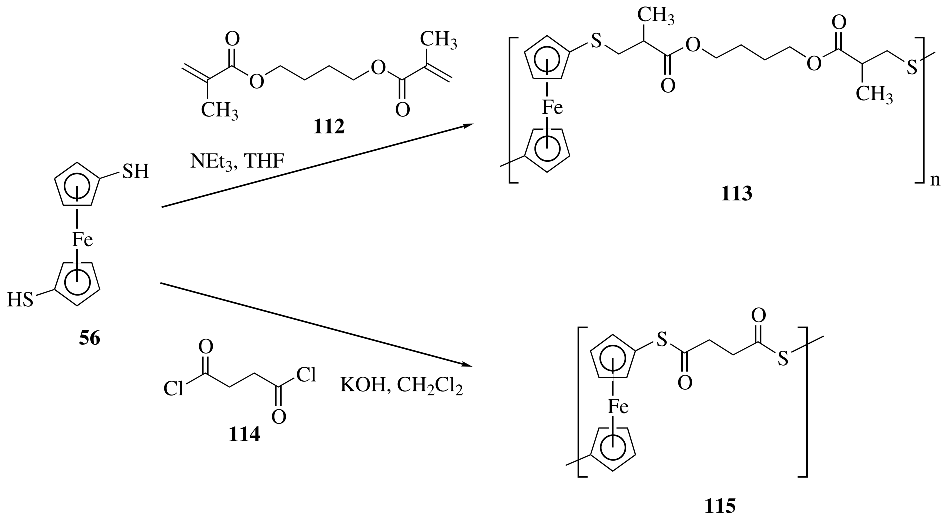
fides) (**110**). It can be seen that reduction of **110** with two equivalents of $LiBHEt_3$ resulted in cleavage of the disulfide linkages in the polymer and generated complex **111**. Reaction of complex **111** with iodomethane allowed for the formation of R,R′-fc$(SMe)_2$ [131,132]. Polymer **110** was regenerated by oxidation of complex **111** with iodine. Reaction of **111** with sulfur or selenium resulted in the formation of a trisulfide (**109**) and a triselenide ferrocene complex, respectively [131,132]. The ROP of a chiral trithiaferrocenophane (R,R′ = *t*-Bu) was also studied and the rates of the polymerization reactions were found to be dependent on the polarities of the solvents used [132]. While insoluble polymers were isolated when the polymerizations of the trithiaferrocenophanes were conducted in THF or DMF, and low molecular weight polymers resulted from reaction in dichloromethane, a mixed solvent system of dichloromethane and THF resulted in soluble high molecular weight polymers [133]. For example, the M_w of **110** (R = H, R′ = *n*-Bu) was 40,000 when the reaction was performed in CH_2Cl_2, 144,000 in 50:50 CH_2Cl_2:THF and 350,000 in 1.5:98.5 CH_2Cl_2:THF [133]. Electrochemical oxidation of the soluble polymers showed that these polymers undergo two distinct reversible oxidation steps separated by about 300 mV, indicating that there is electronic communication between the iron centers. Deselenization of a triselenide monomer in THF yielded a soluble poly(ferrocenylene perselenide) with an M_w of 15,300 [133].



Scheme 28.

Low molecular weight ferrocene-based materials with disulfide bridges have been synthesized by Herberhold et al. [134] via the AIBN-initiated radical oligomerization of 1,1′-ferrocenedithiol. Main-chain polyferrocenes have also been synthesized by polyaddition and polycondensation reactions of 1,1′-ferrocenedithiol (**56**) with various difunctionalized organic monomers [135]. Scheme 29 shows the reaction of **56** with 1,4-butandiyl dimethacrylate (**112**) and succinyl dichloride (**114**) to produce polymers **113** and **115**, respectively. These polymers (**113** and **115**) had weight average molecular weights of 12,600 (PDI = 3.4) and 10,000 (PDI = 5.0). Monomer **56** was also utilized to initiate the ROP of propylene sulfide, which resulted in the isolation of a copolymer with one ferrocene unit in the backbone [135].

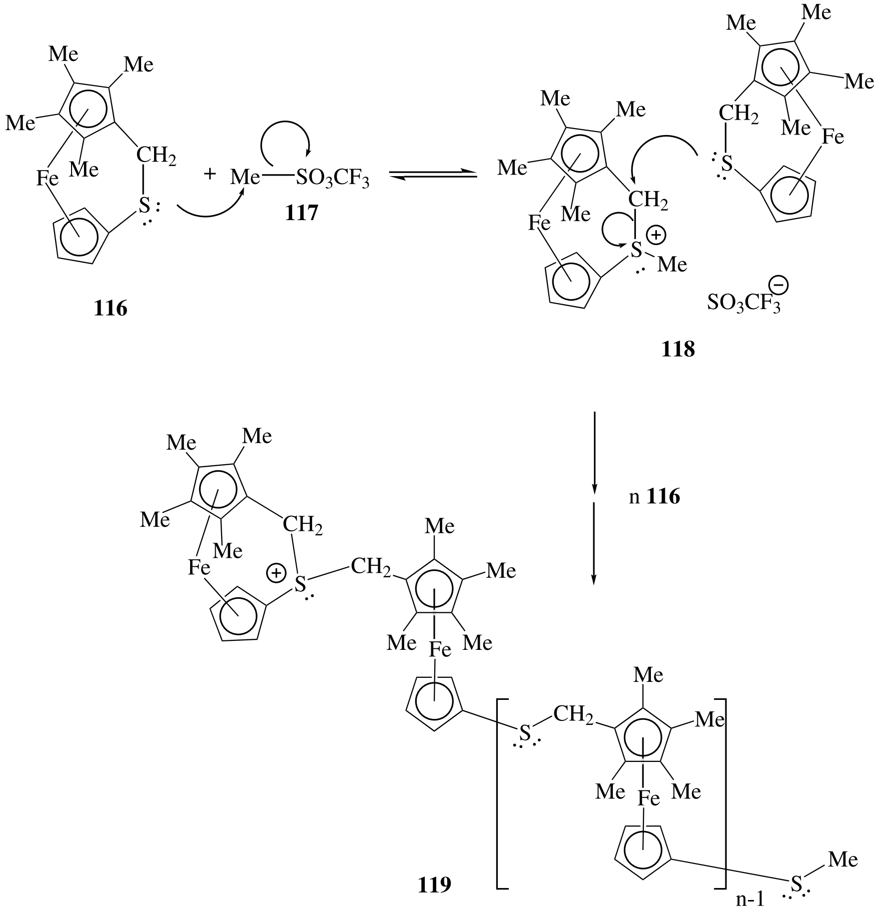
ROP of [1]thia- and [1]selena-ferrocenophanes has also been reported by Manners and coworkers [136] using thermal and anionic initiations. While insoluble poly(ferrocenyl sulfide) and poly(ferrocenyl selenide) were isolated, a low molecular weight soluble poly(ferrocenyl sulfide) was obtained when the cyclopentadienyl rings in this polymer were functionalized with a methyl group. Cyclic voltammetry showed two reversible oxidation waves at −0.07 and + 0.24 V, which indicated that there was strong electronic communication between the iron centers in these polymers [136]. [2]Ferrocenophanes with carbon–sulfur, –silicon and –phosphorus bridges have also been polymerized [137,138]. The ferrocenophane containing a C–Si bridge was resistant to thermal, anionic and transition metal-catalyzed ROP, while the phosphorus- and sulfur-containing polymers underwent thermal ROP [138]. The [2]carbathioferrocenophane (**116**) could also be polymerized in the presence of the cationic initiators methyl triflate and boron trifluoride etherate, however it was resistant to anionic and transition metal-catalyzed ROP [137,138]. When polymerization reactions were initiated with methyl triflate, oxidation of the iron centers resulted. Mechanistic studies showed that the probable initiators for the cationic polymerization reactions were Me^+ and H^+ for methyl triflate and boron trifluoride, respectively [138]. Scheme 30 shows a possible mechanism



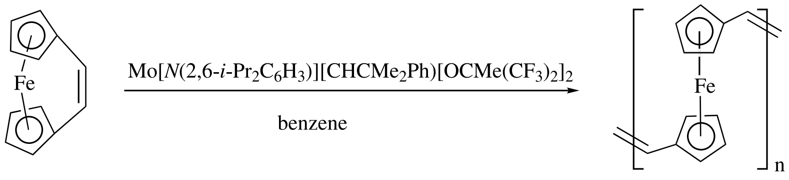
Scheme 29.

for the cationic ROP of **116** using methyl triflate (**117**) to produce the insoluble polymer **119**. Copolymerization of **116** with trimethylene sulfide allowed for the isolation of a high molecular weight soluble random copolymer [138].

Thermal ROP of [2]ferrocenophanes containing ethylene bridges has resulted in the production of poly(ferrocenylethylenes) [139,140]. When the cyclopentadienyl rings were substituted with methyl groups, ROP at 300 °C yielded a soluble polymer with a bimodal molecular weight distribution with number average molecular weights of 86,000 and 3500, respectively. Cyclic voltammetry of this polymer showed two reversible oxidation waves at −0.25 and



Scheme 30.



120

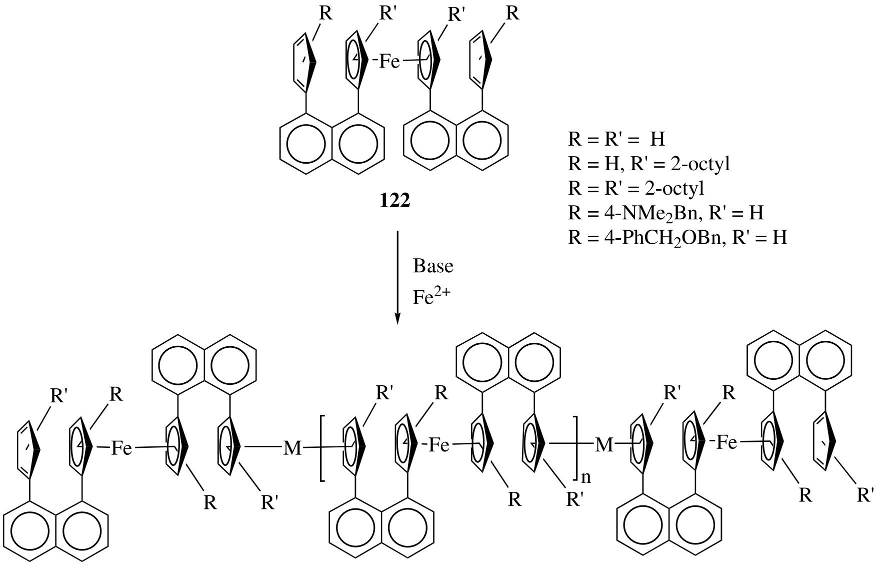
121

Scheme 31.

−0.16 V [140]. Thermogravimetric analysis yielded ferromagnetic iron carbide ceramics at 600 °C. Oxidation of this poly(ferrocenylethylene) with tetracyanoethylene (TCNE) produced soluble and insoluble fractions. Magnetic susceptibility measurements showed that there were significant antiferromagnetic interactions in the soluble fraction of the polymer [140].

Ring-opening metathesis polymerization (ROMP) of a vinyl-bridged [2]ferrocenophane has been reported by Buretea and Tilley [141]. Scheme 31 shows the ROMP of monomer **120** using a molybdenum catalyst to produce an insoluble poly(ferrocenylenevinylene) (**121**). This conjugated polymer was doped with iodine and had an electrical conductivity of 1×10^{-3} Ω^{-1} cm^{-1}. Block copolymers were produced by initiating the polymerization of norbornene and then adding monomer **120**. The resulting copolymers were partially soluble in organic solvents and had M_w and M_n values of 21,000 and 11,000, respectively. Cyclic voltammograms of the copolymer showed the presence of two reversible oxidation waves separated by 250 mV [141]. The ring-opening metathesis polymerization of [4]ferrocenophanes has also been achieved [142,143]. In 1995, Grubbs and coworkers [142] utilized tungsten- and ruthenium-based catalysts to polymerize a number of ferrocenophanes. Conjugated and non-conjugated polymers were both insoluble, and upon doping had electrical conductivities of 10^{-5} and 10^{-4} Ω^{-1} cm^{-1}, respectively. The incorporation of a vinyl ether group in the polymer backbone enhanced the polymer's solubility. Copolymerization reactions with *sec*-butylcyclooctatetraene produced soluble organoiron polymers [142]. Lee and coworkers [143] reported that soluble conjugated polymers with molecular weights greater than 300,000 were isolated when *tert*-butyl groups were attached to a vinyl group in the polymer backbone.

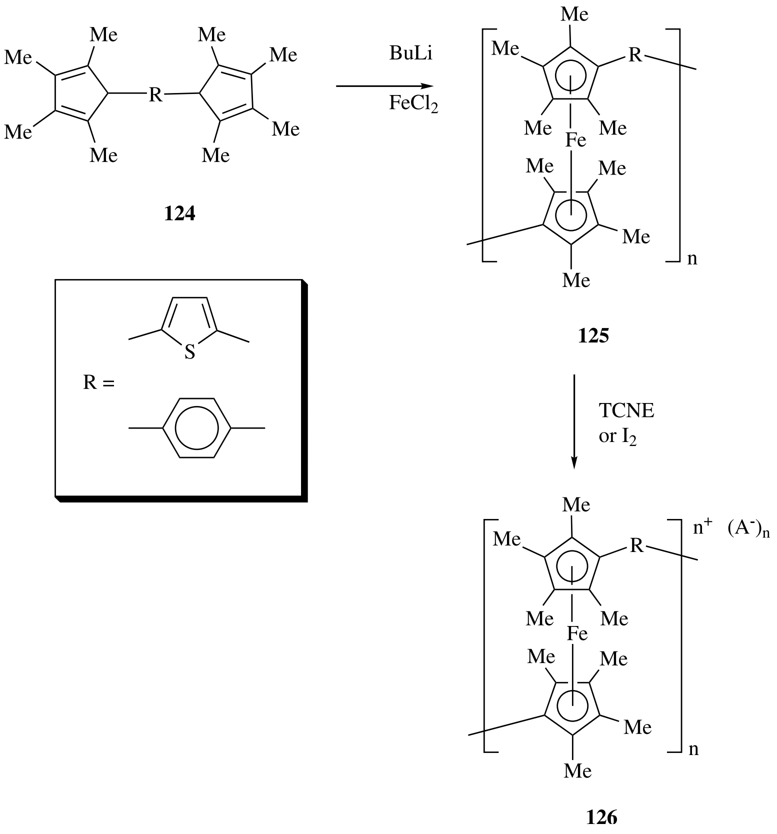
The synthesis of face-to-face polyferrocenes has been described by Rosenblum and coworkers [144–148] by reaction of 1,1′-disubstituted ferrocene complexes with naphthalene derivatives or by reaction of cyclopentadienyl-substituted naphthalene derivatives with ferrous chloride. High molecular weight soluble ferrocene-based polymers (**123**) were obtained by the reaction of monomers (**122**) with base and then by addition of a Fe(II) salt (Scheme 32) [146–148]. The solubilities of these polymers were increased by incorporating substituents on the cyclopentadienyl rings. For example, the non-alkylated polymer had a molecular weight of about 2500, when R = H, R′ = 2-octyl, the polymer's molecular weight was 18,400, and when R and R′ were 2-octyl, a molecular weight of 139,000 was obtained [146]. The elec-



122

123

Scheme 32.



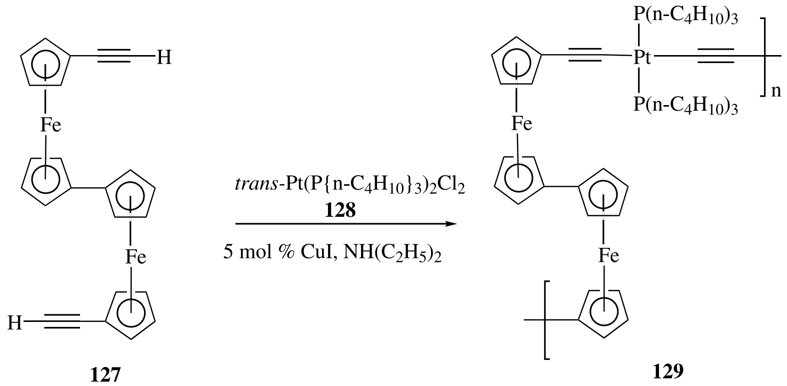
Scheme 33.

trical conductivity of polymer **123**, when R = H, R′ = 2-octyl, was less than 10^{-12} S cm^{-1}, and upon doping with iodine, it increased to 6.7×10^{-3} S cm^{-1}. The incorporation of aryl groups onto the cyclopentadienyl rings increased the solubilities and molecular weights of these polymers [148]. Oligomeric ferrocene-based materials prepared by reaction of dicyclopentadienyl-containing monomers with ferrous chloride have also been reported by Neuenschwander and coworkers [149].

Southard and Curtis [150–152] have utilized a similar methodology to prepare conjugated ferrocene-based polymers (Scheme 33). The formation of conjugated polymetallocenes was accomplished by reaction of an isomeric mixture of dilithio bis(3-hexyl-4-methylcyclopentadienide) arylenes with ferrous iodide [150,151]. The weight average molecular weights of these polymers were between 42,000 and 52,600, with PDI values between 10.5 and 14.6. The electrical conductivities of these polymers ranged from 10^{-10} to 10^{-7} S cm^{-1} upon doping. Scheme 33 shows the reaction of bis(tetramethylcyclopentadienyl)arenes (**124**) with anhydrous ferrous iodide or chloride to produce insoluble polymers (**125**) [152]. These polymers were oxidized with tetracyanoethylene or iodine in dichloromethane to afford soluble ferrocenium-based materials (**126**). Magnetic susceptibility measurements of the oxidized polymers were consistent with antiferromagnetic coupling or ferromagnetic interactions [152].

The synthesis of conjugated polyferrocenes has been the focus of numerous investigations, however, these polymers are often insoluble and have low molecular weights [153–159]. One of the methods utilized to prepare this class of polymer involves the reaction of ethynyl monomers with halogen-substituted monomers [154–158]. Ferrocene-based oligomers containing dithiafulvene moieties in the backbone have been prepared by the cycloaddition polymerization of 1,1′-bis(trimethylsilylethynyl)ferrocene with aldothioketone [156]. The resulting low molecular weight conjugated polymer formed a soluble charge-transfer complex with TCNQ, and upon doping with iodine had an electrical conductivity of 3.6×10^{-3} S cm^{-1}. The synthesis of polymers containing ferrocene and platinum units in the backbone was reported by Long et al. (Scheme 34) [156]. Reaction of the biferrocene monomer **127** with the *trans*-dichloroplatinum complex (**128**) allowed for the production of a polymer with a broad molecular weight distribution and an M_w of 11,800. The molecular weight of this mixed-metal polymer was limited by its poor solubility during the polymerization reaction [156].

The palladium-catalyzed coupling of 1,1′-diiodoferrocene (**130**) with diethynyl monomers (**131a–131d**) has been used by Yamamoto et al. [157,158] to synthesize conjugated polyferrocenes (**132a–132d**) (Scheme 35). Polymers **132a** and **132b** exhibited very limited solubilities in organic solvents, although **132b** was soluble in formic acid. The introduc-



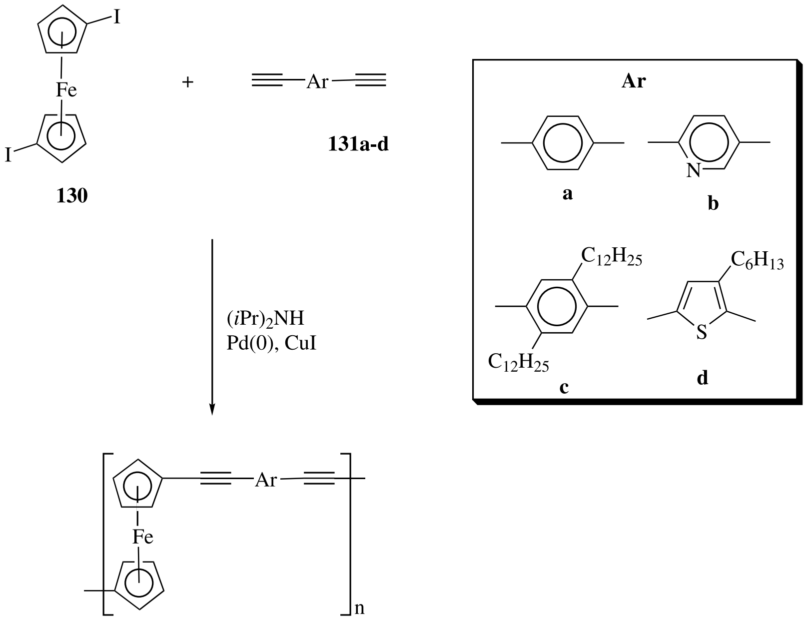
127 **129**

Scheme 34.

tion of alkyl groups into the monomers resulted in the isolation of soluble polymers **132c** and **132d**. Light scattering analysis of the chloroform-soluble fractions of **132b** and **132d** provided M_w values of 21,000 and 34,000, respectively. However, GPC analysis of these polymers indicated that their weight average molecular weights were 5700 and 5800 [158]. The oxidation of polymers **132a** and **132b** was studied with iodine, and the Mössbauer spectrum of polymer **132a** indicated the presence of Fe(II) and Fe(III) centers, while the spectrum of **132b** showed that ferrocenium complexes were not formed, since only Fe(II) signals were observed. Undoped polymers had electrical conductivities around 10^{-12} S cm^{-1}, while doping with iodine or sodium led to conductivities ranging from 10^{-7} to 10^{-5} S cm^{-1}.

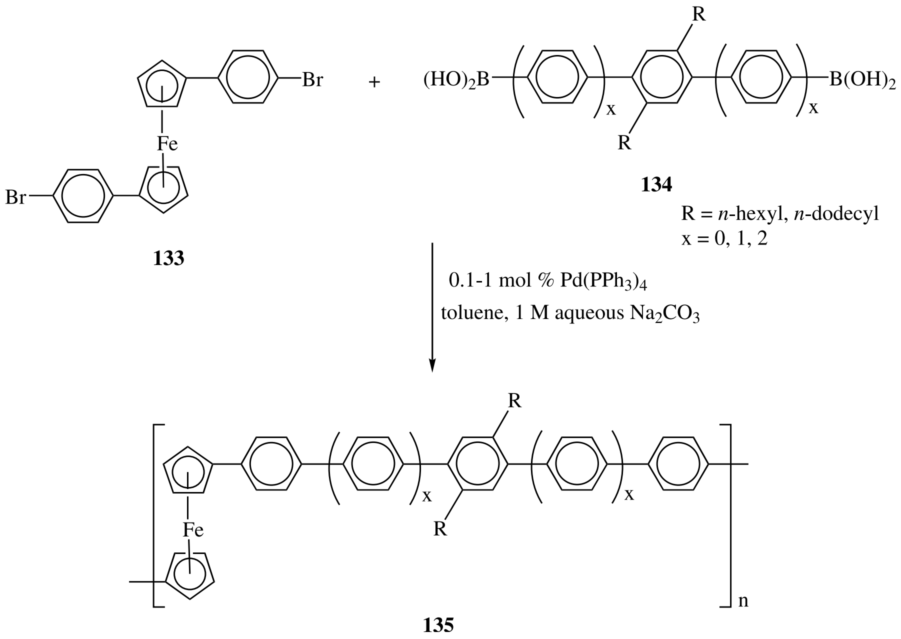
Deck et al. [159] have reported the synthesis of conjugated ferrocene-based polymers with fluorinated arene spacers by reaction of dilithioferrocenes with hexafluorobenzene. These polymers exhibited low solubilities; however, the incorporation of a tertiary amine on the ferrocene ring increased their solubilities such that an oligomer with nine iron centers in its backbone could be identified. Scheme 36 shows the palladium-catalyzed polycondensations of 1,1′-bis(p-bromophenyl)ferrocene (**133**) with oligophenylene diboronic acid derivatives (**134**) [160]. These reactions resulted in the production of polymers (**135**) with degrees of polymerization as high as 62. Increasing the length of the phenylene spacers in the polymer backbones resulted in polymers whose soluble portions possessed lower molecular weights. While both the polymers with $x = 0$ remained in solution during the polymerization reactions, when $x = 1$, only the dodecyl-substituted polymer remained in solution, and when $x = 2$, both the hexyl- and dodecyl-functionalized polymers precipitated from solution.

Plenio et al. [161,162] have reported the synthesis of conjugated homoannular polyferrocenes (**137a–137c**) by the Sonogashira coupling of the ferrocene monomers



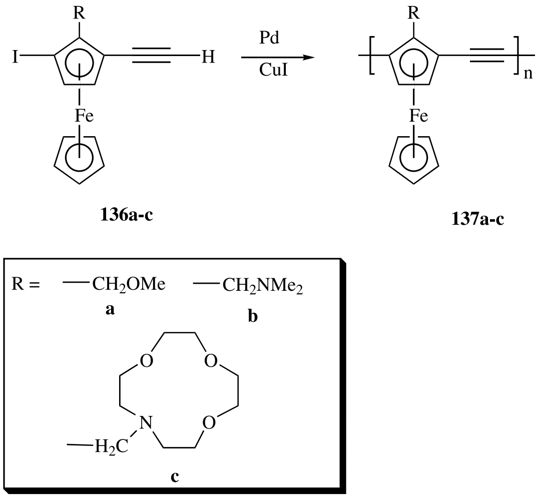
132a-d

Scheme 35.



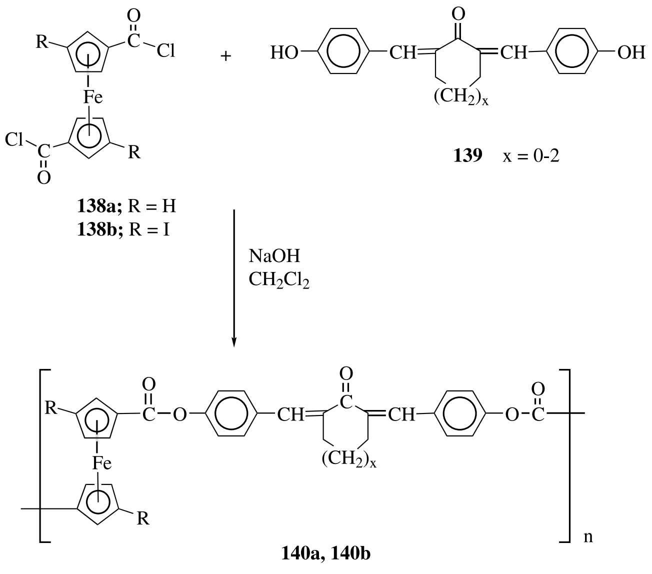
Scheme 36.

136a–136c as shown in Scheme 37. The synthesis of a chiral iodoferroceneacetylene monomer (**136a**) followed by its polymerization produced a soluble polymer (**137a**) [161]. This polymer (**137a**) was optically active with $[\alpha] = -198.0$ per ferrocene unit. Analysis of monomer **136a**, low molecular weight oligomers and polymer **137a** by UV–Vis spectroscopy showed that there was a linear relationship between the λ_{max} values of the d–d transitions and the number of ferrocene units in these materials, which is consistent with its conjugated backbone. In addition, cyclic voltammetry of the polymer showed two redox waves, which suggested that the iron centers were interacting [161]. Diastereomeric mixtures of monomers **136b** and **136c** were also polymerized to yield the soluble amine-substituted poly(ferrocenylacetylides) **137b** and **137c** [162]. GPC-LALLS analysis of polymer **137b** indicated a bimodal distribution with M_w values of 3700 and 7100. Analysis of **137c** provided an M_w of 61,000; however, this molecular weight may have been overestimated due to aggregation of polymer chains.



Scheme 37.

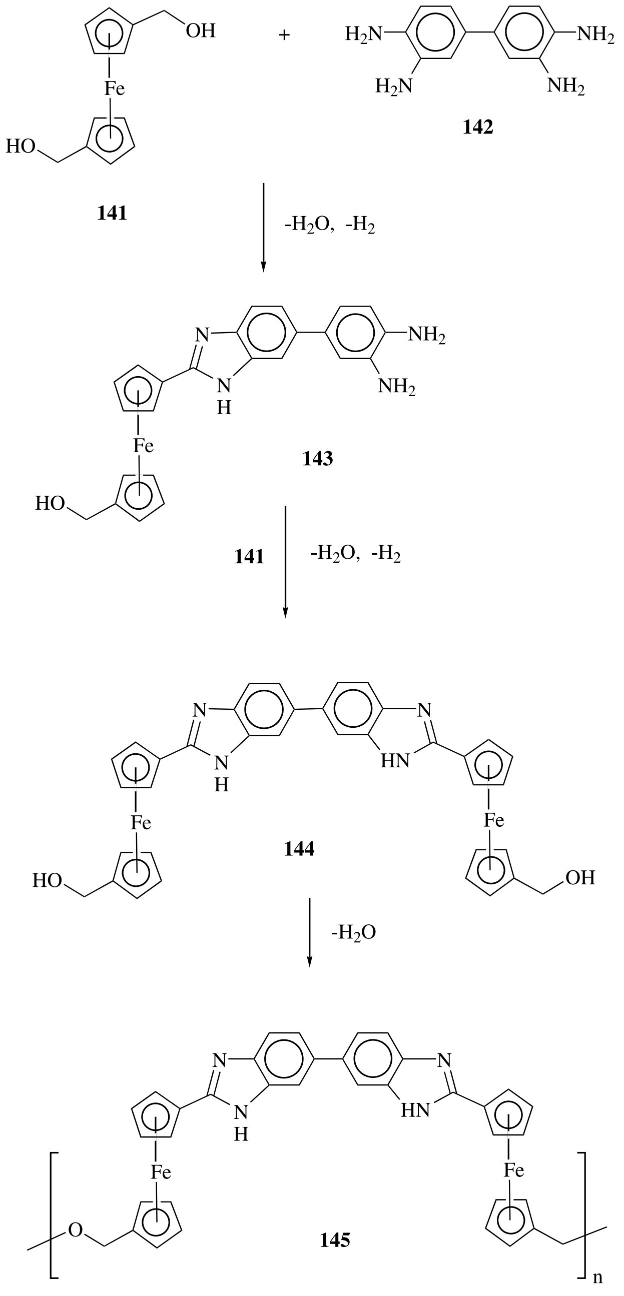
The first ferrocene-based polyesters and polyamides were synthesized by Knobloch and Rauscher in 1961 [163]. Rausch and coworkers [164–168] reported the synthesis and polymerization of a number of new classes of ferrocene derivatives in the 1980s. Polyamides, polyesters, polyureas and polyurethanes were synthesized in these studies and the properties of these materials were examined. The properties of this class of polymer are still receiving considerable attention, even though high molecular weights are not always obtained. It has been reported that the fire retardant properties of polyurethanes can be enhanced by incorporating ferrocenyl groups in the polymer backbone [169]. The electrochemical properties of polyurethanes with polyether spacers in the backbone have also been described [170]. The electrical conductivity and thermal stability of ferrocene-based polyesters has been examined by Abd-Alla et al. (Scheme 38) [171]. It was reported that the interfacial polymerization of **138a** and **138b** with **139** resulted in the isolation of **140a** and **140b**. Increasing the number of CH_2 groups in the polymer backbone increased the solubilities of these materials. The polymers with iodo groups on the cyclopentadienyl rings (**140b**) were less soluble than **140a**, however the iodine-substituted polymers exhibited higher thermal stability. X-ray diffraction studies showed that these were mostly amorphous polymers; however, there were crystalline domains in each. The electrical conductivities of these polymers increased at higher temperatures [171].



Scheme 38.

In 1964, Plummer and Marvel [172] reported the synthesis of a polybenzimidazole-containing ferrocene moieties in the backbone. This polymer had an inherent viscosity of 0.20 in 0.2% formic acid. A polybenzimidazole-containing ferrocenyl units in its backbone (**145**) was recently synthesized by the 1:2 polycondensation of 1,1′-ferrocenedimethanol (**141**) with 3,3′,4,4′-biphenyltetraamine (**142**) in the presence of [$RuCl_2(PPh_3)_3$] [173]. Scheme 39 shows the mechanism proposed by Osakada, Yamamoto and coworkers for polymer formation. GPC analysis of polymer **145** provided a weight average molecular weight of 45,000 and a number average molecular weight of 21,000. Mössbauer spectroscopy showed that ca. 20% of the iron centers were in the Fe(III) state due to their oxidation by the catalyst during the polymerization reaction. Electrochemistry of polymer **145** showed that irreversible oxidation of the iron centers occurred due to deprotonation of the nitrogen atoms in the polymer backbone [173].

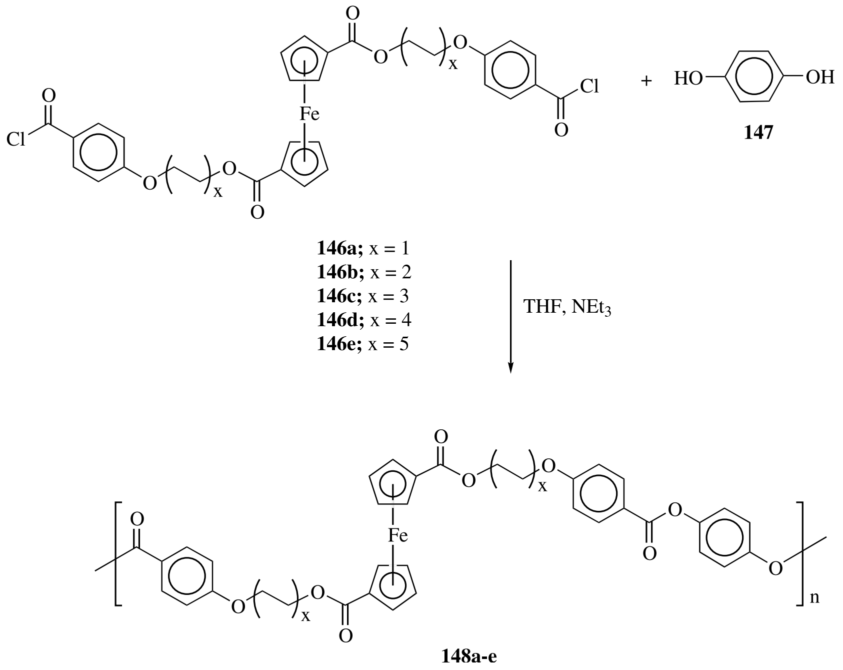
The properties of main-chain ferrocene-based polymers prepared by polycondensation reactions range from nonlinear optical activity [174–176] to liquid crystallinity [177–181]. Ferrocene-containing liquid crystalline polyesters were first reported in 1989 by Singh et al. [177]. The strategy used to synthesize liquid crystalline polymers generally involves the incorporation of flexible and rigid spacers into the polymer backbone [178–181]. Senthil and Kannan [179,180] have recently reported the synthesis of liquid crystalline ferrocene-based polymers containing phosphate groups in their backbones. These phosphorus-containing polymers had high char yields. Scheme 40 shows the synthesis of polyesters **148a**–**148e** by the polycondensation of the ferrocene-containing complexes **146a**–**146e** with hydroquinone (**147**) [181]. Examination of these polymers under a polarizing microscope showed that they all exhibited anisotropic properties. Polymers **148d** and **148e**, with the longest aliphatic spacers in their backbones, possessed nematic schlieren textures, while polymers **148a**–**148c**, with shorter aliphatic spacers, had grainy textures. The duration of the liquid crystalline domains decreased as the number of methylene spacers in the polymer backbone increased [181].



Scheme 39.

3.2. Bis(cyclopentadienyliron) in the side chain

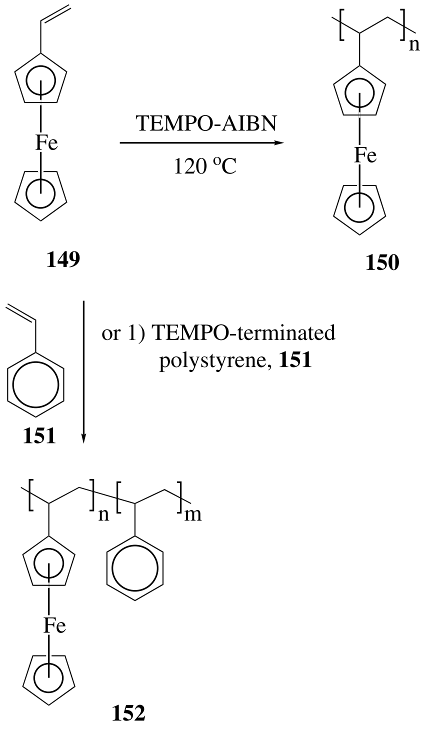
Poly(vinyl ferrocene) and its copolymers with methylmethacrylate, styrene and chloroprene were first reported in 1955 by Arimoto and Haven [12]. In the 1970s, Pittman and coworkers [182–187] and George and Hayes [188,189] described the homo- and co-polymerization of vinyl fer-



Scheme 40.

rocene in detail and reported the rate laws for these reactions. For example, the rate law for the radical-initiated homopolymerization of vinylferrocene did not follow the classic one-half order in initiator concentration that most organic systems follow [187–189]. Pittman reported the homo- and co-polymerization of vinylferrocene with a large number of organic monomers and found that the molecular weight of poly(vinylferrocene) does not increase with a decrease in initiator concentration [182–186]. High molecular weight poly(vinylferrocenes) were produced by adding the radical initiator azobisisobutyronitrile (AIBN) at different stages of the polymerization reactions [185]. In addition, when the reaction temperature was lowered from 80 to 60 °C, higher molecular weight materials were isolated. It was determined that the high molecular weight portions of these materials were branched. The electrical conductivities of poly(vinylferrocene) and poly(3-vinylbisfulvalenediiron) were also examined [190,191]. Upon oxidation of poly(3-vinylbisfulvalenediiron) with TCNQ, the conductivity of this polymer increased to between 6×10^{-3} and 9×10^{-3} Ω^{-1} cm^{-1} [191].

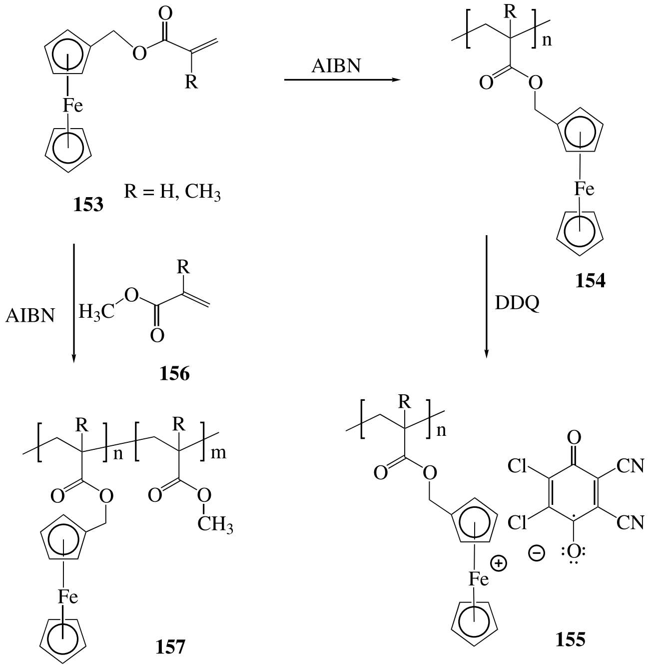
The homo- and co-polymerization of vinylferrocene (**149**) using the radical initiator 2,2,6,6-tetramethyl-1-pyperidinyl-1-oxy (TEMPO) has recently been reported by Frey and coworkers (Scheme 41) [192]. Homopolymerization reactions afforded relatively low molecular weight poly(vinylferrocene) (**150**), while copolymerization of vinylferrocene with styrene (**2**) or TEMPO-terminated polystyrene (**151**) afforded random or block copolymers (**152**), respectively. Random copolymers incorporating 42 mol% of vinylferrocene were isolated with number average molecular weights as high as 10,000. Block copolymers possessing narrow polydispersities were available using this living-radical initiator, and M_n values between 10,900 and 17,600 were obtained. Differential scanning calorimetry showed that there were two glass transition temperatures in these materials between 109 and 123 °C and between 163 and 167 °C, corresponding to the polystyrene and poly(vinylferrocene) blocks, respectively [192].



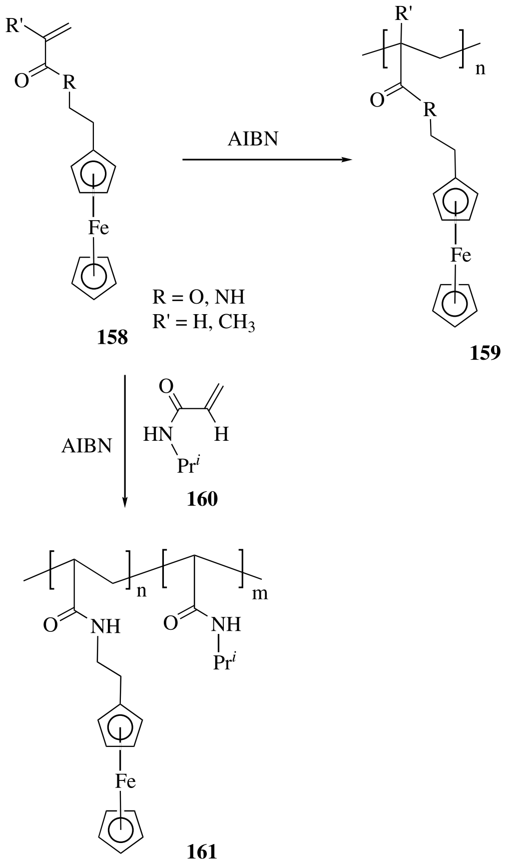
Scheme 41.

Copolymerization of small quantities of vinylferrocene with *N*-ethyl- or *N*,*N*-diethyl-acrylamide resulted in high molecular weight thermosensitive polymers [193]. Increasing the amount of poly(vinylferrocene) in these materials decreased their lower critical solution temperatures (LCST), while chemical oxidation of the iron centers with cerium sulfate resulted in increased LCST values. An interesting example involving grafting a copolymer of poly(vinylferrocene) onto the surface of carbon fiber was recently described by Tsubokawa et al. [193]. Reaction of the copolymers in the presence of aluminum chloride, aluminum powder and carbon fiber resulted in 46.1% of the polymer being grafted to the carbon surface. These reactions involved a ligand exchange reaction between the terminal cyclopentadienyl ring of the poly(vinylferrocene) with the polycondensed aromatic rings of the carbon fiber [194]. Rausch and coworkers [195] reported that the reaction of ferrocene with acetone in the presence of aluminum chloride produced oligomeric poly(isopropenylferrocene). The structure of this polymer was consistent with poly(isopropenylferrocene) prepared by cationic initiation of the vinyl monomer isopropenylferrocene [196]. However, the cationic-initiated polymerization of α-hydroxyisopropylferrocene produced poly (α-hydroxyisopropylferrocene) in which the cyclopentadienyl rings were homo- and hetero-annularly substituted [195]. In the IR spectrum of this polymer, there was no evidence of an absorbance corresponding to hydroxyl groups.

Pittman et al. [197–201] were also researching the polymerization of ferrocene-substituted acrylates and methacrylates. The incorporation of ferrocene moieties into these classes of polymers resulted in materials with much higher glass transition temperatures than their organic analogs [197]. For example, radical polymerization of ferrocenylmethyl acrylate (**153**, R=H) allowed for the isolation of polymer **154**, which had a T_g about 200 °C higher than that of polymethylacrylate [197]. Oxidation of **154** with dichlorodicyanoquinone (DDQ) or *o*-chloroanil led to the production of charge-transfer complexes (**155**) [197,198]. Mössbauer spectroscopy showed that ca. 50% of the iron centers were in the oxidized ferrocenium state. The reactivity ratios of the copolymerization of ferrocenylmethyl acrylate and ferrocenylmethyl methacrylate with styrene, methyl acrylate, methyl methacrylate and vinyl acetate have also been determined [199] (see Scheme 42).

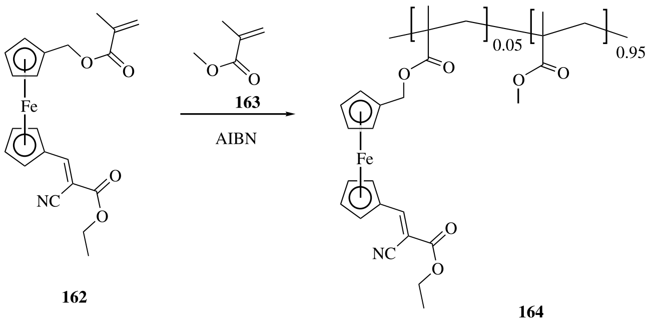


Scheme 42.



Scheme 43.

The homo- and co-polymerizations of 2-ferrocenylethyl acrylate and methacrylate (**158**, R = O) were also reported by Pittman's group in the 1970s [200,201]. It was found that both 2-ferrocenylethyl acrylate and 2-ferrocenylethyl methacrylate were more reactive than ferrocenylmethyl acrylate (**153**). The polymerizations of 2-ferrocenylethyl methacrylate, acrylate, methacrylamide and acrylamide (**158**) were recently reported to produce high molecular weight polymers (**159**) using AIBN as the initiator (Scheme 43) [202]. Copolymerization of 2-ferrocenylethylacrylamide (**158**, R′ = NH, R=H) with isopropylacrylamide (**160**) resulted in a water-soluble polymer

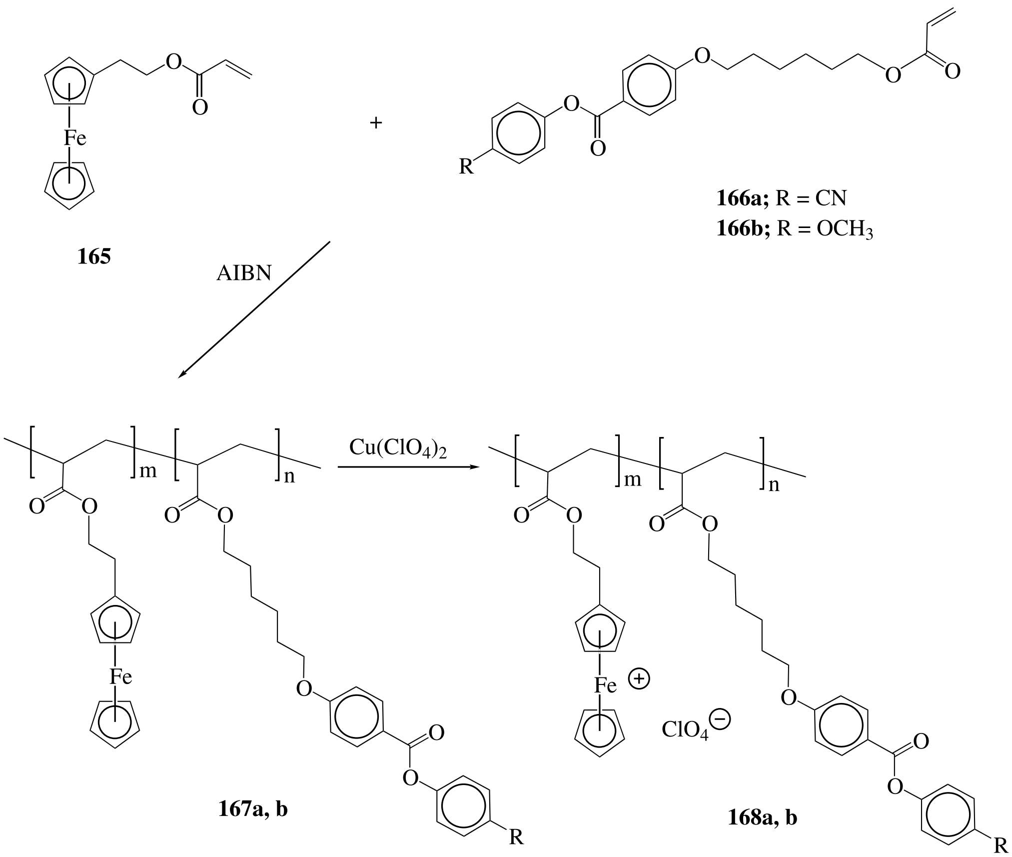


Scheme 44.

(**161**) in which the *n*:*m* ratios were 1:200, 1:100 and 1:50. These thermally sensitive polymers had LCST values of 28.6, 27.2 and 26.0 °C, respectively, as the ratios of organoiron to organic units in the polymer side chains increased [202].

The synthesis of organoiron polymethacrylates with nonlinear optical properties has been described by Wright et al. [203]. Scheme 44 shows the copolymerization of the ferrocenyl-functionalized monomer (**162**) with methylmethacrylate (**163**) resulting in the production of polymer **164** with ferrocenyl groups in the side chain. The efficiency of the second-harmonic-generation activity exhibited by the copolymer was ca. four times greater than that of a quartz standard.

The syntheses of liquid crystalline polymers with ferrocene units in the side chain have also been examined [204–209]. Deschenaux et al. [204,205] have reported the synthesis of organoiron-containing thermotropic side chain liquid crystalline polymethacrylates and polysiloxanes. Zentel and coworkers [206,207] have described the synthesis of polymers with azoxybenzene groups in the backbone and ferrocenyl groups in the side chain by polycondensation reactions. These polymers exhibited smectic A phases with low ferrocene incorporation; however, above 25 mol%, nematic phases were observed [207]. The liquid crystalline properties of polyacrylate ionomers with ferrocene-containing side chains have also been described [208,209]. Scheme 45 shows the free radical polymerization of monomer **165** with **166a** and **166b**, which resulted in the production of polymers **167a** and **167b**. These polymers had M_w values ranging from 15,500 to 43,800, depending on the reaction conditions employed [208]. Polymer **167a** exhibited nematic and isotropic phases, while polymer **167b** exhibited smectic A, nematic and isotropic phases. Oxidation of the ferrocenyl groups was achieved in the presence of copper(II) perchlorate or benzoquinone to produce ionomers such as **168a** and **168b**. Following oxidation, the perchlorate ionomer was unstable above 100 °C, whereas the sulfate ionomer exhibited higher thermal stability. Polymers **168a** and **168b** formed clusters and segregated from the liquid crystalline phase. The incorporation of four alkyl



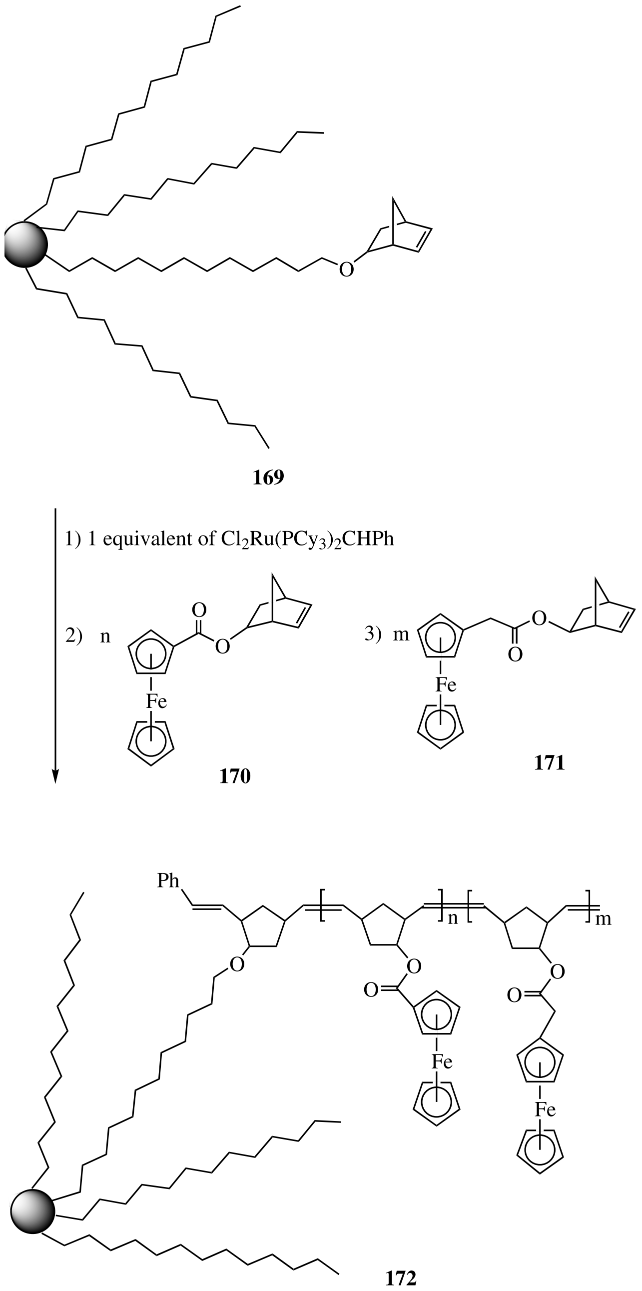
Scheme 45.

substituents on the cyclopentadienyl rings increased the stability of the ferrocenium-based polymers relative to **168a** and **168b** [209].

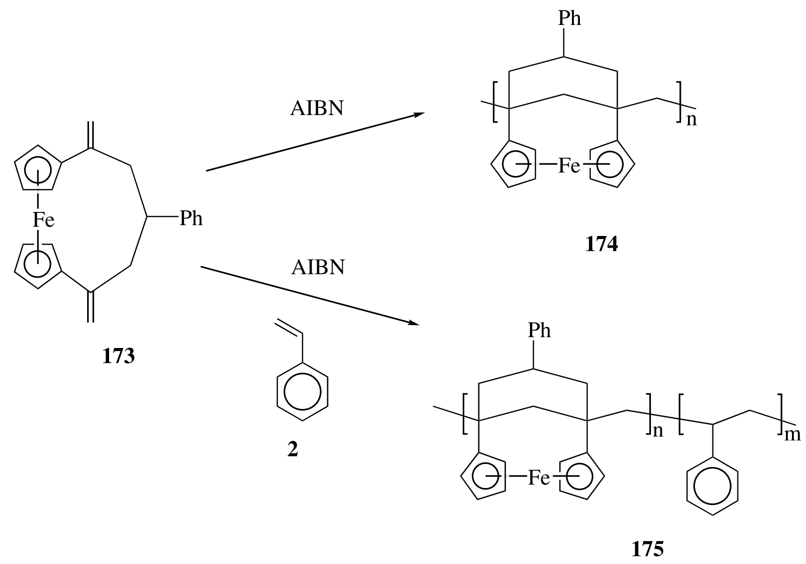
The ring-opening metathesis polymerization of norbornene monomers functionalized with ferrocenyl groups and the use of metathesis catalysts substituted with ferrocene moieties has allowed for the production of polynorbornenes functionalized with organoiron groups [210,211]. Termination of the polymerization reactions by addition of octamethylferrocenecarboxaldehyde also allowed for the incorporation of redox active sites within the polymers. Block copolymers of polynorbornene have also been reported by Nguyen, Mirkin and coworkers [212]. Monomer **169** was prepared by reaction of 3 nm gold particles with 1-dodecanethiol and 1-mercapto-10-(*exo*-5-norbornen-2-oxy)decane in a 3:1 ratio. Reaction of the norbornene groups on the gold nanoparticles with the ruthenium carbene catalyst, $Cl_2Ru(PCy_3)_2CHPh$, followed by consecutive additions of 20 equivalents of **170** and **171** resulted in the isolation of the block copolymer **172** shown in Scheme 46. TEM analysis of homopolymers prepared using a similar strategy showed that the hybrid particles were still about 3 nm in diameter [212].

The radical and cationic cyclopolymerization of 3-phenyl[5]ferrocenophane-1,5-dimethylene (**173**) was studied by Glatzhofer and coworkers (Scheme 47) [213]. Cationic initiators yielded oligomeric species, while AIBN-initiated polymerizations resulted in M_n values as high as 20,800 and polydispersities of about 4. The resulting polymer (**174**) had a [3]ferrocenophane pendent to the polymer backbone. Copolymerization of **173** with styrene produced a low molecular weight copolymer (**175**) in which there were ca. twice as many styrene units as organoiron units. Cyclic voltammetry of polymer **174** showed the presence of two redox waves at -0.13 and $+0.05$ V, indicating that there may be electronic communication between the iron centers. However, copolymer **175** showed only one reversible redox wave at -0.10 V. The electrical conductivities of polymers **174** and **175** were between 10^{-9} and 10^{-8} S cm^{-1}. Doping of **174** and **175** with iodine under argon resulted in an increase in their conductivities to 5.3×10^{-5} and 1.6×10^{-6} S cm^{-1}, respectively. Under ambient conditions, the polymer films exhibited better strength and their doped analogs had conductivities of 7.6×10^{-4} and 9.5×10^{-5} S cm^{-1}, respectively.

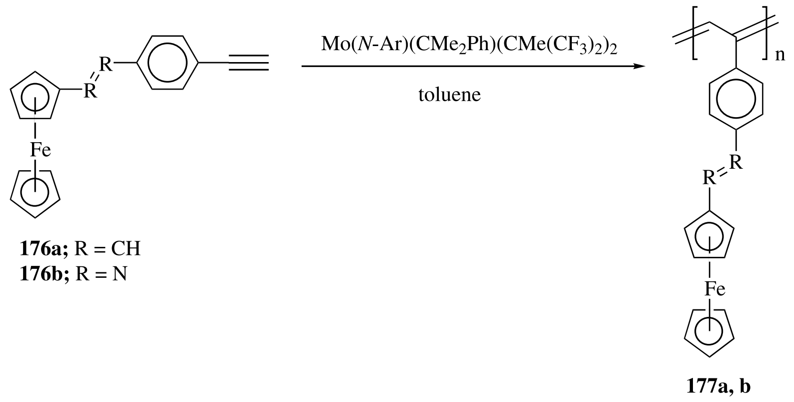
Polyacetylenes with pendent ferrocene groups have been prepared by living metathesis polymerization of acetylene-substituted monomers [214–217]. Scheme 48 shows the polymerization of monomers **176a** and **176b** to produce polymers **177a** and **177b** using molybdenum-based catalysts [215]. NMR analysis indicated that the polymerization reactions proceeded via head-to-tail propagation. Polymer **177b** was soluble up to a degree of polymerization of 60, and an M_n of about 19,000. The solubility of the azobenzene-containing polymer was lower, possibly due to inter- and intra-molecular interactions of the diazene group with other functionalities. The wavelength maxima for polymer **177b** increased with increasing molecular weights; however, the λ_{max} values of polymer **177a** decreased as the degree of polymerization increased [215]. Buchmeiser and coworkers [217] have also described the use of this class of polymer in ion exchange chromatography. Living polyacetylene was grafted to a norbornene-functionalized silica support and the iron centers were then oxidized with iodine to give the corresponding ferrocenium complexes. These organoiron-grafted supports were utilized to separate oligodeoxythymidylic acids using sodium chloride-acetonitrile as the mobile phase. These anion exchange columns lost a great deal of their resolving power within 2–3 days; however, utiliza-



Scheme 46.



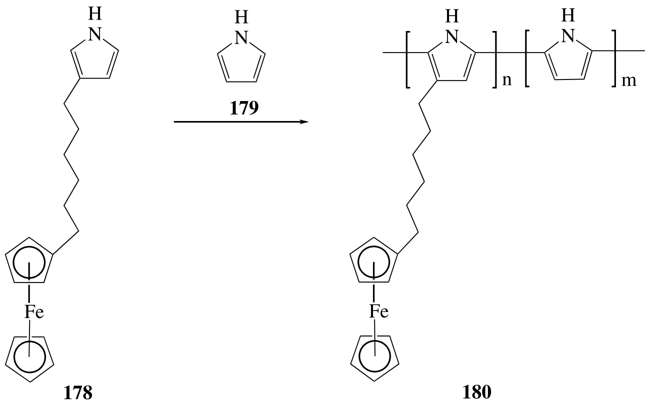
Scheme 47.



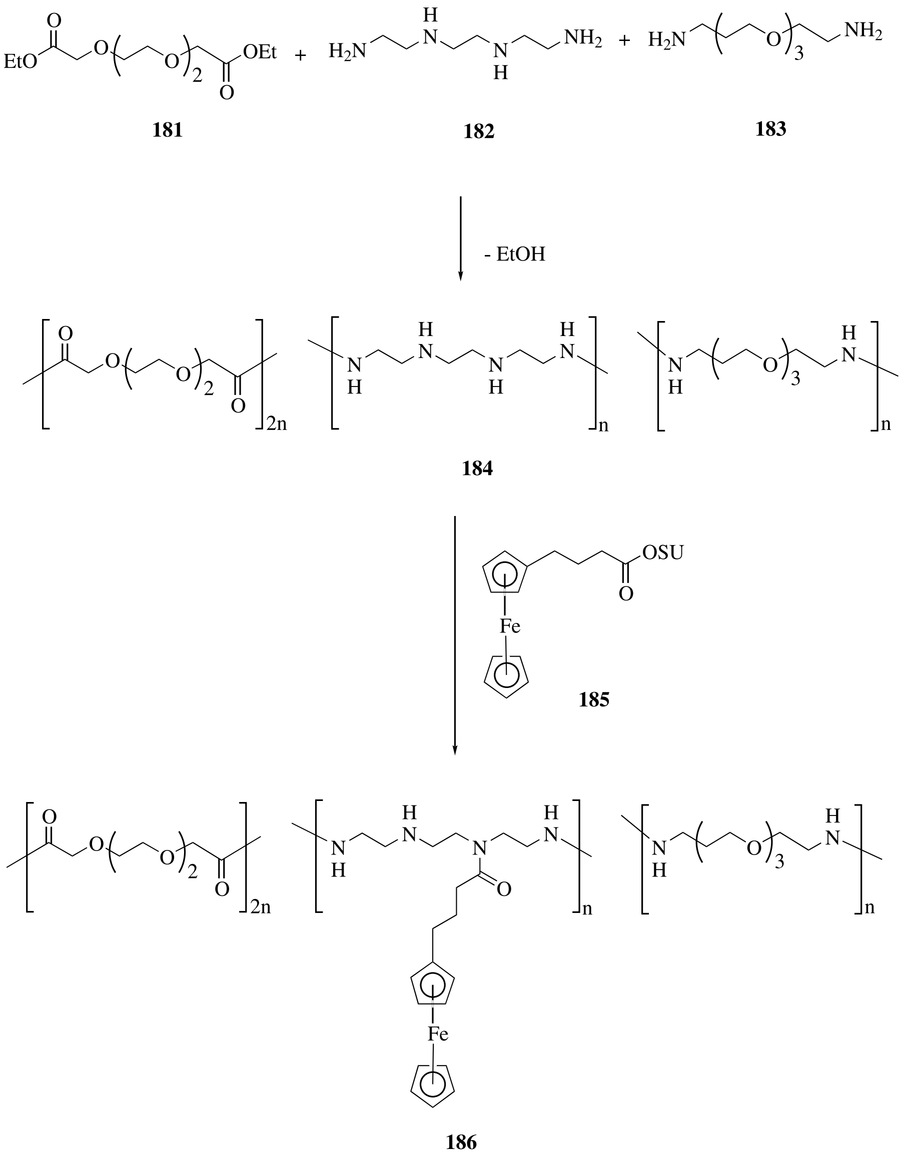
Scheme 48.

tion of an octamethylferrocene derivative allowed for good column resolution for 7–10 days [217].

The electrical conductivities of polypyrroles and polythiophenes containing ferrocene moieties as pendent groups have been reported by Zotti et al. [218,219]. These conjugated organoiron polymers were synthesized electrochemically, and copolymers with pyrrole and thiophene were also examined. Scheme 49 shows the copolymerization of the organoiron pyrrole monomer (**178**) with pyrrole (**179**) to produce polymer **180** [218]. The redox conductivity of **180** was determined to be 1.5×10^{-2} S cm^{-1}. The polymerization of ferrocenyl-substituted thiophenes has also been



Scheme 49.

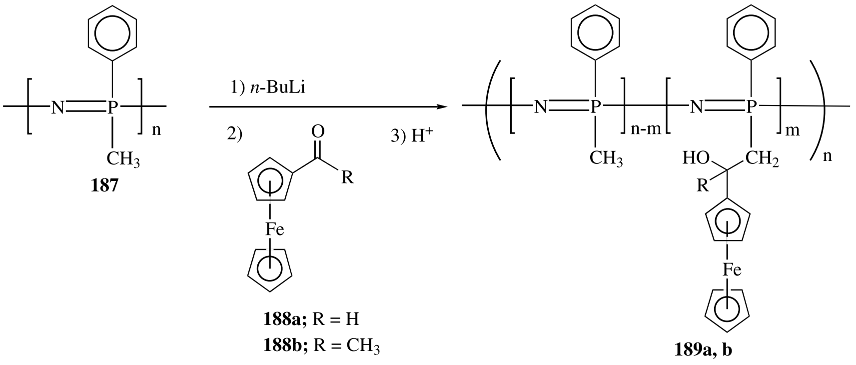


Scheme 50.

examined. The in situ conductivity of a polythiophene containing a side chain ferrocene group was measured to be 40 S cm^{-1}. As the lengths of the spacers between the ferrocene moieties and the polythiophene backbones increased, there was a corresponding decrease in the redox conductivities of these materials [218,219].

Neuse and coworkers [220–225] have studied the use of ferrocene-containing polymers as drugs in cancer research. It has been reported that water-soluble polymers containing ferrocene groups bonded to the polymer backbone via ester or amide linkages possess antiproliferative properties. Ferrocenium salts can react with radical oxygen species, and convert them into less harmful materials. The reaction of the organic polymer (**184**) with the *N*-hydroxysuccinimide ester of 4-ferrocenylbutanoic acid (**185**) afforded a water-soluble polymer (**186**) that contained one ferrocene group in every repeat unit (Scheme 50) [222].

Polyphosphazenes containing ferrocene moieties as pendent groups have been the focus of numerous investigations [226–232]. Allcock et al. [226–230] reported the synthesis of a large number of interesting organoiron polymers by ROP of cyclic phosphazene monomers functionalized with ferrocenyl substituents. The ferrocene moieties were attached to the phosphorus atoms in the polymer backbones via either one or both of their cyclopentadienyl rings. Wisian-Neilson and Ford [231,232] prepared ferrocene-containing polyphosphazenes by reaction of a preformed polyphosphazene with ferrocene derivatives. Scheme 51 shows the reaction of poly(methylphenylphosphazene) (**187**) with 0.5 equivalent of *n*-BuLi, which caused deprotonation of the methyl groups. The resulting anions were then reacted with ferrocenecarboxaldehyde (**188a**) and acetylferrocene (**188b**) to produce the corresponding ferrocene-functionalized polymers **189a** and **189b**. The presence of ferrocenyl groups



Scheme 51.

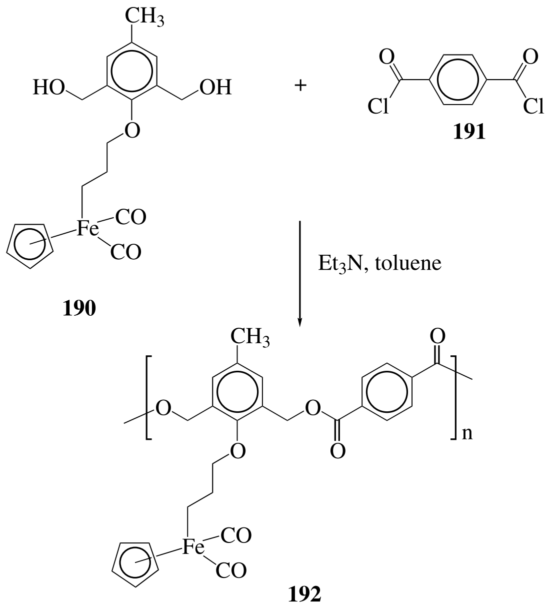
pendent to the backbones of these polymers increased their glass transition temperatures [232]. For example, when polymer **189b** had 23% of its methyl groups substituted with the organoiron functionalities, its T_g was 65 °C, and its T_g was 87 °C when 36% of the side chains were functionalized.

3.3. Cyclopentadienyliron carbonyls

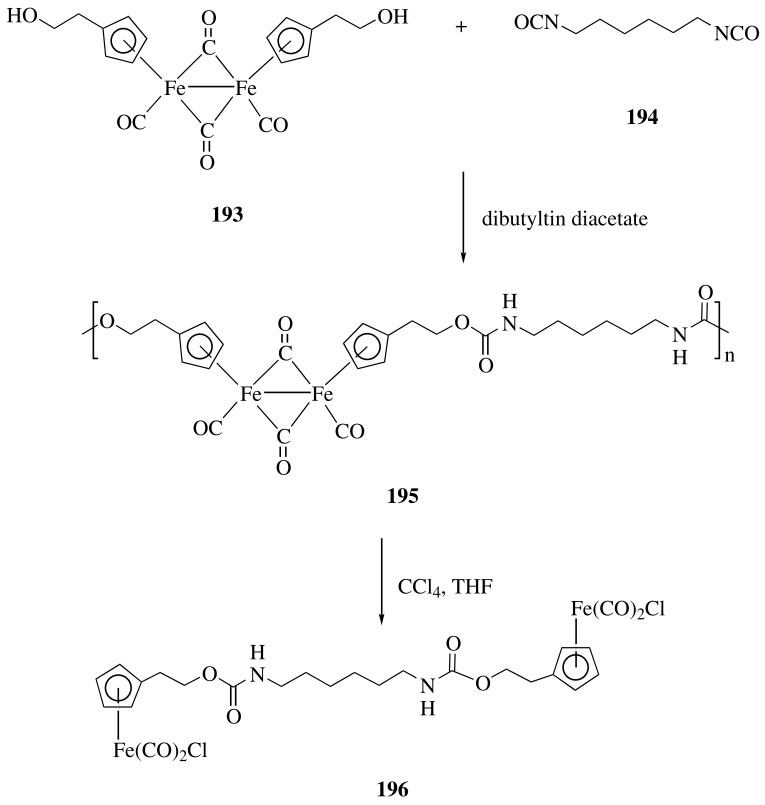
The synthesis of polymers with cyclopentadienyliron dicarbonyl units in the side chains has been reported by Mapolie et al. [233,234]. These polymers were prepared either by the radical polymerization of vinyl monomers or by polycondensation reactions of phenolic monomers. Radical-initiated homo- and co-polymerization reactions of olefinic organoiron monomers with styrene yielded the corresponding organometallic polymers [233]. More recently, reaction of the organoiron monomer (**190**) with terephthaloyl chloride (**191**) produced the low molecular weight oligomer **192** [234]. The reaction yielded soluble and insoluble fractions that had similar IR spectra. When the polycondensation reactions were conducted for 2 or 24 h, similar molecular weights were obtained; however, a larger fraction of insoluble material was isolated after 24 h. Polymer **192** experienced an 8% weight loss starting at 82 °C, which corresponded to loss of the carbonyl ligands on iron [234]. Hanks and coworkers [235,236] have reported the chemical and electrochemical oxidative polymerization of dicarbonyl(η^5-cyclopentadienyl)(η^1-pyrrolyl)iron(II). The electrochemically generated polymers did not conduct electricity, whereas chemical oxidation of the monomer yielded polymers with electrical conductivities as high as 0.25 S cm^{-1}. Refluxing the polypyrrole in solution resulted in loss of carbonyl ligands and the generation of an azaferrocene polymer [236] (see Scheme 52).

Tyler and coworkers [237–240] have examined the synthesis of polyurethanes containing iron–iron bonds in their backbones. Oligomeric urethanes and ether-urethanes containing photodegradable iron–iron bonds in their backbones were synthesized by polycondensation reactions of iron-containing monomers bearing terminal hydroxyl groups with isocyanates. Scheme 53 shows the reaction of monomer **193** with hexamethylene diisocyanate (**194**), resulting in the formation of polymer **195** [237,238]. Photochemical degradation of **195** with carbon tetrachloride resulted in cleavage of the iron–iron bonds and the production of the bimetallic complex **196** [238].

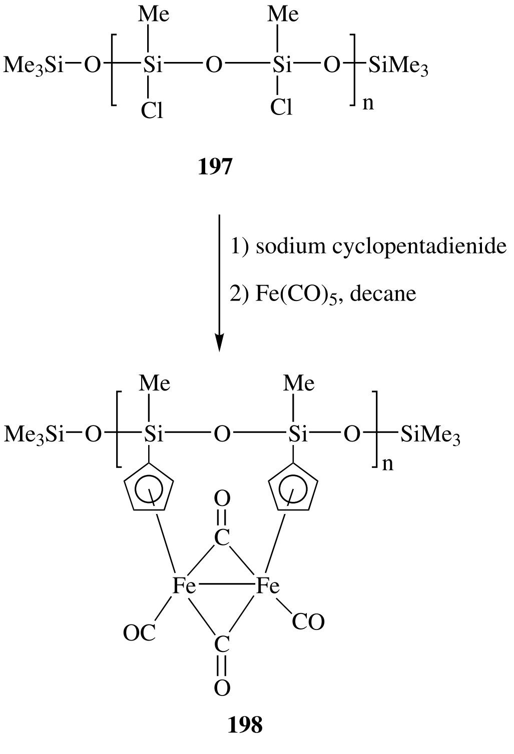
Cuadrado and coworkers [241] have reported the synthesis of low molecular weight polysiloxanes with iron–iron bonds in their backbones by polycondensation reactions of disilanols with a dinuclear iron–iron-bonded complex. Reaction of poly(methylchlorosiloxane) (**197**) with sodium cyclopentadienide resulted in the formation of poly(cyclopentadienylmethylsiloxane). This polymer was then reacted with iron pentacarbonyl to produce the corresponding organoiron polymer (**198**) shown in Scheme 54. The poor solubility and good thermal stability of **198** indicated that cross-linking between polymer chains may have occurred [241].



Scheme 52.



Scheme 53.



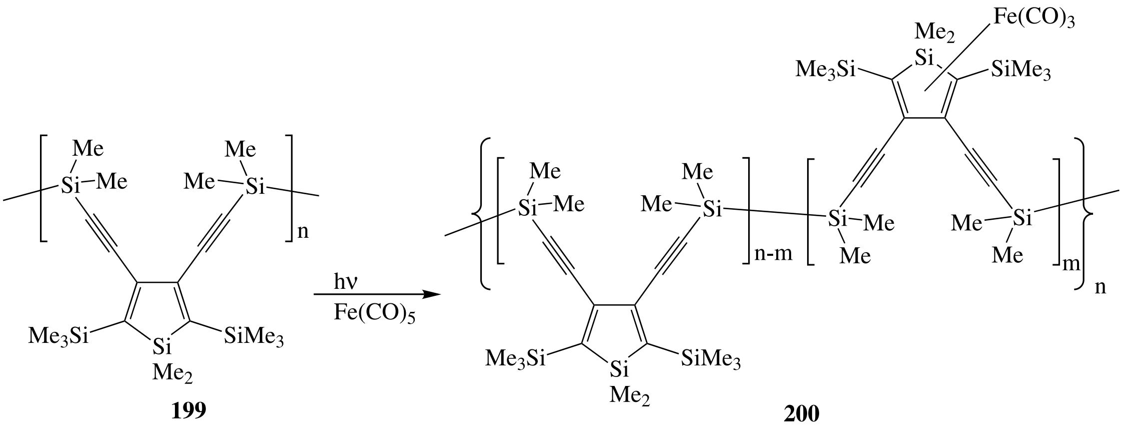
Scheme 54.

3.4. Silole rings

The reaction of polymers containing silole rings in their backbones with an excess of iron pentacarbonyl concurrent with irradiation using a high-pressure mercury lamp produced polymers with $Fe(CO)_3$-coordinated silole rings in their backbones (Scheme 55) [242]. The molecular weights of polymers such as **200** were found to be lower than their organic analogs (**199**) due to photolytic cleavage of the silicon–silicon bonds. NMR analysis revealed that the ratio of coordinated to non-coordinated silole rings was 2:1. The UV spectra of the iron-coordinated polymers showed that they were red-shifted relative to **199**. The electrical conductivity of polymer **199** was less than 10^{-8} S cm^{-1}, while its organoiron analog (**200**) had a conductivity of 3.3×10^{-5} S cm^{-1} upon doping with iodine or ferric chloride.

3.5. Hyperbranched, cross-linked, star and dendritic polymers

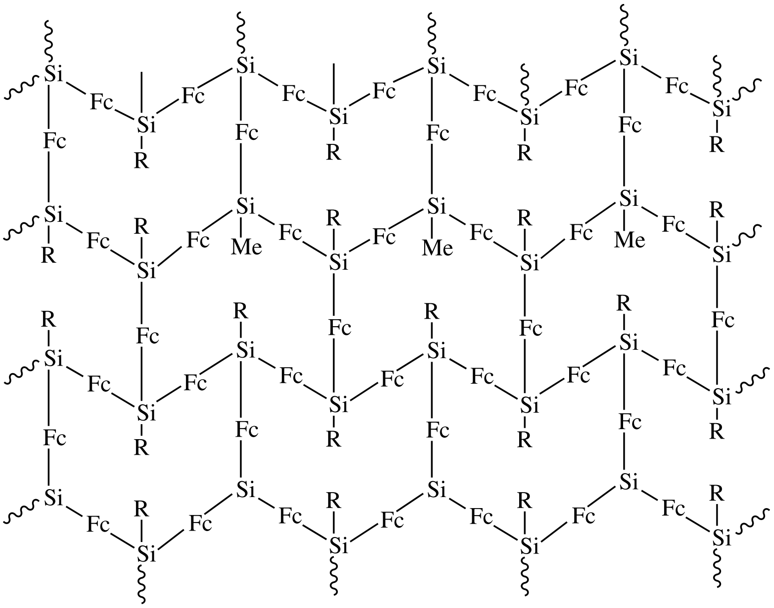
Galloway and Rauchfuss [243] reported that high molecular weight network poly(ferrocenylene persulfides) could be synthesized by desulfurization-induced ROP of monomers **201a** and **201b** (Scheme 56). While polymer **202a** was insoluble, the incorporation of a *t*-butyl group onto one of the cyclopentadienyl rings in **201b** allowed for a soluble high molecular weight network polymer (**202b**). Following pu-



Scheme 55.

rification, polymer **202b** had a weight average molecular weight of about 3,000,000.

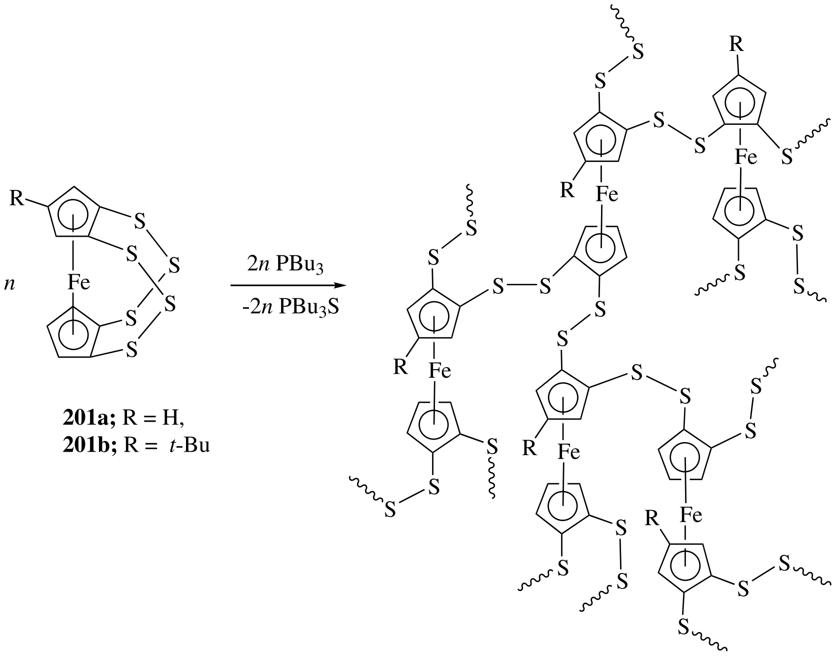
Tang and coworkers [244] have described the synthesis of hyperbranched polymers by reaction of 1,1′-dilithioferrocene with alkyltrichlorosilanes. The resulting polymers (**203**) had M_w values of 2000 and 6300 for the methyl- and *n*-dodecyl-substituted polymers, respectively; however, the methyl-substituted polymer was not completely soluble. Pyrolysis of these hyperbranched poly(ferrocenylsilanes) was accomplished by heating the samples up to 1000 °C under a nitrogen atmosphere or to 1200 °C under an argon atmosphere. The ceramic yield of the methyl-substituted polymer was about 50% and decreased as the length of the alkyl substituents increased. However, all the hyperbranched materials had higher ceramic yields than their corresponding linear poly(ferrocenylsilane) analogs. The pyrolysis products were found to be magnetic and were composed of Fe_3Si, Fe_2O_3 and Fe particles. The ceramic formed under a stream of argon was a soft ferromagnetic material and had a high saturation magnetization (M_s~49 emu g^{-1}) [244].



203

Fc = 1,1'-ferrocenylene
R = Me, *n*-dodecyl

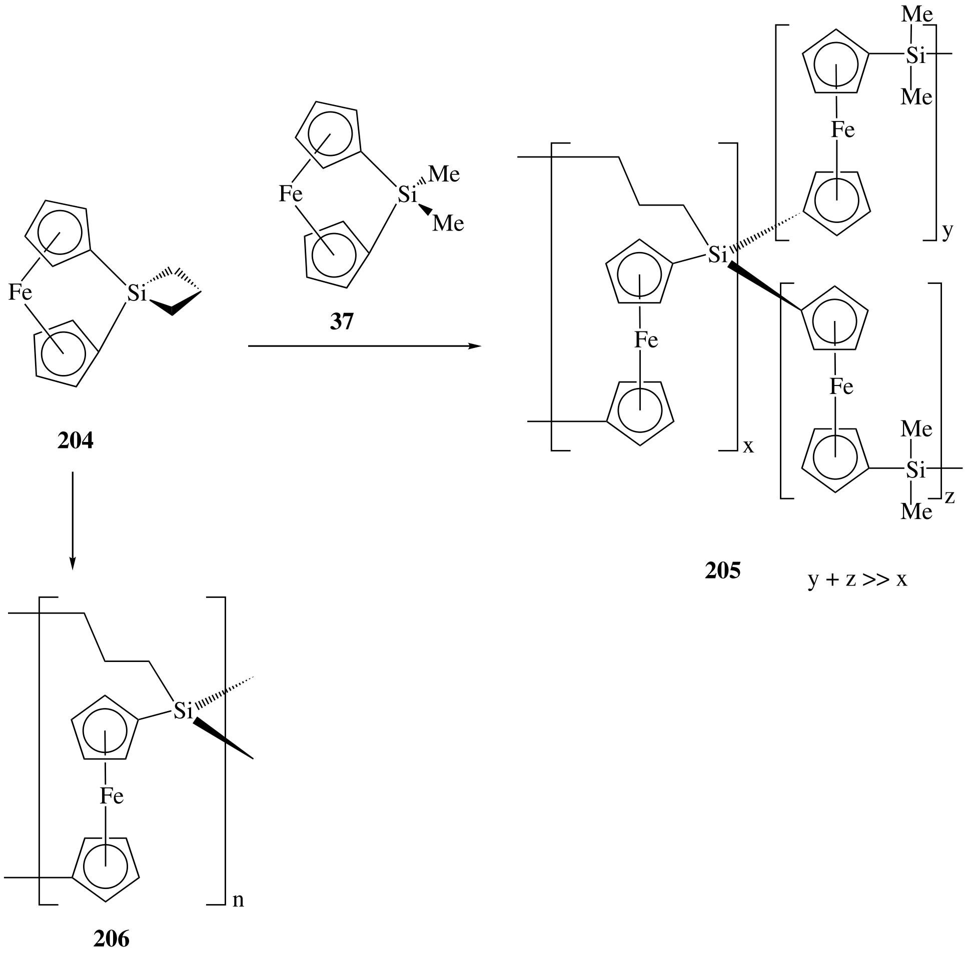
Manners' group has reported the synthesis of cross-linked poly(ferrocenylsilanes) by the thermal ROP of spirocyclic ferrocenophanes [245–250]. Scheme 57 shows the homo- and co-polymerization of the spirocyclic carbosilane-[1]ferrocenophane (**204**) to yield the cross-linked polymers **205** and **206**. Reaction of 2, 5, 10 and 15 mol% of **204** with **37** produced polymers with varying degrees of cross-linking [245]. In addition to thermal ROP, **204** also undergoes transition metal-catalyzed ROP with Pt(1,5-COD)$_2$ or Karstedt's catalyst [245]. These polymers were insoluble, but swelled and formed gels in THF, chloroform and



201a; R = H,
201b; R = *t*-Bu

202a, 202b

Scheme 56.



37

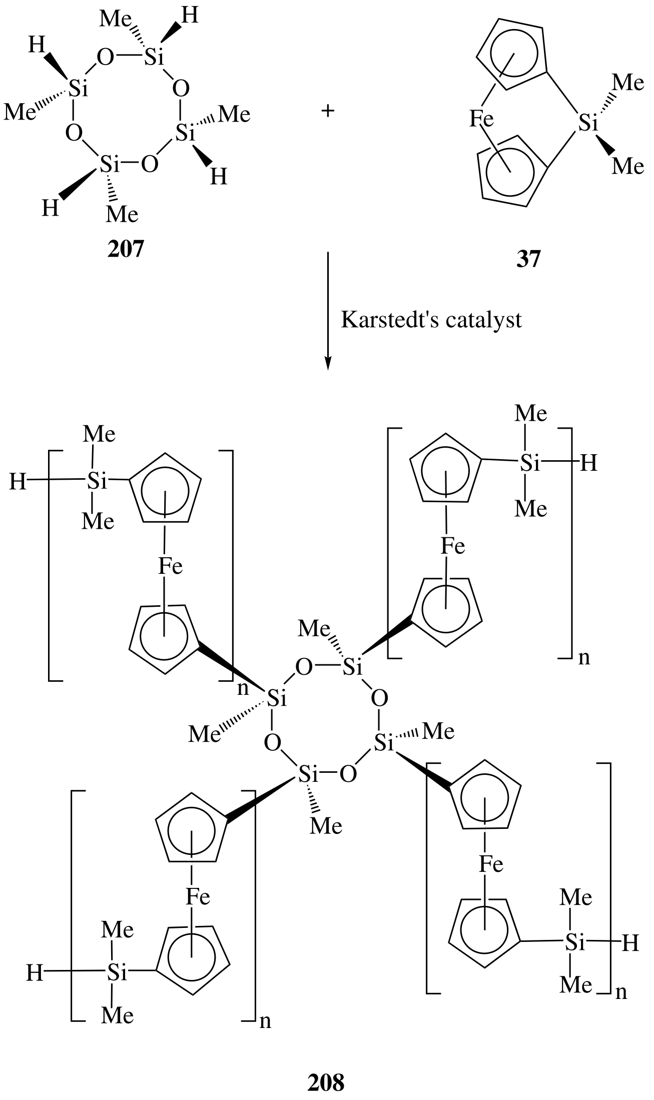
204

205 y + z >> x

206

Scheme 57.

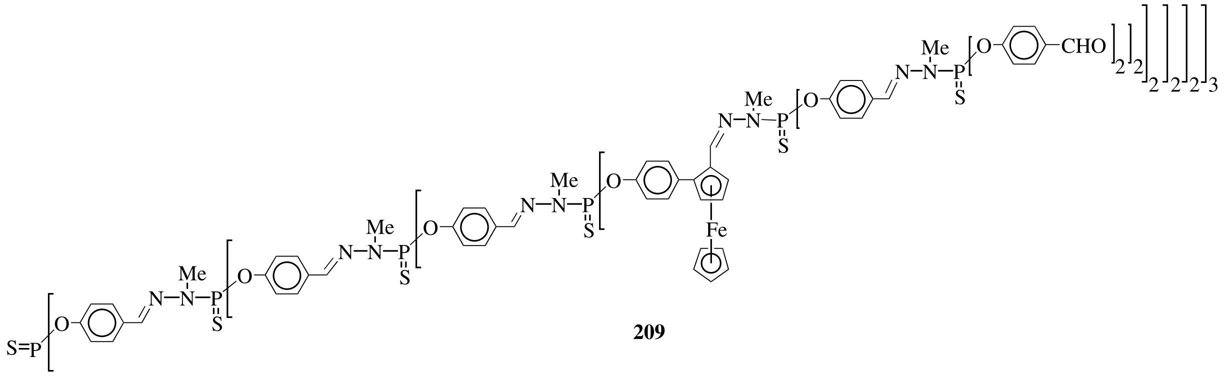
dichloromethane [246]. The swelling properties of these cross-linked polymers were examined and the solubility parameter of the corresponding homopolymer of **37** was determined. DSC analysis showed that in comparison to linear poly(ferrocenylsilanes), the cross-linked polymers did not have observable melting transitions and the glass transition temperatures of the two least cross-linked polymers were higher than the T_g of the linear polymer. The polymers that were 10 and 15% cross-linked did not have T_g's [245,246]. The cross-linked polymers were more thermally stable than their linear analogs and the pyrolysis products of these poly(ferrocenylsilanes) produced ceramics that possessed magnetic properties [246–250]. Poly(ferrocenylsilane) microspheres were formed and upon oxidation, they self-assembled with silica spheres. Upon pyrolysis, the metal-containing materials retained their spherical shapes [249,250]. These ceramic microspheres consisted of α-Fe nanoclusters embedded in a silicon carbide–carbon matrix. The magnetic properties of these iron-containing ceramics could be altered by changing the pyrolysis conditions.



Scheme 58.

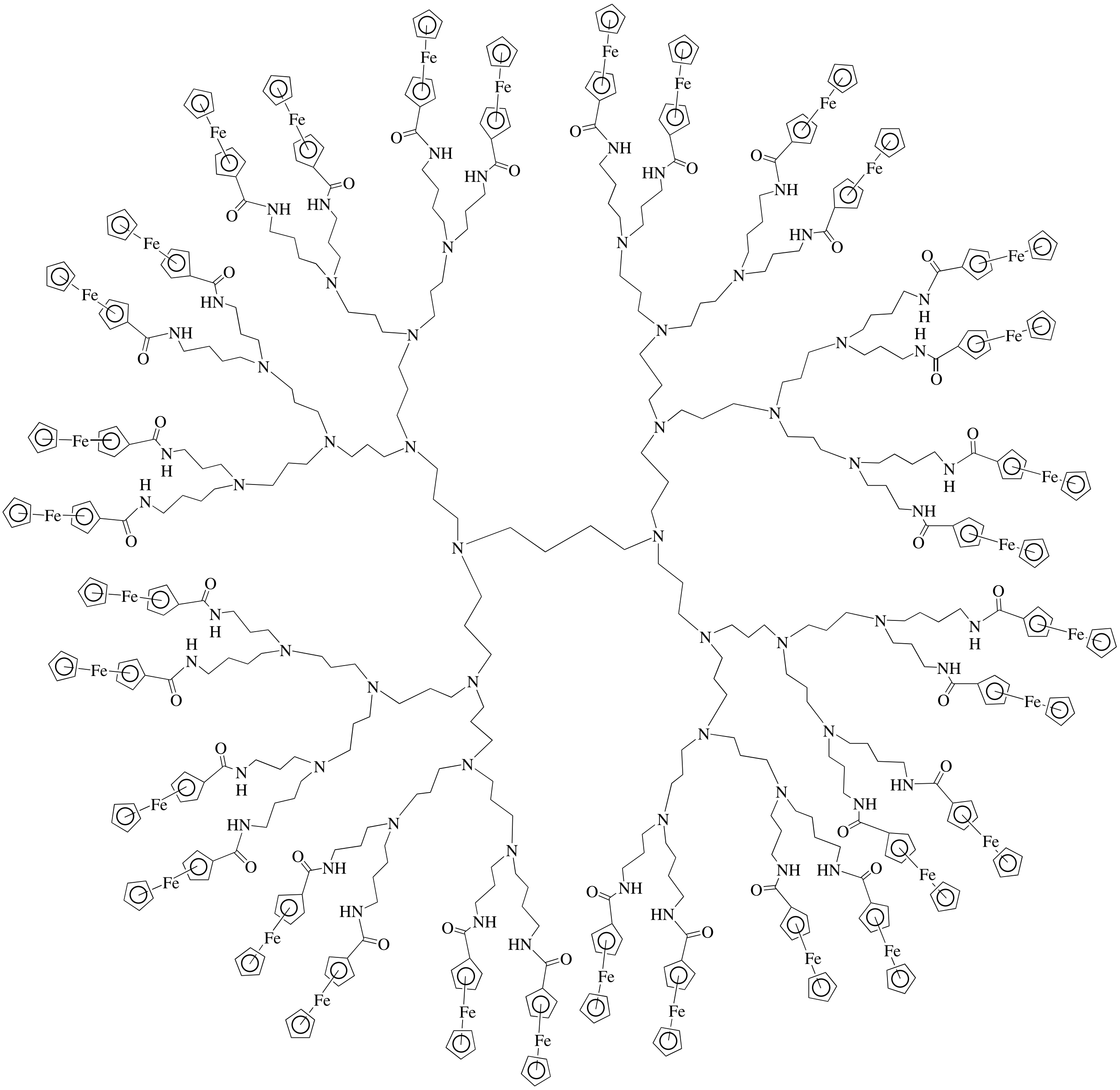
The synthesis of star polymers such as **208** has been accomplished by transition-metal-catalyzed ROP of hydromethylcyclotetrasiloxane (**207**) with [1]dimethylsilaferrocenophane (**37**) as shown in Scheme 58 [251]. Thus, under the correct conditions, linear, cross-linked and star-shaped polymer can be isolated by ROP of strained ferrocenophanes.

The synthesis of high-generation dendrimers containing ferrocenyl units at the core, within the branches and at the periphery have recently been reported by Turrin et al. [252–254]. Polymer **209** is an example of an optically active dendrimer with 24 ferrocenyl units in its branches [254]. The synthesis of dendrimers with up to 1536 ferrocenyl units in their structures have also been synthesized and their electrochemical properties and optical activities have been examined. Polymer **209** has a molecular weight of 35,748 and its $[\alpha]_D$ and $[\alpha]_{mol}$ per chiral group values were + 236.1 and 352, respectively. The chiroptical properties of these ferrocene-containing dendrimers were dependent upon the number of ferrocenyl groups and their chemical environment, but not on their positions within the dendrimer. On the other hand, the electrochemical properties of these materials were dependent on the generation of the dendrimer and the placement of the ferrocenyl moieties within the dendrimer core, branch or terminus [254]. Deschenaux et al. [255,256] have reported the synthesis of liquid crystalline ferrocene-based star polymers. Examination of a fullerene-containing dendrimer using polarized optical microscopy showed the presence of enantiotropic smectic A phases [256].



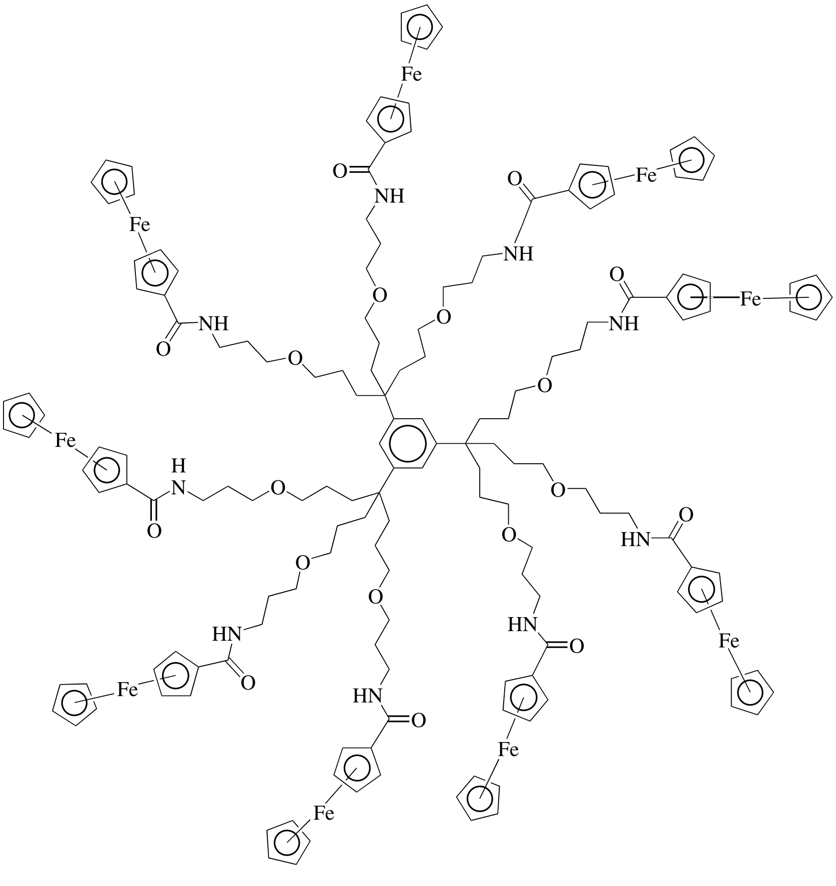
209

Considerable interest has been directed towards the synthesis of high-generation amine dendrimers with ferrocenyl moieties at the periphery [257–260]. Cuadrado and coworkers [257–259] have reported the synthesis of propylenimine-based dendrimers with up to five generations and 64 terminal ferrocenyl groups. Polymer **210** is an example of a dendrimer with 32 ferrocenyl units at the periphery [258,259]. The guest–host relationships of dendrimers containing 4, 8 and 16 terminal ferrocenyl groups with cyclodextrins were examined [257]. The low-generation dendrimers functionalized with 4 and 8 peripheral ferrocene moieties underwent complexation reactions with β-cyclodextrin, while the dendrimer containing 16 peripheral ferrocene groups underwent incomplete complexation, possibly due to steric congestion. Complexation of these materials to the cyclodextrins enhanced their solubilities in aqueous solution; however, reversible binding of the cyclodextrins could be achieved by adding 2-naphthalenesulfonate.



210

Salmon and Jutzi [260] have reported the synthesis of neutral and cationic ferrocene-based poly(propylene imine) dendrimers. Amine containing dendrimers containing 4, 8, 16, 32 and 64 ferrocene groups at the periphery were synthesized and quaternized using HCl. The low-generation cationic dendrimers could be solubilized in aqueous solutions, while the high-generation materials exhibited poor solubility in all solvents [260]. Astruc and coworkers [261] have reported that the reaction of amine-functionalized dendrimers with ferrocenecarbonyl chloride produced organoiron dendrimers (**211**) that were effective as supramolecular redox sensors of inorganic anions. Complexes and dendrimers with 1, 3, 9 and 18 ferrocenyl moieties were titrated with the *n*-Bu_4N^+ salts of $H_2PO_4^-$, HSO_4^-, Cl^-, Br^- and NO_3^- and shifts in the oxidation potential of the iron centers were monitored using cyclic voltammetry. The anions hydrogen-bonded to the amide H and caused a shift in the redox potentials of the ferrocenyl moieties. It was found that as the generation levels of the dendrimers increased, there was increased anion recognition. This dendritic effect was attributed to a more selective shape for the anions to penetrate the dendrimers as their generations increased [261].



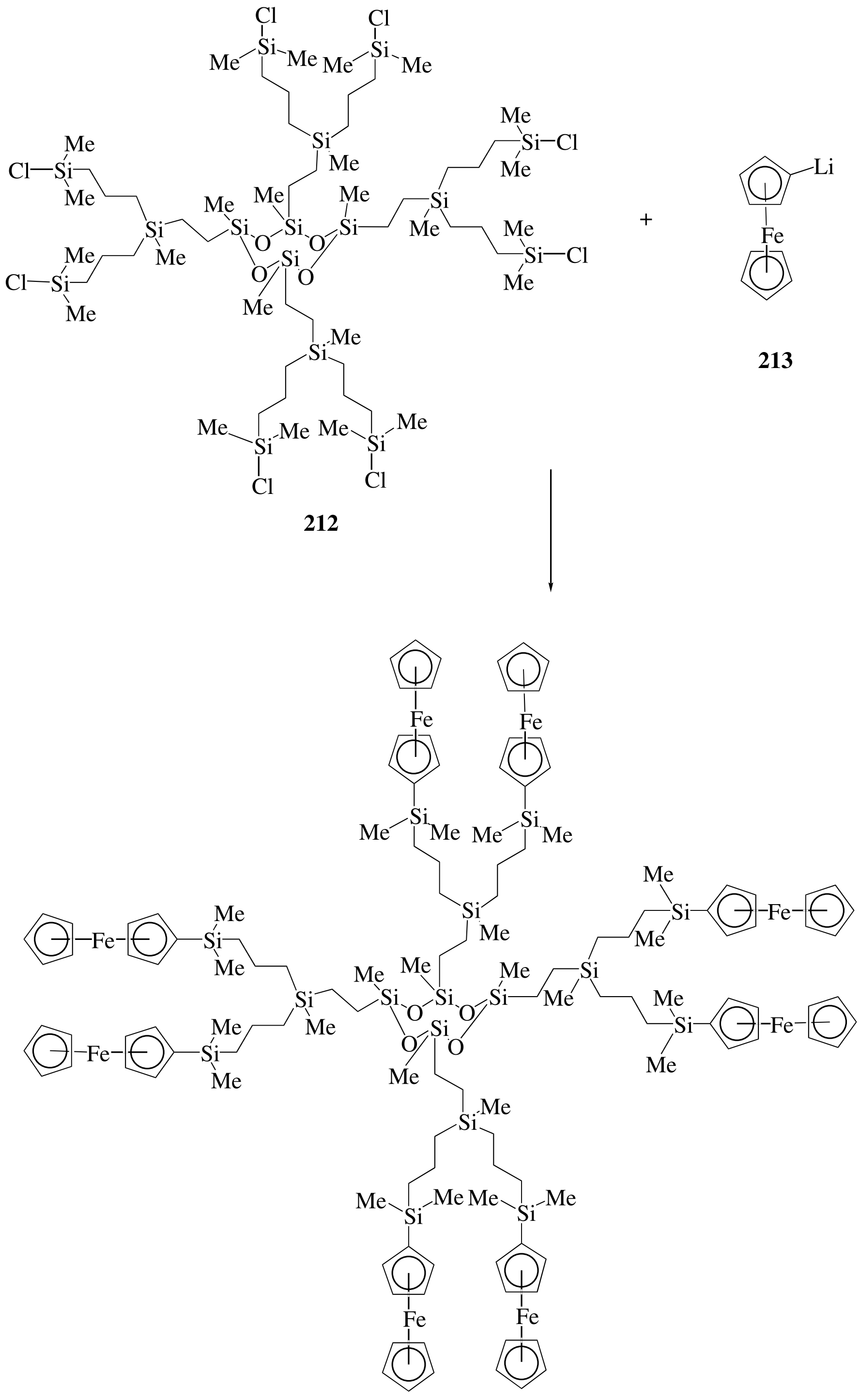
211

Astruc and coworkers [262–264] have synthesized dendrimers with up to 243 ferrocenyl units at the periphery via ferrocenylsilylation reactions of allyl-terminated dendrimers with ferrocenyldimethylsilane using Karstedt's catalyst. These dendrimers underwent chemically and electrochemically reversible oxidation processes [264]. Reversible reduction back to the neutral organoiron dendrimers showed that these materials behave as molecular batteries. Cuadrado et al. [265] have reported that ferrocenyl groups in silicon-containing dendrimers are electronically communicating. Scheme 59 shows the synthesis of a dendrimer with a cyclic siloxane core (**214**) via reaction of a chloro-substituted dendrimer (**212**) with lithioferrocene (**213**) [266]. The iron centers in **214** were found to be electronically independent. A hyperbranched polymer with cubic silsesquioxanes in its structure has been shown to mediate the electrocatalytic oxidation of ascorbic acid [266].

4. Polymers containing η^6-arene-η^5-cyclopentadienyliron cations

4.1. Arene complexes in the backbone

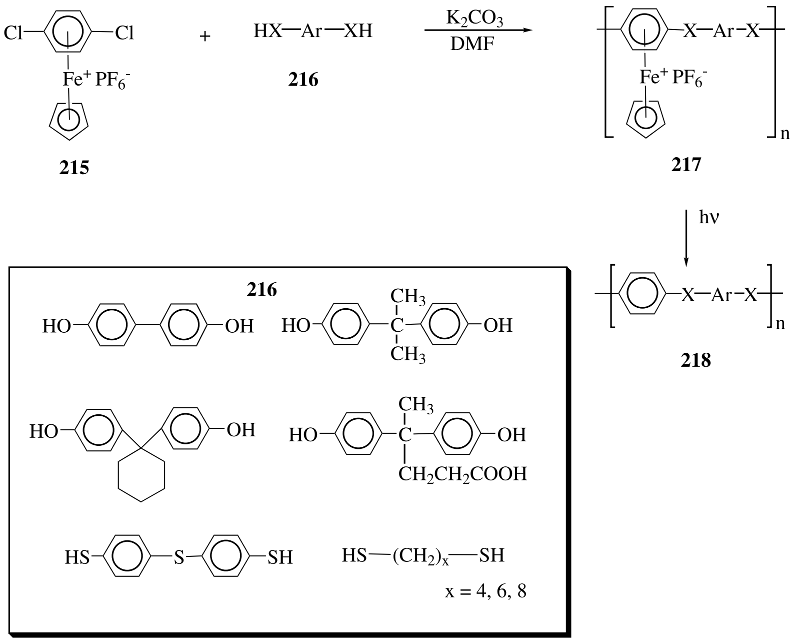
Chloroarenes coordinated to cyclopentadienyliron cations have been utilized to synthesize novel classes of organoiron monomers and polymers [16,267]. Abd-El-Aziz et al. [268] reacted dichlorobenzene complexes of cyclopentadienyliron with hydroquinone in sequential nucleophilic aromatic substitution reactions, which resulted in oligomers and polymers with well-defined molecular weights and molecular weight distributions. Poly(aromatic ethers) with up to 35 cyclopentadienyliron moieties pendent to alternating benzene rings in the polymer backbone were synthesized



212 + **213** → **214**

Scheme 59.

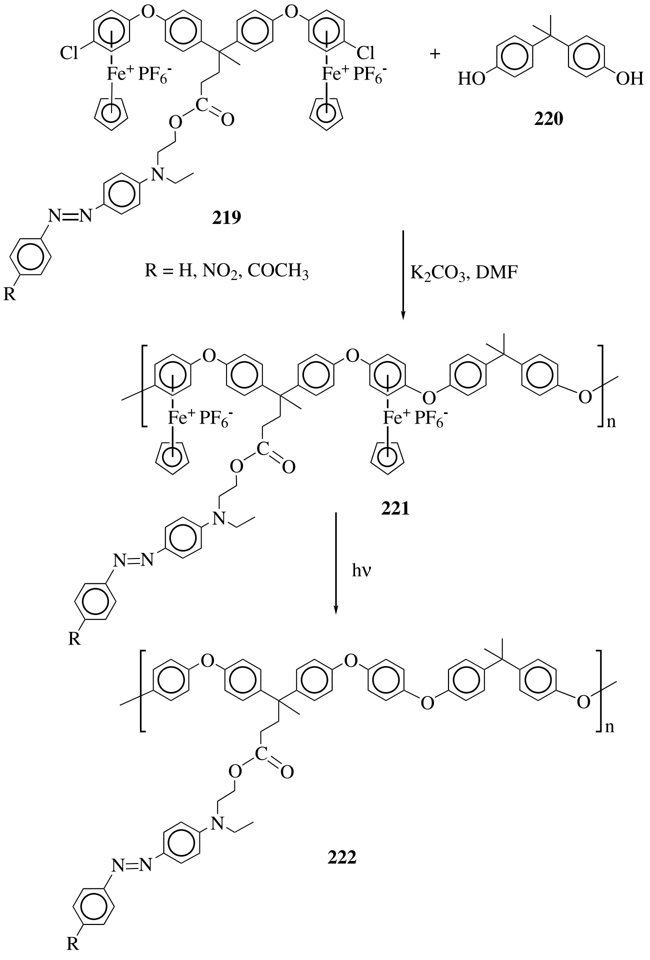
using this strategy. Cyanide addition to these aromatic ether oligomers allowed for the isolation of the corresponding nitrile adducts [269]. More recently, attention has been directed towards the one-step synthesis of polyethers and thioethers coordinated to cyclopentadienyliron cations [270,271]. By reacting the dichloroarene complex (**215**) with various oxygen and sulfur dinucleophiles (**216**), it was possible to isolate cationic organoiron polymers (**217**) as shown in Scheme 60. The cyclopentadienyliron moieties pendent to the polymer backbones had a solubilizing influence on these aromatic polymers (**217**). They exhibited good solubilities in polar organic solvents such as acetone, acetonitrile, DMF and DMSO [271]. The molecular weights of the cyclopentadienyliron-coordinated polymers



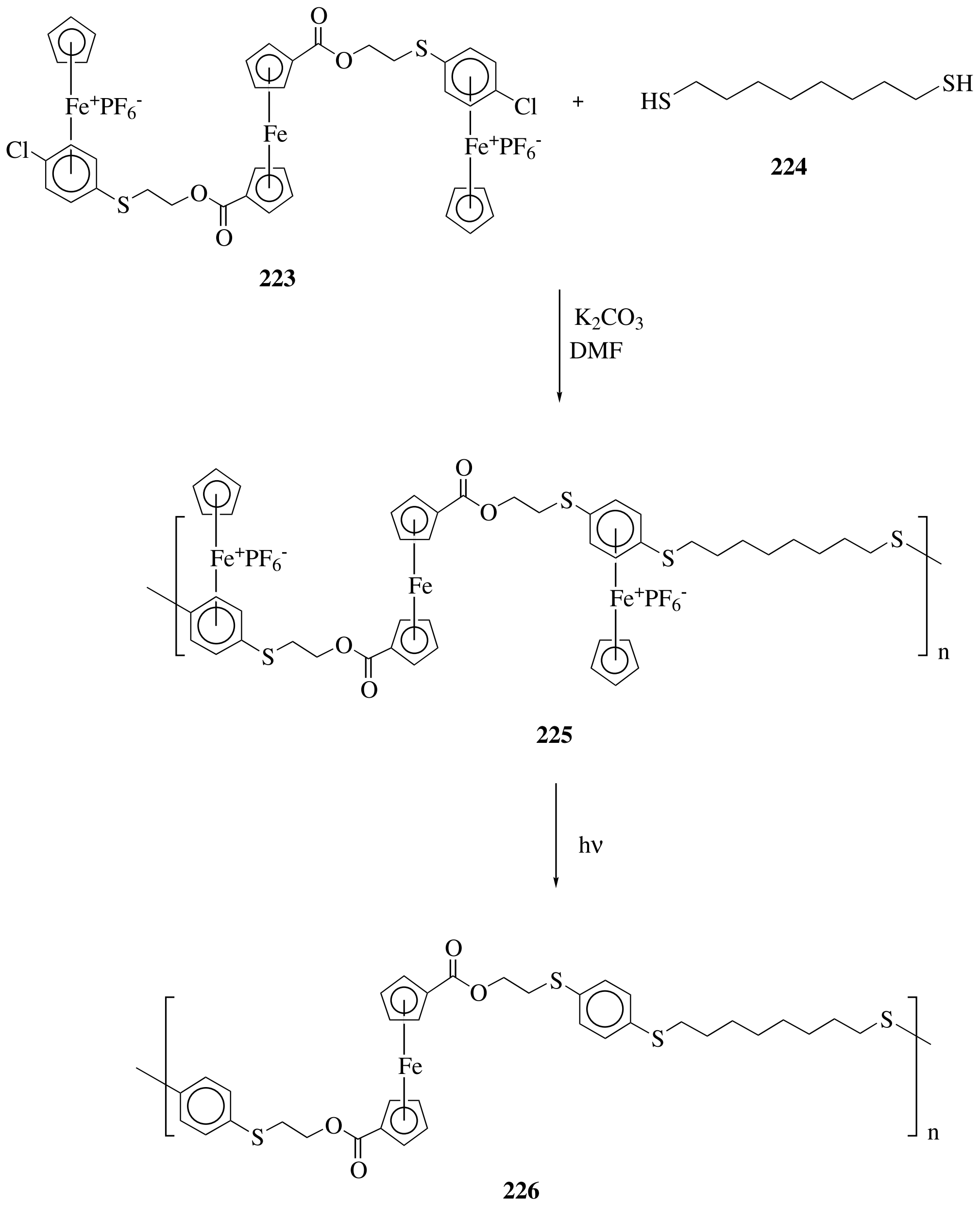
Scheme 60.

could not be determined using GPC due to interactions with the columns. Photolysis of polymers **217** allowed for the isolation of the corresponding organic polymers, whose molecular weights were measured. However, the solubilities of polymers **218** were much lower than their metallated analogs, and some of these polymers were completely insoluble in all organic solvents tested [271]. Molecular weights of the soluble portions of the organic polymers ranged from 7300 to 21,400. Organoiron polymers containing alternating ether–thioether or amine–thioether spacers in their backbones were also synthesized. Thermogravimetric analysis of the organoiron polymers showed that the cyclopentadienyliron moieties were cleaved from the arenes at ca. 200 °C, while degradation of the polymer backbones occurred around 500 °C. Cyclic voltammetric studies of the cyclopentadienyliron-coordinated polyethers and thioethers (**217**) showed that these materials underwent reversible reduction processes. Polyaromatic ethers and thioethers containing alternating cyclopentadienyliron and pentamethylcyclopentadienylruthenium cations pendent to their backbones have also been synthesized [272].

Highly colored organoiron complexes and polymers have been produced by incorporating azobenzene moieties in their structures [273]. The polymers were synthesized by reaction of cyclopentadienyliron-complexed azobenzene monomers (**219**) with various SH- and OH-based dinucleophiles such as bisphenol A (**220**) (Scheme 61). These cationic polymers (**221**) had wavelength maxima at 417, 452 and 489 nm, respectively, when the R groups on the azobenzene moieties were H, $COCH_3$ and NO_2. Photolysis of these polycationic cyclopentadienyliron-coordinated polymers allowed for the isolation of the organic polymers (**222**). The incorporation of cationic cyclopentadienyliron moieties pendent to the



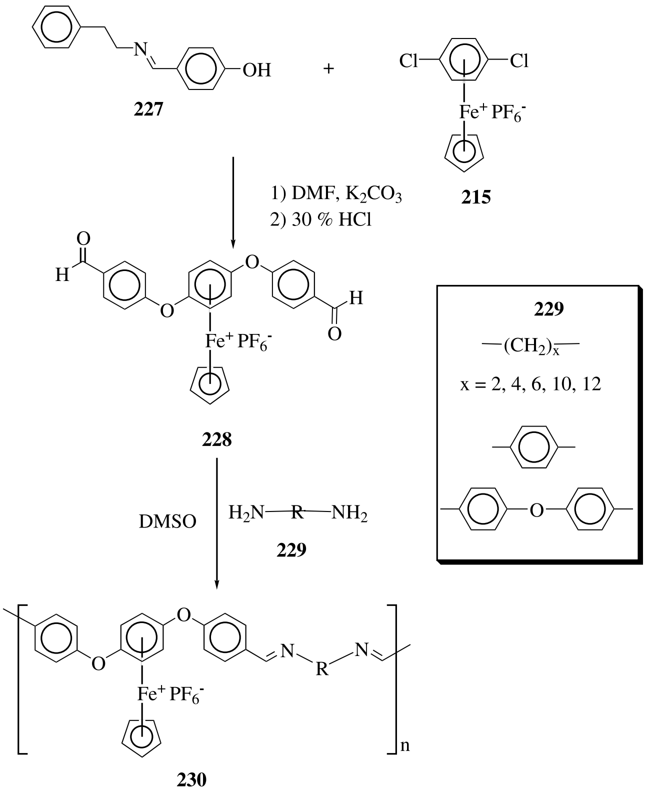
Scheme 61.



Scheme 62.

backbones of these polymers increased their glass transition temperatures relative to their corresponding organic polymers. For example, the T_g of **221** with nitro substituents was 173 °C, while the T_g of its organic analog (**222**) occurred at 112 °C. Photobleaching of these highly colored azo dye-functionalized polymers was achieved in the presence of hydrogen peroxide.

New classes of polymers containing neutral ferrocene units in their backbones and cationic cyclopentadienyliron moieties pendent to their backbones have recently been reported by Abd-El-Aziz's group [274]. Scheme 62 shows the synthesis of one of these organoiron polymers (**225**) via nucleophilic aromatic substitution reactions of trimetallic complexes such as **223** with 1,8-octanedithiol (**224**). Photolysis of the polymers resulted in cleavage of the pendent cationic iron groups, allowing for the isolation of novel ferrocene-containing polymers such as **226**. Thermal analysis indicated that the ferrocene-containing polymers possessed higher thermal stability but lower glass transition temperatures than their cationic analogs. For example, the glass transition temperatures of the polymers with pendent cationic cyclopentadienyliron moieties ranged from 65 to 161 °C, while their neutral organoiron analogs had T_g values ranging from 10 to 92 °C. Cyclic voltammetry of the polymers showed that the neutral and cationic organoiron complexes underwent reversible oxidation and reduction processes, respectively. The molecular weight of polymer **225** was estimated to be 14,500 with a polydispersity of 1.37 [274].



Scheme 63.

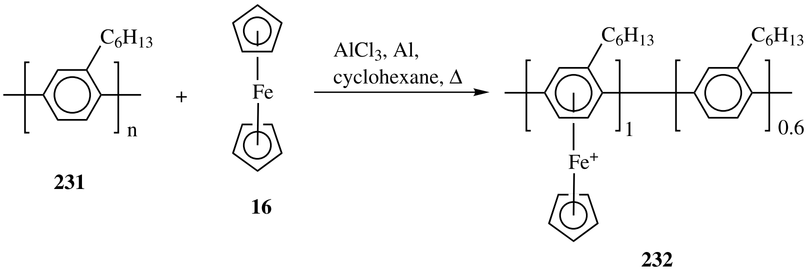
The synthesis of polymers containing imine and aromatic ether spacers in their backbones has been accomplished by polycondensation reactions (Scheme 63) [275,276]. Reaction of the dichlorobenzene complex **215** with compound **227** resulted in a diimine complex, which was decomposed in situ to yield the dialdehyde monomer **228**. This dialdehyde monomer was subsequently reacted with a variety of aliphatic and aromatic diamines (**229**) to give the corresponding cationic organoiron polymers (**230**). While the cyclopentadienyliron-coordinated polymers were soluble in a number of polar aprotic solvents, following photolytic removal of the organoiron moieties, the organic polyetherimines were insoluble [276]. Viscosity measurements of the metallated polymers (**230**) showed that they exhibited polyelectrolyte effects in DMSO. Thermogravimetric analysis of the organoiron polymers with aliphatic spacers showed that these materials were thermally stable up to about 300 °C, while polymers prepared with the aromatic diamines were stable to about 200 °C.

Nishihara and coworkers [277] have reported that the reaction of poly(hexyl phenylene) (**231**) with ferrocene (**16**) resulted in complexation of ca. 1 in every 1.6 aromatic rings with cyclopentadienyliron cations. Scheme 64 shows the formation of this iron-coordinated polymer (**232**) using aluminum and aluminum chloride. Cyclic voltammetry experiments showed that the iron centers in this polymer were reduced at −1.7 V. An increase in ΔE_p with increasing sweep rate indicated that the heterogeneous electron transfer in this system was fairly slow. Spectroelectrochemical analysis of **232** indicated that following reduction of the iron centers, a network was formed between aromatic rings of neighboring polymer chains [277].

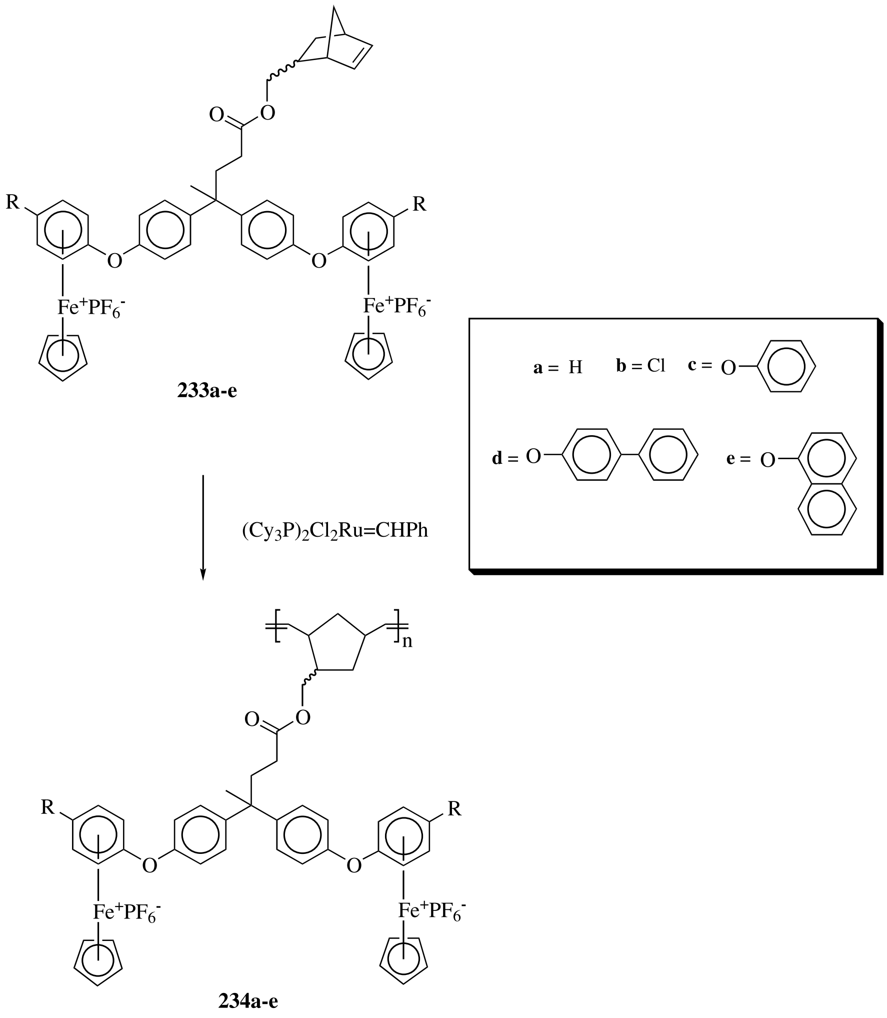
4.2. Arene complexes in the side chain

Chloroarene complexes of cyclopentadienyliron have been utilized to synthesize a number of organoiron norbornene monomers containing aromatic and aliphatic ether spacers [278–282]. While some of these monomers were demetallated prior to ring-opening metathesis polymerization [278,279], it has recently been reported that ROMP of cationic organoiron norbornenes can also be achieved using the Grubbs catalyst [280–282]. Scheme 65 shows the polymerization of monomers **233a–233e**, which resulted in the isolation of polymers **234a–234e** [280,281]. The polymerization reactions proceeded rapidly to produce the corresponding soluble organoiron polynorbornenes. The incorporation of larger aromatic ether groups increased the thermal stability of these polymers and the glass transition temperatures of their organic analogs. Thermogravimetric analysis showed that following loss of the cyclopentadienyliron moieties, the onset for weight loss in polymer **234a** occurred at 368 °C, while polymer **234e** was thermally stable up to 431 °C. Cyclic voltammetric investigations of polymers **234a–234e** showed that the iron centers in these materials were reduced in single steps between −1.2 and −1.5 V [280,281].

Polynorbornenes containing cationic organoiron azobenzene side chains have also been prepared via ring-opening metathesis polymerization reactions (Scheme 66) [282]. Organoiron norbornene complexes functionalized with azobenzene chromophores (**235a** and **235b**) were reacted



Scheme 64.

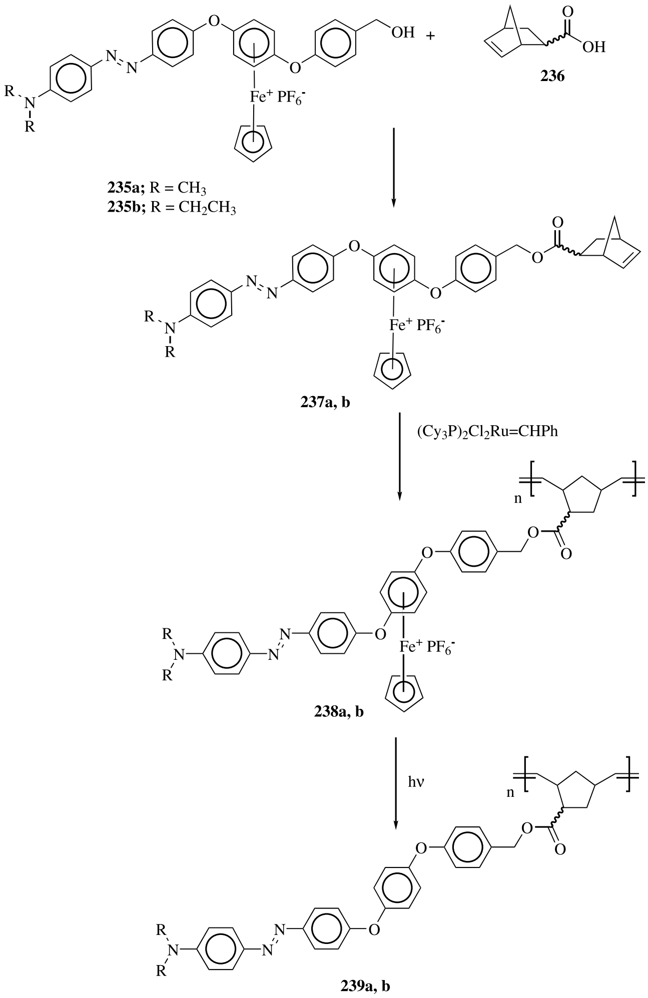


Scheme 65.

with 5-norbornene-2-carboxylic acid (**236**) to produce the norbornene monomers **237a** and **237b**. ROMP of these monomers using the Grubbs catalyst produced the corresponding cationic organoiron polynorbornenes **238a** and **238b** in good yields. UV–Vis analysis of these polymers in DMF showed maxima between 420 and 430 nm, and upon protonation of the azo groups, there was a bathochromic shift to between 510 and 520 nm. Cyclic voltammetric studies showed that the iron centers underwent reversible reduction steps between −1.2 and −1.4 V. It was also found that the polymers with cationic cyclopentadienyliron moieties pendent to their side chains (**238a** and **238b**) had much higher T_g values than their organic counterparts (**239a** and **239b**).

Polymethacrylates (**241**) containing cationic arene cyclopentadienyliron complexes in their side chains have been prepared by the radical initiated polymerization of methacrylate monomers (**240**) as shown in Scheme 67 [283]. Photolysis of **241** resulted in the cleavage of the metallic moieties from the polymer side chains and isolation of the organic polymethacrylates (**242**). The weight average molecular weights (M_w) of these organic polymers ($R = H$, CH_3) ranged from 17,800 to 48,500 with PDI values of 2.6 and 2.4, respectively. Electrochemical studies of the metallated polymethacrylates showed that reduction of the iron centers occurred between $E_{1/2} = -1.1$ and -1.3 V [284].

The polymerization of methacrylates and styrenes with cationic chloroarene cyclopentadienyliron complexes in their structures has also been accomplished via radical polymerization and nucleophilic aromatic substitution reactions [284]. The radical polymerization of the methacrylate monomers yielded soluble organoiron polymers with high molecular weights. The polystyrenes (**244**) with organoiron groups in their side chains exhibited fair solubility in organic solvents; however, their organic analogs were insoluble. Nucleophilic aromatic substitution polymerization of these monomers allowed for the isolation of soluble polyaromatic ethers and ether/thioethers with methacrylate and styrene moieties (**246**) as pendent groups. The molecular weights of the metallated polyethers ranged from 22,500 to 22,800,

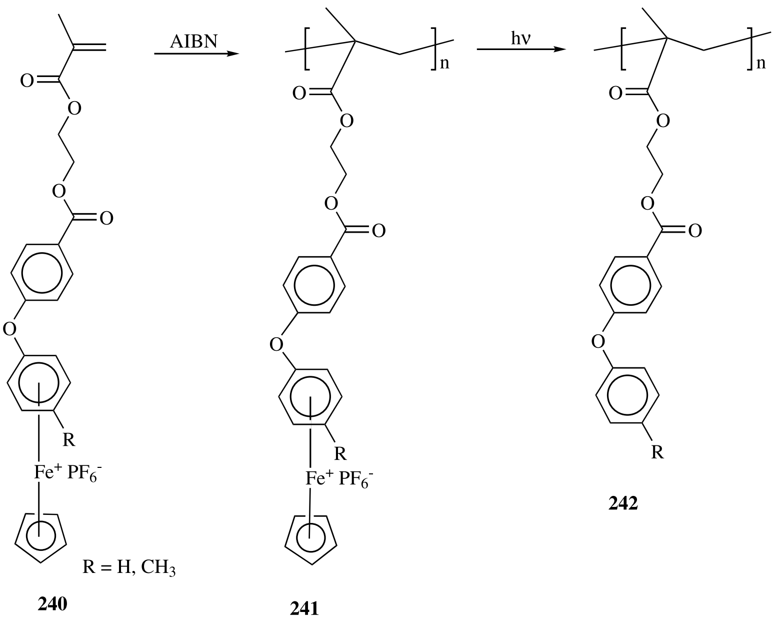


Scheme 66.

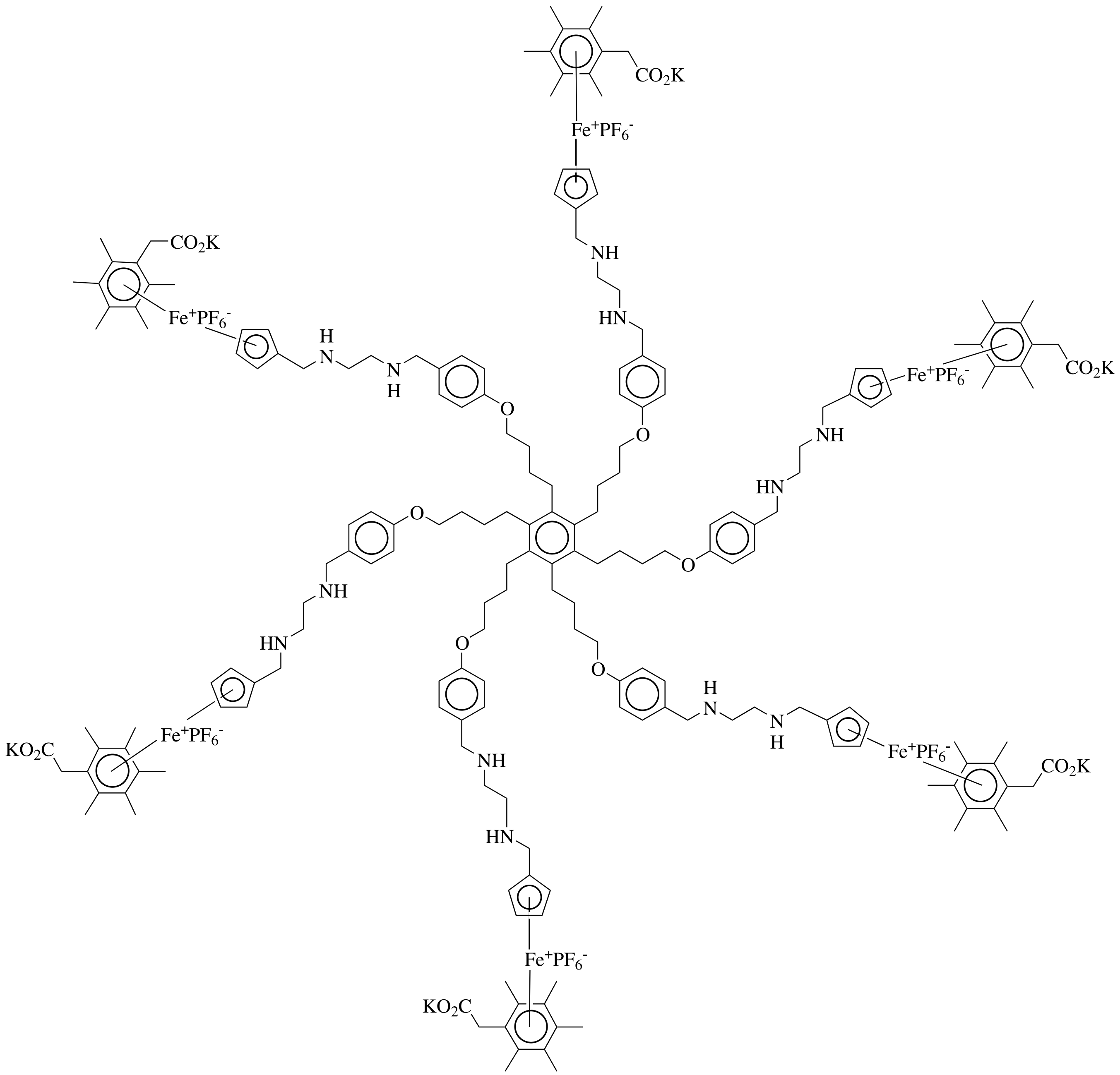
while the soluble portions of the polyether/thioethers ranged from 10,500 to 13,800. These polymers display good thermal stability following loss of the metallic moieties. Electrochemical analysis of these polymers showed that the iron centers in these materials were reversibly reduced. The polymers prepared by nucleophilic aromatic substitution reactions possessed higher thermal stability than the polymers prepared by radical polymerization of the methacrylate or styrene groups. Cross-linking did not result in significant increases in thermal stability; however, the polymers (**247**) did become insoluble (Scheme 68) [284].

4.3. Stars and dendrimers

Astruc and coworkers [285–297] have synthesized a number of star polymers and dendrimers containing arene cyclopentadienyliron complexes at the core and/or periphery. Cyclopentadienyliron-mediated per-alkylation, -benzylation and -allylation reactions of cationic tri-, tetra- and hexamethylbenzene complexes have allowed for the preparation of multifunctional materials that have been utilized to synthesize branched organic and organometallic polymers. It has been reported that the water-soluble dendrimer (**248**), containing six cationic cyclopentadienyliron moieties, can be utilized to cathodically reduce nitrates and nitrites to ammonia [287]. Scheme 69 shows the synthesis of a star-shaped organoiron complex containing eight terminal cyclopentadienyliron moieties [297]. This polymer (**251**) was synthesized by reaction of the organic molecule **249** with the organoiron nucleophile (**250**). The octametallic star molecule (**249**) was previously prepared by deprotonation of a permethylated iron complex.

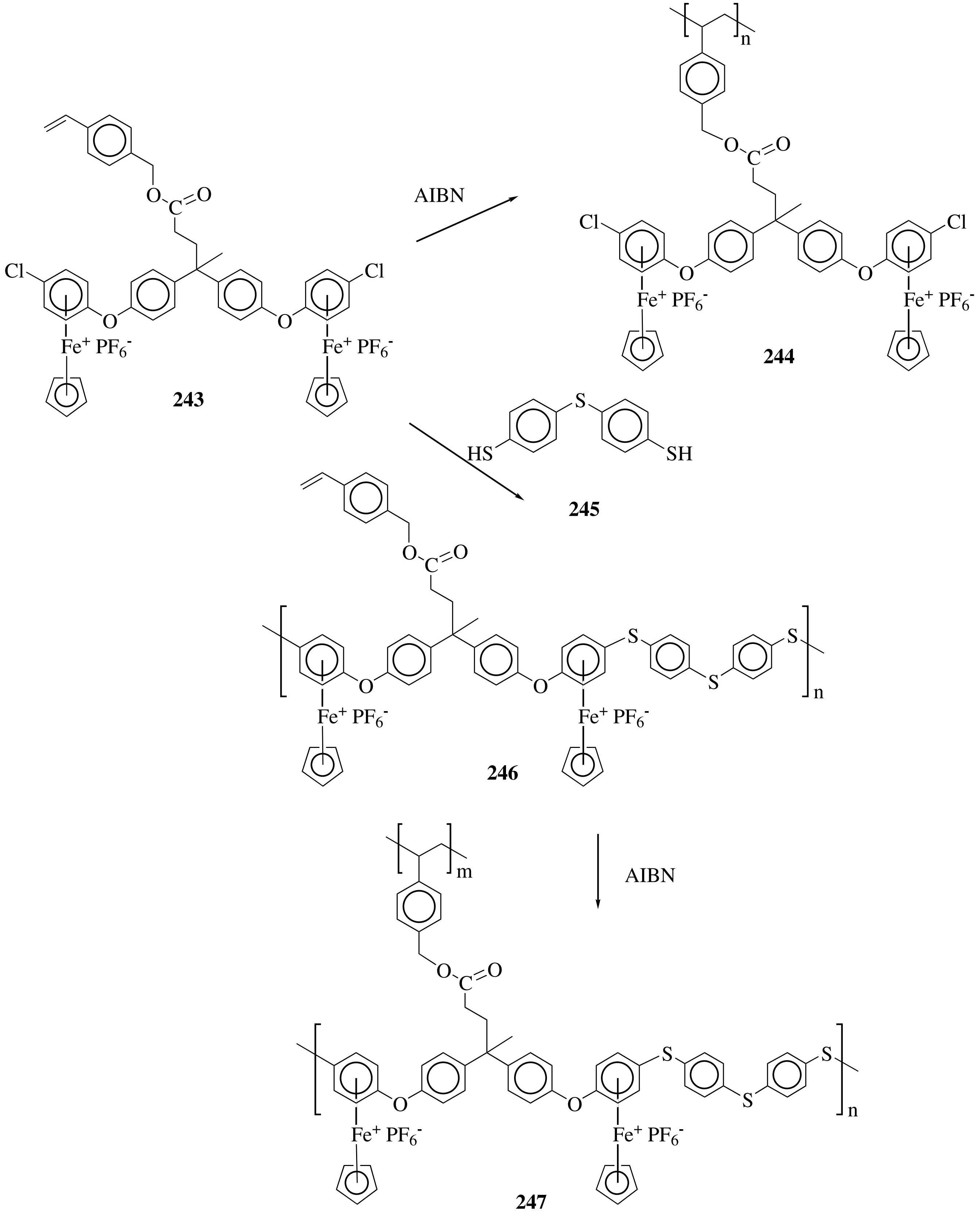


Scheme 67.

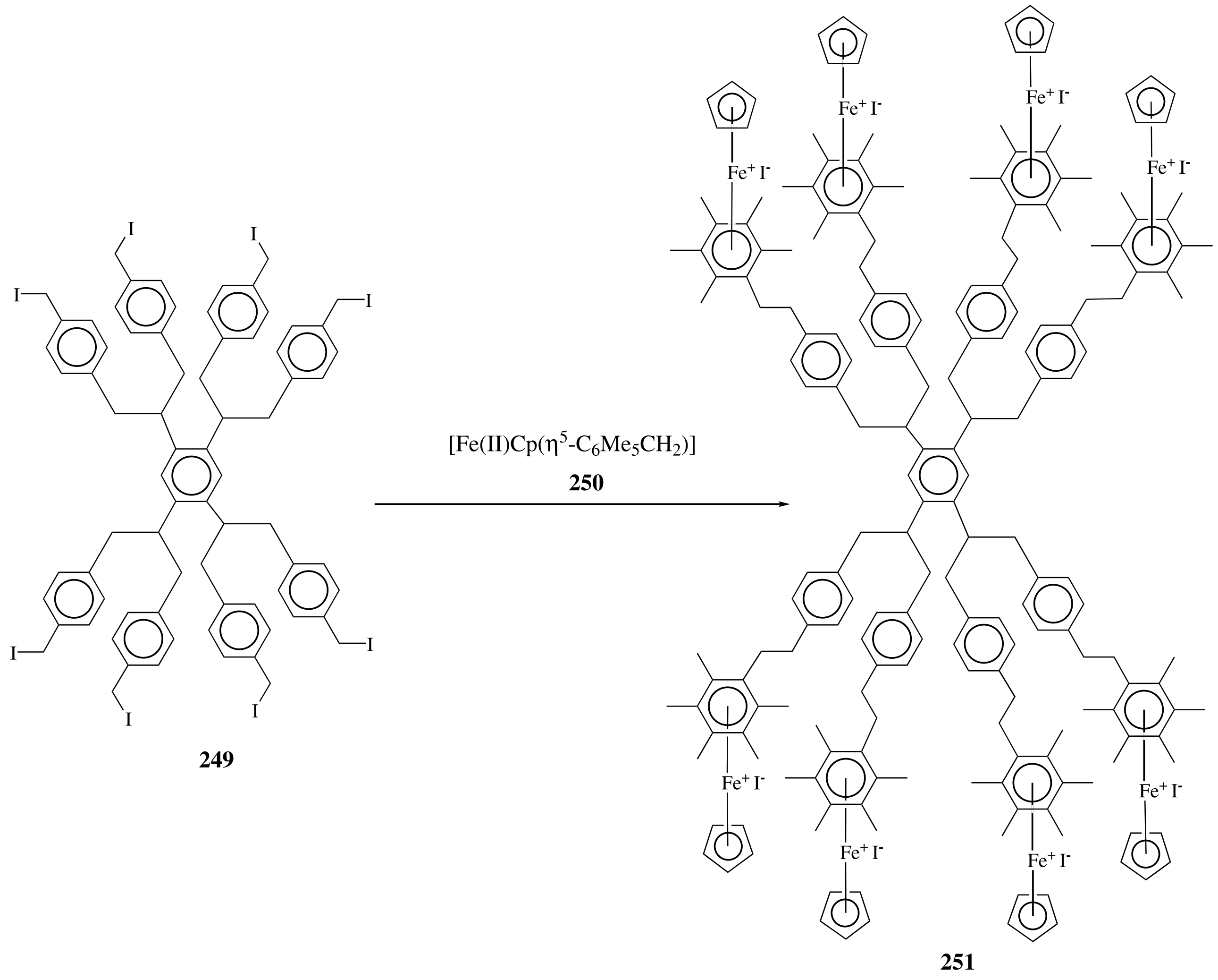


248

A trimetallic complex containing three chloroarene complexes at the periphery (**252**) was reacted with a number of organoiron complexes containing terminal phenolic groups to produce star-shaped polymers [298]. Scheme 70 shows the reaction of **252** with the carboxylic acid-functionalized complex (**253**), which resulted in the isolation of the hexametallic star **254**. Polymer **254** was found to be soluble in polar organic solvents and also in aqueous solutions. A number of different organoiron complexes were reacted with **252** to produce polymers with 6, 9, 12 and 15 cationic cyclopentadienyliron moieties pendent to the polymer branches. Cyclic voltammetric studies of star-shaped polyaromatic ethers showed that the 18-electron iron centers were reduced between −0.99 and −1.4 V, and



Scheme 68.



Scheme 69.

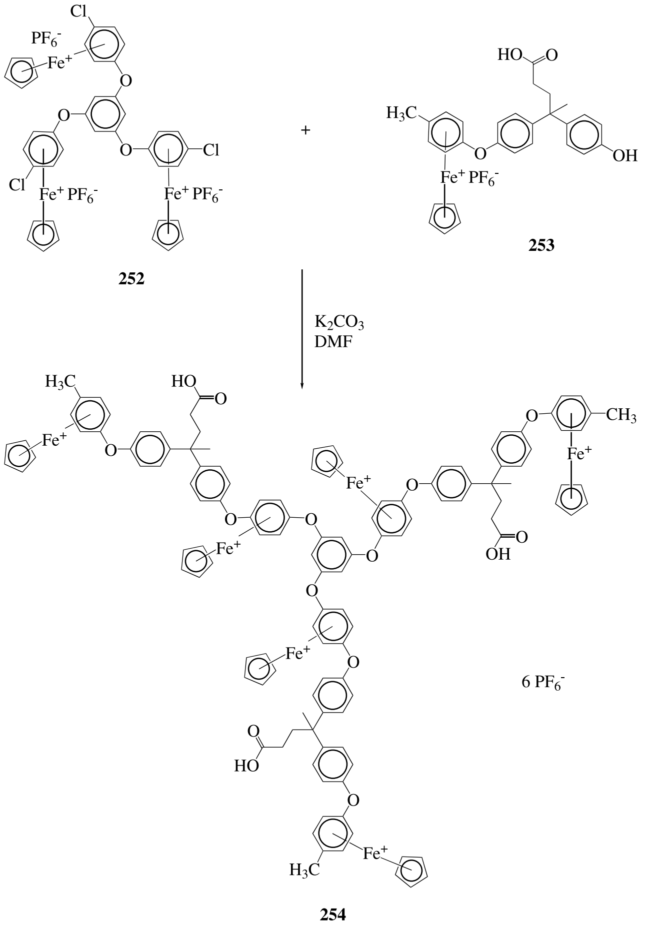
that the iron moieties behaved as isolated redox centers [298].

5. Iron polyynes

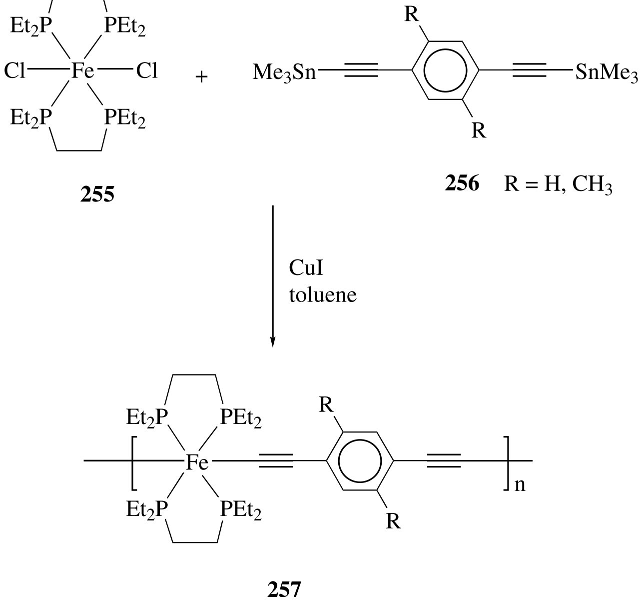
Poly(metal acetylides) containing iron complexes in their backbones have been reported by Lewis and coworkers [299,300]. Scheme 71 shows the reaction of an iron-chelating phosphine dichloride complex (**255**) with bis-trimethylstannylalkynes (**256**) in the presence of a catalytic amount of CuI to yield high molecular weight polymers (**257**). The weight average molecular weight of polymer **257**, when $R = CH_3$, was 173,000, which corresponds to a degree of polymerization of **279**. Lo Sterzo and coworkers [301] have reported the synthesis of oligomeric complexes containing iron acetylide units in their backbones.

6. Summary

Since the first examples of organoiron polymers were reported in the 1950s, there have been numerous developments in this area. Iron-containing polymers have been synthesized using all the traditional polymerization methods, including chain growth, step growth and ROP. Interest in this field stems from the relative ease in handling and synthesizing iron-containing monomers and polymers as well as the potential applications that these organoiron polymers possess. Examples of polymers with iron atoms π-coordinated and σ-bonded to carbon were described. The organoiron complexes exist within the polymer backbones and in the polymer side chains. It is anticipated that this research area will continue to expand within the near future in light of the interesting properties that organoiron polymers have already been shown to possess. Future studies may be directed towards tailoring existing systems in order to optimize the properties of these polymers. However, in light of the large number of stable complexes that iron makes with organic ligands, the development of new classes of iron-containing macromolecules will undoubtedly produce materials with new sets of interesting properties and applications. This review covers research in this field from the early 1950s until this year and provides a comprehensive reference section.



Scheme 70.



Scheme 71.

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