
 CHAPTER 1

Overview of Organoiron Polymers

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I. INTRODUCTION

Iron is the second most abundant metal and the fourth most abundant element found in Earth's crust. In 1951, Kealy and Pauson made the extraordinary discovery of ferrocene.¹ Prior to that time, complexes containing transition metal-carbon bonds were rare, and it was thought that these bonds must be unstable. The high thermal stability of ferrocene changed many of these ideas, and organoiron chemistry

*Macromolecules Containing Metal and Metal-like Elements,
Volume 2: Organoiron Polymers*, Edited by Alaa S. Abd-El-Aziz,
Charles E. Carraher, Jr., Charles U. Pittman, Jr., John E. Sheats, and Martin Zeldin
ISBN 0-471-45078-2 Copyright © 2004 John Wiley & Sons, Inc.

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became the focus of numerous investigations. From the initial reports on the synthesis and structure of ferrocene, there have been countless studies examining the chemistry of organoiron complexes.¹⁻³

The rich chemistry of ferrocene stems from the nucleophilicity of the cyclopentadienyl rings, which allows for their reactions with numerous electrophiles. Within a few years of its discovery, a number of functionalized ferrocene molecules had been prepared, and in 1955, the first polymer containing ferrocene in its structure was reported by Arimoto and Haven.⁴ In the years to follow, the fascinating chemistry associated with ferrocene led to research in the synthesis of ferrocene-based polymers in which the organometallic group exists in sidechains, the mainchain, or discrete locations within the polymer.⁵⁻⁷ Ferrocene-based polymers are the most well-examined class of organometallic polymer, and their methods of synthesis and their properties cover a wide spectrum. These types of polymers have been shown to exhibit interesting electrochemical, optical, thermal, morphological, pharmacological, and magnetic properties.^{5,6}

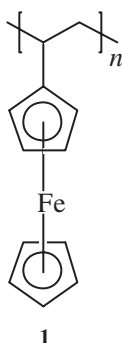
The displacement of one of the cyclopentadienyl rings of ferrocene by an arene allows for the isolation of cationic η^6 -arene- η^5 -cyclopentadienyliron complexes.⁸ While Coffield and coworkers reported the first cyclopentadienyliron coordinated arene in 1957 by refluxing mesitylene with cyclopentadienyliron dicarbonyl chloride,⁹ it was 6 years later when Nesmeyanov and coworkers prepared these complexes using ferrocene.^{10,11} These cationic organoiron complexes had properties very different from those exhibited by ferrocene. For example, the complexed benzene rings were found to be susceptible to attack by nucleophiles, and did not show the same reactivity as did uncomplexed benzenes. Also, while the iron centers in ferrocene undergo stable electrochemical oxidation, arene cyclopentadienyliron complexes are reduced electrochemically.¹² It is also important to note that the arene iron bond does not show the same thermal stability, and is readily cleaved by pyrolysis, photolysis, and electrolysis. While arene complexes of cyclopentadienyliron have been known since the 1950s, it was not until the 1990s that polymers containing these organometallic groups in their structures were reported.

While many studies have reported the interesting chemistry associated with the cyclopentadienyl and benzene complexes of iron, a number of other studies have reported the synthesis of other classes of organoiron polymers. For example, iron carbonyl moieties π -coordinated to dienes and cyclopentadienyl compounds have been investigated, and each new class of polymer relates new information about organoiron polymers and the chemistry of organoiron complexes. Polymers possessing iron-carbon σ and π bonds or only iron-carbon σ bonds within the polymer's backbones are classes of polymers that have not received a great deal of attention. Polymers containing iron-iron bonds within, or pendent to their backbones have also been synthesized using a number of different strategies, and have exhibited interesting properties.

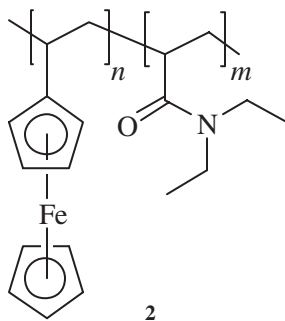
This chapter presents an overview of all classes of macromolecules containing iron-carbon bonds and highlights some examples of these materials. The methods utilized to synthesize and characterize these polymers are described and the properties of some of the organoiron-based polymers are noted. This chapter focuses on the diversity found in the area of organoiron polymer chemistry and briefly introduces the materials covered in the remaining chapters in this volume.

II. FERROCENE-BASED POLYMERS

Soon after the monumental discovery and elucidation of the structure of ferrocene, the homo- and copolymerization of vinylferrocene was reported using a number of different catalysts.⁴ The solution and bulk synthesis of polyvinylferrocene (**1**) has been studied in detail, as have the properties of polyvinylferrocene.¹³⁻¹⁵ While many of these studies were undertaken in the 1960s and 1970s, the polymerization of vinylferrocene continues to be an active area of research. The copolymerization of vinylferrocene with styrene using a “living” radical initiator (viz., TEMPO) was also reported.¹⁶

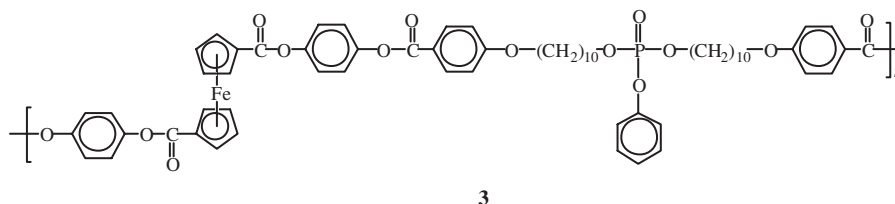


The properties that the ferrocenyl groups introduce into polymers have been the focus of numerous investigations. Kuramoto and coworkers have shown that copolymers (**2**) prepared from *N,N*-diethylacrylamide and vinyl ferrocene had decreasing low critical solution temperature (LCST) values with increasing ferrocene incorporation because of their reduced solubility in aqueous solution.¹⁷ Oxidation of the ferrocene units increased their hydrophilicity and resulted in increased LCST values for these materials. The same observations were observed for copolymers prepared with ferrocenylethylacrylamide and isopropylacrylamide.¹⁸ These organoiron polymers had lower LCST values than did poly(*N*-isopropylacrylamide). In both of these studies, there was only a low incorporation of the organometallic monomer into these materials.

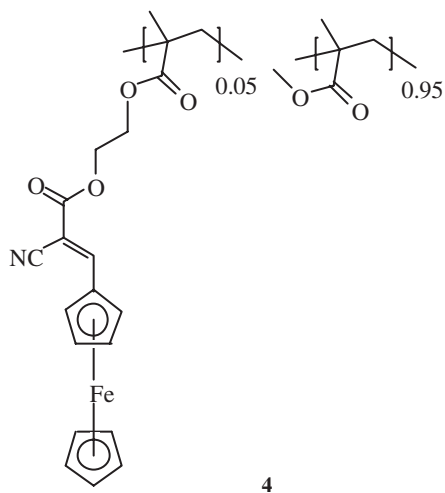


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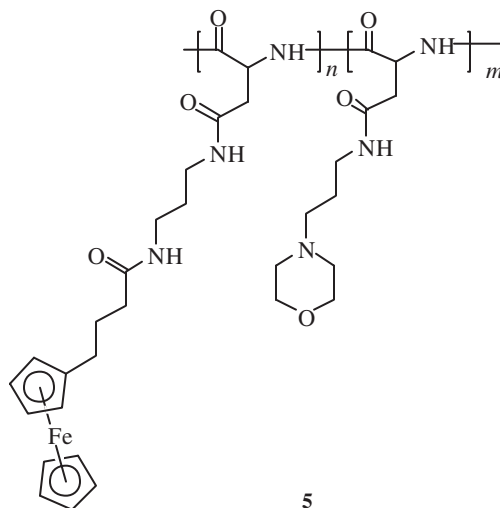
It has also been reported that polymers containing ferrocene units in the main-chain or sidechains may possess liquid crystalline characteristics.^{19–23} Ferrocene-based liquid crystalline polyesters (**3**) containing phosphorous groups in their backbones have been reported by Senthil and Kannan.²³



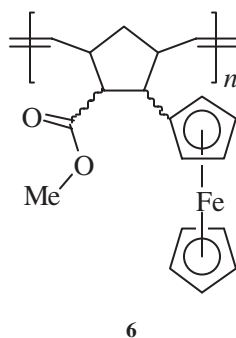
Polymers containing sidechain and mainchain ferrocenyl moieties have also been reported to possess nonlinear optical (NLO) properties.^{24–26} By incorporating 5 mol% of the organometallic monomer into the polymethacrylate (**4**), it was possible to generate NLO properties.²⁶



Similarly, Neuse and coworkers have reported that the incorporation of a small amount of a ferrocene-containing sidechain into polyaspartamide introduces antiproliferative properties into these materials.^{27–29} Polymer **5** is an example of an organoiron-functionalized polymer prepared from reaction of the preformed organic polymer with 4-ferrocenylbutanoic acid.²⁹

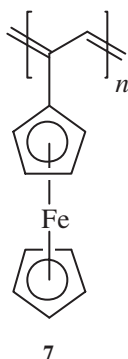


The redox stability of the ferrocenyl group has led to the incorporation of this organoiron unit into a number of different classes of macromolecules.³⁰⁻³² An amperometric glucose sensing electrode has been prepared utilizing a polymethylsiloxane with ferrocene groups in its sidechain.³⁰ Peptides functionalized with ferrocene units interact with each other through hydrogen bonds resulting in supramolecular assemblies.³¹ Schrock and Wrighton have reported the synthesis of polynorbornenes with ferrocenyl moieties pendent to the norbornene unit (6).³²

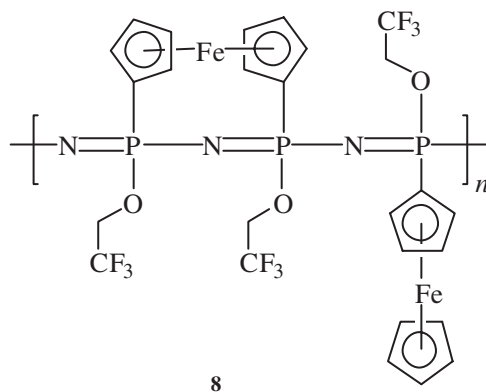


The synthesis of metallocenes functionalized with alkyne groups has been reported using a molybdenum catalyst to produce polyacetylenes with ferrocene groups in their sidechains (7).^{33,34} The living polymerization reactions produced head-to-tail polymers with *trans* double bonds. The living polyacetylene could be surface grafted to a norbornene-functionalized silica support and used in anion exchange chromatography following oxidation of the iron centers.³⁴

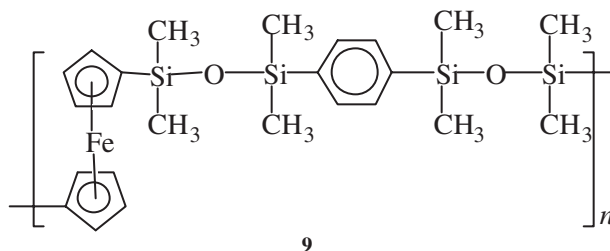
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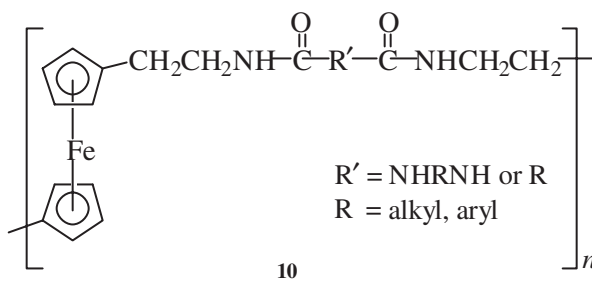
Allcock and coworkers have reported the ring-opening polymerization of cyclic phosphazenes functionalized with ferrocenyl groups.^{35,36} The polymers were attached to the metallocenes by the phosphorous atoms to either one or both of the cyclopentadienyl rings (**8**).³⁶



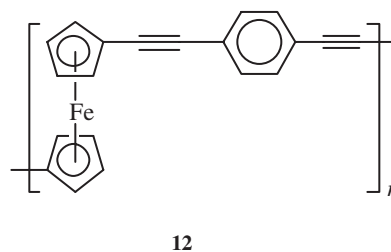
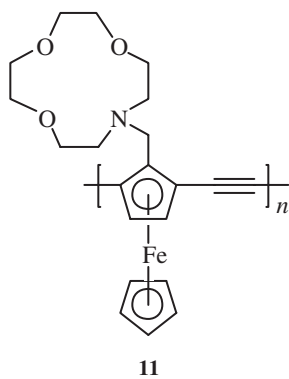
Polycondensation reactions have produced mainchain ferrocene polymers since 1961, and since that time, there have countless studies outlining the preparation of this class of material.³⁷ The functional groups and reaction conditions utilized to prepare these materials are varied, as are the properties of the resulting materials. In the 1970s, Pittman and coworkers reported the synthesis of a thermally stable, high molecular weight polymer (**9**) via polycondensation of disilanolols with *bis*-dimethylaminodimethylsilylferrocene.³⁸



Polyamides and polyureas (**10**) have also been synthesized by polycondensation reactions of 1,1'-bis(β -aminoethyl)ferrocene with diisocyanates or diacid chlorides, respectively.³⁹

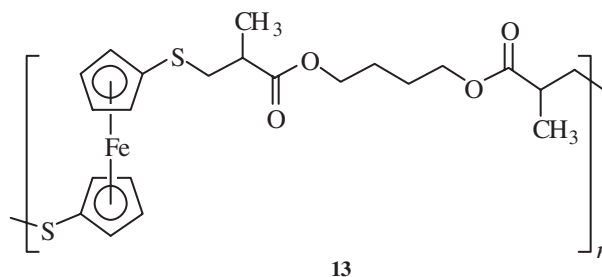


The polymerization of 1,2,3-substituted ferrocenes containing one iodo and one acetylene group using Sonogashira coupling resulted in the production of polymers with functionalized sidechains (**11**).⁴⁰ The reaction of 1,1'-diiodoferrocene with diethynyl monomers has also been used in the production of polymetallocenes with semiconducting properties (**12**).⁴¹

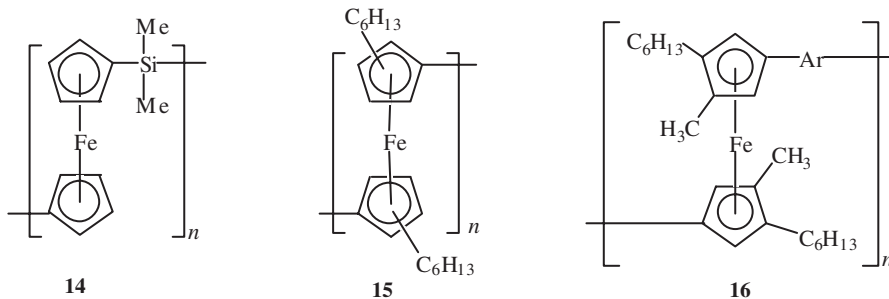


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Mainchain ferrocene-based polymers have also been synthesized by polyaddition reactions.⁴² For example, the reaction of 1,1'-dimercaptoferrocene with 1,4-butandiyil dimethacrylate resulted in the isolation of polymer **13**.

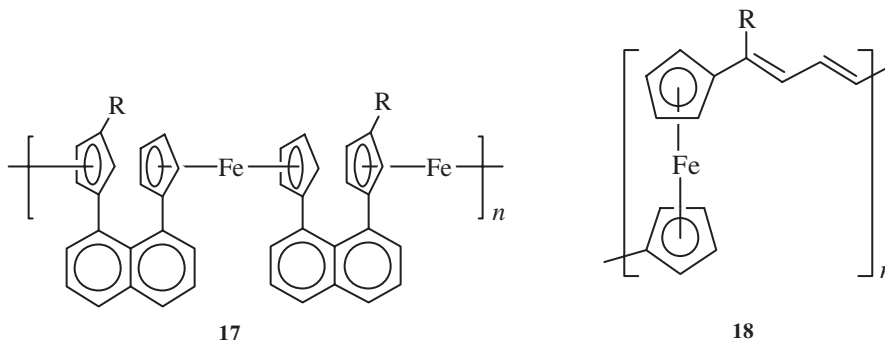


A polyferrocenylsilane (**14**) has been prepared via the reaction of the dilithium salt of dicyclopentadienyldimethylsilane with ferrous chloride.⁴³ Polyferrocenylene substituted with hexyl groups (**15**) has been reported by reaction of the dihexylfulvalene dianion with $[\text{FeCl}_2(\text{THF})_2]$.⁴⁴ The hexyl groups attached to the cyclopentadienyl rings resulted in an enhanced solubility of these materials, and electrochemical studies showed that the iron centers were interacting. Southard and Curtis have used a similar strategy to prepare soluble conjugated polymetalloenes (**16**) by reaction of an isomeric mixture of *bis*(alkylcyclopentadienide arenes) with ferrous iodide.⁴⁵

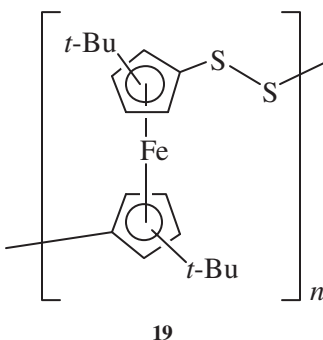


High molecular weight face-to-face polymetalloenes (**17**) have been prepared by Rosenblum and coworkers.⁴⁶ These polyferrocenes were found to be electrically conducting on doping with I_2 .

The ring-opening metathesis polymerization of ferrocenophanes containing bridging vinyl groups has also been reported.^{47–49} The incorporation of alkyl groups pendent to their backbones increased the solubility of these polymers (**18**). An enhancement of solubility could also be achieved by copolymerization reactions. Some of these polymers exhibited electrical conductivity.

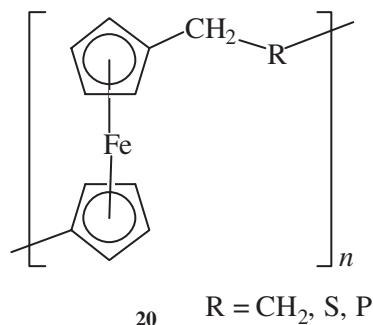


Rauchfuss and coworkers have reported the ring-opening polymerization of [3]trithiaferrocenes and [3]trisenaferrocenes with PBU_3 .^{50,51} The ring-opening-induced desulfurization and deselenization reactions resulted in the formation of high molecular weight polymers. The polyferrocenylene persulfides (**19**) can be reductively decomposed with LiBHET_3 and regenerated on oxidation. The thermal and anionic ROP of [1]thia- and [1]senaferrocenophanes has also been reported by Manners.⁵² The presence of two reversible oxidation processes in the cyclic voltammograms of the polyferrocenyl sulfides indicates that these polymers possess strong metal–metal interactions.

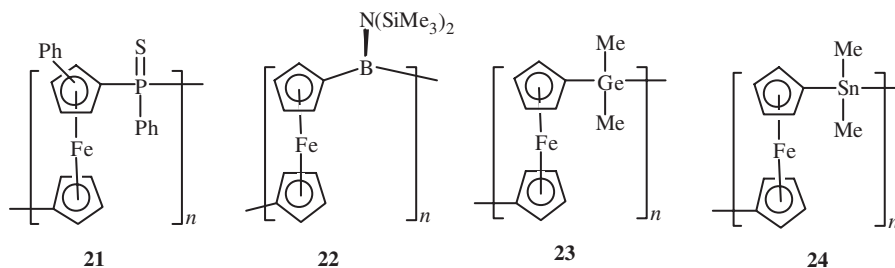


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Thermal ring-opening polymerization of [2]ferrocenophanes has also been reported by Manners and coworkers (**20**).^{53,54} Oxidation of the polyferrocenylethylene with tetracyanoethylene resulted in antiferromagnetic interactions.⁵³ Unsymmetric [2]ferrocenophanes (R=S, P) have also been synthesized and ring-opened; however, a ferrocenophane containing a C–Si bridge was resistant to thermal, anionic, and transition-metal-catalyzed ROP.⁵⁴ The [2]carbathioferrocenophane could also be polymerized in the presence of cationic initiators.

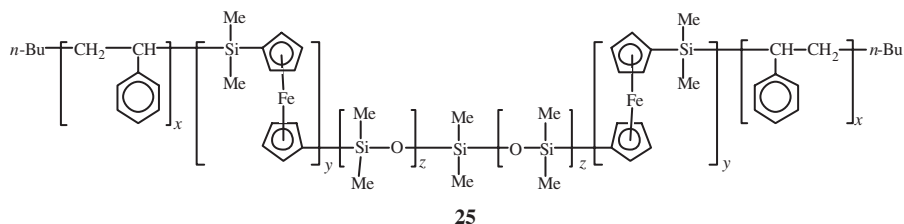


Polyferrocenylphosphines have been synthesized by the ring-opening polymerization of [1]ferrocenophanes.^{55–57} These polymers can be further reacted with elemental sulfur to produce the corresponding polyferrocenylphosphine sulfides (**21**).⁵⁵ Borane adducts of polyferrocenylphosphines have been isolated via thermal ROP of the functionalized ferrocenophane, or by addition of the borane to the preformed polyferrocenylphosphine.⁵⁶ Manganese and tungsten complexes have also been reacted with a [1]ferrocenophane bearing a bridging phosphine ligand.⁵⁷ [1]Ferrocenophanes containing boron bridges have been found to possess large ring tilts, and have been ring-opened thermally to produce the corresponding polymers (**22**).⁵⁸ [1]Germaferrocenophanes undergo facile ROP to yield high molecular weight poly(ferrocenyl germanes) (**23**) thermally and with transition metal catalysts.^{59,60} The ROP of ferrocenophanes with tin bridges has also been described by the research groups of Manners and Pannell.^{61,62} High molecular weight tin polymers (**24**) have been produced by thermal ring-opening polymerization, or at room temperature in solution. It was reported that the ring opening of tin- and germanium-bridged [1]ferrocenophanes is facilitated by the addition of amines.⁶¹

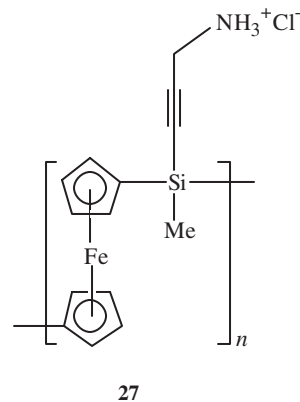
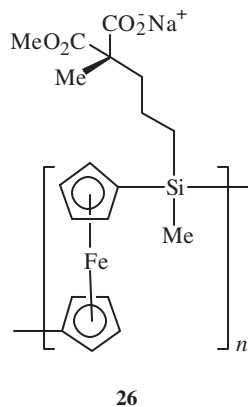


Since the first report on the ring-opening polymerization of [1]silaferrocenophanes in 1992, there have been many developments in this area of research.^{63–65} Polymerization of [1]silaferrocenophanes has now been achieved thermally, anionically and with transition metal catalysts. The solid-state polymerization of $\text{Fe}(\eta\text{-C}_5\text{H}_4)_2\text{SiMeR}$ ($\text{R}=\text{Me}, \text{Ph}$) has also been accomplished using a ^{60}C γ -ray source.⁶⁶ It was determined that irradiation of the unsymmetric ferrocenophane ($\text{R}=\text{Ph}$) resulted in a stereoregular polymer.

A number of copolymers have been prepared by anionic polymerization of silicon-bridged [1]ferrocenophanes.^{67–69} For example, the copolymerization of dimethylsilaferrocenophane with living polystyrene produced a polymer to which 12-crown-4 and $[\text{Me}_2\text{SiO}]_3$ was added. The living polymer ends of the resulting triblock copolymer were subsequently coupled with Me_2SiCl_2 to produce polymer **25**.⁶⁷

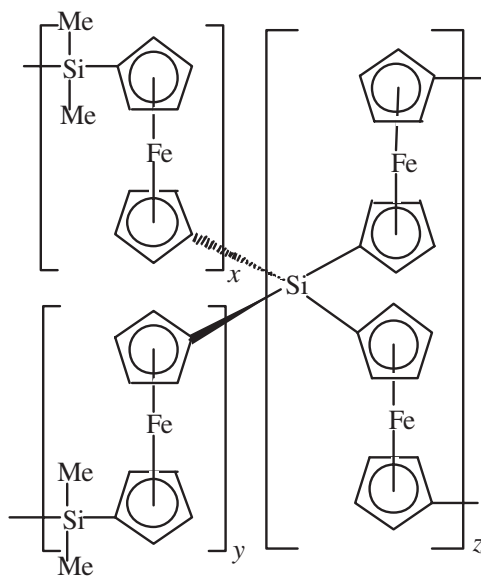


Copolymerization reactions with ferrocenophanes using transition metal catalysts have also been accomplished.^{70,71} The self-assembly of block copolymers has been examined, and polymers with dimethylsiloxane or ethyleneoxide blocks have been found to be soluble in aqueous solution.^{72,73} These ferrocene-based polymers have been found to self-assemble in solution, and their morphologies have been investigated.^{70–73} A number of water-soluble anionic (**26**)⁷⁴ and cationic (**27**)⁷⁵ polyelectrolytes have also been produced by sidechain functionalization.



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Tang and coworkers have reported that pyrolyzed hyperbranched polyferrocenylsilanes have greater ceramic yields than their linear polymeric counterparts.⁷⁶ Manners has reported that thermally crosslinked polyferrocenylsilanes (**28**) possessed greater thermal stability than their linear analogs.⁷⁷ The swelling properties of these crosslinked polymers were examined, and the solubility parameter of the corresponding linear homopolymer was determined. The pyrolysis of linear, hyperbranched, and crosslinked polyferrocenylsilanes has resulted in the production of ceramics that possess magnetic properties.⁷⁶⁻⁷⁸



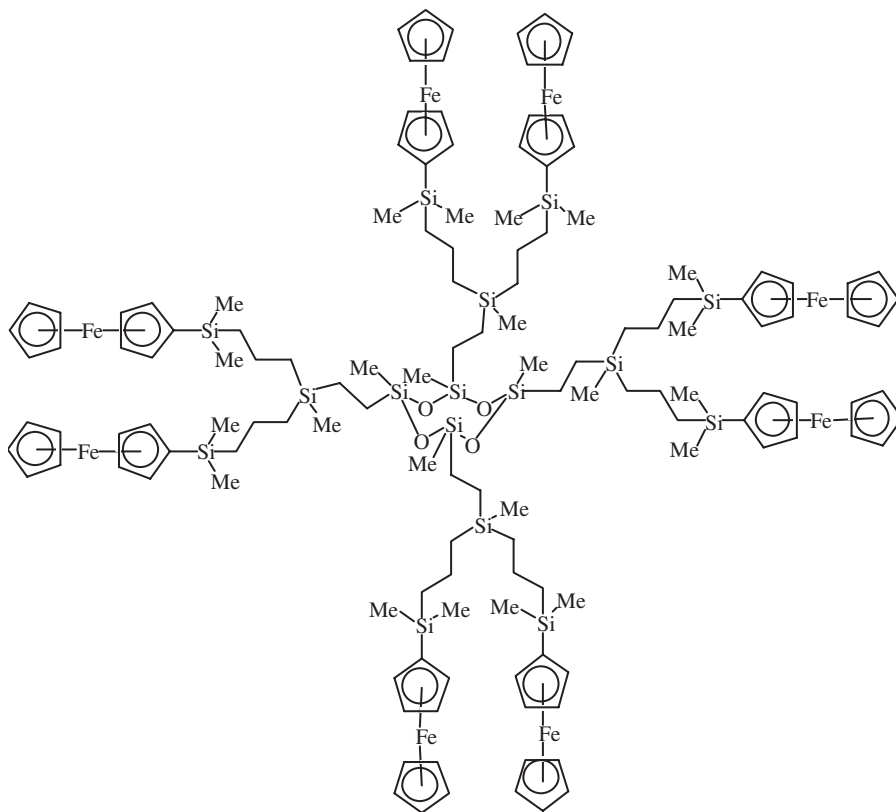
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The synthesis and properties of star polymers and dendrimers functionalized with ferrocene units has attracted a great deal of attention. The synthesis of high-generation dendrimers functionalized with chiral ferrocenyl units in their structures has been reported.⁷⁹ The chiroptical properties of this class of dendrimer was dependent on the number of ferrocenyl groups and their chemical environment, but not on their position within the dendrimer. Deschenaux has reported the synthesis of liquid crystalline ferrocene-based polymers possessing an enantiotropic smectic A phase.⁸⁰ Ferrocene-functionalized cyclic siloxane (**29**) and silsesquioxane branched polymers have also been reported.⁸¹ A hyperbranched polymer with a cubic silsesquioxane core was used to mediate the electrocatalytic oxidation of ascorbic acid.

The guest-host relationship of dendrimers containing 4, 6, and 8 ferrocene groups with cyclodextrins has been examined by Cuadrado and coworkers.⁸² It was found that the low-generation dendrimers formed reversible complexes with β -cyclodextrin, while the dendrimer with 16 peripheral ferrocene groups underwent incomplete complexation reactions. The synthesis of a dendrimer containing nine

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peripheral organoiron groups (**30**) was prepared by reaction of an amine-functionalized dendrimer with the acid chlorides of ferrocene.⁸³ These polymers were utilized as supramolecular redox sensors for the recognition of small inorganic anions. Ferrocenylsilation reactions were also used by Astruc and coworkers to prepare dendrimers with up to 243 ferrocenyl units at the periphery.⁸⁴

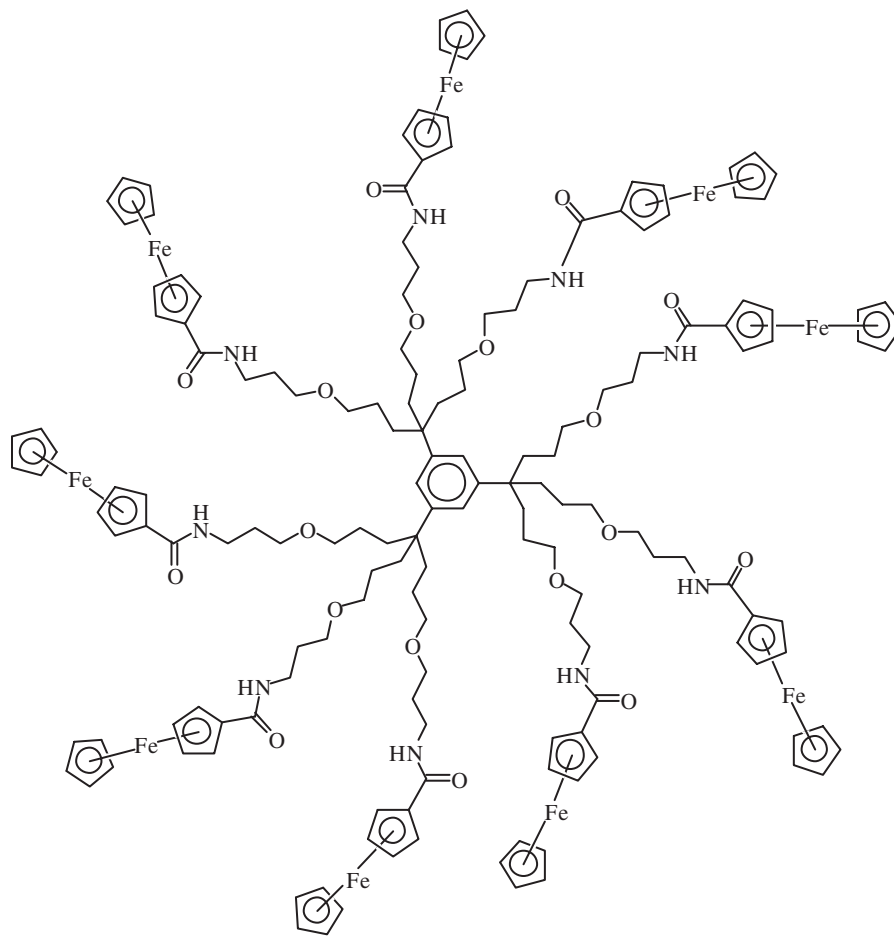


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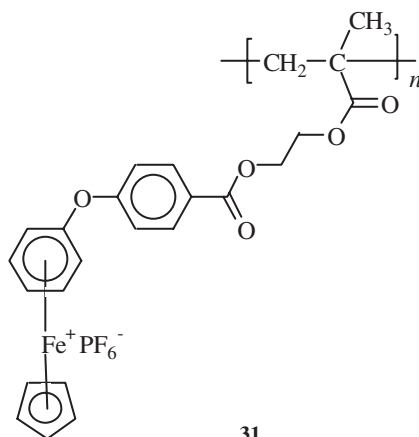
III. POLYMERS CONTAINING CYCLOPENTADIENYLIRON-COMPLEXED ARENES

We have reported the synthesis of polymethacrylates (**31**) and polystyrenes with cationic cyclopentadienyliron moieties coordinated to their sidechains using AIBN.^{85,86} Photolysis of these organoiron polymethacrylates allowed for the isolation of the corresponding organic polymethacrylates. The weight-average molecular weights (M_w) of these organic polymers ranged from 48,000 to 68,000. Electrochemical studies of the metallated polymethacrylates showed reductions of the iron centers occurring between $E_{1/2} = -1.1$ and -1.3 V.

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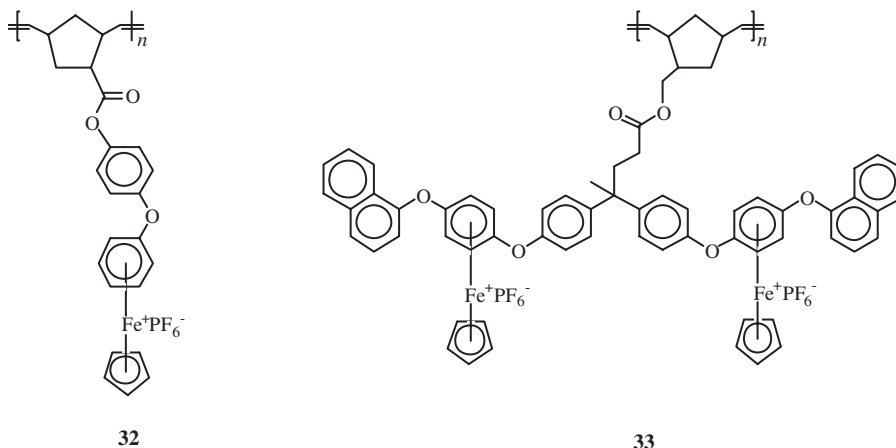
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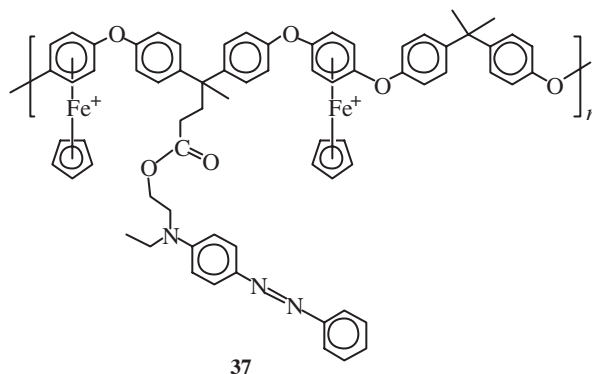
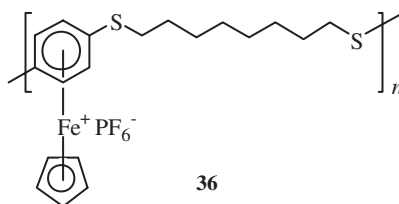
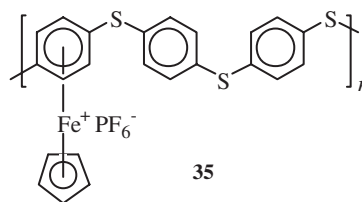
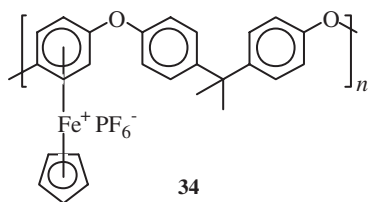
The ring-opening metathesis polymerization of norbornene monomers functionalized with arene complexes of cyclopentadienyliron has been reported using Grubbs' catalyst.⁸⁷ These polymerization reactions proceeded rapidly to produce the corresponding polynorbornenes (**32** and **33**). It was found that the incorporation of bulkier aromatic groups in the sidechains of these materials increased their glass transition temperatures and thermal stability.



The synthesis of cyclopentadienyliron-coordinated polyaromatic ethers and thioethers has been achieved by reaction of dichlorobenzene complexes with various oxygen and sulfur dinucleophiles.⁸⁸ These polymers exhibited good solubility in polar organic solvents such as acetone, acetonitrile, DMF, and DMSO. Photolysis of these polymers allowed for the isolation of the corresponding organic polymers; however, the solubilities of these polymers were much lower than those of their metallated analogues. Thermogravimetric analysis of the organoiron polymers indicated that the metallic moieties were cleaved from the polymers at approximately 200°C, while degradation of the polymer backbones occurred around 500°C. By designing diiron complexes containing terminal chloroarenes, polymers with alternating ether–thioether or amine–thioether spacers were also synthesized.⁸⁸ Differential scanning calorimetry (DSC) showed that the organic polyethers had the highest glass transition temperatures and polymers with thioether bridges had the lowest. Cyclic voltammetric studies of the cyclopentadienyliron-coordinated polyethers and thioethers (**34–36**) showed that these polymers underwent reversible reduction processes. Polymers containing CpFe⁺ and Cp^{*}Ru⁺ moieties pendent to their backbones have also been synthesized.⁸⁹

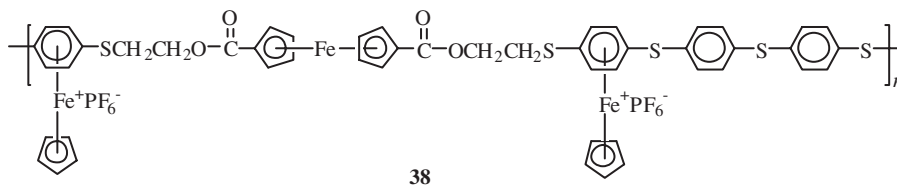
The synthesis of polyaromatic ethers (**37**) and thioethers containing azobenzene dyes in their sidechains has been achieved.⁹⁰ These polymers were prepared by reaction of cyclopentadienyliron-complexed azobenzene monomers with various dinucleophiles. These organoiron polymers were bright orange or red, and could be bleached by irradiating the polymer in a solution containing hydrogen peroxide.

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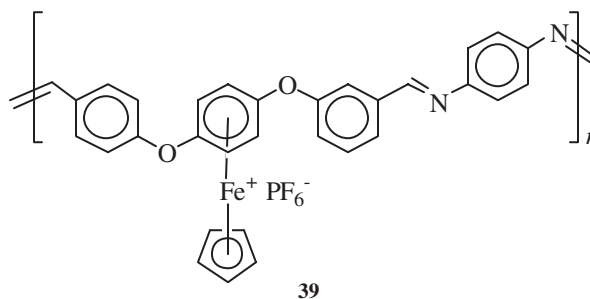


The synthesis of polymers containing cyclopentadienyliron moieties within and pendent to their backbones (**38**) was reported by Abd-El-Aziz and coworkers.⁹¹ The cationic cyclopentadienyliron moieties were pendent to the polymer backbones, while the neutral ferrocene units were incorporated into the polymer backbones. The cationic iron centers underwent reversible reduction processes, while the neutral iron centers underwent reversible oxidation processes. The cationic cyclopentadienyliron moieties were cleaved from the polymer backbones by photolysis; however, the ferrocene units in the polymer backbones were not degraded.

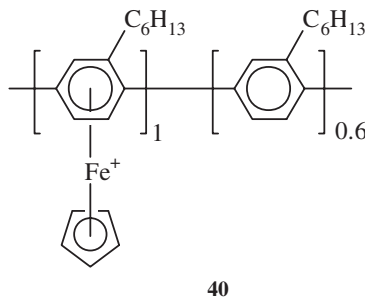
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The design of polyether/imines coordinated to cyclopentadienyliron moieties (**39**) has been achieved via the reaction of a dialdehyde complex of cyclopentadienyliron with a number of aliphatic and aromatic diamines.⁹² The polycondensation reactions resulted in the isolation of the polyether/imines in good yields.

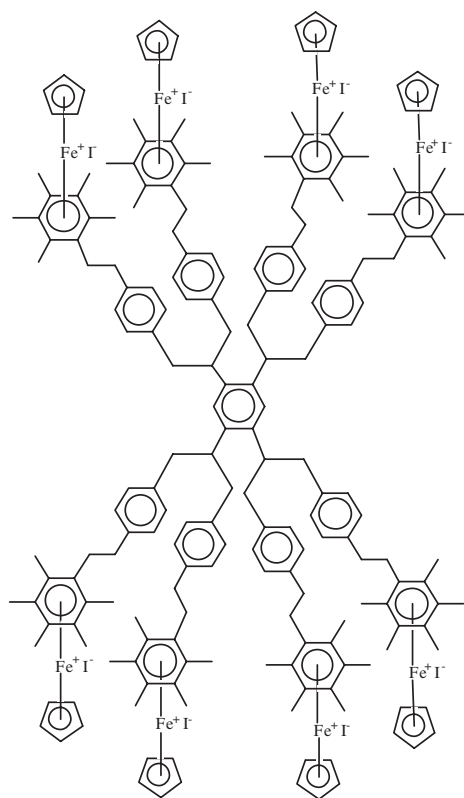


Nishihara has reported the complexation of poly(hexyl phenylene) with cyclopentadienyliron, where approximately 1 in every 1.6 aromatic rings was coordinated to the metallic moiety.⁹³ Spectroelectrochemical analysis of this organoiron polymer (**40**) suggested that a network was formed between the aromatic rings of neighboring polymer chains following reduction of the cationic iron centers to the neutral radicals.



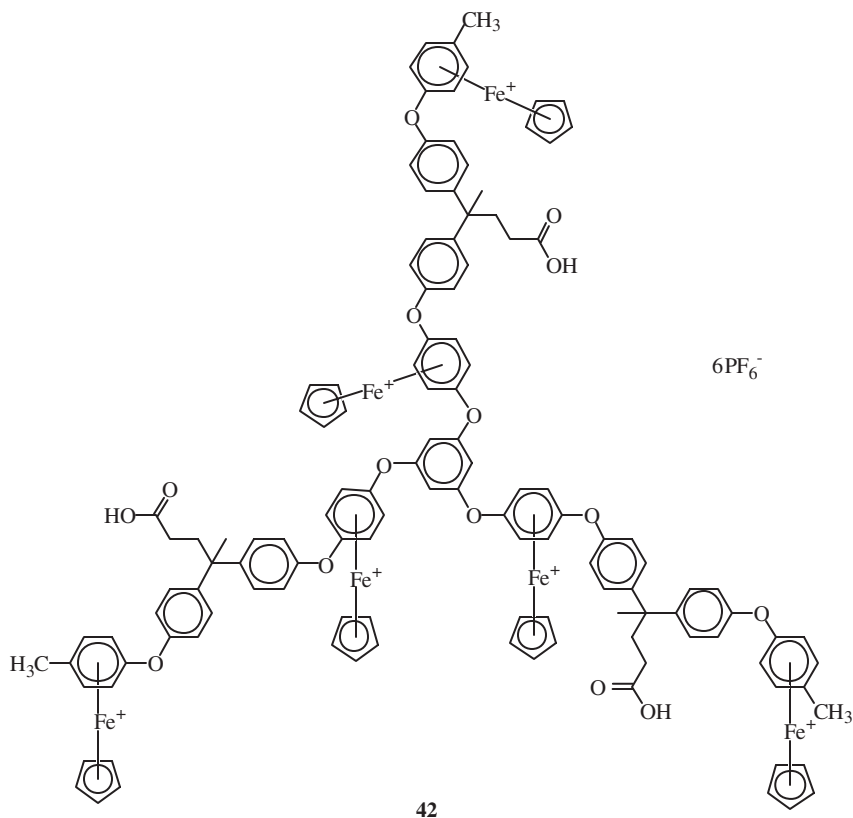
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Star polymers and dendrimers have been synthesized by Astruc using cyclopentadienyliron-mediated peralkylation, benzylation, and allylation reactions of cationic tri-, *tetra*-, and *hexa*-methylbenzene cyclopentadienyliron complexes.⁹⁴⁻⁹⁶ These star and dendritic polymers contained cationic cyclopentadienyliron moieties at the core and/or the periphery. The cathodic reduction of nitrates and nitrites to ammonia has been achieved using a water-soluble dendrimer containing six cationic cyclopentadienyliron moieties as a redox catalyst.⁹⁴ The octametallallic star (**41**) was prepared by deprotonation of permethylated iron complexes.⁹⁶



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Abd-El-Aziz and coworkers have reported the synthesis of star-shaped polyaromatic ethers containing up to 15 cyclopentadienyliron cations pendent to aromatic rings.⁹⁷ Polymer **42** is an example of a water-soluble *hexa*-metallallic star complex. Electrochemical studies showed that reduction processes for the inner and outer iron complexes could be distinguished for the *hexa*- and nonametallallic stars.

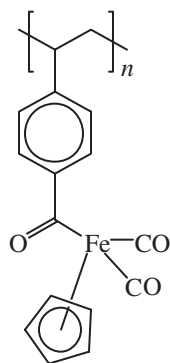


IV. POLYMERS CONTAINING IRON CARBONYL COMPLEXES

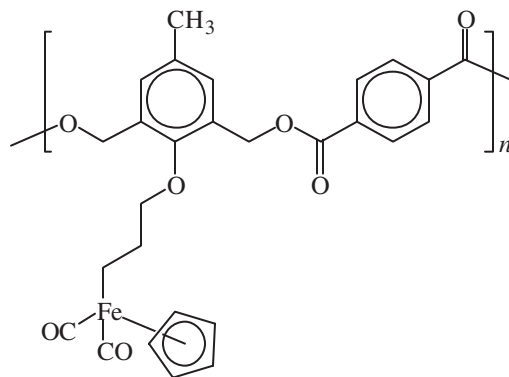
Polymers containing metal-carbon σ and π bonds were reported by Mapolie and coworkers.⁹⁸ Homo- and copolymerization reactions of organoiron monomers containing olefins with AIBN yielded the corresponding organometallic polymers (**43**). Bifunctional hydroxyl monomers functionalized with iron complexes were subjected to polycondensation with terephthaloyl chloride to produce low molecular weight polyesters (**44**).⁹⁹

Martin and Hanks have reported the oxidative polymerization of dicarbonyl $(\eta^5\text{-cyclopentadienyl})(\eta^1\text{-pyrrolyl})\text{iron(II)}$.^{100,101} The resulting polymer (**45**) yielded an azaferrocene polymer (**46**) on refluxing. The electrical conductivities of polymers **45** and **46** were found to be 7×10^{-3} and 1.5×10^{-4} S/cm, respectively.

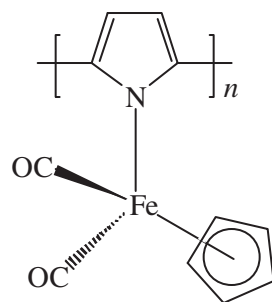
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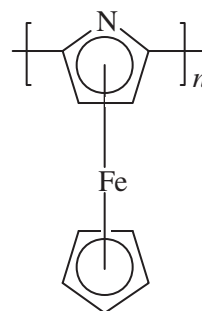
43



44



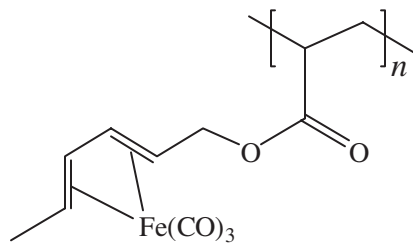
45



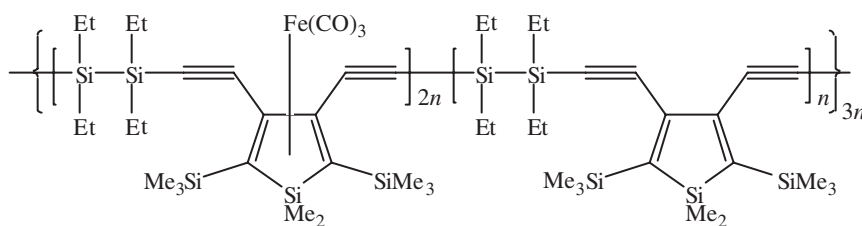
46

In 1973, the homo- and copolymerization of π -(2,4-hexa-dienyl acrylate)tricarbonyliron with styrene, methyl acrylate, acrylonitrile, and vinyl acetate was reported by Pittman and coworkers.^{102,103} It was reported that these polymers (47) could be protonated to produce the π -allyliron derivatives.¹⁰³ Nakamura and coworkers have also reported the synthesis and electrochemical properties of polymers containing dienes coordinated to iron tricarbonyl moieties in the polymer sidechains.¹⁰⁴

UV irradiation of polymers containing silole units in their backbones in the presence of iron pentacarbonyl resulted in the coordination of iron tricarbonyl units to one of every two silole rings in the polymer backbone.¹⁰⁵ On doping, these organoiron polymers (48) become electrically conducting and their UV absorption bands are red shifted relative to the uncoordinated polymers.



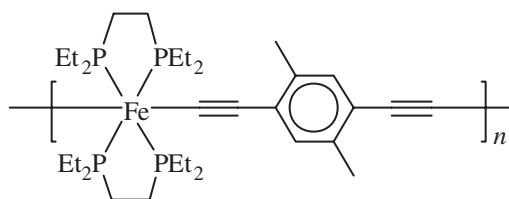
47



48

V. IRON POLYINES

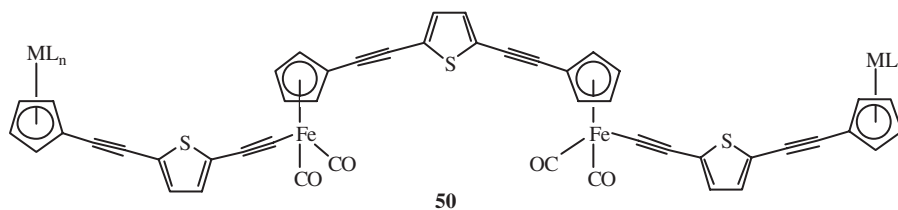
Since the late 1970s, poly(metal acetylide)s have been examined for group 9 and 10 transition metals. Lewis and coworkers have also demonstrated that group 8 metals, including iron, can form σ bonds with alkynes via reaction of an iron-chelating phosphine dichloro complex with *bis*-trimethylstannylalkynes to form high molecular weight polymers in the presence of a catalytic amount of CuI.^{106,107} The weight-average molecular weight of polymer **49** was determined to be 173,000 by GPC.



49

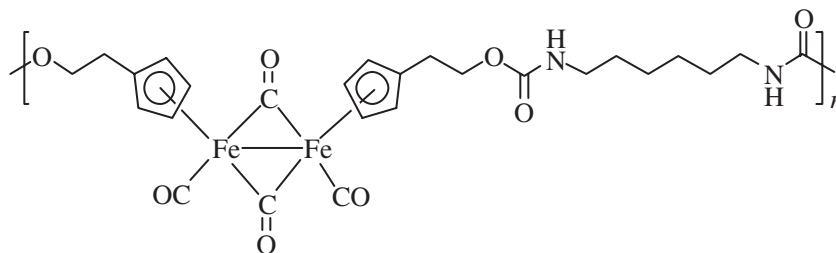
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Oligomeric complexes containing iron acetylide units in units in their structures (**50**) were also examined by Lo Sterzo and coworkers.¹⁰⁸

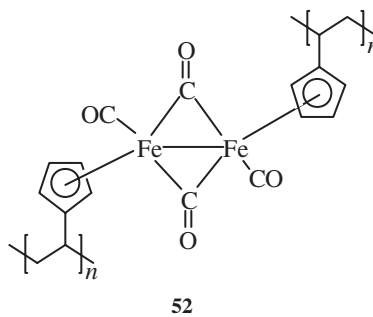


VI. POLYMERS WITH IRON-IRON BONDS

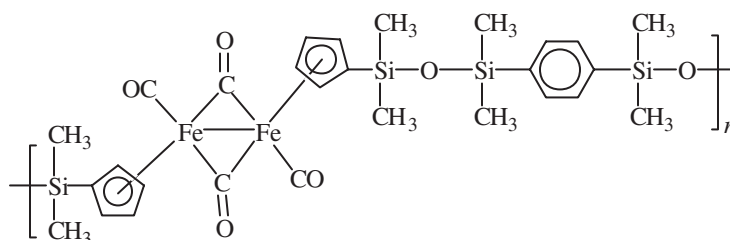
In the early 1990s, Tyler and coworkers described the synthesis of oligomeric urethanes and ether urethanes containing photodegradable iron-iron bonds in their backbones.¹⁰⁹⁻¹¹² The solid-state photochemical degradation of low molecular weight polyurethanes such as **51** was also examined in the presence of light and oxygen.



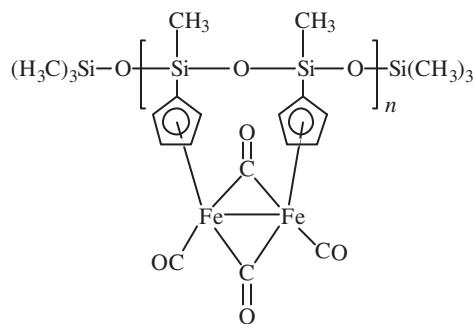
Vinyl monomers were also homo- and copolymerized in the presence of AIBN to produce polymers (**52**) with Fe-Fe bonds in their backbones.



Cuadrado and coworkers have reported the synthesis of polysiloxanes with Fe–Fe bonds using two different methodologies.¹¹³ Polymers with the metal–metal bonds within their backbones (**53**) were synthesized by polycondensation reactions of disilanol with a dinuclear iron–iron bonded complex, while reaction of a polysiloxane with $\text{Fe}(\text{CO})_5$ resulted in polymer **54**. Polymer **54** possessed good thermal stability and poor solubility, which indicates that crosslinking between polymer chains may have occurred. Molecular weight analysis of polymers prepared by polycondensation reactions shows that these polymers have degrees of polymerization between 5 and 10.



53



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VII. OUTLOOK

The history of organoiron polymers can be traced to the 1950s, and much of the fundamental knowledge we possess of these materials, and organometallic polymers in general, stems from work done in and prior to the 1970s. However, there have been significant advances in organoiron polymers since the early 1990s. Within this time, we have seen a huge variety of organoiron polymers emerge. The discovery that the ring opening of ferrocenophanes produces high molecular weight

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polymers, and that these polymers possess a wide range of properties, has changed the perceptions of organometallic polymers. Many of the difficulties that early researchers in this area had in producing well-defined, high molecular weight polymers have since been overcome. New classes of polymers containing organoiron groups continue to emerge, leading to new properties and applications.

This chapter was intended to briefly introduce the types of organoiron polymers that have been developed since the early 1950s. Subsequent chapters in this volume will detail some of the advances that have taken place in recent years. The synthesis and properties of ferrocene-based polymers and polymers containing arene complexes of cyclopentadienyliron will be described. The properties and applications of some of these materials will be described, and the reader will hopefully gain an appreciation of organoiron polymers.

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