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Monomers, oligomers and polymers containing arenes with pendent transition metal moieties

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Contents

Abstract

A number of synthetic routes have been utilized in the production of organometallic monomers and polymers containing arenes coordinated to the Group VI, VII and VIII transition metals. Transition metal-coordinated monomers were prepared either by nucleophilic aromatic substitution reactions of transition metal-coordinated haloarenes with phenolic compounds or via ligand exchange reactions. These monomers were polymerized directly or following removal of the metallic moieties to produce the resulting organometallic or organic polymers. Well-defined oligomeric ethers prepared via sequential nucleophilic displacement reactions were functionalized via nucleophilic addition reactions. The synthesis and characterization of heterometallic oligomers and complexes containing both neutral and cationic metallic moieties are also reviewed. The synthesis of polymers containing arenes coordinated to transition metal moieties was investigated using metal-mediated reactions. The introduction of transition metal moieties into pre-existing polymeric materials has also proven to be an effective methodology to isolate this class of organometallic polymer. Supramolecular assembly of arene complexes of transition metals was explored as a route to macromolecular materials. The use of arene complexes has allowed for the preparation of a number of polyfunctional molecules used in the design of dendrimers and star polymers. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Transition metal-complexed arenes; Chromium; Molybdenum; Manganese; Iron; Ruthenium; Monomers; Polymers; Nucleophilic aromatic substitution

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1. Introduction

In recent years, there has been a growing interest in the use of Groups VI, VII and VIII transition metal arene complexes in monomer and polymer synthesis [1–3]. The most studied transition metal moieties coordinated to arenes are $Cr(CO)_3$, $Mn^+(CO)_3$, $CpFe^+$ and Cp^*Ru^+ [1–4]. The significance of these materials stems from their ability to undergo nucleophilic aromatic substitution (S_NAr) and addition reactions. The magnitude of the electron-withdrawing capacity of these metallic moieties has been studied, and it was found that their strengths decrease in the order $Mn^+(CO)_3 >$ $CpFe^+$ and $Cp^*Ru^+ \gg Cr(CO)_3$ [5–9]. While manganese tricarbonyl is the most electron-withdrawing fragment, difficulties involved in the preparation of its dihaloarene complexes have limited its use in polymer synthesis [2]. Nucleophilic addition reactions to arene–$Mn^+(CO)_3$ complexes have proven to be an effective method to functionalize aromatic rings [2]. The chromium tricarbonyl fragment has often been used in organic synthesis to mediate S_NAr reactions, even though it is the least electron-withdrawing system [2,10]. Cyclopentadienyliron and ruthenium moieties exert very similar influences on arenes, however, the preparation of the iron analogues is much more facile [1–4]. The introduction of metallic moieties into organic polymers results in materials that exhibit magnetism, hardness, enhanced solubility and interesting optical and redox behavior [11–14]. Manners have recently reviewed the synthesis and properties of organometallic polymers with a focus on those polymers with transition metals in the main chain [11].

This review describes the synthesis of monomeric and polymeric materials containing arenes coordinated to Groups VI, VII and VIII transition metal moieties. The role of these arene complexes in monomer and polymer design, as well as the influence of the transition metals on the properties of the organometallic polymers, is also surveyed.

2. Monomer design for the synthesis of organometallic and organic macromolecules

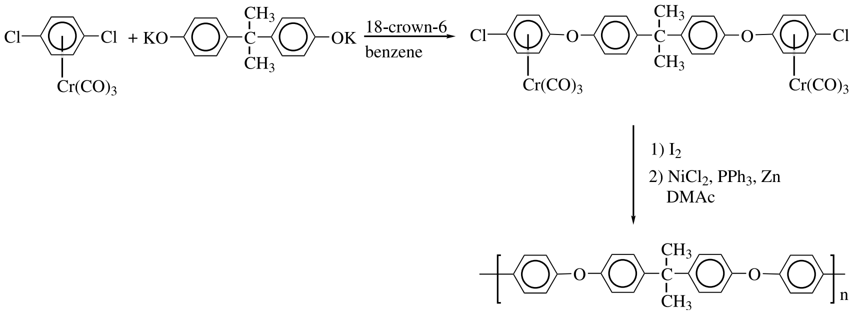
2.1. Arylethers

Transition metal arene complexes have proven to be excellent precursors in the design of functionalized monomers [1,2]. The mild reaction conditions associated with S_NAr reactions of chloroarene complexes allowed for the formation of aryl ether bonds. This is important since the traditional synthetic routes to aromatic ethers require harsh conditions, catalysts, and often give mixtures of products [15,16]. In 1993, Percec and Okita reported the synthesis of monomeric ethers prepared via $Cr(CO)_3$-mediated S_NAr reactions of *p*-dichlorobenzene complexes with diphenolic compounds [17]. Oxidative demetallation of the chromium tricarbonyl moieties from the monomeric units was achieved prior to polymerization. An aryl ether monomer containing terminal chloro groups was polymerized using a Ni(0) catalyzed reaction as shown in Scheme 1. The resulting amorphous polyaromatic ethers were determined to have number average molecular weights (M_n) up to 11,200.

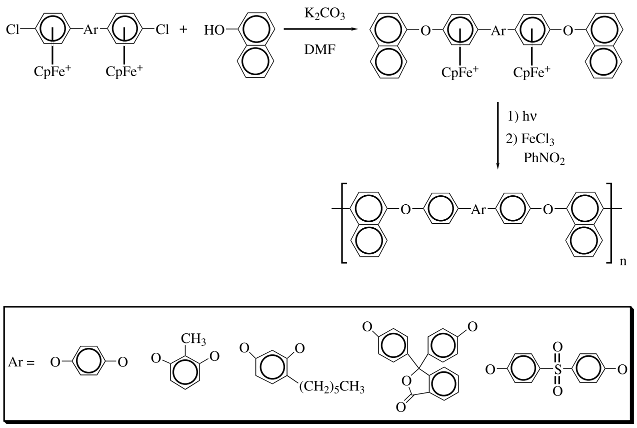
Pearson and co-workers have utilized chloroarene–cyclopentadienyliron complexes in the synthesis of various aromatic ether monomers [18–20]. These materials were designed to contain terminal phenolic and carboxylic acid groups. Following photolytic cleavage of the cyclopentadienyliron moieties, polycondensation of these monomers produced polyaromatic ether esters, as shown in Scheme 2. Polymers with tailored thermal properties were obtained through the use of either *m*- or *p*-dichloroarene complexes, as well as by varying the nature of the aromatic linkages. Some of these polymers have also displayed liquid crystallinity.

A metal-mediated approach to the monomeric precursors of polyaromatic ethers was developed via reaction of chloroarene–cyclopentadienyliron complexes with phenolic compounds [21]. Reaction of *p*-dichlorobenzene cyclopentadienyliron complexes with dinucleophiles yielded diiron complexes with terminal chloro groups. These complexes were then capped with naphthyl groups, producing the organoiron-complexed aryl ether monomers. Upon photolytic removal of the cyclopentadienyliron moieties pendent to the monomers' backbones, the organic aromatic ethers were isolated as shown in Scheme 3. Polymerization of these monomers was achieved via the Scholl reaction, which proceeds via a radical–cation mechanism [22,23]. Carbon–carbon bond formation between the terminal aromatic rings was achieved using $FeCl_3$ as initiator. The resulting polyaromatic ethers had weight average molecular weights (M_w) as high as 124,000, and glass transition temperatures ranging from 147 to 226 °C. Thermogravimetric analysis of these polymers showed that they were thermally stable from 458 to 575 °C.

Ring-opening polymerization of cyclic aryl ethers is another route that has been explored in the design of polyaromatic ethers. It has been established by a number of research groups that cyclic aryl ethers can be polymerized thermally in the presence of an anionic initiator [24–27]. The synthesis of cyclic aromatic molecules has been reported using a number of organic and organometallic strategies [24–33]. A number of the organic routes yield macrocycles with various cycle sizes as well as linear oligomers [24–27]. These reactions are often low yielding and operate using high dilution techniques. $Cr(CO)_3$, $CpRu^+$ and $CpFe^+$ complexes were utilized in the preparation of macrocylic com-



Scheme 1.



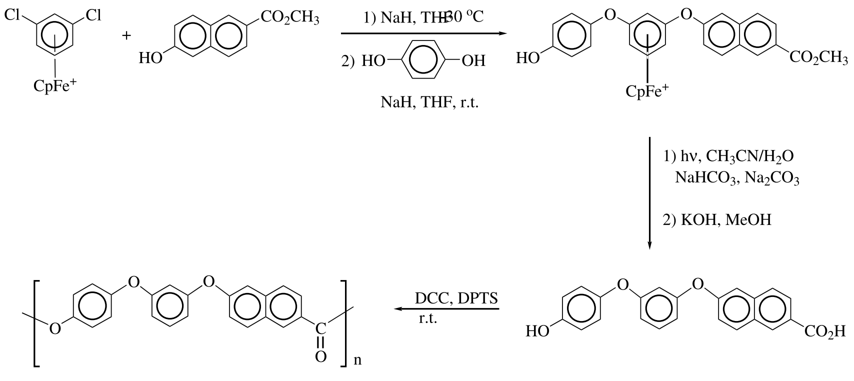
Scheme 3.

pounds [28–33]. Recently, we reported the synthesis of cyclic aryl ethers containing symmetric and asymmetric bridges via nucleophilic displacement reactions of *o*- and *m*-dichlorobenzene cyclopentadienyliron complexes (Scheme 4) [34,35]. Following removal of the metallic moieties, ring-opening polymerization of these cyclic monomers was achieved in the presence of potassium carbonate at 350 °C (Scheme 5) [36].

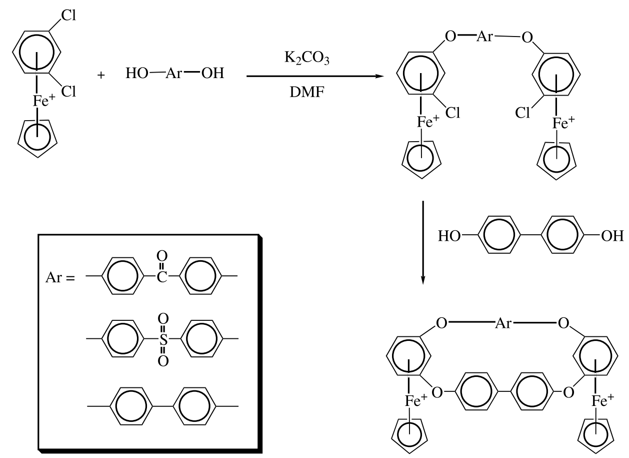
2.2. Styrenes and acrylates

In the 1970s, Pittman and co-workers reported the synthesis of polystyrenes and polyacrylates functionalized with arenes coordinated to chromium tricarbonyl [37,38]. Using the methodology previously reported by Rausch and co-workers, a styrene monomer coordinated to $Cr(CO)_3$ was prepared [39]. This organometallic monomer was subsequently co-polymerized with either styrene or methyl acrylate using azobisisobutyronitrile (AIBN) as shown in Scheme 6. Homo- and co-polymerization of an acrylate monomer containing an arene with a pendent $Cr(CO)_3$ moiety was also accomplished with a number of organic and organometallic co-monomers [38]. The soluble organochromium homo- and co-polymers had M_n values ranging from about 20,000 to 60,000.

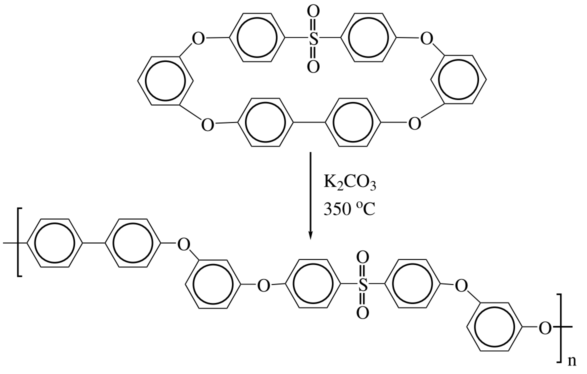
The synthesis of polymethacrylates with cationic cyclopentadienyliron moieties coordinated to their side chains has recently been reported [40]. Scheme 7 shows the synthesis of a polymethacrylate containing diaryl ether spacers in its side chains. These cationic monomers were polymerized using AIBN as the initiator, resulting in the isolation of the polymeric materials with cationic organoiron side chains. Photolytic demetallation of the cyclopentadienyliron-coordinated polymethacrylates resulted in the isolation of the corresponding organic analogues, whose M_w's ranged from 48,000 to 68,000. The electrochemical behavior of the metallated polymethacrylates was explored using cyclic voltammetry [41]. The cyclic voltammogram (CV) in Fig. 1 shows reduction of the iron centers occurring at $E_{1/2} = -1.23$ V.



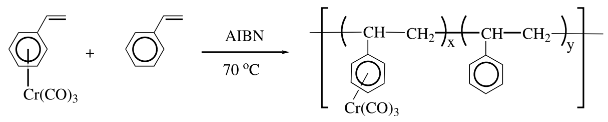
Scheme 2.



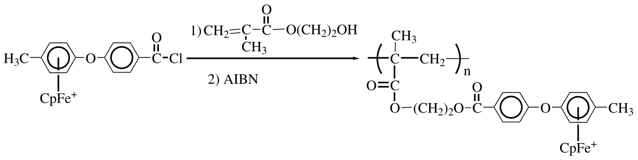
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 7.

2.3. Norbornenes

The industrial importance of polynorbornene stems from its use as a noise- and vibration-dampening agent as well as its applications as a specialty elastomer [42,43]. The functionalization of the side chains of polynorbornene has been explored in order to determine the effects of various functional groups on polymer properties [44,45]. The reaction of chloroarene complexes with 5-norbornene-2-methanol allowed for the formation of an aryl ether bridged norbornene monomer, which was polymerized following removal of the iron moiety from its structure [46,47]. Polymerization of the monomer using ruthenium chloride in 1:1 EtOH–H_2O gave the aryl ether functionalized polynorbornene with $M_w = 535{,}000$.

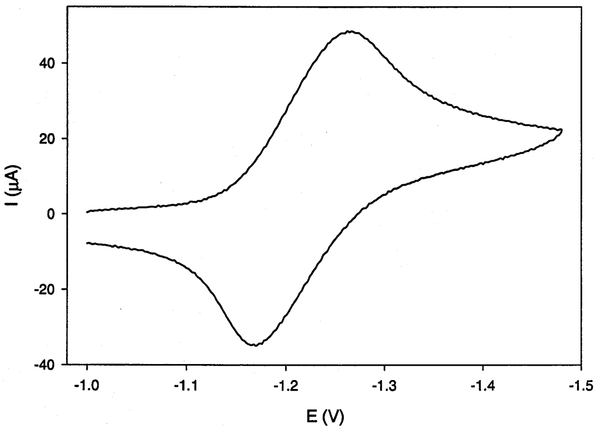
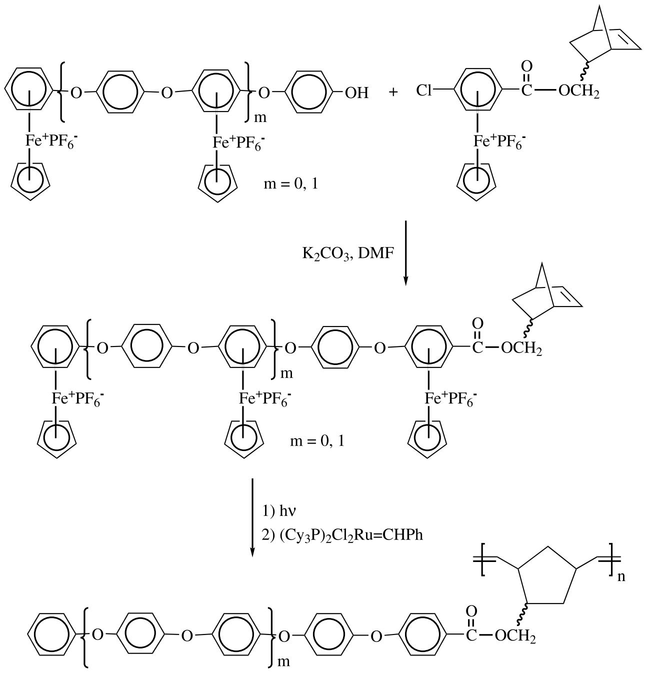


Fig. 1. Cyclic voltammogram of an iron-coordinated polymethacrylate.

Reaction of oligomeric ether complexes containing terminal phenolic groups with a substituted norbornene complex led to the isolation of norbornene monomers as shown in Scheme 8 [46,47]. Polymerization of these monomers was studied using ruthenium chloride as well as bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride (Grubbs' catalyst). It was found that



Scheme 8.

the ester linkage within the monomers resulted in deactivation of the $RuCl_3$, and thus Grubbs' catalyst was utilized in the polymerization of these functionalized norbornenes. The resulting norbornene-based polymers contained one, three and five aromatic rings within their side chains.

Thermal analysis of these polynorbornenes showed that as the number of aromatic ether linkages in the polymer side chains increased, the glass transition temperatures and thermal stability of the polymers also increased. For example, the onset for weight loss in the polymers' thermograms commenced at 385 °C for the polynorbornene that contained one aromatic ring per side chain, and this temperature increased to 409 °C for the polymer with five phenyl rings in each of its side chains. As well, the glass transition temperatures of the polymers increased from 55 to 73 °C as the number of aromatic rings in the polymer side chains increased from one to five. It was also notable that the solubility of the polymers decreased with an increased number of aromatic rings in their side chains [47].

The incorporation of aliphatic ether spacers into the side chains of polynorbornenes has also been reported [48]. It was found that the thermal stability of these high molecular weight polymers ($M_w = 397{,}000$) increased with respect to unfunctionalized polynorbornene, while their glass transition temperatures were much lower. Analysis of the organic monomers was achieved using 2D-NMR techniques in order to characterize their *endo* and *exo* isomers. Fig. 2 shows the HH COSY of the monomer containing a hexamethylene bridge. The olefinic resonances in the spectrum of the substituted norbornenes appeared between 5.93 and 6.21 ppm, and following polymerization, new olefinic resonances indicative of the polymers' unsaturated backbones appeared between 5.04 and 5.57 ppm.

Polymerization of norbornenes functionalized with cationic cyclopentadienyliron-coordinated aryl ethers was recently reported [49]. The ring-opening metathesis polymerization of these metallated monomers was accomplished using Grubbs' catalyst, which is known to be tolerant to polar functional groups. While the cyclopentadienyliron-coordinated monomers were successfully polymerized using this ruthenium alkylidene catalyst, the molecular weights of the resulting polymers were lower than those obtained when analogous organic monomers were polymerized (Scheme 9).

3. Stepwise design of polyethers with pendent cyclopentadienyliron cations

The synthesis of polyaromatic ethers with well-defined molecular weights has been accomplished by sequential S_NAr reactions of chloroarene complexes of cyclopentadienyliron with hydroquinone [50–52]. This methodology allowed for the preparation of aromatic ether complexes with as many as 35 metallic moieties

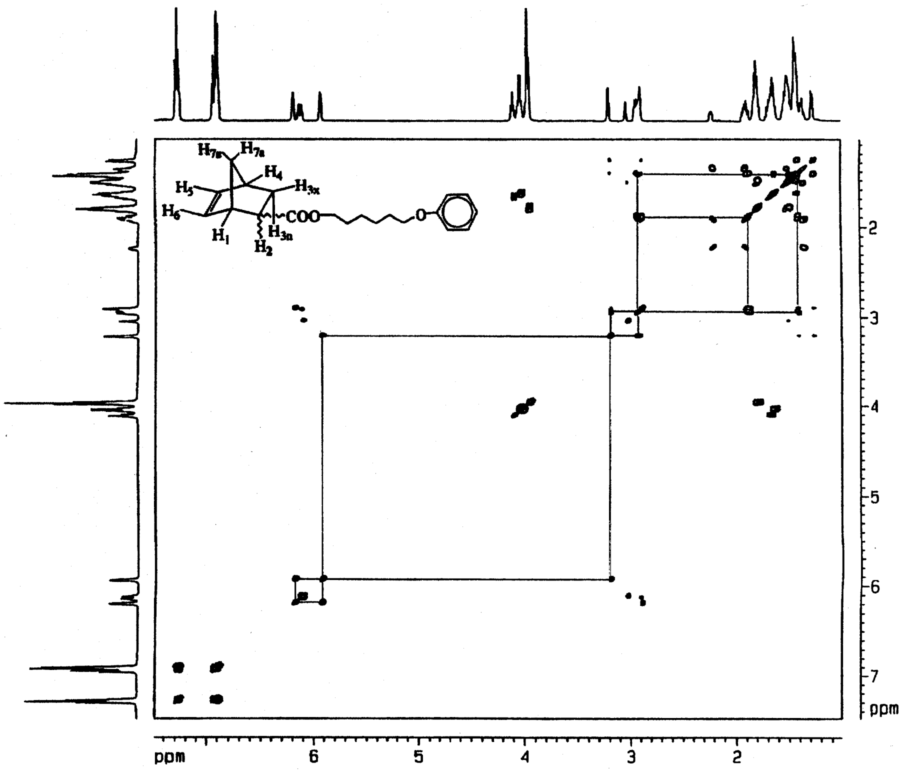
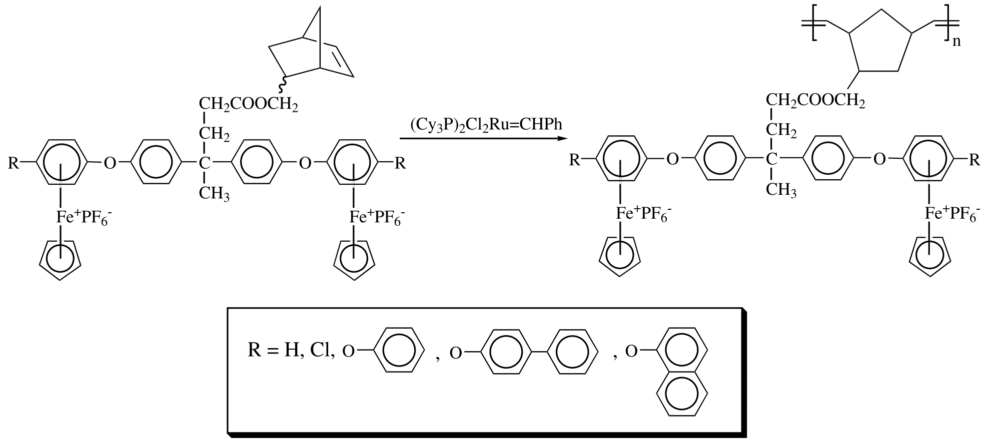
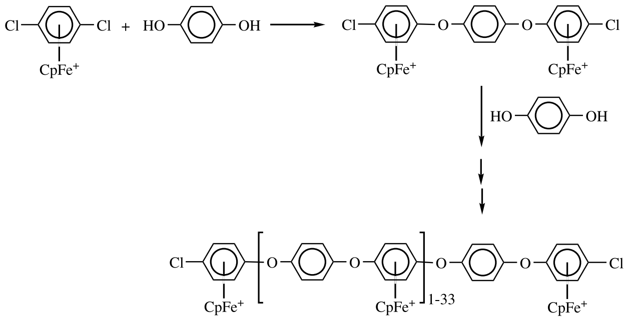


Fig. 2. COSY spectrum of substituted norbornene monitor.



Scheme 9.

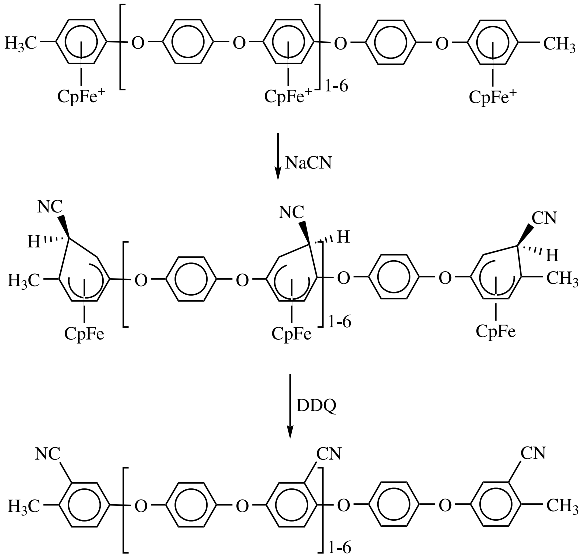


Scheme 10.

pendent to their backbones [51]. Scheme 10 shows the general synthesis of these materials, which contained cyclopentadienyliron cations pendent to alternating aromatic rings.

The electrochemical behavior of cationic aromatic ether, thioether and sulfone complexes of cyclopentadienyliron was studied using cyclic voltammetry and coulometry [52,53]. The redox potentials of the complexes were dependent on the nature of the heteroatoms between the complexed aromatic rings [53]. Diiron complexes with aromatic ether, thioether or sulfonyl linkages were reduced to neutral and anionic complexes in two separate redox steps. In the etheric diiron complex, the iron centers were electronically isolated on the time scale of the experiment, while in the complex with thioetheric linkages, the CV's showed that there was some communication between the iron centers [53]. These results are consistent with other studies on the electrochemical behavior of arene complexes of cyclopentadienyliron [54].

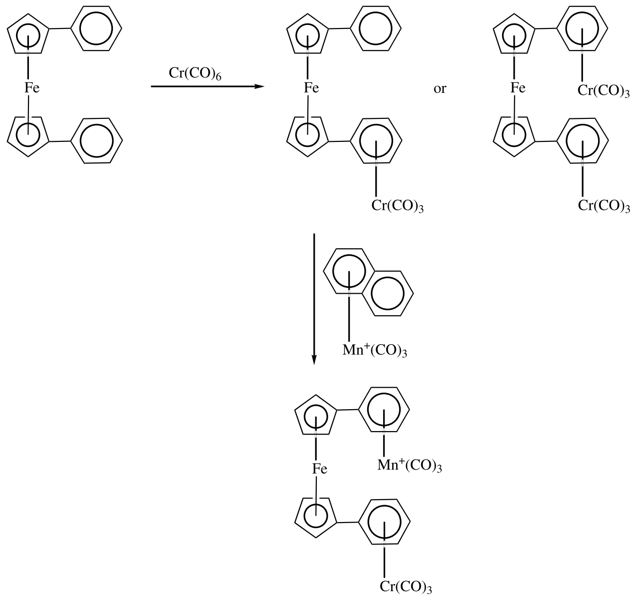
Functionalization of these aromatic ether complexes was achieved via nucleophilic addition to the complexed aromatic rings [55,56]. Scheme 11 shows the reaction of aromatic ether oligomers with sodium cyanide, leading to the formation of the neutral adducts [55]. It was determined that addition of the cyano group to the complexed aromatic rings occurred *meta*- to the etheric linkages on the terminal arenes. The ^{1}H-NMR spectra of the cationic aromatic ether complexes and their corresponding neutral cyano adduct was utilized to characterize these materials [55]. The unstable adducts were treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), resulting in the oxidative cleavage of the iron moieties, and generation of the organic nitriles.



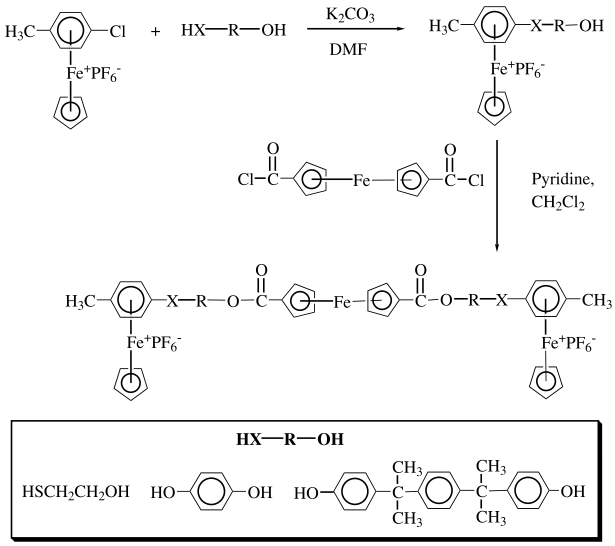
Scheme 11.

4. Heterometallic oligomers

Chung and co-workers have reported the preparation of oligomeric complexes containing neutral ferrocenyl moieties as well as η^6-arene–Cr(CO)$_3$ and Mn$^+$(CO)$_3$ moieties within their structures [57,58]. Scheme 12 shows the method used to prepare a trimetallic complex



Scheme 12.



Scheme 13.

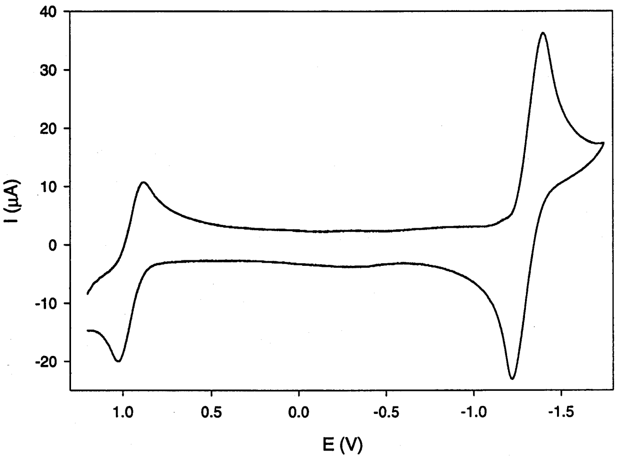


Fig. 3. Cyclic voltammogram of trimetallic complex containing one neutral and two cationic iron centers.

containing iron, chromium and manganese atoms. Complexes containing iron and manganese or chromium and manganese metal centers were also synthesized using similar strategies. The synthesis of a pentametallic complex with a ferrocenyl core bonded to four η^6-arene–Cr(CO)$_3$ branches was also reported [58]. This heterometallic complex was prepared by reaction of the tetra-phenyl substituted ferrocene complex with chromium hexacarbonyl.

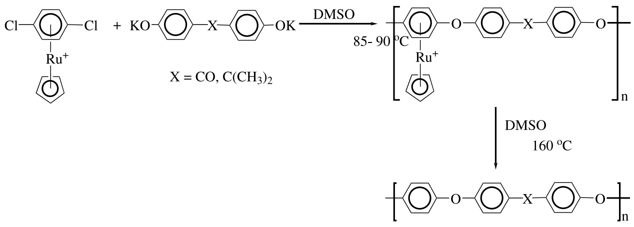
Complexes containing both neutral and cationic iron centers were prepared according to the method described in Scheme 13 [59]. This work involved the reaction of ferrocene derivatives with arene–cyclopentadienyliron complexes. The cationic iron complexes were prepared via displacement of the chloro group from the η^6-chlorotoluene–η^5-cyclopentadienyliron complex by dinucleophilic compounds. These complexes were then coupled to 1,1′-ferrocenedicarbonyl chloride, yielding the trimetallic complexes with one neutral and two cationic iron centers.

The electrochemical behavior of these systems was studied using cyclic voltammetry. The CV of the trimetallic complex containing the alkyl bridge can be seen in Fig. 3. The neutral iron centers underwent a reversible oxidation process at $E_{1/2} = 0.96$ V, while the cationic iron centers underwent a reversible reduction process at $E_{1/2} = -1.31$ V. This research has been extended to include the preparation of polymeric materials containing neutral ferrocenyl complexes within their backbones and cationic cyclopentadienyliron moieties pendent to their structures [60].

5. Synthesis of polymeric materials with pendent transition metal moieties

5.1. *Polymers with etheric, thioetheric and amine bridges*

In 1985, Segal reported the synthesis of polyaromatic ethers prepared via cyclopentadienylruthenium



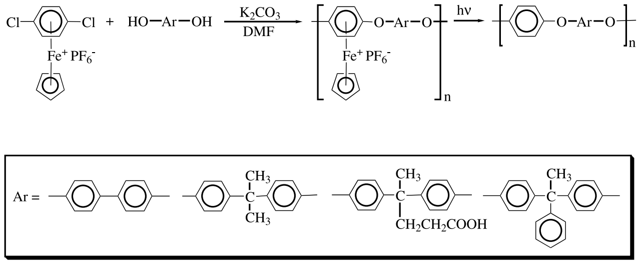
Scheme 14.

(CpRu$^+$)-mediated S_NAr reactions [61]. This study demonstrated that the presence of metallic moieties pendent to the backbone of poly(aromatic ether)s resulted in an enhancement of the solubilities of these materials relative to their organic analogues. While the metallated polyether-ketone shown in Scheme 14 was soluble in polar aprotic solvents such as DMF and DMSO, upon thermolysis of the polymer, the corresponding organic polyether-ketone was insoluble in most organic solvents. The presence of an isopropylidene bridge in the polymers allowed for the isolation of the soluble organic polyether whose M_w was found to be 15,600 in 1,2-dichloroethane. The glass transition temperatures of these organic polyethers ranged from 115 to 144 °C [61].

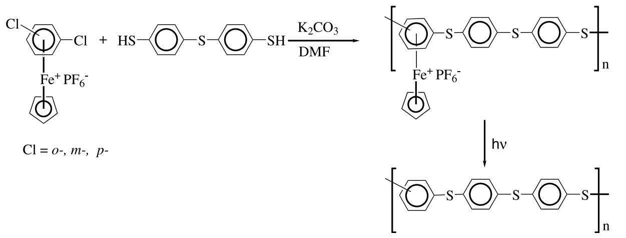
In 1993, Dembek and co-workers utilized a similar strategy to prepare poly(aromatic ethers and thioethers) with pendent pentamethylcyclopentadienyl–ruthenium (Cp*Ru$^+$) moieties [62,63]. A number of oxygen and sulfur dinucleophiles were utilized in the preparation of these polymers. This investigation also demonstrated that the solubility of the polymers increased due to metal coordination. Viscosity and NMR studies of these materials provided evidence of polymerization. The inherent viscosity of the polymers ranged from 0.52 to 1.49 dl g^{-1} in 0.5% DMF at 30 °C.

Recently, we have reported the synthesis, thermal and molecular weight analysis of polymers containing aromatic ether, thioether, thioether/amine and ether/thioether bridges [64,65]. The synthesis of these classes of organometallic polymers involved either the reaction of cyclopentadienyliron complexes of dichloroarenes with oxygen and sulfur dinucleophiles or the reaction of ether- or amine-containing diiron complexes with dithiols. Scheme 15 shows the synthesis of a number of soluble polyaromatic ethers that were prepared. Following photolytic demetallation of the polyaromatic ethers, only the polymers with alkyl groups in their backbones were soluble in organic solvents such as chloroform and THF. The molecular weights of the polymers were determined following removal of the cationic iron moieties, and the M_w's of the soluble portions of these materials ranged from 7,300 to 21,400 [65].

Scheme 16 describes the synthesis of poly(phenylene sulfide)s (PPS) via displacement of the chloro groups of *o*-, *m*-, and *p*-dichlorobenzene complexes with 4,4′-thiobisbenzenethiol. These polymers represent a soluble class of PPS, whose preparation can be achieved using very mild reaction conditions. Removal of the iron moieties from the backbone of these polymers allowed for the isolation of the corresponding organic analogues. *Para*-substituted PPS is a well-known polymer due to its excellent thermal stability, chemical resistance and conductivity [66,67]. It was found that the *m*- and *p*-substituted polymers were insoluble in common organic solvents at room temperature. DSC analysis of the polymers showed that the *o*-, *m*-, and *p*-substituted polymers had T_g's of 88, 72 and 86 °C, respectively. The *p*-substituted PPS also had a crystallization exotherm at 140 °C and a melting endotherm at 278 °C. The T_g, T_c and T_m for this polymer are consistent with literature values reported for PPS [67].

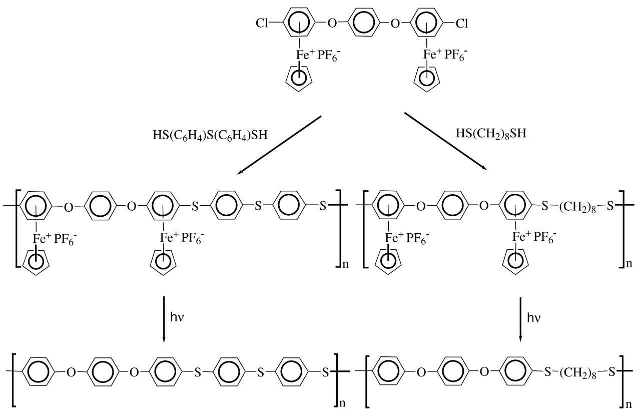


Scheme 15.



Scheme 16.

Polymers with alternating ether and thioether or amine and thioether bridges were synthesized by reaction of diiron complexes containing ether or amine bridges with dithiols [65]. Scheme 17 shows the synthesis of polymers containing alternating ether/thioether linkages. Following the removal of the metallic moieties, only the polymer with the alkyl bridge in its backbone was soluble in organic solvents at room temperature. Thermogravimetric analysis of the organoiron polymers indicated that these materials lost their metallic moieties at ca. 200 °C, while degradation of the polymer backbones occurred around 500 °C. Fig. 4 shows the TGA thermograms of an organoiron-coordinated polyaromatic ether (a), and its corresponding organic polymer



Scheme 17.

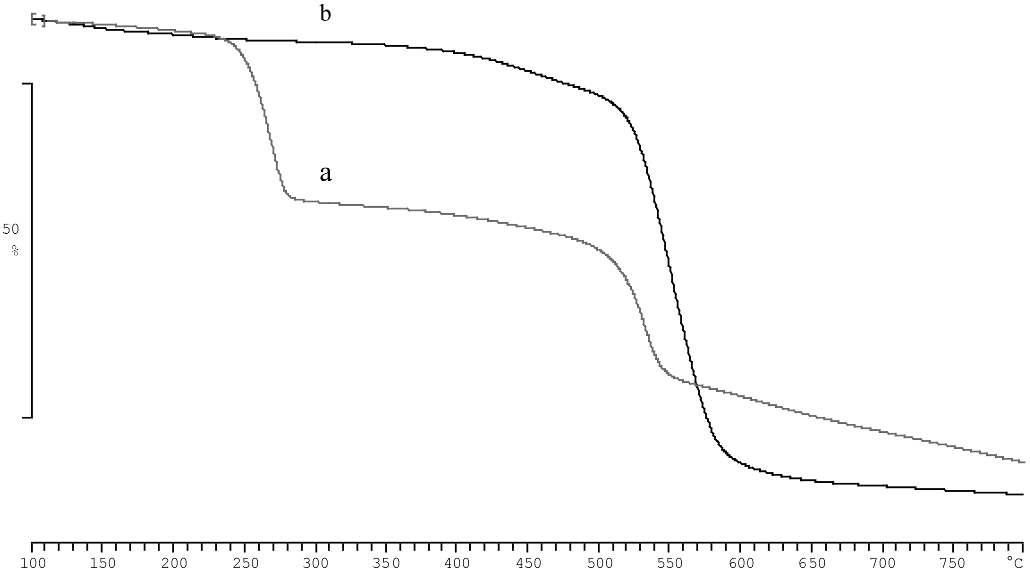


Fig. 4. TGA thermograms of complexed (a) and uncomplexed (b) polyaromatic ethers.

(b), which was isolated following cleavage of the cyclopentadienyliron moieties. By incorporating different heteroatoms and organic bridges between the complexed aromatic rings, the thermal properties of the polymers could be tailored. While the polymers with aromatic ether bridges had the highest glass transition temperatures, and the polymers with thioether bridges had the lowest T_g's, copolymers incorporating both oxygen and sulfur bridges in their backbones had intermediate values. The glass transition temperatures observed for the organic polymers ranged from 33 to 165 °C [65].

Cyclic voltammetry of the cyclopentadienyliron-coordinated polymers with etheric or thioetheric spacers in their backbones gave some insight into the electrochemical behavior of these materials. The CV in Fig. 5 shows the reduction processes observed in a cyclopentadienyliron-coordinated polythioether. This CV shows reduction of all cationic 18-electron iron centers to the neutral 19-electron species, and a further reduction of these iron centers to the anionic 20-electron species [68].

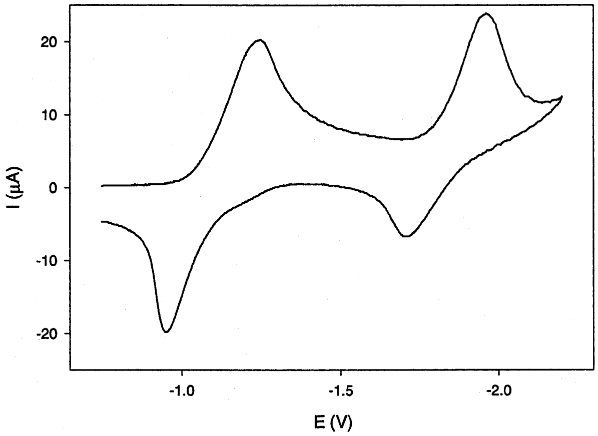
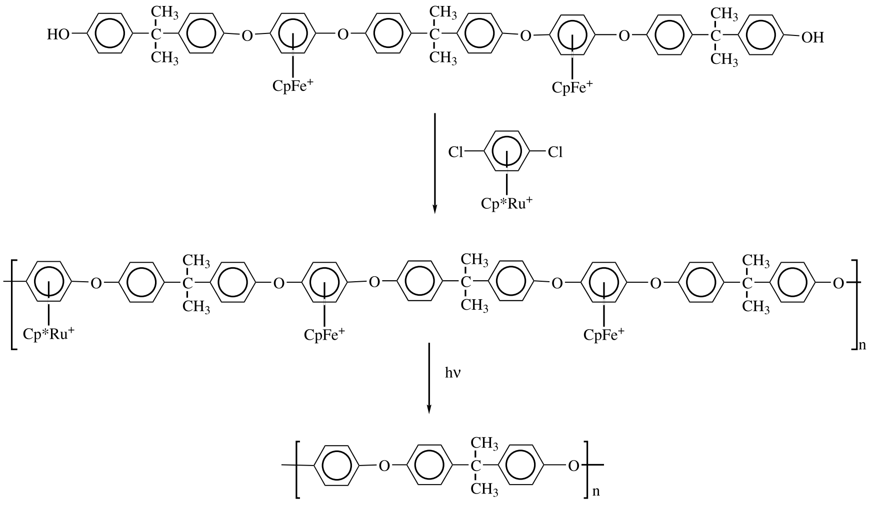


Fig. 5. Cyclic voltammogram of an iron-coordinated polythioether.

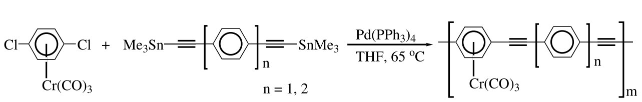
In a recent report, polymers containing both CpFe$^+$ and Cp*Ru$^+$ moieties pendent to their backbones were synthesized [69]. Scheme 18 describes the synthesis of a diiron aromatic ether complex prepared via reactions of bisphenol A with the *p*-dichlorobenzene cyclopentadienyliron complex. This diiron complex with terminal phenolic groups was subsequently reacted with *p*-dichlorobenzene pentamethylcyclopentadienylruthenium to produce the heterometallic polymer. Following cleavage of the iron and ruthenium moieties pendent to the polymer backbone, GPC analysis showed that the molecular weight of the organic polymer was 12,600, corresponding to a molecular weight of ca. 19,000 for its metallated analogue [69].

5.2. *Poly(phenyl ethynyl)s*

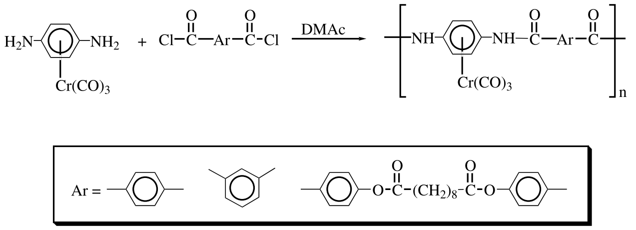
In 1989, Wright reported the synthesis of conjugated polymers coordinated to chromium tricarbonyl moieties [70]. These polymers were synthesized via a palladium catalyzed cross-coupling reaction of η^6-1,3- and 1,4-dichloroarene–chromium tricarbonyl complexes with organostannane reagents as shown in Scheme 19. Combustion analysis of these polymers indicated that the degree of polymerization (DP) was about 18, corresponding to molecular weights of about 7800. These poly(phenyl ethynyl)s displayed low solubility in organic solvents due to their high degree of rigidity and conjugation. TGA analysis showed that these polymers displayed excellent thermal stability under an argon atmosphere following an initial 10–12% weight loss, corresponding to loss of the $Cr(CO)_3$ units. Combustion and IR analysis of polymers heated past 200 °C



Scheme 18.



Scheme 19.



Scheme 20.

indicated that these materials underwent cross-linking reactions following loss of carbon monoxide from the metallic moieties.

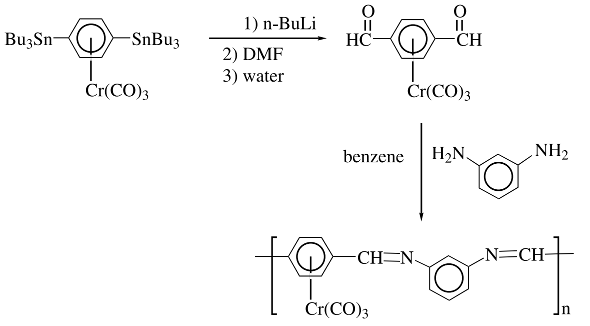
5.3. Polyamides

In 1987, Jin and Kim reported the synthesis of polyamides coordinated to chromium tricarbonyl moieties via condensation reactions of phenylenediamine–$Cr(CO)_3$ with various acid chlorides (Scheme 20) [71]. The desire to prepare these materials stemmed from the interesting properties associated with poly(*p*-phenylene terephthalamide) (PPTA), which is known to form a lyotropic liquid crystal in strong acids. This polymer exhibits low solubility in organic solvents, and can be processed into high strength and modulus fibers [71]. An enhancement of PPTA's solubility was achieved via the incorporation of chromium tricarbonyl moieties pendent to its backbone. The analogous organic polyamides were also prepared under similar reaction conditions in order to compare its solubility to that of its metallated counterpart. While the organometallic polyamides remained in solution during the polymerization reactions, the organic polymers formed gels or precipitated out of solution during their preparation. The viscosities of the organic and organometallic polymers were determined in concentrated sulfuric acid. The organometallic polymers had higher viscosities than the organic polymers, probably due to the higher solubilities of the former during the polymerization reactions. This study also determined that all chromium tricarbonyl moieties were cleaved from the polymer backbones upon addition to sulfuric acid. While initially the solubility of the organochromium polymers was good, upon drying, it became difficult to redissolve the polymers in polar organic solvents.

In 1993, Dembek and co-workers prepared high molecular weight PPTA in *N*,*N′*-dimethylacetamide (DMAc) using a methodology similar to that of Jin and Kim [72,73]. It was shown that when the concentration of the high molecular weight polyamide was greater than 4–6% in DMAc, nematic liquid crystalline texture was observed using polarizing optical microscopy [72,73]. This lyotropic behavior suggests that although the solubility of the polymer increased dramatically upon metal coordination, the rigid rod nature of the polymer was retained. Following isolation of the organometallic polymer as a precipitate or film, it would no longer dissolve in polar aprotic solvents. A copolymer, consisting of only half of the phenylenediamine rings coordinated to $Cr(CO)_3$ was prepared, and this polymer also displayed enhanced solubility and liquid crystalline behavior.

5.4. Polyimines

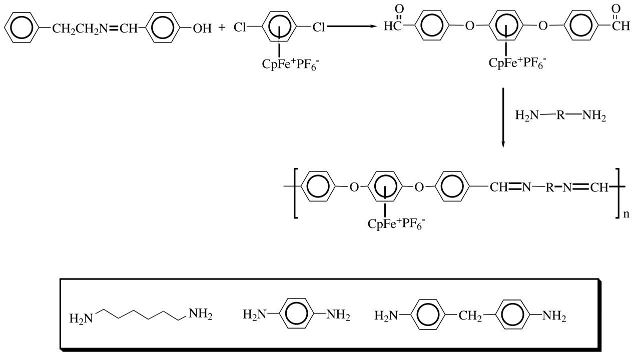
Wright and Lowe-Ma reported the first example of an organometallic polyimine prepared via reaction of η^6-



Scheme 21.

terephthaldialdehyde chromium tricarbonyl complexes with 1,3-phenylenediamine (Scheme 21) [74]. The resulting conjugated polyimine precipitated from the reaction solution and was insoluble in common organic solvents. The chromium complex was prepared via reaction of the 1,4-bis(tri-*n*-butylstannyl)benzene complex with *n*-BuLi in a Seyferth transmetallation reaction, and quenched with *N*,*N*-dimethylformamide to give the dialdehyde complex shown in Scheme 21.

The synthesis of polyether/imines coordinated to cyclopentadienyliron moieties has recently been communicated [75]. The organoiron polymers shown in Scheme 22 were prepared by reaction of a dialdehyde complex of cyclopentadienyliron with a number of aliphatic and aromatic diamines. These polycondensation reactions resulted in the isolation of the polyether/imines in good yields. Alternatively, polyether/imines were prepared by synthesizing diiron complexes of arenes with bridging imine groups. The terminal complexed aromatic rings containing chloro groups were subjected to S_NAr reactions with diphenolic organic compounds to give the polymeric materials. Although both methodologies resulted in similarly structured polymeric materials, the first method used the cyclopentadienyliron moieties only to synthesize the monomers, and they did not facilitate the polymerization process. The second methodology, however, required the presence of the metallic moiety to mediate the polymerization reactions.



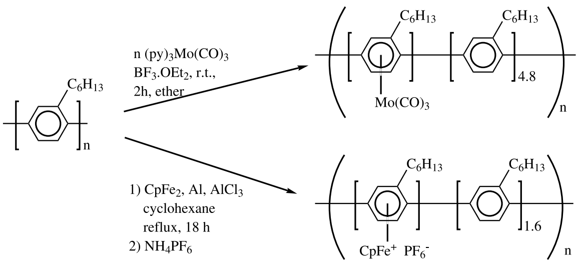
Scheme 22.

6. Incorporation of transition metal moieties into polymers

6.1. Polyphenylenes

Another strategy that has been used to prepare polymers with transition metal moieties coordinated to arenes within their backbones or side chains involves metal complexation to arenes in preformed polymeric materials [76–80]. This approach was first taken in 1984 by Eyring and co-workers when they complexed molybdenum tricarbonyl to about 25% of the aromatic rings in polyparaphenylene (PPP) [76,77]. Using IR photoacoustic spectroscopy, it was found that the organomolybdenum polymer showed similar shifts in its spectrum as potassium doped PPP relative to the unmodified organic polymer.

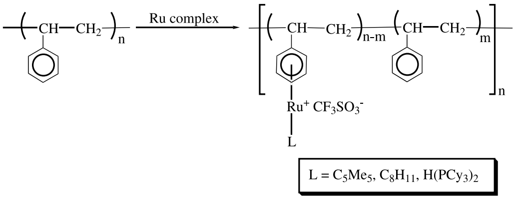
Nishihara and co-workers adapted these systems by forming poly(*n*-hexylphenylene) (PHP) coordinated to metallic moieties (Scheme 23) [78–80]. The use of alkylated aromatic rings increased the solubility of the polymers, thus making their characterization much simpler. It was estimated by elemental analysis that 1 in every 4.8 aromatic rings was coordinated to $Mo(CO)_3$. The organic and organometallic polymers were analyzed using electrochemical and spectroscopic techniques. The results of these studies showed that the band gap of the polymer did not change appreciably upon coordination to $Mo(CO)_3$, whereas the redox potential and conductivity of the polymer were affected. A cyclopentadienyliron complex of PHP was also prepared, and it was determined that on average, 1 in every 1.6 aromatic rings was coordinated to a metallic moiety. Cyclic voltammetric studies of the polymer showed reduction of the iron centers around −1.7 V, and the increase in ΔE_p with increasing sweep rate indicated that the heterogeneous electron transfer within the system was fairly slow. Spectroelectrochemical measurements of the organoiron polymer suggest that a network was formed between aromatic rings of neighboring polymer chains following reduction of the cationic iron centers to the neutral radicals. These results showed that the π-coordination of metallic moieties to aromatic rings in polymers is an effective way to alter their electronic properties.



Scheme 23.

6.2. Polystyrenes

Interest in transition metal catalysts on polymeric supports led to a report by Chaudret and co-workers regarding the coordination of organoruthenium moieties to the aromatic rings in polystyrene [81]. In the work, the proposed structures of the polymers contained pendent Ru^+Cp^*, $Ru^+C_8H_{11}$ or $Ru^+H(PCy_3)_2$ moieties pendent to the aromatic rings of polystyrene [81]. Depending on the bulkiness of the ligand attached to the ruthenium; anywhere from 25 to 100% of the aromatic rings in the polymer side chains became coordinated to ruthenium moieties. This article also reported the first polymer supported hydrido transition metal complex, whose synthesis is shown in Scheme 24.



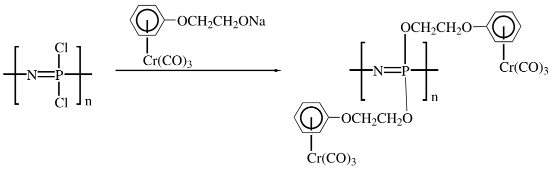
Scheme 24.

6.3. Polyphosphazenes

In 1991, Allcock and co-workers incorporated arene chromium tricarbonyl moieties into the side chains of polyphosphazenes as shown in Scheme 25 [82,83]. Two approaches were taken in the production of these inorganic polymers, however, in both cases, the chromium tricarbonyl units were incorporated into the preformed polyphosphazenes. The first, and most effective method involved the displacement of chloro groups of the polyphosphazene by aryloxy or arylalkoxy groups containing the $Cr(CO)_3$ fragment [82]. In order to effect complete displacement of the chloro groups by the organometallic nucleophiles, it was found that alkyl spacers were required in order to decrease the steric bulk surrounding the polymer backbone. It was important that complete displacement of the chloro groups was achieved due to the instability of the P–Cl bond. The second method involved the reaction of an aryl-functionalized polyphosphazene with $Cr(CO)_6$. Differential scanning calorimetry showed that the glass transition temperatures of the chromium tricarbonyl functionalized polymers were higher than that of their organic analogues by ca. 50 °C.

7. Supramolecular assembly of polymers

Brammer and co-workers have recently reported the use of arene chromium tricarbonyl complexes as building blocks in supramolecular assembly [84,85]. Carboxylate-functionalized arenes coordinated to chromium tricarbonyl moieties were connected via hydrogen bonds on the arene carboxyl substituents. Complexed arenes functionalized with one to three carboxylic acid groups were synthesized. While complexes containing one carboxylic acid group formed discrete dimers, di- and tri-functionalized complexes formed extended supramolecular assemblies. The dimers were found to assemble into a sheet-like structure through hydrogen bonding. In addition to hydrogen bonding via the carboxylic acid groups on the arenes, the three carbonyl oxygen atoms attached to chromium also acted as hydrogen bond acceptors to C–H donors in the 2- and 5-positions on the arene rings. In addition the C–H group in the 3-position of the arene formed a C–H···O hydrogen bond to neighboring hydroxy oxygen atoms.



Scheme 25.

8. Dendrimers and star polymers

The study of organometallic three-dimensional macromolecules has been the focus of a number of recent studies [86–90]. Astruc and co-workers have developed a number of different dendrimeric and star polymer systems containing organometallic functionalities [90–100]. Although metals such as cobalt [98] and ruthenium [99] have been incorporated into these materials, a number of Astruc's studies have focused on the design of organoiron dendrimers. Two different classes of organoiron systems have been utilized consistently in his research on dendrimers; these include substituted ferrocenes and arene–cyclopentadienyliron complexes. An efficient method for the design of star cores and dendrimers was developed using cyclopentadienyliron-mediated peralkylation, benzylation and allylation reactions of cationic tri-, tetra- and hexamethylbenzene cyclopentadienyliron complexes [91–97]. The presence of the iron moieties coordinated to the arenes was found to activate the C–H bonds towards C–C bond formation. These branched starting materials were reacted with organic, inorganic and organometallic reagents to give the star and dendrimeric polymers directly or following cleavage of the cationic iron species. One of the star complexes was also derivatized following removal of the iron centers and used as a catalyst in the living cationic polymerization of star-shaped polystyrene, and was later functionalized with fullerene moieties [96]. Demetallation, followed by

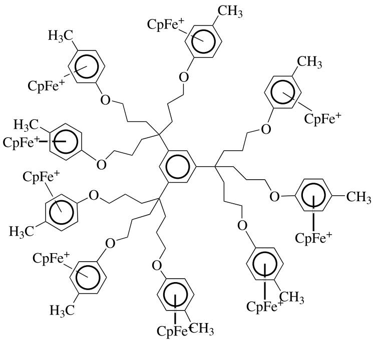


Fig. 6. Star complex with nine cathionic organoiron moieties.

oxidation of the allyl-functionalized mesitylene complex gave rise to a branched compound containing nine terminal hydroxyl groups [97]. This compound was then reacted with nine equivalents of η^6-*p*-fluorotoluene–η^5-cyclopentadienyliron hexafluorophosphate to yield the nonairon complex (Fig. 6). Cyclic voltammetry of this complex showed that the cationic organometallic dendrimer underwent nine reversible quasi-equivalent reduction processes at −1.37 V versus SCE.

The synthesis of a water-soluble metallodendrimer containing six cationic cyclopentadienyliron moieties was also reported by Astruc and co-workers [100]. In contrast to most studies of arene–cyclopentadienyliron complexes, the functionalization of these materials was accomplished via the Cp rather than the arene rings (Fig. 7). This star-shaped organoiron complex was studied as a redox catalyst for the cathodic reduction of nitrates and nitrites to ammonia [100].

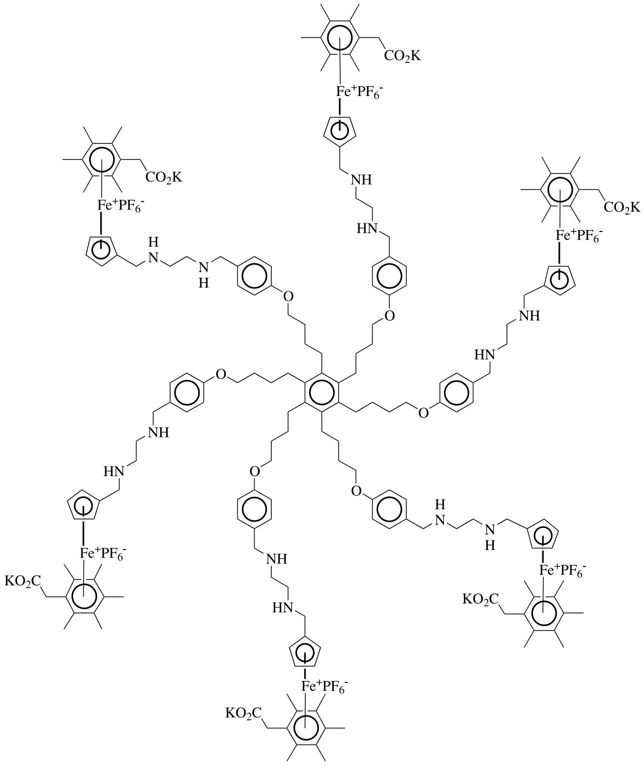


Fig. 7. Water soluble star shaped complex.

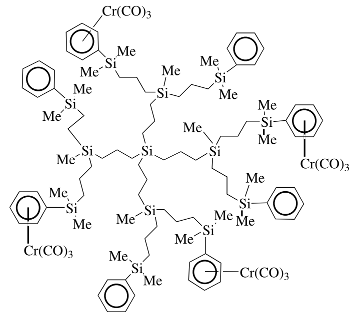
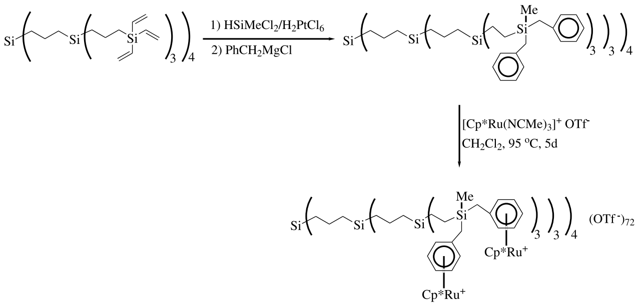


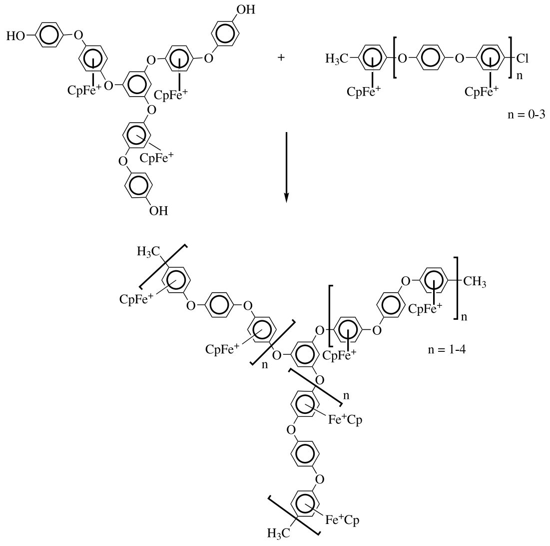
Fig. 8. Organochromium dendrimer.

Cuadrado and co-workers have been very active in the development of new classes of inorganic and organometallic dendrimers [89,101,102]. In 1996, the synthesis of organosilicon dendrimers containing chromium tricarbonyl moieties pendent to four peripheral aromatic rings was reported (Fig. 8) [101]. Although there were eight possible sites where coordination of the $Cr(CO)_3$ moieties could have occurred, the harsh conditions required to coordinate the other four aromatic rings resulted in decomposition of the dendrimers. Electrochemical oxidation of the chromium atoms was studied using voltammetry and the isolated redox centers were found to be stable on the electrochemical time scale in the absence of nucleophilic species.

Tilley and co-workers have reported the synthesis of organosilane dendrimers that were coordinated to 12, 24, 36 and 72 pentamethylcyclopentadienylruthenium cations [103]. These highly branched polymers were prepared with the intent to eventually combine the polycationic dendrimers with polyanions to form superlattices. The dendrimer containing 12 cationic ruthenium centers was analyzed by single-crystal X-ray diffraction, and all of the polymetallic complexes were analyzed by mass spectrometry. The presence of the dendrimer containing 72 positively charged ruthenium moieties was identified in its mass spectrum, however, the authors did suggest that incomplete coordination to the Cp^*Ru^+ moieties may have occurred as a result of high steric crowding (Scheme 26).



Scheme 26.



Scheme 27.

Currently, we are exploring the synthesis of star polymers prepared by repeated S_NAr reactions of chloroarene complexes of cyclopentadienyliron with di- and tri-phenolic compounds [104,105]. The synthesis of star polymers containing up to 15 cationic metal centers pendent to the branches of the polymers was achieved as shown in Scheme 27. The preparation of star polymers and dendrimers coordinated to cyclopentadienyliron ($CpFe^+$) moieties via sequential S_NAr reactions had not previously been reported. The metallic moieties in the polymers were positioned at regular intervals rather than at the core or periphery of the polymers, as has been the case in the previous examples.

9. Conclusions

The use of arene complexes of transition metals in monomer and polymer synthesis has been explored over the past few decades, however, it is only in the past 15 years that an exploration into these materials has flourished. This class of polymers combines the properties of arene transition metal complexes and organic polymers. The introduction of metallic moieties coordinated to arenes within the side chains or the backbones of polymers gave rise to materials that displayed conductivity, liquid crystallinity and catalytic properties. Of particular significance, many of these metal-coordinated polymers demonstrated enhanced solubility relative to their organic analogues.

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