Articles

Macromolecules Containing Redox-Active Neutral and Cationic Iron Complexes

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ABSTRACT: Nucleophilic aromatic substitution reactions of chloroarene cyclopentadienyliron complexes were utilized to prepare new classes of oligomers and polymers containing both neutral and cationic organoiron complexes in their structures. Photolysis of these polymers resulted in the removal of the cationic cyclopentadienyliron moieties, while the neutral organoiron complexes remained intact within the polymer structures. The weight-average molecular weights of these polymers after photolysis ranged from 8700 to 56 200 with polydispersities from 1.1 to 3.1. Thermal analysis established that the cationic polymers possess higher glass transition temperatures, but lower thermal stability than the neutral ferrocene-based polymers. The glass transition temperatures of the cationic polymers ranged from 65 to 161 °C, while the T_gs of the neutral polymers ranged from 10 to 92 °C. Electrochemical studies showed that the iron centers in the neutral complexes were oxidized, while the cationic complexes were reduced. Viscosity studies showed that the cationic polymers exhibited a polyelectrolyte effect.

Introduction

There is an ever-growing interest in the development of organometallic polymers in light of their uses as chemical sensors, electrocatalysts, modified electrodes, and photoactive molecular devices.[1] The incorporation of organometallic moieties into the backbone of organic molecules has been shown to modify the optical, magnetic, and thermal properties of these systems. Macromolecular complexes containing ferrocenyl units are of particular interest as a result of the exceptional thermal and chemical stability that these units possess.[2] Polymers containing ferrocenyl units in their backbones or side chains represent the largest and best studied class of organometallic macromolecules.[3] These types of materials have been shown to display liquid crystallinity, ferromagnetism, and nonlinear optical and catalytic properties.

There have been numerous investigations into the electrochemical properties of polymetallic complexes due to possible communication between the metal centers.[1−4] The introduction of two different electrochemically active sites into a polymer is of interest due to potential applications in electric devices, electrocatalysis, and sensors.[5] Ferrocene-based polymeric systems are some of the most well-studied organometallic macromolecules, and their electrochemical properties have also been studied extensively.[2c,6] It has been shown by Manners and co-workers that communication between iron centers in polymers is dependent on the nature of the organic/inorganic bridging groups.[1e] Recently, it was shown that silicon-bridged [1]ferrocenophanes undergo photolytic living ring-opening polymerization in the presence of nucleophilic anionic initiators.[7] It was proposed that the ring-opening of the [1]ferrocenophanes was facilitated via photoinduced MLCT transitions, which further weakened the already weak Fe−Cp bonds, thus allowing for nucleophilic attack at the iron centers.[7a] The resulting poly(ferrocenylsilanes) were not photoactive since the HOMO−LUMO transition for these polymers was similar to that of ferrocene and exhibit no significant MLCT character.

It has been well established that ferrocene derivatives undergo a highly reversible $1e^-$ oxidation to give cationic $17e^-$ complexes.[3] The exceptional electrochemical stability of ferrocene has made it one of the most widely used internal references for electrochemical cells. Electrochemical studies of cationic η^6-arene−η^5-cyclopentadienyliron complexes have shown that they undergo two successive one-electron reduction steps.[8] The first reduction is chemically reversible and produces the neutral $19e^-$ complex, while the second reduction step leads to an anionic 20 e^- complex. In 1998, Astruc and co-workers reported that 18-electron arene cyclopentadienyliron complexes could undergo electrochemical oxidation with SO_2 to give 17-electron dicationic complexes.[2c,9] It had previously been communicated by Solodovnikov and co-workers that arene complexes could be oxidized at low temperature using $SbCl_5$; however, there was very little data provided to prove that the 17-electron complex was isolated.[10] For fully methylated sandwich complexes (arene and cyclopentadienyl), the oxidation processes were chemically and electrochemically reversible; however, the reversibility decreased by decreasing the number of methyl substituents on the arenes. The oxidation potentials of these complexes occurred between 0.9 and 1.7 V vs ferrocene.[10]

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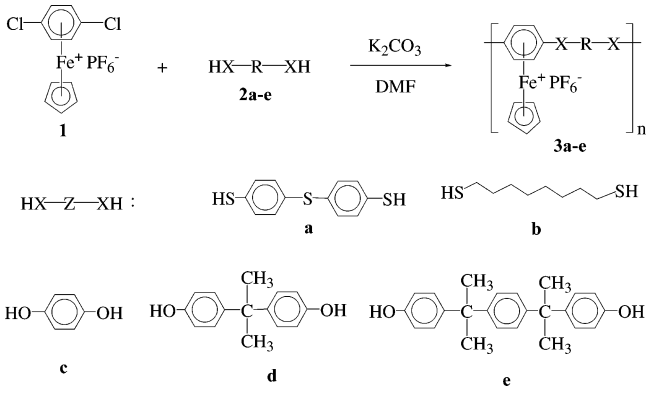
Scheme 1



The organoiron complexes presented in this work were prepared by taking advantage of the different chemical properties associated with these two types of iron complexes. The electron-rich cyclopentadienyl rings of ferrocene make the η^5-Cp rings susceptible to electrophilic attack, while the electron-withdrawing effect of the $CpFe^+$ moiety on arenes makes these rings susceptible to nucleophilic addition and substitution reactions.[11] A number of studies have shown that oligomeric and polymeric ethers, thioethers, and amines can be synthesized under mild conditions via nucleophilic displacement reactions of cyclopentadienyliron-complexed chloroarenes with nucleophiles.[12] Recently, the synthesis and electrochemical properties of bi- and trimetallic complexes containing ferrocene groups conjugated to arenes coordinated to cyclopentadienyliron cations were described.[13] We have also reported the synthesis of macromolecules containing both cyclopentadienyliron and pentamethylcyclopentadienylruthenium moieties pendent to their backbones.[12]

This work describes the synthesis of polymetallic complexes containing neutral cyclopentadienyliron units in or pendent to the main chain as well as pendent cationic cyclopentadienyliron moieties.

Experimental Section

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, on a Gemini 200 NMR spectrometer, with chemical shifts calculated in hertz, referenced to solvent residues. Gel permeation chromatography (GPC) was performed using a Waters 1525 HPLC pump and 2410 refractive index detector with THF as the eluent. Molecular weights were calculated relative to polystyrene standards. Cyclic voltammetric experiments were performed using a conventional three-electrode cell. In these studies the working electrode was a glassy carbon disk electrode (ca. 2 mm diameter), the auxiliary electrode was a Pt wire, and a (Ag/AgCl) reference electrode was utilized. Temperatures ranging from 293 to 243 K were obtained using a dry ice−acetone mixture. The concentration of the complex was 2.0 mM, while that of the supporting electrolyte (TBAH or TBAP) was 0.1 M. The solutions were deaerated with nitrogen prior to use. An EG&G Princeton Applied Research model 263A potentiostat was used in all experiments. All viscosity measurements were preformed on a Brookfield model DV-II+ viscometer using a low-volume spindle code S00 and a ULA adapter. Measurements were in 18 mL of DMSO at 25 °C constant temperature using a Brookfield TC200 water bath.

Materials. Chloroarene complexes **1**, **4**, and **5** were synthesized according to an established procedure.[14] Complexes **7c, 8c**, **17, 18, 21, 22,** and **30** were prepared according to previously reported methodologies.[12d,15−19] All nucleophiles were available from the Aldrich Chemical Co. and were used without purification. Solvents were HPLC grade and were used without further purification, with the exception of THF, which was distilled under N_2 from sodium metal and benzophenone prior to use. Tetrabutylammonium hexafluorophosphate (TBAH) and tetrabutylammonium perchlorate (TBAP) were received from Aldrich and Fluka, respectively.

Preparation of 7a−e and 8a−e. The chlorobenzene and chlorotoluene complexes **4** and **5** (3 mmol) were reacted with 2-mercaptoethanol (**6a**), 4-hydroxybenzyl alcohol (**6b**), hydroquinone (**2c**), bisphenol A (**2d**), or bisphenol P (**2e**) (3 mmol) in the presence of potassium carbonate (0.525 g, 3.8 mmol) and stirred in 15 mL of DMF under a nitrogen atmosphere for 16 h at room temperature to give **7a−e** and **8a−e**, respectively. The solutions were poured into 10% HCl, and ammonium hexafluorophosphate was added. If the complexes precipitated from solution, the solid was collected in a crucible and washed with water, followed by ether. If an oily product resulted, the complex was extracted with dichloromethane, washed with water, dried over magnesium sulfate, and concentrated by rotary evaporation. The solution was subsequently added dropwise to ether. Spectroscopic data for complex **7a** are provided as a representative example.

7a: Yield: 61%. ^{1}H NMR (acetone-d_6): δ = 3.41 (t, J = 5.3 Hz, 2H, CH_2), 3.92 (t, J = 5.5 Hz, 2H, CH_2), 5.18 (s, 5H, Cp), 6.35 (t, J = 5.5 Hz, 1H, complexed Ar), 6.46 (t, J = 6.0 Hz, 2H, complexed Ar), 6.60 (d, J = 6.3 Hz, 2H, complexed Ar). ^{13}C NMR (acetone-d_6): δ = 35.49, 60.77 (CH_2), 78.49 (Cp), 85.28, 86.01, 87.71 (complexed Ar−CH), 110.61 (complexed Ar−C). IR (KBr), υ/cm^{-1}: 3382 (OH).

Preparation of 9a,b. *p*-Dichlorobenzene−cyclopentadienyliron complex **1** (1.239 g, 3 mmol), 3 mmol of either 2-mercaptoethanol (**6a**) or 4-hydroxybenzyl alcohol (**6b**), and potassium carbonate (0.525 g, 3.8 mmol) were stirred in 15 mL of DMF under a nitrogen atmosphere for 16 h at room temperature to give **9a** and **9b**, respectively. Workup of these complexes followed the previous procedure outlined for complexes **7** and **8**. Spectroscopic data for complex **9a** are provided as a representative example.

9a: Yield: 89%. ^{1}H NMR (acetone-d_6): δ = 3.41 (t, J = 5.9 Hz, 2H, CH_2), 3.92 (q, J = 5.5 Hz, 2H, CH_2), 4.32 (t, J = 5.3 Hz, 1H, OH), 5.27 (s, 5H, Cp), 6.70 (d, J = 6.6 Hz, 2H, complexed Ar), 6.81 (d, J = 6.6 Hz, 2H, complexed Ar). ^{13}C NMR (acetone-d_6): δ = 35.73, 60.87 (CH_2), 80.93 (Cp), 84.61, 87.97 (complexed Ar−CH), 105.59, 110.88 (complexed Ar−C). IR (NaCl): 3589 cm^{-1} (OH).

Preparation of 11a−e and 12a−e. Ferrocenecarboxylic acid **(10)** (0.12 g, 0.5 mmol), **7a−e** or **8a−e** (0.5 mmol), and (*N*,*N*-dimethylamino)pyridine (DMAP) (0.07 g, 0.6 mmol) were combined in 10 mL of CH_2Cl_2. Dicyclohexylcarbodiimide (DCC) (0.12 g, 0.6 mmol) was dissolved in 2 mL of CH_2Cl_2 and added to the solution at 0 °C, and the mixture was stirred under N_2 at room temperature for 12 h. The resulting solution was gravity filtered, washed with water, dried with $MgSO_4$, concentrated by rotary evaporation, and precipitated with ether. Spectroscopic and analytical data for complex **11a** are provided as a representative example.

11a: Yield: 66%. ^{1}H NMR (acetone-d_6): δ = 3.67 (t, J = 6.3 Hz, 2H, CH_2), 4.23 (s, 5H, Cp), 4.47 (br s, 2H, Cp), 4.55 (t, J = 6.3 Hz, 2H, CH_2), 4.73 (br s, 2H, Cp), 5.23 (s, 5H, Cp), 6.42 (t, J = 5.9 Hz, 1H, complexed Ar), 6.54 (t, J = 6.3 Hz, 2H, complexed Ar), 6.71 (d, J = 6.6 Hz, 2H, complexed Ar). ^{13}C NMR (acetone-d_6): δ = 32.07, 62.61 (CH_2), 70.57, 70.83, 71.44 (Cp-CH), 72.33 (Cp-C), 78.98 (Cp-CH), 86.41, 86.83, 88.41 (complexed Ar−CH), 109.60 (complexed Ar−C), 171.54 (C=O). IR (KBr), υ/cm^{-1}: 1711 (C=O). ($C_{24}H_{23}F_6Fe_2O_2PS$) (632.17): Calcd: C 45.60, H 3.67. Found: C 45.82, H 3.78.

Preparation of 14a−e, 15a−e, and 16a,b. 1,1′-Ferrocenedicarbonyl chloride (**13**) (0.31 g, 1.0 mmol), **7a−e**, **8a−e**, **9a**,**b** (2.0 mmol), and pyridine (0.12 mL, 1.5 mmol) were stirred in 8.0 mL of CH_2Cl_2 under a nitrogen atmosphere for 24 h at room temperature. The solvent was removed via rotary evaporation; the residue was dissolved in acetone and poured into 10% HCl. Ammonium hexafluorophosphate (0.13 g, 0.8 mmol) was added. The yellow precipitate was collected in a crucible, washed with water, and rinsed with ether. Spectro-

scopic and analytical data for complex **14a** are provided as a representative example.

14a: Yield: 77%. ^{1}H NMR (acetone-d_6): δ = 3.69 (t, J = 6.0 Hz, 4H, CH_2), 4.40 (t, J = 6.9 Hz, 4H, CH_2), 4.54 (br s, 4H, Cp), 4.80 (br. s, 4H, Cp), 5.20 (s, 10H, Cp), 6.39 (t, J = 5.9 Hz, 2H, complexed Ar), 6.51 (t, J = 5.8 Hz, 4H, complexed Ar), 6.68 (d, J = 6.2 Hz, 4H, complexed Ar). ^{13}C NMR (acetone-d_6): δ = 32.48, 63.53 (CH_2), 73.12 (Cp-CH), 73.82 (Cp-C), 74.50, 79.60 (Cp-CH), 86.90, 87.37, 88.97 (complexed Ar−CH), 109.97 (complexed Ar−C), 170.86 (C=O). ($C_{38}H_{36}P_2F_{12}Fe_3O_4S_2$) (1078.28): Calcd: C 42.33, H 3.37. Found: C 42.46, H 3.36.

Preparation of 19 and 20. 1,1′-Ferrocenedicarbonyl chloride (**13**) (0.311 g, 1 mmol), **17**, **18** (2 mmol), and pyridine (0.4 mL, 5 mmol) were stirred in 10 mL of CH_2Cl_2 under a nitrogen atmosphere for 16 h at room temperature. The solution was poured into 10% HCl, and an excess of ammonium hexafluorophosphate was added. The complex was extracted with dichloromethane, washed with water, and then dried over $MgSO_4$. The solution was filtered and dried by rotary evaporation, and the complex was dissolved in acetone and passed through a short neutral alumina column and added to ether. The resulting yellow precipitate was collected in a crucible and dried under reduced pressure. Spectroscopic and analytical data for complex **19** are provided as a representative example.

19: Yield: 79%. ^{1}H NMR (acetone-d_6): δ = 2.51 (s, 6H, CH_3), 4.79 (t, J = 2.0 Hz, 4H, Cp), 5.10 (t, J = 2.0 Hz, 4H, Cp), 5.21 (s, 10H, Cp), 5.34 (s, 10H, Cp), 6.35−6.40 (m, 12H, complexed Ar), 6.45 (d, J = 7.4 Hz, 4H, complexed Ar), 7.39 (d, J = 9.4 Hz, 4H, Ar), 7.47 (d, J = 9.4 Hz, 4H, Ar), 7.54 (s, 8H, Ar). ^{13}C NMR (acetone-d_6): δ = 19.82 (CH_3), 72.71 (Cp−C), 73.14, 74.44 (Cp−CH), 75.73, 75.94, 76.78 (complexed Ar−CH), 78.45, 78.96 (Cp−CH), 87.71 (complexed Ar−CH), 101.46 (complexed Ar−C), 122.20, 124.02, 124.20, 125.16 (Ar−CH), 131.61, 131.99, 133.47 (complexed Ar−C), 149.53, 151.78, 151.92, 152.13 (Ar−C), 169.30 (C=O). IR (KBr): 1728 cm^{-1} (C=O) ($C_{82}H_{66}P_4F_{24}Fe_5O_{10}$) (2070.5): Calcd: C 47.57, H 3.21. Found: C 47.42, H 3.11.

Preparation of 24 and 25. Complexes **21**, **22** (1 mmol), 1,1′-bis(hydroxymethyl)ferrocene (**23**) (0.12 g, 0.5 mmol), and (*N*,*N*-dimethylamino)pyridine (0.15 g, 1.2 mmol) were combined in 5 mL of CH_2Cl_2. Dicyclohexylcarbodiimide (0.25 g, 1.2 mmol) was dissolved in 2.0 mL of CH_2Cl_2 and added to the stirring mixture at 0 °C. The solution was stirred at room temperature under N_2 for 14 h and then poured into 10% HCl, and ammonium hexafluorophosphate was added. The solution was extracted with CH_2Cl_2, washed with water, dried with $MgSO_4$, concentrated by rotary evaporation, and precipitated in ether. Spectroscopic and analytical data for complex **24** are provided as a representative example.

24: Yield: 60%. ^{1}H NMR (acetone-d_6): δ 4.33 (br s, 4H, Cp), 4.48 (br s, 4H, Cp), 5.27 (s, 4H, CH_2), 5.30 (s, 10H, Cp), 6.51 (s, 8H, complexed Ar), 7.45 (d, J = 8.6 Hz, 4H, Ar), 8.18 (d, J = 8.6 Hz, 4H, Ar). ^{13}C NMR (acetone-d_6): δ (ppm) 63.89 (2 CH_2), 70.25, 71.00, 78.37 (Cp−CH), 79.01 (complexed Ar−CH), 83.14 (Cp−C), 86.36, 87.99 (complexed Ar−CH), 121.09 (Ar−CH), 128.82 (Ar−C), 129.14 (complexed Ar−C), 132.98 (Ar−CH), 158.22 (Ar−C), 165.58 (C=O). IR (KBr), υ/cm^{-1}: 1697 (C=O). ($C_{48}H_{40}P_2F_{12}Fe_3O_6$) (1170.31): Calcd: C 49.26, H 3.45. Found: C 49.45, H 3.49.

Preparation of 26a−c and 27a−c. Complex **16a**,**b** (0.4 mmol), compound **2a**,**b**,**d** (0.4 mmol), and K_2CO_3 (0.138 g, 1 mmol) were stirred in 1.5 mL of DMF under N_2 at 60 °C for 8 h. The viscous solution was poured into10% HCl, and NH_4PF_6 (0.065 g, 0.4 mmol) was added. The resulting precipitate was collected in a sintered glass crucible and washed with water and then ether. Spectroscopic data for polymer **26a** are provided as a representative example.

26a: Yield: 88%. ^{1}H NMR (DMSO-d_6): δ = 3.55 (br s, 4H, CH_2), 4.44 (br s, 4H, CH_2), 4.52 (s, 4H, Cp), 4.73 (s, 4H, Cp), 5.11 (s, 10H, Cp), 6.35 (br d, 4H, complexed Ar), 6.58−6.61 (br d, 4H, complexed Ar), 7.49−7.53 (br d, 4H, Ar), 7.63 (br d, 4H, Ar). ^{13}C NMR (DMSO-d_6): δ = 30.39, 61.65 (CH_2), 70.89 (Cp−CH), 71.37 (Cp−C), 72.68, 79.03 (Cp−CH), 83.97, 84.63 (complexed Ar−CH), 104.74, 106.08 (complexed Ar−C), 127.86 (Ar−C), 131.62, 134.76 (Ar−CH), 136.05 (Ar−C), 168.74 (CO). IR (KBr): 1714 cm^{-1} (C=O).

Preparation of 28a−c and 29a−c. Polymers **26a−c** and **27a−c** (0.25 mmol) were dissolved in 40 mL of CH_3CN:CH_2Cl_2 (1:1) and placed in a Pyrex tube. The solution was purged with nitrogen and then photolyzed for 4 h in a Rayonett photoreactor equipped with 300 nm lamps. The solvents were removed, and the residue was extracted with chloroform. The solution was washed with water and then dried over $MgSO_4$ and filtered. The solution was concentrated and added to pentane. The resulting precipitate was collected in a crucible and dried under reduced pressure. Spectroscopic data for polymer **28a** are provided as a representative example.

28a: Yield: 87%. ^{1}H NMR ($CDCl_3$): δ = 3.22 (t, J = 6.6 Hz, 4H, CH_2), 4.34 (br s, 4H, CH_2), 4.39 (br s, 4H, Cp), 4.77 (s, 4H, Cp), 7.19 (br s, 4H, Ar), 7.28 (br s, 8H, Ar), 7.32 (br s, 4H, Ar). ^{13}C NMR ($CDCl_3$): 32.10, 61.69 (CH_2), 71.24 (Cp−CH), 72.25 (Cp−C), 73.01 (Cp−CH), 129.83, 131.07 (Ar−CH), 132.21, 135.30 (Ar−C), 170.25 (CO). δ = IR (KBr): 1712 cm^{-1} (CO).

Synthesis of Complexes 32a−c. Complex **30** (1.04 g, 1 mmol), compounds **31a−c** (1 mmol), (*N*,*N*-dimethylamino)-pyridine (0.244 g, 2 mmol), and 8 mL of CH_2Cl_2 were placed in a 50 mL round-bottom flask. Dicyclohexylcarbodiimide (0.413 g, 2 mmol) was dissolved in 2 mL of CH_2Cl_2 and added to the stirring mixture at 0 °C. The reaction was carried out at room temperature under a N_2 atmosphere for 18 h. After removal of the solvent, the product was dissolved in acetone and poured into 10% HCl, and NH_4PF_6 (0.163 g, 1 mmol) was added. The resulting precipitate was collected in a crucible then dissolved in acetone and passed through a short neutral alumina column and added to ether. The resulting yellow precipitate was collected in a crucible and dried under reduced pressure. Spectroscopic data for complex **32a** are provided as a representative example.

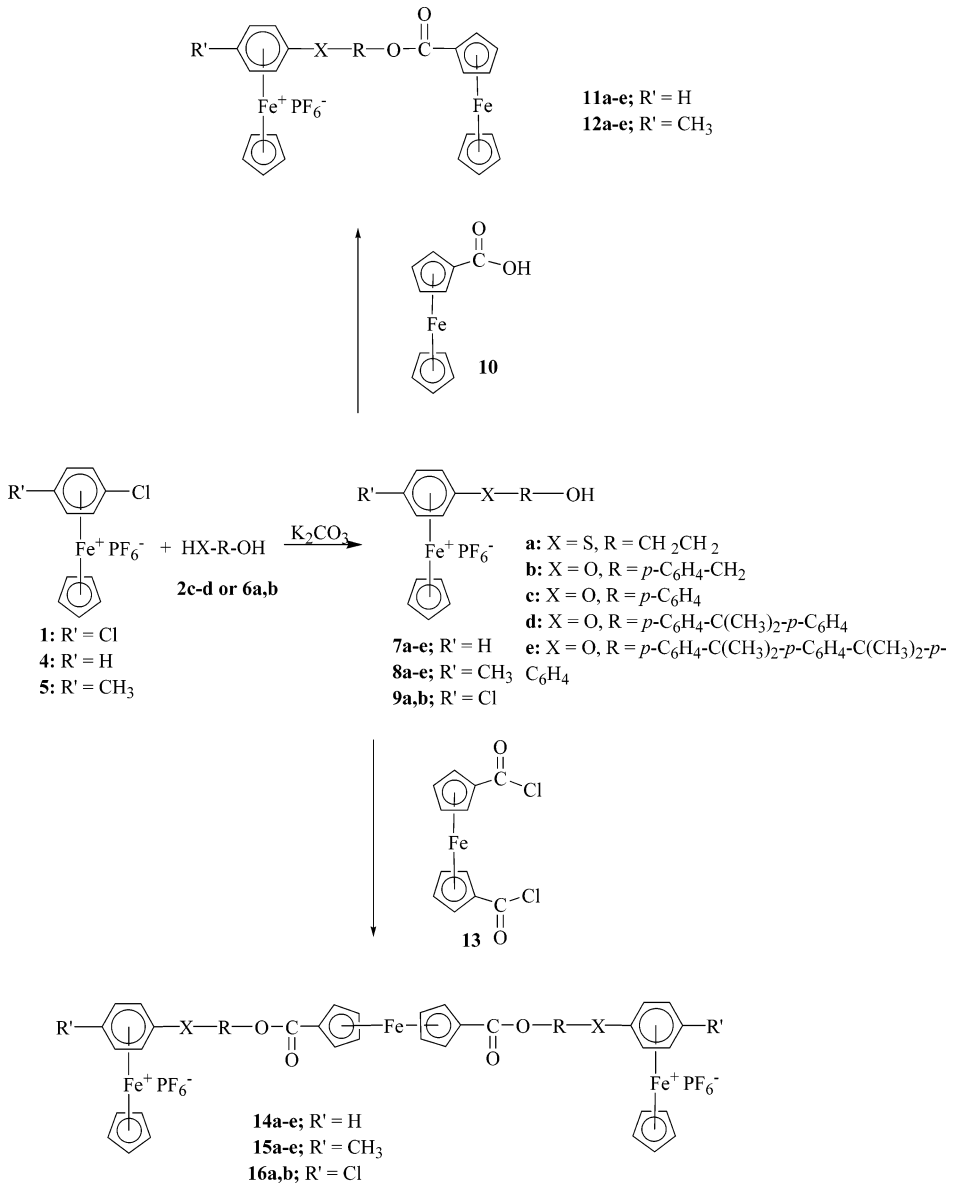
32a: Yield: 92%. ^{1}H NMR (acetone-d_6): δ = 1.74 (s, 3H, CH_3), 2.23 (t, J = 8.2 Hz, 2H, CH_2), 2.55 (t, J = 5.9 Hz, 2H, CH_2), 3.78 (t, J = 5.3 Hz, 2H, CH_2), 4.10 (t, J = 4.9 Hz, 1H, OH), 4.31 (t, J = 5.5 Hz, 2H, CH_2), 5.35 (s, 10H, Cp), 6.48 (d, J = 7.0 Hz, 4H, complexed Ar), 6.78 (d, J = 7.0 Hz, 4H, complexed Ar), 7.32 (d, J = 9.0 Hz, 4H, Ar), 7.48 (d, J = 9.0 Hz, 4H, Ar). ^{13}C NMR (DMSO-d_6): δ = 26.73 (CH_3), 29.38, 42.31 (CH_2), 44.83 (C), 58.67, 63.77 (CH_2), 76.11 (complexed Ar−CH), 79.10 (Cp−CH), 86.56 (complexed Ar−CH), 103.34 (complexed Ar−C), 119.92, 129.09 (Ar−CH), 131.72 (complexed Ar−C), 146.03, 150.86 (Ar−C), 172.33 (CO). IR (KBr), υ/cm^{-1}: 1725 (CO).

Synthesis of Monomers 33a−c. The same procedure utilized to prepare complexes **11** and **12** was followed. Spectroscopic and analytical data for complex **33a** are provided as a representative example.

33a: Yield: 85 %. ^{1}H NMR (acetone-d_6): δ = 1.72 (s, 3H, CH_3), 2.19 (br s, 2H, CH_2), 2.48 (m, 2H, CH_2), 4.36 (br s, 2H, CH_2), 4.07 (t, J = 7.0 Hz, 2H, CH_2), 4.24 (s, 5H, Cp), 4.43 (br s, 2H, Cp), 4.75 (br s, 2H, Cp), 5.36 (s, 10H, Cp), 6.48 (d, J = 6.6 Hz, 4H, complexed Ar), 6.78 (d, J = 6.6 Hz, 4H, complexed Ar), 7.30 (d, J = 8.6 Hz, 4H, Ar), 7.46 (d, J = 9.0 Hz, 4H, Ar). ^{13}C NMR (acetone-d_6): δ = 26.03 (CH_2), 27.75 (CH_3), 37.03 (CH_2), 46.03 (C), 64.29, 64.75 (CH_2), 70.49 (Cp−CH), 70.73 (complexed Ar−CH), 71.58 (complexed Ar−C), 72.29, 77.32 (complexed Ar−CH), 80.58 (Cp-CH), 88.00 (complexed Ar−CH), 104.79 (complexed Ar−C), 121.23, 130.62 (Ar−CH), 133.95 (complexed Ar−C), 147.79, 151.88 (Ar−C), 171.29, 173.34 (CO). IR (KBr), υ/cm^{-1}: 1737 (CO). ($C_{52}H_{46}Cl_2P_2F_{12}Fe_3O_6$) (1295.30): Calcd: C 48.22, H 3.58. Found: C 48.49, H 3.69.

Synthesis of 34a−c and 35a−c. Complexes **33a−c** (0.4 mmol), compounds **2a**,**b** (0.4 mmol), and K_2CO_3 (0.138 g, 1 mmol) were stirred in 1 mL of DMF under N_2 at 60 °C for 1 h and then at room temperature for 6 h. The viscous solution was poured into 10% HCl, and NH_4PF_6 (0.065 g, 0.4 mmol) was added. The resulting precipitate was collected in a sintered glass crucible and washed with water and then ether. Spectroscopic data for polymer **34a** are provided as a representative example.

Scheme 2



34a: Yield: 80%. ^{1}H NMR (acetone-d_6): $\delta = 1.36$ (br s, 12H, CH_2), 1.69 (br s, 3H, CH_3), 2.14 (br s, 2H, CH_2), 2.50 (br s, 2H, CH_2), 3.16 (br s, 4H, CH_2), 4.19 (br s, 5H, Cp), 4.39 (br s, 2H, CH_2), 4.44 (br s, 4H, CH_2, Cp), 4.75 (br s, 2H, Cp), 5.19 (s, 10H, Cp), 6.37 (br s, 4H, complexed Ar), 6.47 (br s, 4H, complexed Ar), 7.26 (br s, 4H, Ar), 7.39 (br s, 4H, Ar). ^{13}C NMR (DMSO-d_6): $\delta = 24.18$ (CH_2), 26.51 (CH_3), 27.70, 28.02, 29.35, 31.85, 38.26 (CH_2), 44.33 (C), 61.30, 61.89 (CH_2), 69.18 (Cp−CH), 69.36 (complexed Ar−CH), 69.89 (complexed Ar−C), 71.09, 75.56 (complexed Ar−CH), 78.15 (Cp−CH), 82.41 (complexed Ar−CH), 105.40 (complexed Ar−C), 119.67, 128.81 (Ar−CH), 130.49 (complexed Ar−C), 145.48, 150.87 (Ar−C), 170.09, 172.26 (CO). IR (KBr), υ/cm^{-1}: 1734 (CO).

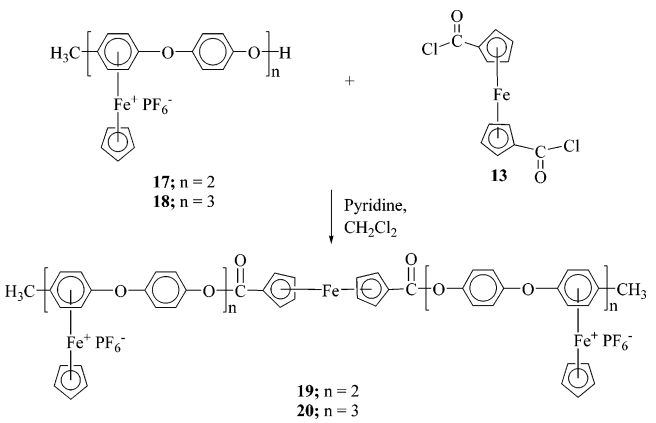
Synthesis of 36a−c and 37a−c. Polymers **34a−c** and **35a−c** (0.25 mmol) were dissolved in 40 mL of CH_3CN:DMSO (1:1) and placed in a Pyrex tube. The solution was purged with nitrogen and then photolyzed for 4 h in a Rayonett photoreactor equipped with 300 nm lamps. The solvents were removed, and the residue was extracted with chloroform. The solution was washed with water and then dried over $MgSO_4$ and filtered. The solution was concentrated and added to pentane. The resulting precipitate was collected in a crucible and dried under reduced pressure. Spectroscopic data for polymer **36a** are provided as a representative example.

36a: Yield: 77 %. ^{1}H NMR (DMSO-d_6): $\delta = 1.53$ (br s, 12H, CH_2), 1.71 (br s, 3H, CH_3), 2.10 (br s, 2H, CH_2), 2.40 (br s, 2H, CH_2), 3.19 (br s, 4H, CH_2), 4.15 (br s, 5H, Cp), 4.28 (br s, 2H, CH_2), 4.41 (br s, 4H, CH_2, Cp), 4.71 (br s, 2H, Cp), 6.90 (br s, 8H, ArH), 7.13 (br s, 4H, ArH), 7.29 (br s, 4H, ArH). IR (KBr), υ/cm^{-1}: 1732 (CO).

Results and Discussion

In our previous studies, we have demonstrated that the strong electron-withdrawing ability of the cationic cyclopentadienyliron moiety allows for facile nucleophilic aromatic substitution reactions of complexed chloroarenes under mild reaction conditions.[12,15−19] In this work, we report the synthesis and characterization of complexes and polymers containing cyclopentadienyliron cations pendent to the backbones and neutral ferrocenyl moieties pendent or within the backbones of the materials. The synthesis of cyclopentadienyliron complexed arenes containing terminal hydroxyl groups (**7a−e**, **8a−e**, and **9a**,**b)** was accomplished by reaction of chloroarene complexes with various dinucleophiles. Monometallic complexes **7a−e** and **8a−e** were subsequently reacted with ferrocene carboxylic acid (**10**) to yield bimetallic complexes **11a−e** and **12a−e**, respectively, as shown in Scheme 2. Complexes **7**−**9** were also reacted with 1,1′-ferrocenedicarbonyl chloride (**13**) to

Scheme 3



produce the trimetallic complexes **14a**−**e**, **15a**−**e,** and **16a**,**b** in good yields. The synthesis of these small complexes allowed for an understanding of the spectroscopic and electrochemical properties of this class of mixed charge organoiron species. In addition, the synthesis of complexes **16a** and **16b** further allows for the preparation of polymeric materials due to the presence of the activated terminal chloroarene complexes.

This methodology was also extended to produce larger oligomeric complexes as shown in Scheme 3. Bi- and triiron complexes containing terminal phenolic groups (**17** and **18)** were reacted with 1,1′-ferrocenedicarbonyl chloride to produce penta- and hepta-metallic complexes **19** and **20**, respectively. The electrochemical properties of these complexes were examined using cyclic voltammetry. The cyclic voltammograms of oligomers **15c**, **19**, and **20** showed that the arene complexes of cyclopentadienyliron possess substantially different electrochemical properties compared to the neutral organoiron complexes. As well, the cationic iron complexes underwent reduction processes that could be distinguished based on the electron-withdrawing/donating abilities of the substituents on the arenes. While the cyclic voltammogram of the trimetallic complex **15c** showed that the neutral iron centers underwent reversible oxidation at $E_{1/2} = 1.00$ V, the cationic iron centers pendent to the aromatic rings in this complex underwent reversible reduction at $E_{1/2} = -1.34$ V. By increasing the number of cationic iron centers in the complexes from two in **15c** to four in complex **19**, the intensity of the reduction processes increased relative to the oxidation process. In the cyclic voltammogram of complex **19** there are two distinct reduction processes visible due to the two terminal and two inner complexed arenes. This behavior is consistent of our previous study of η^6-susbstituted arene−η^5-cyclopentadientyliron complexes in which arenes with electron-withdrawing groups were reduced at lower negative values compared to arenes with electron-donating groups.[20] The neutral iron center underwent reversible oxidation at $E_{1/2} = 1.24$ V, while the cationic iron centers underwent reversible reduction at $E_{1/2} = -1.02$ and -1.11 V and behaved as isolated centers (Figure 1).[8a] In the cyclic voltammogram of complex **20**, the reduction waves of the three different cationic iron centers were overlapped, and it was not possible to distinguish them. Oxidation of the ferrocenyl iron occurred at $E_{1/2} = 1.19$ V, while the cationic iron complexes were reduced at approximately $E_{1/2} = -1.11$ V. In comparison to the cyclic voltammograms of complexes **15c** and **19**, the cyclic voltammogram of **20** showed a much smaller redox wave for oxidation of the

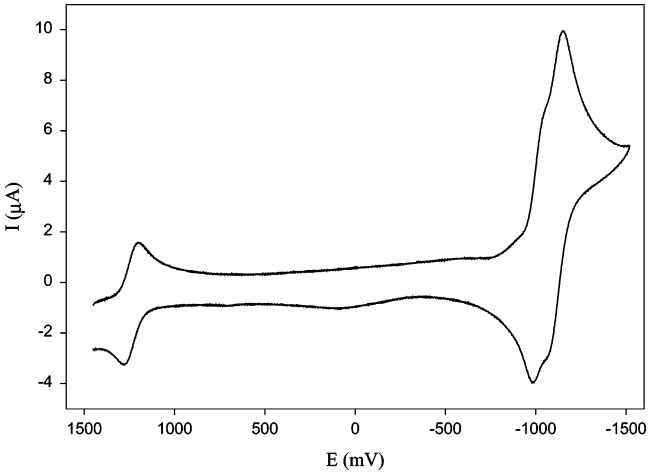
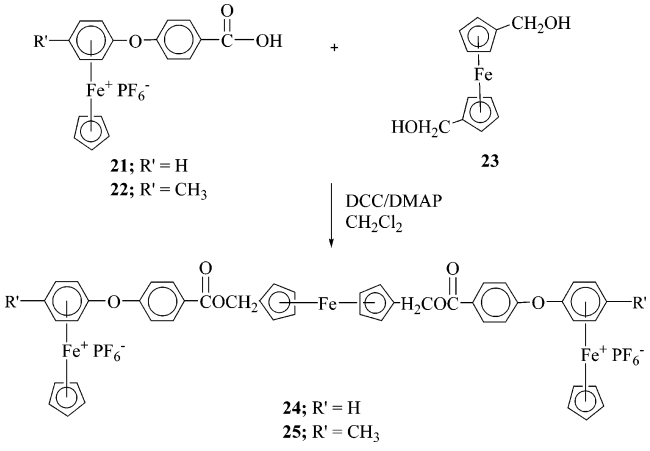


Figure 1. Cyclic voltammogram using glassy carbon electrode, Ag/AgCl reference electrode, and 0.002 M **19** in 0.1 M TBAP in propylene carbonate; $\nu = 0.1$ V/s at 0 °C.

neutral iron since there was only one of these redox centers for every six of the cationic iron centers.

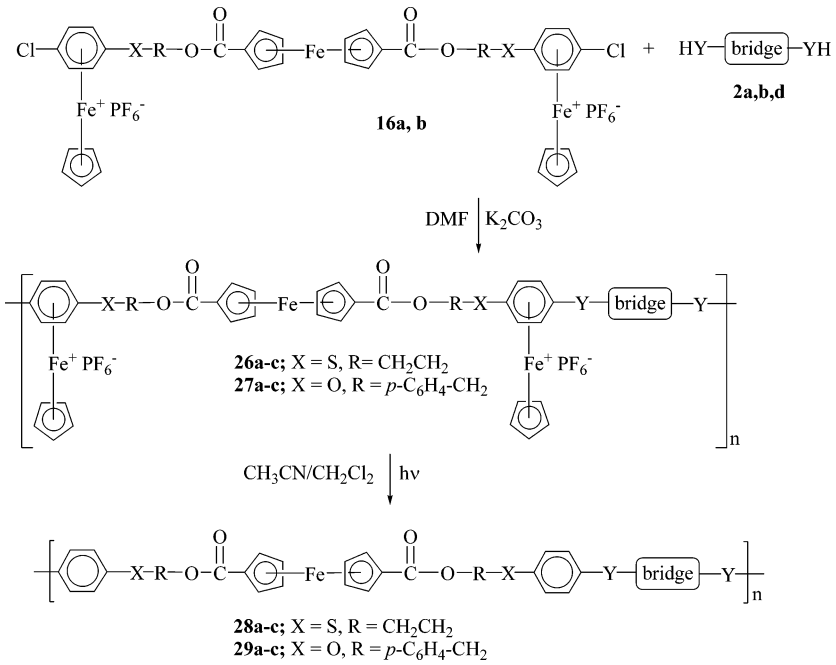
Trimetallic complexes could also be synthesized by reaction of 1,1′-bis(hydroxymethyl)ferrocene (**23**) with carboxylic acid functionalized arene complexes of cyclopentadienyliron. Scheme 4 shows the synthesis of complexes **24** and **25** using this strategy utilizing complexes **21** and **22**, which were prepared using our previously reported methodology.[12d] It is known that ferrocene derivatives with electron-withdrawing substituents have more positive redox potentials than those with electron-donating substituents.[11] This was seen in the cyclic voltammogram of complex **25**, where the $E_{1/2}$ corresponding to oxidation of the neutral ferrocenyl moiety occurred at 0.463 V. This is in contrast to the ferrocenyl moieties containing ester substituents, where the half-wave potentials were above 1 V.

Scheme 4



Two different strategies were utilized to prepare polymers containing both neutral and cationic cyclopentadienyliron complexes within their structures. Scheme 5 shows the reaction of complexes **16a**,**b** with 4,4′-thiobisbenzenethiol (**2a**), 1,8-octanedithiol (**2b**), and bisphenol A (**2d**) to produce the mixed-charge organoiron polymers **26a**−**c** and **27a**−**c**. These polymers are unique in that they contain neutral ferrocenyl units in their backbones and cationic cyclopentadienyliron moieties pendent to their backbones. These polymers were isolated as orange-brown solids in yields that ranged

Scheme 5



from 86 to 91% and demonstrated good solubility in polar organic solvents such as DMF and DMSO.

Scheme 6 shows another class of organoiron polymers that were synthesized, in which the ferrocenyl moieties are present in the polymer side chains rather than the polymer backbones. Reaction of the carboxylic acid functionalized diiron complex (**30**) with various diols (**31a**−**c**) followed by coupling reactions with ferrocene carboxylic acid (**10**) produced monomers **33a**−**c** in very good yields. These monomers were subsequently polymerized with 4,4′-thiobisbenzenethiol (**2a**) and 1,8-octanedithiol (**2b**) to give polymers **34a**−**c** and **35a**−**c**, respectively.

Measurement of the viscosities of the mixed charge organoiron polymers was performed. Figure 2 shows a plot of the inherent viscosity of polymer **27b** versus concentration in DMSO. It can be seen that as the polymer concentration decreased, the inherent viscosity of the solution increased, which is diagnostic of polyelectrolyte solutions.[21d] We have previously reported similar results for polyimines and star-shaped polymers coordinated to cyclopentadienyliron cations.[12d,17,19] Water-soluble poly(ferrocenylsilane) polyelectrolytes have been reported by the research groups of Manners and Vancso.[21] However, in those cases, cationic or anionic substituents were incorporated as pendent groups on the polymer backbones, whereas in this study the cations are the iron centers.

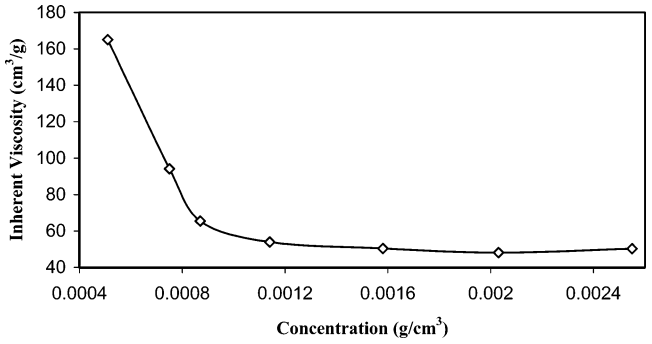


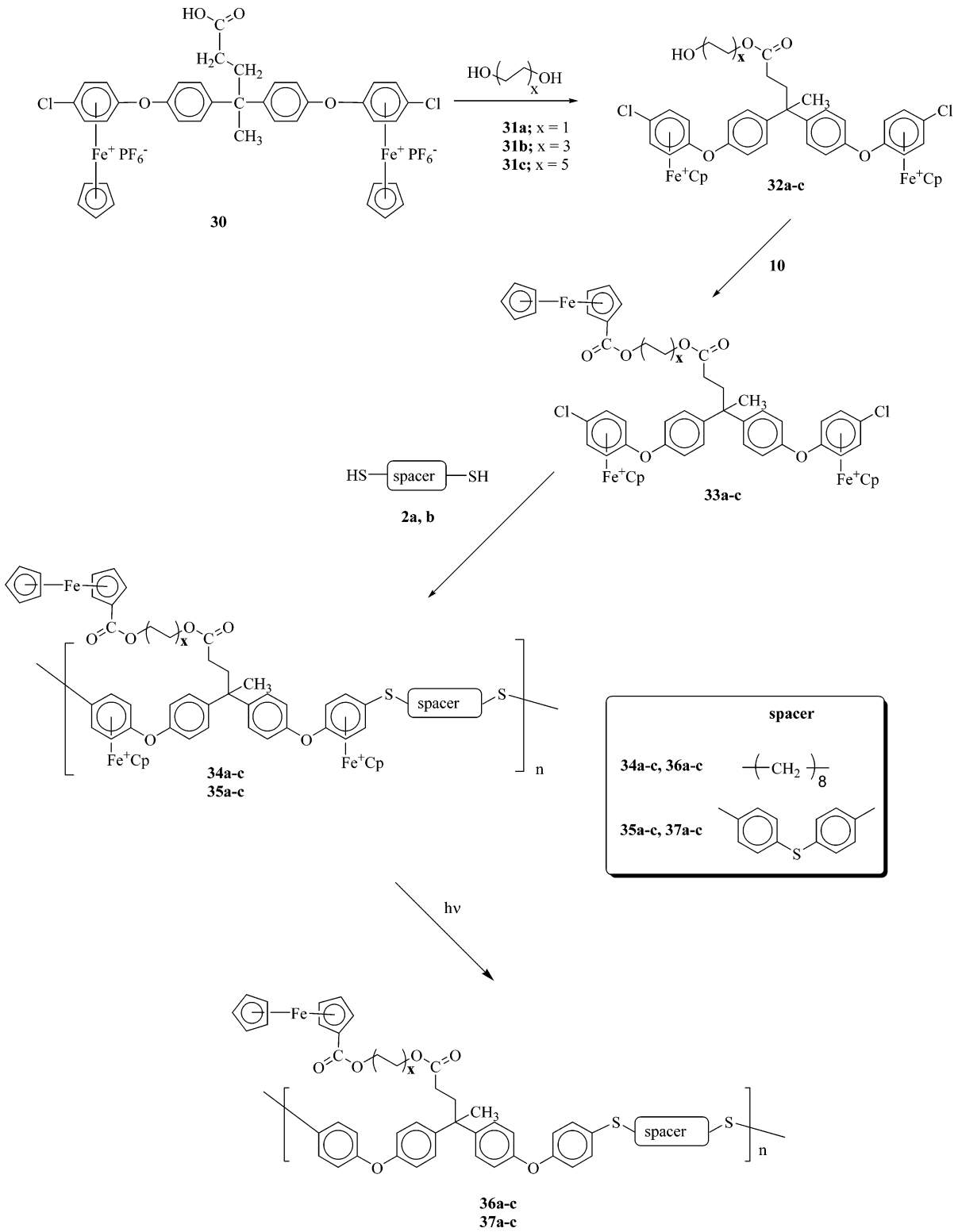
Figure 2. Plot of inherent viscosity versus concentration for polymer **27b**.

It has been established that ionic polymers such as those described in this work cannot be analyzed using GPC due to interactions with the column.[10] Therefore, photolytic reactions were used to remove the cationic cyclopentadienyliron moieties from the polymer backbones. It was found that the cationic organoiron complexes were cleaved from the arenes, while the neutral organoiron complexes were unaffected using these conditions. Therefore, the molecular weights of the neutral ferrocene-based polymers were measured by GPC in THF. The weight-average molecular weights of polymers **28a**−**c** and **29a**−**c** ranged from 8700 to 13 500 with relatively low polydispersities between 1.1 and 2.2. From these values, the molecular weights of the corresponding cationic polymers could be estimated. For example, it was determined that the average number of repeating units in polymer **28a** was 18 by GPC, corresponding to a weight-average molecular weight (M_w) of 13 500. The M_w of its cationic analogue (**26a**) could then be estimated to be 22 800. This indicates that polymer **26a** contained ∼18 neutral iron centers in its backbone and 36 cationic iron centers pendent to its backbone. While polymers **37a**−**c** possessed similar molecular weights as polymers **28** and **29**, polymers **36a**−**c** had markedly higher molecular weights. This is due to the long aliphatic chain in the polymer backbones in addition to the flexible side chains, which allowed for higher solubility. The weight-average molecular weights of polymers **36a**−**c** and **37a**−**c** ranged from 11 100 to 56 200 with polydispersity indices between 1.2

Table 1. Molecular Weight Analysis of Polymers 28a−c, 29a−c, 36a−c, and 37a−c

polymer	M_w	PDI	polymer	M_w	PDI
28a	13 500	1.3	**36a**	18 700	1.2
28b	11 000	1.2	**36b**	56 200	3.1
28c	9 300	1.4	**36c**	29 600	1.3
29a	8 700	1.1	**37a**	14 200	1.4
29b	13 100	2.2	**37b**	13 100	1.2
29c	11 300	1.7	**37c**	11 100	1.2

Scheme 6



and 3.1. The molecular weight data for all of the neutral ferrocene-based polymers can be found in Table 1.

An examination of the electrochemical stability of the iron complexes in these polymers was accomplished by varying the temperature of the solutions from −30 to +30 °C in propylene carbonate containing TBAP.[22] At −30 °C, both the oxidation and reduction waves were reversible; however, at 30 °C, the reduction processes became irreversible. Electrochemical analysis showed that the cationic organoiron complexes were reversibly reduced between −1.02 and −1.28 V, and the neutral ferrocenyl groups were oxidized between 0.891 and 1.03 V vs Ag/AgCl. Electrochemical analysis of the photolyzed polymers was also performed. It was found that the iron centers in the polymers were oxidized at a lower positive potential in the neutral polymers due to the absence of the cationic iron species. For example, the cyclic voltammogram of polymer **29b** obtained in dichloromethane showed that oxidation of the iron centers occurred at $E_{1/2}$ = 0.609 V, whereas in the cationic organoiron polymer **27b**, oxidation of the ferrocenyl groups occurred at $E_{1/2}$ = 1.03 V vs Ag/AgCl. The

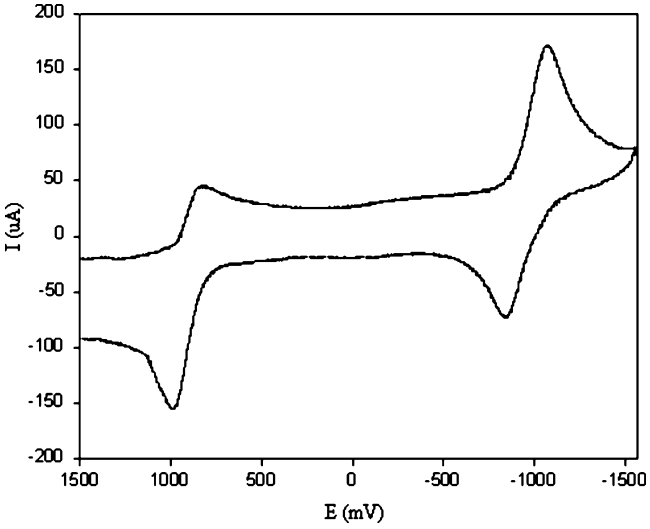


Figure 3. Cyclic voltammogram of polymer **35b** in 0.1 M TBAP in propylene carbonate at −20 °C.

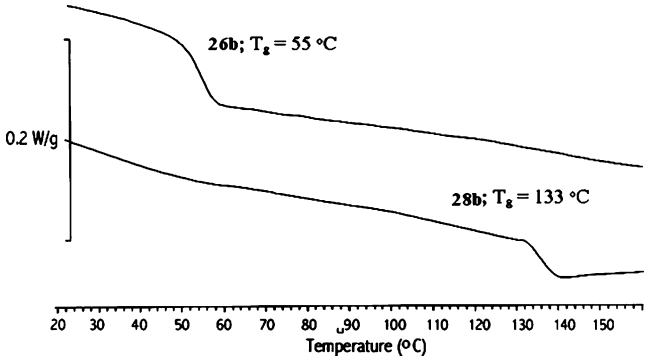


Figure 4. DSC traces of cationic and neutral organoiron polymers **26b** and **28b**.

electrochemical studies of polymers **34a**−**c** and **35a**−**c** showed two separate redox couples for the two different iron species. Polymer **35b**, as an example, showed that the cationic iron moiety underwent a reversible reduction at −1.1 V and that the neutral iron species displayed an oxidation at 0.7 V, as shown in Figure 3.

The thermal properties of the cationic and neutral organoiron polymers were studied using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The polymers containing cyclopentadienyliron cations coordinated to arenes in their backbones experienced weight losses at ∼210 °C due to the loss of the pendent iron complexes. Additional weight loss steps were observed starting between 343 and 465 °C, which were attributed to degradation of the polymer backbones. Following photolytic demetalation of the polymers, the resulting ferrocene-based polymers experienced weight losses starting at temperatures ranging from 290 to 433 °C. Polymers **28a**−**c** and **29a**−**c** underwent at least two weight loss steps, while polymers **36a**−**c** and **37a**−**c** underwent only one significant weight loss step. However, the weight percentages lost were comparable in all polymers. DSC analysis of the cationic and neutral organoiron polymers demonstrated that the cationic polymers had significantly higher glass transition temperatures (T_g) than their neutral analogues. For example, polymer **26b** had a T_g at 133 °C, while polymer **28b** had a T_g at 55 °C, as shown in Figure 4. The T_gs of the cationic polymers ranged from 65 to 161 °C, and the T_gs of the ferrocene based polymers ranged from 10 to 92 °C. The TGA and DSC data for the cationic and neutral organoiron polymers are provided in Tables 2 and 3, respectively.

Table 2. Thermal Analysis of Cationic Organoiron Polymers

polymer	T_g (°C)	weight loss (%)	T_{onset} (°C)	$T_{midpoint}$ (°C)	T_{endest} (°C)
26a	117	12	208	241	264
		32	360	428	493
26b	133	14	210	241	263
		10	343	367	371
		18	426	459	490
26c	65	14	207	239	283
		36	344	393	433
27a	141	5	208	231	247
		37	448	493	529
27b	161	8	207	240	253
		22	436	496	554
27c	104	5	208	219	221
		35	395	435	473
34a	116	23	206	244	262
		35	397	449	482
34b	115	21	209	222	226
		36	412	432	466
34c	113	18	206	224	235
		43	412	433	463
35a	135	25	215	275	277
		24	465	475	497
35b	132	15	213	230	236
		40	428	461	497
35c	118	17	213	232	235
		40	427	453	499

Table 3. Thermal Analysis of Neutral Organoiron Polymers

polymer	T_g (°C)	weight loss (%)	T_{onset} (°C)	$T_{midpoint}$ (°C)	T_{endest} (°C)
28a	59	27	360	428	493
28b	55	23	426	459	490
28c	10	49	344	393	433
29a	92	28	448	493	529
29b	84	33	436	496	554
29c	24	50	395	435	473
36a	66	36	397	449	482
36b	62	36	412	432	466
36c	61	59	412	433	463
37a	75	28	465	475	497
37b	71	21	428	461	497
37c	61	33	412	442	502

Conclusions

A series of model oligomeric complexes containing neutral cyclopentadienyliron complexes in the backbone and pendent cyclopentadienyliron cations were synthesized using metal-mediated nucleophilic aromatic substitution reactions. It was established that these complexes underwent one-electron redox reactions, involving oxidation of the neutral iron centers and reduction of the cationic iron centers. Two different classes of mixed-charge organoiron polymers were also synthesized. The first strategy yielded polymers with the ferrocenyl units in the backbones, while the second strategy produced polymers with ferrocene groups in the side chains. These polymers also underwent reversible redox reactions and were found to show polyelectrolyte effects by viscosity. Photolysis of the cationic polymers resulted in the selective cleavage of the cationic cyclopentadienyliron moieties yielding new classes of ferrocene-based polymers. Thermal analysis established that the cationic polymers possess higher glass transition temperatures but lower thermal stability than their neutral analogues.

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Supporting Information Available: Full experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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