Polyethers and Thioethers Incorporating Neutral and Cationic Organoiron Complexes

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Summary: The synthesis of linear and star-shaped oligomers containing cationic and neutral organoiron groups in their structures was achieved by reaction of cationic arene complexes of cyclopentadienyliron containing terminal hydroxyl groups with 1,1'-ferrocenedicarbonyl chloride or ferrocene carboxylic acid. The use of chloroarene complexes allowed for the formation of triiron complexes that were subsequently polymerized via nucleophilic aromatic substitution with various oxygen- and sulfur-based dinucleophiles. The corresponding polyethers and thioethers were isolated in good yields and these materials exhibited excellent solubilities in polar organic solvents. Cyclic voltammetric investigations revealed that the cationic iron centers pendent to the polymer backbones underwent reversible reduction steps, while the neutral iron centers within the polymer backbones underwent reversible oxidation steps. Photolysis of these polymers resulted in the removal of the cationic cyclopentadienyliron moieties pendent to the polymer backbones. Thermogravimetric analysis (TGA) revealed that the cationic iron complexes were cleaved from the polymers at approximately 210 °C. Differentials scanning calorimetry (DSC) revealed that the glass transition temperatures of the cationic polymers occurred at higher temperatures than their neutral analogs.

Keywords: arene cyclopentadienyliron complexes; ferrocene; organoiron polymers; soluble polymers; star polymers

Introduction

The synthesis of organoiron polymers has been the focus of numerous investigations in recent years in light of the interesting properties that this class of material possesses.[1-4] Two of the most prevalent organoiron groups that have been incorporated into polymers are the ferrocene and arene cyclopentadienyliron complexes. The ferrocene group is a very stable organometallic functionality and undergoes reversible oxidation processes.[5] On the other hand, cationic arene

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cyclopentadienyliron complexes undergo reversible reduction steps.[5, 6] Astruc has reported the synthesis of star and dendritic complexes containing arene complexes of cyclopentadienyliron and ferrocene moieties in their structures.[7, 8] The synthesis of a bimetallic amide complex incorporating one ferrocene and one cobaltocenium complex in the backbone has been described by Cuadrado and coworkers.[9] The ferrocene complex was oxidized at 0.56 V, while the cobaltocenium unit was reduced at –0.75 V vs. SCE. The synthesis of a dendrimer containing these isoelectronic metallocene groups at their periphery was also reported.[10] It was found that the cationic cobalt-based metallocenes functionalized with carboxylic acid groups reacted with amines more rapidly than their neutral iron-based analogs.[9, 10]

Our research focuses on the use of arene complexes in monomer and polymer synthesis. Mono- and di-chloroarene complexes undergo nucleophilic aromatic substitution reactions with a large variety of oxygen, sulfur and nitrogen nucleophiles to produce novel materials.[11-15] Polymerization of dichloroarene complexes of cyclopentadienyliron with dinucleophiles readily affords soluble cationic polymers.[12] Photolysis of these polymers allows for the removal of the organoiron moieties and isolation of the corresponding organic polymers. Monomers containing unsaturated centers have been subjected to radical and ring-opening metathesis polymerization reaction, yielding high molecular weight cationic organoiron polymers.[16-18]

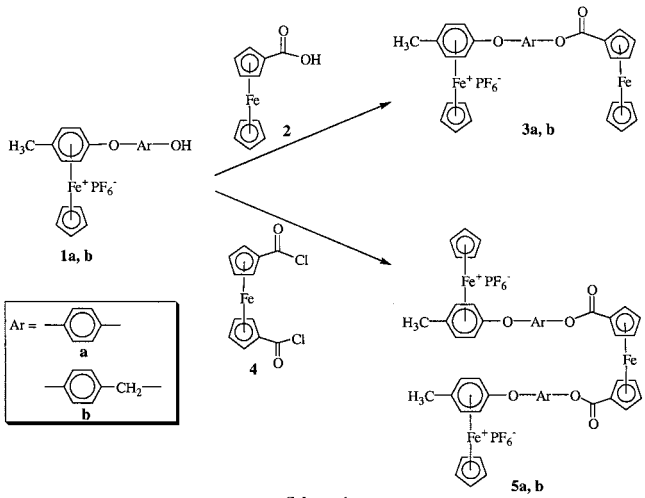
Our success in the design of polymeric materials containing arene cyclopentadienyliron complexes combined with the attractive properties that ferrocene-based polymers possess, prompted our investigation into the development of polymers containing these two organoiron groups. To that end, we recently reported the synthesis of oligomers and polymers containing cationic cyclopentadienyliron moieties and neutral ferrocenyl moieties in their structures.[15] While the neutral ferrocene groups were incorporated as integral parts of these materials, the cationic cyclopentadienyliron moieties were introduced as pendent groups. This article will highlight our results in this area and describe some of our recent findings.

Results and Discussion

Oligomers

Our initial investigations into the synthesis of complexes containing arene complexes of cyclopentadienyliron and ferrocene led to the synthesis of diiron and triiron complexes. Scheme

1 shows the synthesis of some of these complexes by reaction of arene complexes containing terminal -OH groups with carboxylic acid and diacid chloride derivatives of ferrocene. While reaction of complexes **1a** and **1b** with ferrocene carboxylic acid (**2**) in the presence of dicyclohexylcarbodiimide (DCC) and *N,N*-dimethylamino pyridine (DMAP) resulted in the production of bimetallic complexes **3a** and **3b**, reaction of **1a** and **1b** with ferrocene dicarbonyl chloride (**4**) in the presence of pyridine produced the trimetallic complexes **5a** and **5b**, respectively.



Scheme 1

The electrochemical properties of these complexes were examined using cyclic voltammetry. It was possible to distinguish the two types of iron complexes by their distinct redox behaviors. Figure 1 shows the cyclic voltammogram of the trimetallic complex **5a**. The neutral iron centers in this complex underwent reversible oxidation at $E_{1/2}$ = 1.00 V and the cationic iron centers pendent to the aromatic rings underwent reversible reduction at $E_{1/2}$ = -1.34 V. It is also important to note that the redox wave corresponding to the two cationic iron centers is twice as large as the redox wave corresponding to the central ferrocenyl moiety. In contrast, the cyclic voltammograms for complexes **3a** and **3b** exhibited reduction and oxidation processes of equal current intensities. For penta- and hepta-metallic complexes containing one central ferrocene group each, the ratios of the current intensities for the oxidation to reduction peaks were 1 to 4 and 1 to 6, respectively.

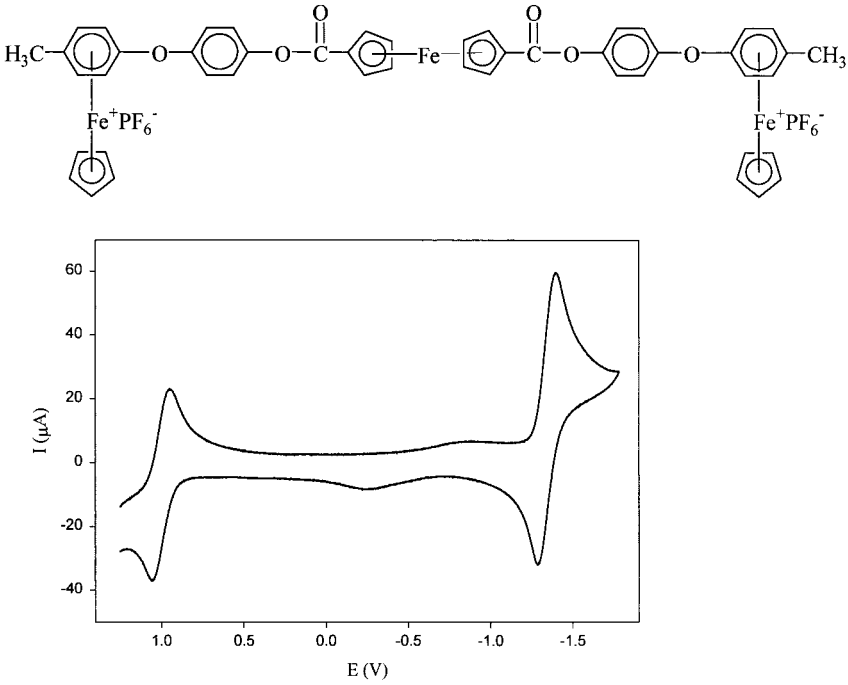
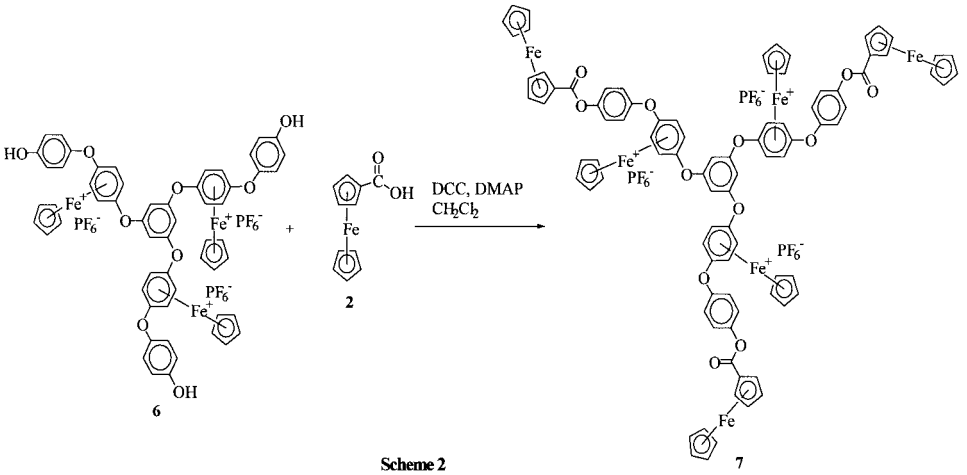


Figure 1. Cyclic voltammogram at glassy carbon of 0.002 M 5a in 0.1 M TBAP in propylene carbonate, $\nu = 0.1$ V/s at 0 °C.

Star-Shaped Complexes

It was also of interest to prepare star-shaped complexes containing these two different redox active organoiron groups. The synthesis of a hexametallic complex containing neutral and cationic cyclopentadienyliron moieties in its structure is shown in Scheme 2. We have recently reported the synthesis of complex **6**, which served as a core molecule in the synthesis of star-shaped polyaromatic ethers.[13] Reaction of trimetallic star complex **6** with ferrocene carboxylic acid (**2**) allowed for the isolation of the hexametallic star complex **7**. A slight excess of complex **2** was utilized in the reaction in order to ensure complete coupling of the carboxylic acid groups to the phenolic groups.



Scheme 2

The ^{1}H NMR spectrum of complex **7** is shown in Figure 2a. The cyclopentadienyl protons of the unsubstituted ferrocenyl groups appear as a singlet at 4.33 ppm, while the protons of the substituted cyclopentadienyl ring appear as two sets of triplets at 4.40 and 4.94 ppm. The protons of the cyclopentadienyl ring coordinated to the cationic iron center appear as a singlet further downfield at 5.35 ppm. The complexed aromatic protons appear as two sets of doublets at 6.41 and 6.63 ppm, which is consistent with the proposed structure. The protons of the central aromatic ring appear as a singlet at 7.35 ppm, while the protons of the three other aromatic rings appear as a singlet at 7.38 ppm. The ^{13}C NMR (APT) spectrum displayed in Figure 2b shows the cyclopentadienyl carbons (CH) of the ferrocenyl unit at 70.68, 71.23 and 72.95 ppm, while the *ipso* carbons appear at 70.46 ppm. The cyclopentadienyl resonance of the rings coordinated to the cationic iron centers appear at 78.99 ppm. The complexed aromatic carbons (CH) appear at 75.84 and 76.87 ppm, while the *ipso* complexed aromatic carbons resonate at 130.70 and 131.94 ppm. The carbons *alpha* to the ether linkages in the central arene and the branches appear at 110.71 ppm, and 122.17 and 124.84 ppm, respectively. The three *ipso* aromatic carbons appear at 149.57, 151.70 and 157.62 ppm. The peak at 170.35 ppm corresponds to the carbonyl carbons of the ester functionalities.

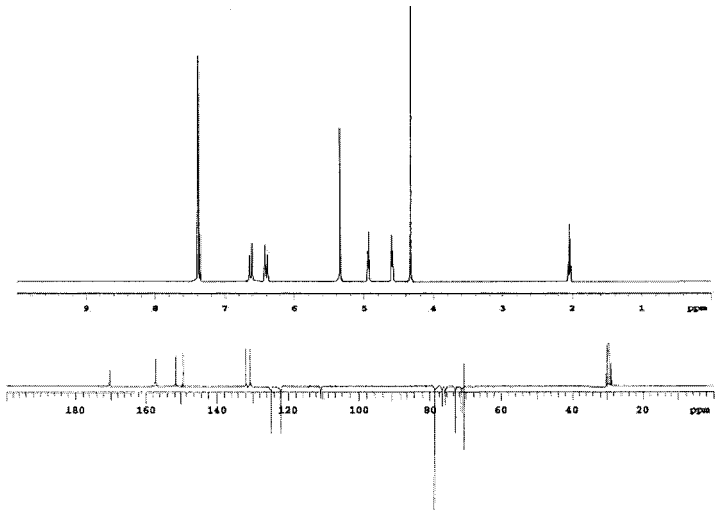


Figure 2. (a) top, ^{1}H NMR spectrum of complex **7** in acetone-d_6 (a) bottom, ^{13}C NMR spectrum of complex **7** in acetone-d_6.

The electrochemical properties of complex **7** were examined in order to determine the redox potentials of the two cationic and neutral iron centers within its structure. These cyclic voltammograms were obtained in propylene carbonate from –30 to +10 °C and were found to be reversible. The cyclic voltammogram in Figure 3 shows the oxidation of the neutral iron centers at $E_{1/2} = 0.694$ V and reduction of the cationic iron centers at $E_{1/2} = -1.29$ V.

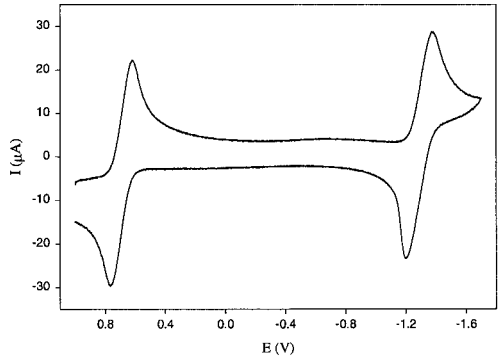
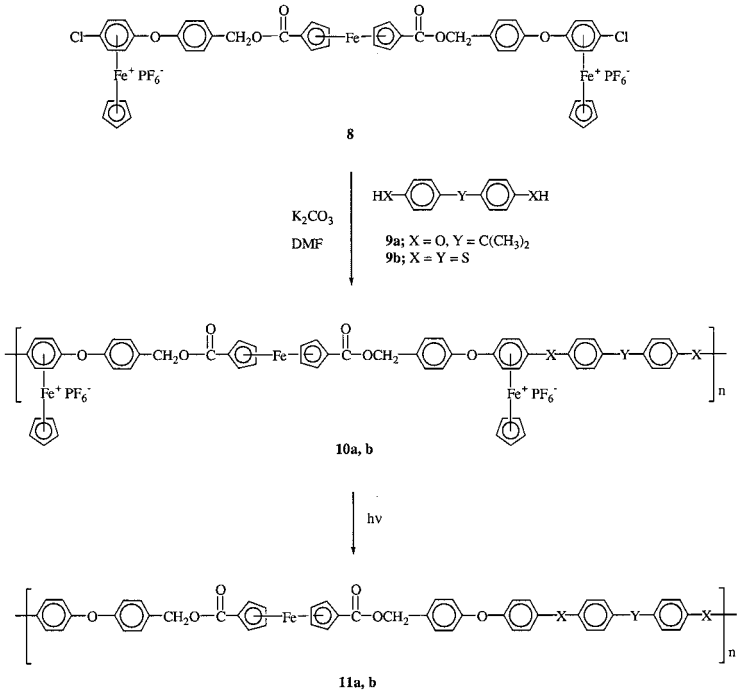


Figure 3. Cyclic voltammogram at glassy carbon of 0.001 M of the star-shaped hexametallic complex **7** in 0.1 M TBAP in propylene carbonate, v = 0.2 V/s at –30 °C.

Polymers

The synthesis of polymers containing both neutral and cationic cyclopentadienyliron complexes in their structures has recently been communicated.[15] Reaction of trimetallic complexes containing terminal chloroarene complexes of cyclopentadienyliron were reacted with various dinucleophiles in the presence of potassium carbonate. Scheme 3 shows the reaction of complex **8** with bisphenol A (**9a**) and 4,4'-thiobisbenzenethiol (**9b**), producing the mixed-charge organoiron polymers **10a** and **10b**, respectively. NMR analysis of these polymers was consistent with successful polymerization. In order to measure the molecular weights of these materials, the cationic cyclopentadienyliron moieties were first cleaved from the polymer backbones due to interactions between these complexes and GPC columns. Irradiation of **10a** and **10b** in acetonitrile/dichloromethane solutions allowed for the isolation of the novel ferrocene-containing polymers **11a** and **11b**.



Scheme 3

^{1}H and ^{13}C NMR analysis of these polymers clearly showed that the cyclopentadienyl resonances corresponding to the cyclopentadienyliron cations were no longer present in the spectra of **11a** and **11b**, however the cyclopentadienyl resonances corresponding to the neutral organoiron groups were still observed. Figure 4 shows the ^{1}H NMR spectrum of polymer **11a**. It is clear that the ferrocenyl cyclopentadienyl resonances are present at 4.24 and 4.75 ppm, while the cyclopentadienyl resonance of the cationic complex is not visible. The peak at 5.18 ppm corresponds to the methylene protons and the singlet at 1.63 ppm corresponds to the methyl protons of the isopropylidene groups. The aromatic protons appear as three sets of doublets and two singlets between 6.86 and 7.34 ppm.

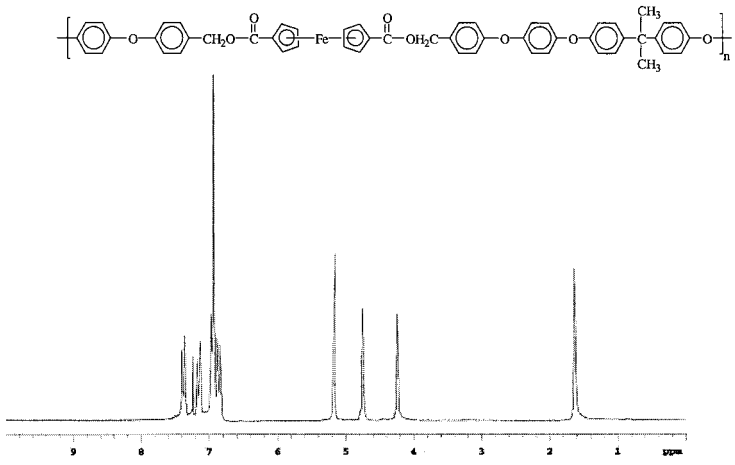


Figure 4. ^{1}H NMR spectrum of the ferrocene-based polymer **11a** in $CDCl_3$.

The cyclic voltammogram of polymer **10b** is shown in Figure 5. It can be seen that the neutral iron centers in the polymer backbone were oxidized at $E_{1/2}$ = 1.05 V, while the cationic iron centers pendent to the polymer backbone were reduced at $E_{1/2}$ = -0.995 V. While the redox patterns of the polymers were similar to the smaller oligomeric complexes, it can be seen that the oxidation and reduction waves are broader in the polymeric materials.

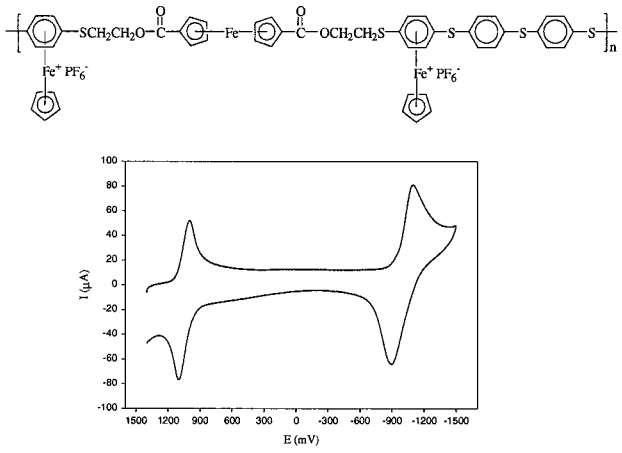


Figure 5. Cyclic voltammogram at glassy carbon of 0.002 M of the organoiron polymer **10b** in 0.1 M TBAP in propylene carbonate, ν = 0.5 V/s at –20 °C.

Electrochemical analysis of the photolyzed polymers was also performed. Since polymers **11a** and **11b** still contained redox active groups, cyclic voltammetry was a useful method to compare the properties of the cationic and neutral organoiron polymers. Figure 6 shows the cyclic voltammogram of polymer **11b**, which was obtained in dichloromethane. It can be seen that oxidation of the iron centers in this polymer occurs at $E_{1/2}$ = 0.609 V. In contrast, the CV of polymer **10b** showed that the neutral iron centers were oxidized at a much more positive potential.

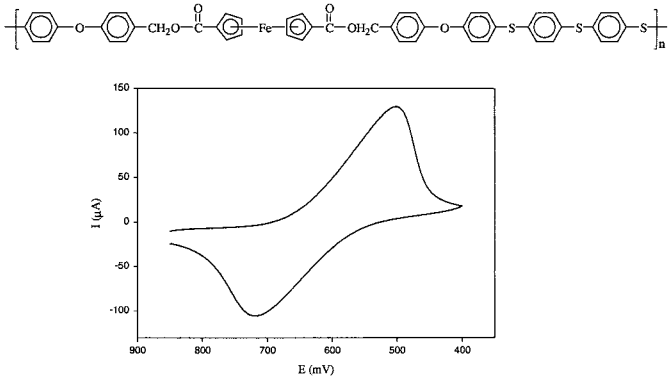


Figure 6. Cyclic voltammogram at glassy carbon of 0.001 M of the neutral organoiron polymer **4.18** in 0.1 M TBAP in dichloromethane, ν = 0.1 V/s at –30 °C.

The molecular weights of polymers **11a** and **11b** were measured using gel permeation chromatography. It was not possible to measure the molecular weights of polymers **10a** and **10b** directly due to interactions of the cationic iron centers with GPC columns. Therefore, the molecular weights of the organometallic polymer were calculated based on the average weights determined for their corresponding neutral analogs. The number average molecular weights of polymers **10a** and **10b** were determined to be 9,700 and 9,100 with polydispersities of 1.13 and 2.19.

Thermogravimetric analysis of the organoiron polymers showed that the cyclopentadienyliron cations were cleaved from the polymer backbones at about 210 °C. These values are consistent with our other thermal tests of cyclopentadienyliron-coordinated polyethers and thioethers.[12] Degradation of the polymer backbones began at about 440 °C. Following photolytic cleavage of the cyclopentadienyliron moieties from the backbones of the polymers, the weight losses at 210 °C were not present. However, two weight losses were present in the thermograms of **11a** and **11b**. Small weight loss steps were observed at about 290 °C and more significant decomposition began at about 400 °C.

Differential scanning calorimetry of polymers **10a,b** and **11a,b** was performed in order to examine the glass transition temperatures of these organoiron polymers. The glass transition temperatures of polymers **10a** and **10b** were 141 and 161 °C, respectively. Upon removal of the cationic cyclopentadienyliron moieties pendent to the polymer backbones, the T_gs of these polymers decreased to 92 to 84 °C, for **11a** and **11b**, respectively. These results indicate that the presence of bulky cationic cyclopentadienyliron moieties pendent to the backbones of polymers causes significant increases in their glass transition temperatures.

Conclusion

New classes of oligomers and polymers containing neutral ferrocene units in their backbones and cationic cyclopentadienyliron moieties pendent to their backbones were synthesized via nucleophilic aromatic substitution reactions. Photolysis of these polymers resulted in cleavage of the pendent cationic iron groups, allowing for the isolation of novel ferrocene-containing polymers. Thermal analysis indicated that these polymers possessed higher thermal stability but lower glass transition temperatures than their cationic analogs. Cyclic voltammetry of the

complexes and polymers incorporating neutral and cationic organoiron complexes in their structures showed that the iron centers underwent reversible oxidation and reduction processes, respectively.

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