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Synthesis of Sulfone-Containing Monomers and Polymers Using Cationic Cyclopentadienyliron Complexes

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Summary: The synthesis of sulfone-containing monomers with pendent cationic cyclopentadienyliron ($CpFe^+$) moieties has been accomplished via nucleophilic aromatic substitution of dichloroarene complexes with a number aliphatic dithiols. These complexes were further oxidized using m-CPBA to give the sulfone-based monomers. Polymerization of the sulfone-based monomers with O-containing nucleophiles produced the sulfone-based polymers. Direct nucleophilic aromatic substitution of dichloroarene complexes with dinucleophiles allowed for the formation of organoiron sulfide-based polymers. Oxidation of these polymers led to the formation of sulfone polymers with the pendent iron moieties. The organometallic monomers and polymers were found to be more soluble in polar solvents in comparison to their organic analogues.

Keywords: arene complexes; cyclopentadienyliron; organoiron polymers; polyether and thioethers; sulfur- and sulfone-based polymers

Introduction

There has been a tremendous interest in the development of sulfur-containing polymers due to their wide spread industrial applications as electrical components and in the manufacturing of car engine parts.[1] Sulfone-based polymers such as poly(aromatic ether sulfone)s are known as engineering thermoplastics.[2-5] This class of macromolecules is known for its excellent thermal stability and mechanical properties. These polymers also have good hydrolytic stability, outstanding toughness, low smoke emission, and electrical insulating properties.[2, 6] Introduction of pendent groups to the sulfone-based polymers could lead to improved transport properties.[6] There are a number of traditional organic routes to the synthesis of sulfone-containing monomers and polymers.[7] An alternative method is using arenes coordinated to the cyclopentadienyliron

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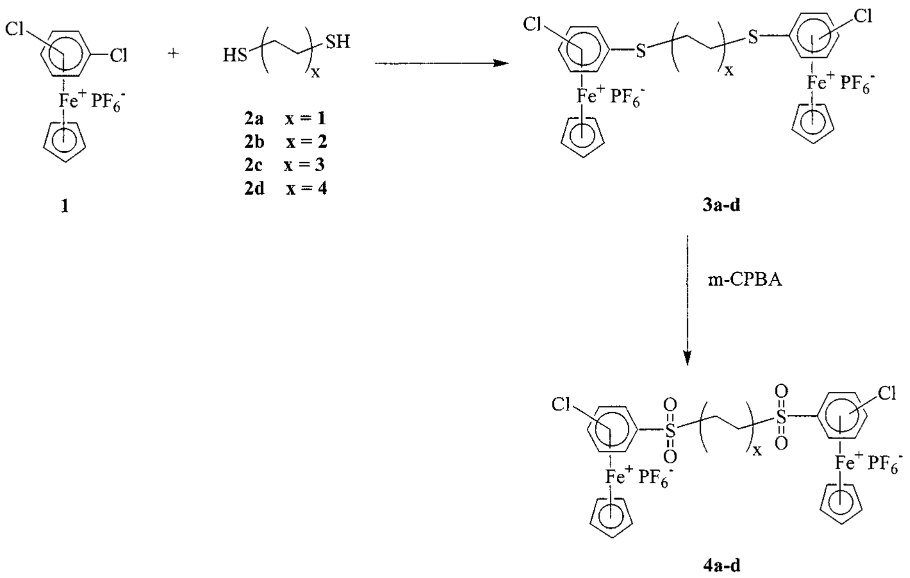
moiety.[8] Complexation of chloroarenes to cyclopentadienyliron cations increases the reactivity of the arene towards nucleophiles, therefore decreasing reaction times and reducing extremely harsh conditions. For example, reaction of a dichlorobenzene with ferrocene in the presence of a Lewis acid produces the organoiron complex, which can then be reacted with various thiols or thiophenols to produce the corresponding sulfide-functionalized complexes.[9-11] Oxidation of the sulfide groups produces sulfones, which are excellent activating groups for nucleophilic aromatic substitution reactions. Polymerization of the sulfone-substituted chloroarenes can be achieved directly, or following demetallation of the organoiron complexes.

Results and Discussion

Over the past decade, we have been interested in the development of synthetic routes to organometallic as well as organic monomers and polymers using cationic cyclopentadienyliron ($CpFe^+$) and pentamethylcyclopentadienylruthenium (Cp^*Ru^+) complexes.[12-18] In this study, two strategies were developed for the preparation of sulfone-based polymers. The first strategy involved the synthesis of diiron sulfide complexes via metal-mediated aromatic nucleophilic substitution reactions. Oxidation of these complexes using m-CPBA allowed for the isolation of their corresponding sulfones. The complexes were then demetallated using pyrolysis to give the organic sulfones. These sulfone monomers were then polymerized to produce the sulfone-based polymers. The second strategy entailed the direct polymerization of the dichlorobenzene with ethane-, butane-, hexane-, and octane-dithiol. The resulting polymeric sulfides were then oxidized to give the organoiron sulfone-based polymers.

The bimetallic aliphatic sulfide complexes (**3a-d**) were prepared via the nucleophilic aromatic substitution reactions of (dichlorobenzene)$CpFe^+$ complexes with dithiols in DMF in the presence of K_2CO_3 as shown in Scheme 1. Oxidation of the diiron sulfide complex **3a-d** gave rise to the sulfone complex **4a-d** in good yields.



Scheme 1

The following ^{1}H-NMR spectra (Figure 1) are of the bimetallic sulfide **3b** and bimetallic sulfone complex **4b**. The strong electron-withdrawing capabilities of the sulfones caused a downfield shift of the cyclopentadienyl and complexed aromatic resonances in the NMR spectra compared to the corresponding sulfide complexes.

Pyrolysis of the organometallic monomers **4a-d** resulted in the isolation of their corresponding organic analogues **5a-d** (Scheme 2). These monomers were then characterized by ^{1}H- and ^{13}C-NMR as well as IR spectroscopy. Figure 2 shows the ^{1}H-NMR of monomer **5b**. The cyclopentadienyliron peak is no longer there in the spectrum and the formerly complexed aromatic protons are shifted downfield in the spectrum of the organic sulfone monomer. The two peaks at approximately 3.0 ppm and 2.8 ppm are the two CH_2 groups, with the peak resonating more downfield being the one bonded α to the sulfone and the other peak, being the methyl group β to the sulfone group.

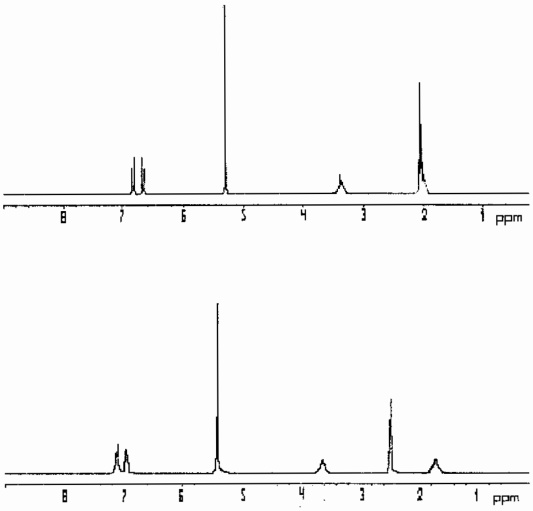


Figure 1. ^{1}H-NMR spectra of sulfide, 3b (top, acetone-d_6) and sulfone, 4b (bottom, DMSO-d_6)

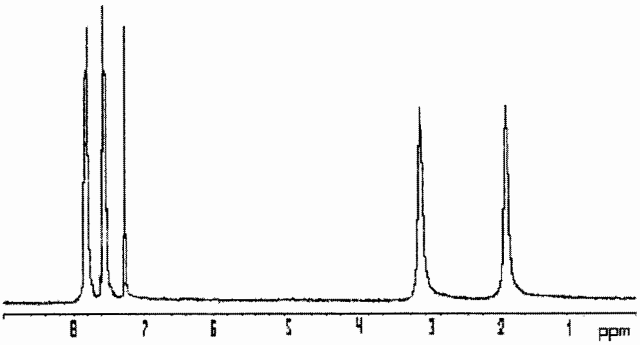
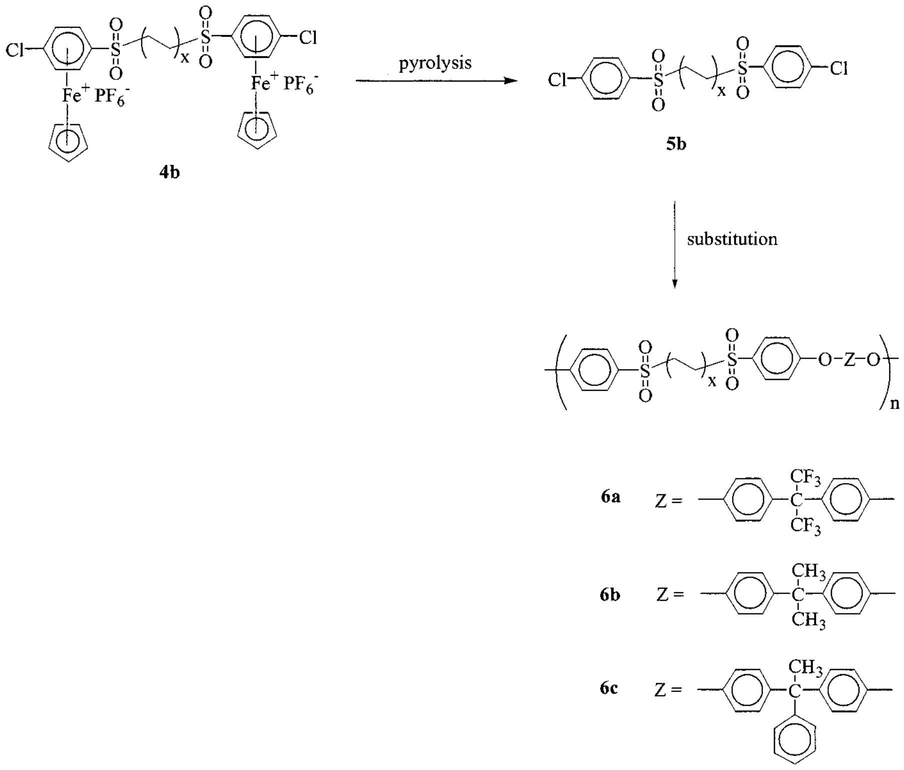


Figure 2. ^{1}H- NMR of demetallated sulfone monomer 5b ($CDCl_3$)

Demetallation of **4b,** as an example, was achieved by first grinding it into a fine powder and placing it in the pyrolytic chamber where it was heated to 250 °C under reduced pressure for 2 h. After purification through a silica column, the solution was then concentrated and precipitated into hexane affording the sulfone monomer **5b**. The synthesis of **6a-c** was performed in DMF and K_2CO_3 under a nitrogen atmosphere, where the temperature was maintained between 155-165 °C for 16 h. The solution was then precipitated in 10% HCl filtered and washed with water.

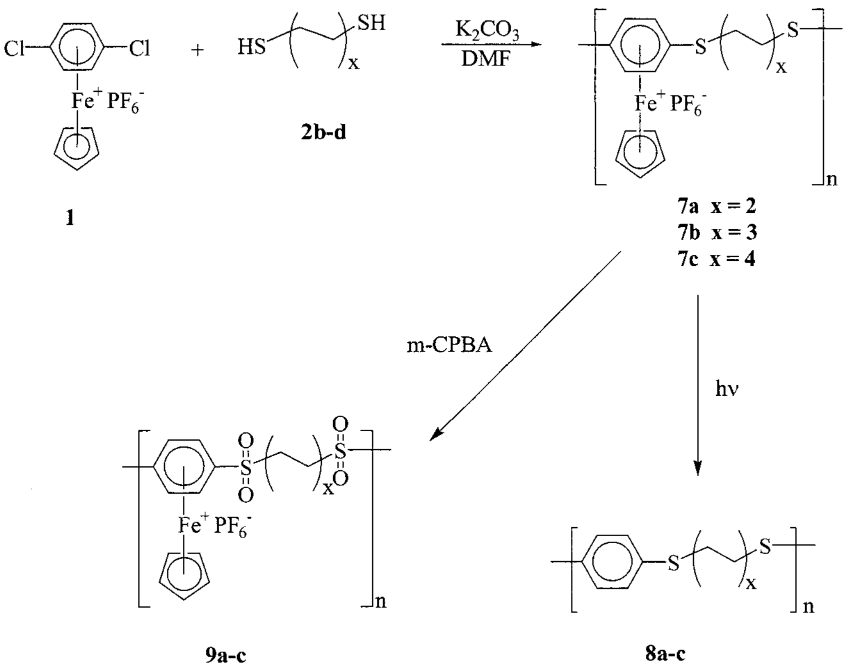


Scheme 2

The successful polymerization of the monomer **5b** with bisphenol A was determined by the upfield shift of the resonances of the protons that are adjacent to the chloro groups. The protons adjacent or α to the sulfone resonate at 2.94 ppm, the β protons appeared at 1.59 ppm, and the methyl groups on the bisphenol A appeared at 1.70 ppm. The aromatic protons appeared at 6.84-6.97 ppm (m, 8H), 7.16 (d, 4H, J = 8.2 Hz), 7.67 (d, 4H, *J* = *8.2* Hz). The APT (attached proton test) ^{13}C-NMR is further proof that the polymerization occurred, as shown by the quaternary ArC peaks appearing at 132.02, 147.26, 152.61, and 162.62 ppm. The ArCH peaks appear at 117.61, 119.86, 128.47, and 129.63 ppm. The α CH_2 peak appears at 55.58 ppm, the β CH_2 appears at 21.58 ppm; the methyl group resonates at 30.9 ppm; finally the quaternary carbon appears at 42.38 ppm.

Infrared analysis was also performed to confirm the presence of the sulfone and the ether groups. The sulfone group should show stretching in the range of 1 160-1 120 cm^{-1} and the C-O-C should stretch at around 1 230-1 250 cm^{-1}. The IR shows that the sulfone appears at 1 145 cm^{-1} and the ether at 1 245 cm^{-1}. Gel permeation chromatography was used to determine that the M_w was 9 100 with a polydispersity of 2.03, indicating that the degree of polymerization was 16. TGA showed that the onset and endset of decomposition for this polymer occur at 421 and 482 °C, respectively, while DSC analysis showed that the T_g was 142 °C.

The influence of aliphatic chains in the backbones of polythioethers was analysed by reacting complex **1** with **2** as shown in Scheme 3.[13] Polymers **7a-c** were isolated in 88-91% yield as beige coloured precipitates.



Scheme 3

Polymer **7a** displayed very low solubility in various polar solvents and precipitated from DMF during the polymerization process. It was observed that with the increase in the size of the aliphatic chains in the polymer backbones, there was a corresponding increase in polymer solubility. As an example, the polymer that incorporated the octamethylene groups in the backbone was formed more rapidly, was more soluble, and had a higher molecular weight than polymers with shorter aliphatic chains in the polymer backbone. As well, the 1,6-hexanedithiol (**7b**) and 1,8-octanedithiol (**7c**) polymers were much more stable at high temperatures during the polymerization reactions, which was most likely due to their higher solubilities in the reaction medium.

Figure 3 shows the ^{1}H NMR spectrum of polymer **7b**. There are three resonances corresponding to the methylene peaks in the polymer backbone at 1.42, 1.71, and 3.26 ppm. The cyclopentadienyl protons appear as a singlet at 5.01 ppm, while the complexed aromatic protons appear as a singlet at 6.41 ppm. After demetallation, the aromatic peak in **8b** shifted downfield and appeared as a singlet at 7.20 ppm.

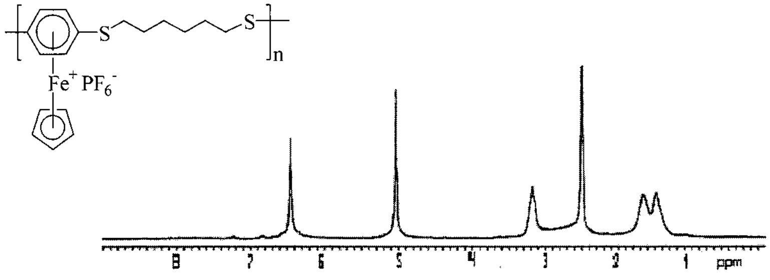


Figure 3. ^{1}H NMR spectrum of polymer 7b in DMSO-d_6

When oxidation of **7a** was performed, the ^{1}H-NMR of both **7a** and **9a** were compared to confirm that the oxidation was successful. For the Cp peak, it shifted downfield from 5.01 ppm in the sulfide polymer to 5.45 ppm in the sulfone polymer. The aromatic peaks appear at 6.46 ppm and 7.33 ppm for the sulfide and sulfone polymers, respectively. The α CH_2 peak resonates at 3.45 ppm in the sulfide polymer and at 3.71 ppm in the sulfone polymer. Lastly, the β CH_2 group resonates at 1.70 ppm and at 1.75 ppm for the sulfide and sulfone polymers, respectively.

The solubilities of polymer **8a-c** were also highly dependent on the number of methylene units in their backbones. It was found that polymers **8b** and **8c** were soluble in organic solvents such as THF and chloroform due to the flexible six-and eight-carbon aliphatic chains in their backbones. These polymers were determined to have weight average molecular weights of 13 500 and 21 400, respectively. Due to the short aliphatic spacer in polymer **8a**, this polymer was found to be only partially soluble. The TGA thermograms of **8a-c** were as follows: for **8a** the start of decomposition occurred at 344 °C with the end of decomposition at 400 °C; for **8b** the onset was at 372 °C and the endset at 428 °C; finally for **8c** the onset was at 327 °C and the endset occurred at 447 °C. The T_gs of **8a-c** was 37, 34, and 33 °C, respectively.

The cyclic voltammogram of polymer **7c** is shown in Figure 4. At a scan rate of 5 V/s, this CV shows the two sequential one-electron reduction steps of the iron centres pendent to the polymer backbone. It was found that at low scan rates, the second reduction step was irreversible. The $E_{1/2}$ values corresponding to formation of the neutral nineteen-electron, and anionic twenty-electron iron species occurring at –1.07 and –1.77 V, respectively.

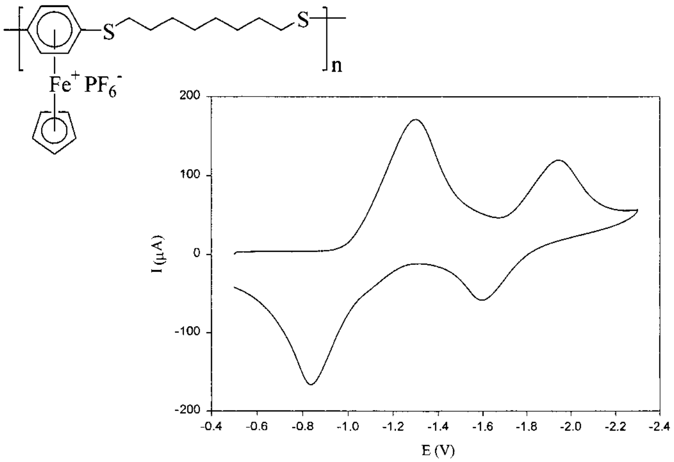


Figure 4. Cyclic voltammogram of 7c obtained at a scan rate of 5 V/s

Conclusion

The synthesis of sulfone-based polymers can be successfully conducted via metal-mediated methodology. Two different routes were followed in order to achieve this goal. The first route involved the synthesis of disulfide monomers, that were oxidized, followed by pyrolytic demetallation to give the sulfone-based monomers, which were then polymerized. The second route involved the direct polymerization of a dichlorobenzene complex with a number of aliphatic dithiols. Oxidation of these polymers with m-CPBA produced the corresponding organometallic polysulfones. The length of the aliphatic chains in the backbone showed a direct correlation of the solubilities of these polymers. While the hexane and octane spacers in the polymers enhanced the solubilities, the incorporation of butane spacers gave rise to partially insoluble polymers.

Acknowledgements

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