*Macromol. Symp.* **2004**, *209,* 185-193

# Synthesis of Iron-Containing Polymers with Azo Dyes in the Backbones or Side Chains

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**Summary:** The synthesis of cationic cyclopentadienyliron-containing polymers with pendent azobenzene chromophores was accomplished via metal-mediated nucleophilic aromatic substitution reactions. All of the desired polymers were isolated as vibrantly coloured materials and displayed excellent solubility in polar aprotic solvents. Cationic and neutral cyclopentadienyliron polymers incorporating azo dyes in the backbone were also prepared. Reactions of azo dyes with dichlorobenzene complexes allowed for the isolation of cationic cyclopentdienyliron ($CpFe^+$) complexes with azo dye chromophores. These complexes were then reacted with 1,1'-ferrocenedicarbonyl chloride to produce the trimetallic monomers with terminal chloro groups. These monomers contained two pendent $CpFe^+$ cations and a neutral iron moiety in the backbone. Nucleophilic substitution reactions of these monomers with oxygen and sulfur containing dinucleophiles gave rise to a new class of polymeric materials. The pendent $CpFe^+$ moieties could also be cleaved from the polymer backbones using photolysis to afford novel ferrocene based polymers. The UV-vis spectra of the organoiron monomers and polymers display similar wavelength maxima however incorporating azobenzene chromophores with electron-withdrawing substituent into the polymer chains resulted in bathochromic shifts of the $\lambda_{max}$ values.

**Keywords:** arene complexes; azo dyes; ferrocene-based polymers; iron-containing polymers; nucleophilic substitution reactions; polyethers; polythioethers

DOI: 10.1002/masy.200450513

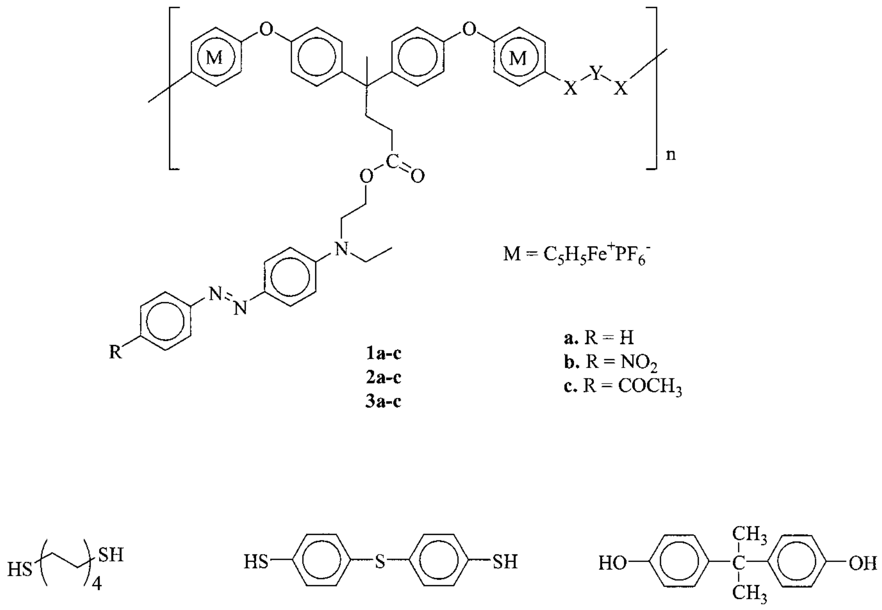
## Introduction

Interest in the field of organometallic polymers stems from the wide spread applications that these materials find, and the synthesis of organoiron polymers is a major contributor in these studies.[1-7] The first reports of ferrocene-based polymers in 1955 initiated a number of research groups to develop various routes to prepare organometallic polymers.[8] The past twenty years have seen a significant increase in the synthesis of these polymers in light of their potential applications as electrocatalysts, modified electrodes, chemical sensors and photoactive molecular devices.[5-7, 9-11] Our group has focused on the use of cyclopentadienyliron coordinated chloroarenes in the synthesis of cationic iron-based polymers.[12-16] The mild reaction conditions and the use of various nucleophiles has allowed for the synthesis of many functionalized monomeric and polymeric ethers, thioethers, amines and imines.[12-15] It has been documented that the incorporation of azo dyes into the backbones or the side chains of organic and organometallic macromolecules generates interesting properties such as liquid crystallinity and non-linear-optical activity. The properties that this class of polymers possess make them potential candidates for a wide variety of applications such as reversible optical storage systems, electrooptic modulators, and photorefractive switches.[17-27] Manners and coworkers have prepared liquid crystalline poly(ferrocenyl silanes) containing azo dyes in their side chains.[28] These polymers were prepared via thermal ring opening polymerization of a methyl silyl-bridged [1]ferrocenophane which was subsequently functionalized with azobenzene moieties through a platinum-catalyzed hydrosilylation reaction.[28] This article will focus on the synthesis of cationic iron-coordinated polyaromatic ethers and thioethers functionalized with azo dyes in their side chains as well as the incorporation of azo dyes directly into the polymeric backbones.

## Results and Discussion

### *Polymers with Pendent Azobenzene Moieties*

Recently, our group has been focusing on the preparation of organometallic and organic polyethers, thioethers and amines using metal-mediated nucleophilic aromatic substitution reactions. Condensation reactions of bimetallic organoiron complexes containing terminal carboxylic acid groups with a phenolic substituent on an azo dye in the presence of dicyclohexylcarbodiimide (DCC) and N,N-dimethylamino pyridine (DMAP), allowed for the isolation of brightly coloured azobenzene substituted diiron complexes. These complexes were then polymerized via nucleophilic aromatic substitution reactions with S- and O-based nucleophiles to yield polyaromatic ethers and ether/thioethers with pendent azobenzene chromophores **1a-c** to **3a-c** (Scheme 1). The functionalized polymers were isolated in good yields as bright orange-red solids. These materials displayed good solubility in polar organic solvents such as acetonitrile, DMF and DMSO. The electron-withdrawing properties of the R groups on the azobenzene moieties gave rise to bathochromic shifts of the $\lambda_{max}$ values. For example, the $\lambda_{max}$ of polymers **1a-c** were 417, 452 and 489 nm, respectively.



**1a-c**
**2a-c**
**3a-c**

$M = C_5H_5Fe^+PF_6^-$

**a.** R = H
**b.** $R = NO_2$
**c.** $R = COCH_3$

**1** **2** **3**

**Scheme 1**

Characterizations of the monomeric and polymeric materials were conducted using spectroscopic and analytical techniques. Figure 1 shows the $^1H$ and $^{13}C$ NMR spectra of polymer **2a**. In the $^1H$ NMR spectrum, the uncomplexed aromatic protons appear as four doublets and two sets of multiplets and resonate between 6.85 and 7.73 ppm, while the complexed aromatic protons appear as a singlet at 6.26 ppm. The cyclopentadienyl protons show as an intense singlet at 5.14 ppm and the remaining methyl and methylene protons appear between 4.22 and 1.12 ppm. The $^{13}$C-NMR spectrum was run as an attached proton test (APT). The two methyl carbons peaks resonate at 12.32 and 27.30 ppm and the methylene carbons resonate between 30.22 and 61.95 ppm. The cyclopentadienyl carbons appear as a large peak at 79.00 ppm, and the complexed aromatic carbons can be seen at 76.52 and 85.43 ppm, however, the hydrogen-attached aromatic carbons resonate between 111.79 and 135.16 ppm.

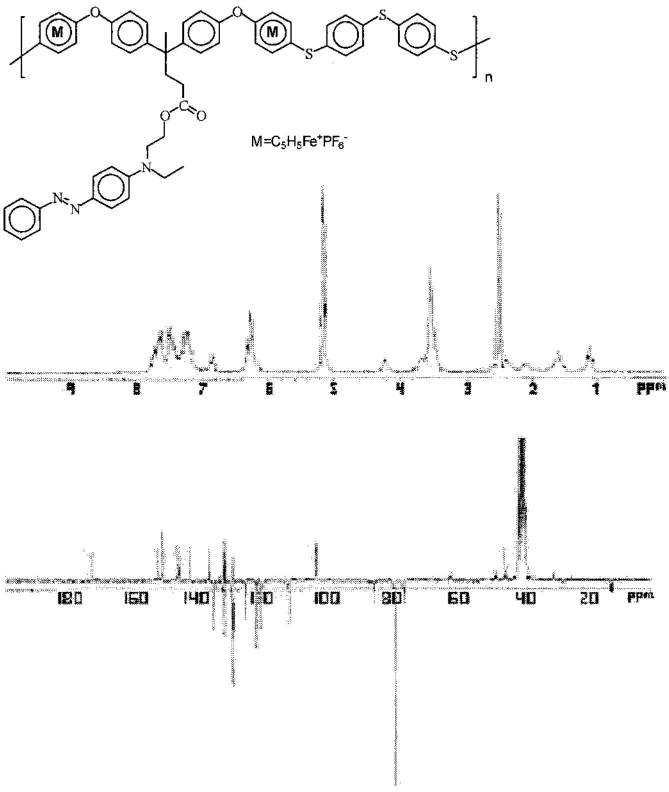


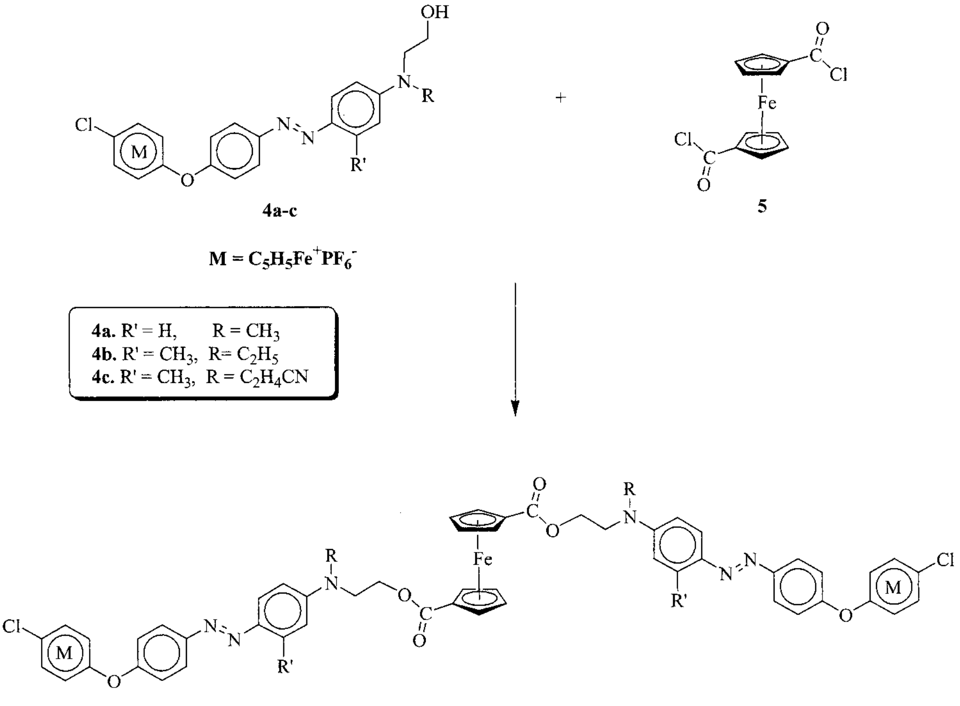
Figure 1. $^{1}$H-NMR and $^{13}$C-NMR spectra of organoiron polymer **2a**.

The molecular weights of the polymers were determined using gel permeation chromatography (GPC). Photolytic demetallation of the organoiron polymers was performed prior to molecular weight deremination in order to avoid interactions of the metal moieties with the GPC columns. The weight average molecular weights of the metallated polymers were estimated to be in the range of 13,400 to 18,200 with polydispersities between 1.2 to 2.0.

Thermal properties of both the metallated and demetallated polymers were analyzed using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The thermograms of the metallated and demetallated polymers containing azobenzene groups in their side chains showed multiple weight losses. TGA analysis of the metallated polymers showed that the weight losses between 220-240 °C correspond to the cleavage of the cyclopentadienyliron moieties. The decomposition of the azo group was in the range of 250-290 °C, however the degradation of the polymer backbones was in the range of 420-460 °C. The DSC analysis showed that the glass transition temperatures ($T_g$'s) of the metallated polymers occurred between 167 and 173 °C, whereas the demetallated polymers exhibited glass transition temperatures between 111 and 123 °C. It was observed that the $T_g$'s of the metallated polymers were higher than the $T_g$'s of the demetallated ones. This observation was attributed to the presence of the bulky cationic cyclopentadienyliron moieties. Furthermore, the organoiron polymers with aromatic spacers possessed higher $T_g$'s than the polymers containing aliphatic spacers; this trend was also observed in the demetallated polymers.

### *Azobenzene Moieties in the Polymer Backbone*

Synthesis of the monomers occurred through nucleophillic aromatic substitution of the *p*-dichlorobenzene cyclopentadienyliron complex with azo dyes in the presence of $K_2CO_3$ and DMF. These vibrantly coloured azobenzene complexes were isolated in good yields, and the azobenzene complexes were subsequently reacted with 1,1' ferrocenedicarbonyl chloride in dichloromethane (Scheme 2) to form triiron monomers with terminal cationic cyclopentadienyliron moieties and an inner disubstituted bis(cyclopentadienyliron) group (**6a-c**).



**4a-c**

**5**

**M = $C_5H_5Fe^+PF_6^-$**

**4a.** R' = H, R = $CH_3$
**4b.** R' = $CH_3$, R= $C_2H_5$
**4c.** R' = $CH_3$, R = $C_2H_4CN$

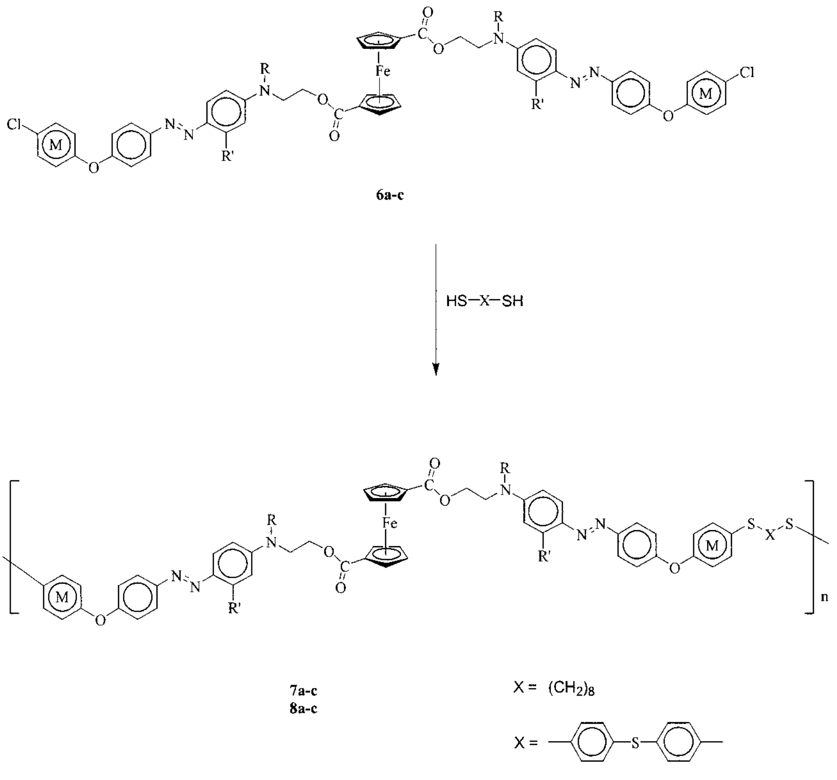
**6a-c**

**Scheme 2**

Characterization of all complexes was preformed using $^1$H-NMR, $^{13}$C-NMR, and IR spectroscopy. For example, the $^1$H-NMR spectrum of monomer **6a** shows that the ferrocenyl protons appear at 4.4 and 4.8 ppm and the cyclopentadienyl protons of the cationic complex resonate as a singlet at 5.41 ppm. The complexed aromatic protons shift upfield between 6.6 and 6.9 ppm, while the uncomplexed aromatic protons appear between 7.5 and 8.0 ppm. Polymerization of the azobenzene functionalized complexes, accomplished with oxygen and sulfur based nucleophiles, allowed for the isolation of novel organoiron polymers containing azobenzene chromophores in the backbones (Scheme 2). The polymerization was carried out at 50 °C for 7 h, and the resulting brightly coloured polymers displayed good solubility in polar organic solvents.

Cleavage of the cationic iron moieties was performed via photolytic demetallation reactions that resulted in the isolation of the ferrocene-based polymers functionalized with azobenzene dyes. Molecular weight determination of these polymers was performed using gel permeation chromatography. The weight average molecular weights of the ferrocene polymers were in the range of 8 000-12 000 while the molecular weights of the cationic-neutral organoiron polymers were estimated using these values to be in range of 11 000-16 000.

Thermal gravimetric analysis showed that the cleavage of the cationic cyclopentadienyliron moieties occurred between 230 and 249 °C, while the polymeric backbone degraded between 424 and 465 °C.



Scheme 3

UV-vis analysis illustrated that the monomeric and polymeric materials display similar wavelength maxima, which was attributed to the π-π* and n- π* transitions of the incorporated azo dyes. The UV-vis studies were carried out in DMF and DMF/HCl solutions to examine the halochromisim of these polymers. Figure 2 shows the visible spectra of polymer **7b**, which displays a $\lambda_{max}$ at 433 nm in DMF solution. Addition of 10% HCl to the polymer solution produced a bathochromic shift ($\lambda_{max}$ at 525 nm). This bathocrhomic shift has been attributed to the formation of the azonium ion.

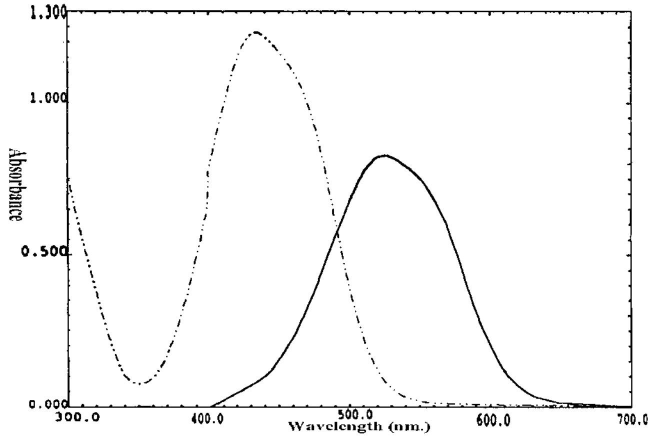


Figure 2. Visible spectra of polymer **7b** in DMF and DMF/HCl solution.

## Conclusions

Organoiron macromolecules containing azo dyes in the backbones or pendant to the side chains were synthesized under very mild reaction conditions using a metal-mediated methodology. Thermal analysis of the metallated polymers showed two weight losses corresponding to the cleavage of the cationic moieties and the degradation of the polymer backbones. Design of trimetallic complexes with terminal $CpFe^+$ and inner bis(cyclopentadienyliron) moieties was accomplished and their polymerization afforded coloured macromolecules containing neutral and cationic organoiron centers. It is also important to note that photolytic demetallation of these polymeric materials resulted in the cleavege of $CpFe^+$ and therefore the isolation of novel ferrocene-based polymers with azo dyes in the backbone.

## Acknowledgements

Financial support provided by the Natural Sciences and Research Council of Canada (NSERC) and Manitoba Hydro are gratefully acknowledged. R.M.O. would also like to thank the Department of Chemistry, University of Manitoba.

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