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# Articles

## Design of Polyaromatic Ethers Using Cyclopentadienyliron Complexes

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ABSTRACT: Nucleophilic aromatic substitution of cyclopentadienyliron complexes of chloroarenes with oxygen-containing nucleophiles led to the isolation of a number of aromatic ether complexes (**2**, **5a**−**e**) in very good yields. Reactions of these complexes with 1-naphthol, followed by removal of the cyclopentadienyliron moieties produced aromatic ether compounds with terminal naphthoxy groups (**3**, **7a**−**e**). Polymerization of these monomers in the presence of ferric chloride gave the poly(aryl ethers) **4** and **8a**−**e**. These materials were obtained with weight-average molecular weights up to 139 900 g/mol. Thermogravimetric analysis of the poly(aryl ethers) showed that these materials displayed no significant weight loss until 458−575 °C. The glass transition temperatures for these polymers ranged from 147 to 226 °C, as measured by differential scanning calorimetry.

## Introduction

Over the past few decades, there has been tremendous interest in the production of thermally stable polymers as replacements for metals and ceramics in the aerospace and automotive industries.[1] Poly(aryl ethers) are a class of thermally stable polymers that are able to withstand temperatures in excess of 200 °C and exhibit excellent resistance to acids, bases, and organic solvents.[1c,d] The limited solubility of poly(aryl ethers) in organic solvents at room temperature, and their high melting points decrease their processability.[2] It has been found, however, that the introduction of bulky groups into the polymer chains enhances the solubility of these materials.[3] Wang and co-workers have also demonstrated that the presence of naphthalene units in the backbone of polyethers reduces their crystallinity and increases their glass transition temperatures ($T_g$).[4]

There are a limited number of methodological approaches to the synthesis of poly(aryl ethers).[1b] Electrophilic aromatic sulfonylation or acylation reactions, metal-catalyzed coupling reactions, and nucleophilic aromatic substitution ($S_NAr$) are the most common. Of these methodologies, the only synthetic route that allows for the direct incorporation of an etheric bond into the backbone of a polymer chain is nucleophilic aromatic substitution.[3−6] The Ullmann ether synthesis is a nucleophilic substitution reaction that uses a copper activator to synthesize aryl ether bonds.[7] The drawbacks to this reaction include the harsh reaction conditions, low yields, and side products. Electrophilic aromatic substitution of diphenyl ethers allows for the synthesis of poly(aryl ethers) that incorporate sulfonyl or carbonyl groups into the backbone of polymeric chains through a Friedel−Crafts mechanism.[5a,8] The disadvantage to this methodology is the number of substitution patterns that can take place. Another route to the synthesis of poly(aryl ethers) is through coupling reactions catalyzed by metal salts.[9] The Scholl reaction is a coupling reaction that can be used to prepare poly(aryl ethers) by reacting monomers that contain aryl ether linkages. Carbon−carbon bonds are formed between terminal phenyl or naphthyl groups in the presence of a Lewis acid via a radical-cation mechanism.[10]

Nucleophilic aromatic substitution of haloarenes complexed to transition metal moieties with oxygen-, sulfur-, and nitrogen-containing nucleophiles allows for the synthesis of a wide variety of aryl ethers, thioethers, and amines.[11] These metal-mediated reactions proceed under very mild conditions and allow for the incorporation of a number of different functional groups. Pearson and co-workers were successful in the preparation of monomers with terminal hydroxyl and carboxylic acid groups using cyclopentadienyliron-coordinated arenes.[12] Coupling of these two functional groups led to the preparation of isoregic poly(aromatic ether−esters). Percec and Okita synthesized a number of monomeric aromatic ether complexes with pendent chromium tricarbonyl moieties.[13]

We have been successful in the stepwise design of oligomeric aryl ethers with up to 35 cyclopentadienyliron moieties pendent to the aromatic backbone.[11h] A one-step preparation of polyaromatic ethers, sulfides, and amines with pendent cyclopentadienyliron cations has also been reported.[14] We have also demonstrated that norbornenes with etheric side chains could be prepared in good yields using cyclopentadienyliron as an activating group.[15] Ring-opening metathesis polymerization of these bicyclic compounds led to the isolation of substituted polynorbornenes. In this article, the design of aromatic ether compounds with terminal naphthoxy groups using cyclopentadienyliron complexes and their subsequent polymerization is described.

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## Experimental Section

$^1$H and $^{13}$C NMR spectra were recorded at 200 and 50 MHz, respectively, on a Gemini 200 NMR spectrometer, with chemical shifts referenced to solvent residues and coupling constants calculated in hertz. Molecular weight measurements were accomplished using gel permeation chromatography, with a BL-gel mixed D column (Phenomenex) equipped with a CH-30 column heater (Eppendorf) and a PL-DCU (Polymer Laboratories) data station. Molecular weights were calculated versus polystyrene standards with $CHCl_3$ as the eluent, at a flow rate of 0.7 mL/min using a Gilson model 302 pump and a model 131 refractive index detector. Thermogravimetric analysis (TGA) was carried out using a Mettler-Toledo TGA/SDTA851$^e$ at heating rates of 30 °C/min. Glass transition temperatures were determined by differential scanning calorimetry (DSC), using a Mettler-Toledo DSC 25 with a TC15 controller at heating rates of 20 °C/min. $T_g$ values are reported for the second heating as the temperature at the midpoint of the transition. All of the reagents used are commercially available and were used without further purification, with the exception of nitrobenzene, which was dried over calcium hydride and vacuum distilled prior to use.

**A. Monomers. a. Preparation of Complex 2.** For the preparation of complexed monomer **2**, $\eta^6$-1,4-dichlorobenzene-$\eta^5$-cyclopentadienyliron(II) hexafluorophosphate (413 mg, 1 mmol), 1-naphthol (360 mg, 2.5 mmol), and potassium carbonate (346 mg, 2.5 mmol) were stirred under nitrogen in 10 mL of DMF at room temperature for 16 h. The reaction mixture was poured into a 10% (v/v) HCl solution, resulting in the formation of a yellow precipitate. A concentrated solution of ammonium hexafluorophosphate was added, and the precipitate was collected on sintered glass, washed liberally with water, and finally washed with two aliquots of ether.

**2**: Yield: 91%. $\delta_H$ (acetone-$d_6$): 5.42 (5H, s, CpH); 6.52 (4H, s, complexed ArH); 7.46 (2H, d, $J = 7.6$, ArH); 7.56−7.66 (6H, m, ArH); 7.94 (2H, d, $J = 8.3$, ArH); 8.06−8.10 (4H, m, ArH). $\delta_C$ (acetone-$d_6$): 76.54 (complexed ArC); 79.32 (CpC); 116.72, 121.74 (ArC); 126.77 (q, complexed ArC); 126.83, 127.03, 127.98, 128.12, 129.19 (ArC); 132.07, 136.10, 150.71 (q, ArC).

**b. Preparation of Complexes 5a−e.** In a 50 mL round-bottom flask, $\eta^6$-1,4-dichlorobenzene-$\eta^5$-cyclopentadienyliron(II) hexafluorophosphate (413 mg, 1.0 mmol) was combined with a biphenol nucleophile (0.5 mmol) and potassium carbonate (346 mg, 2.5 mmol) in 10 mL of DMF. The mixture was allowed to stir under a nitrogen atmosphere at room temperature for 16 h. The solutions were then subjected to the same workup procedure as **2** to give complexes **5a−e**.

**5a**: Yield: 88%. $\delta_H$ (acetone-$d_6$): 5.38 (10H, s, CpH); 6.56 (4H, d, $J = 7.0$, complexed ArH); 6.78 (4H, d, $J = 7.0$, complexed ArH); 7.59 (4H, s, ArH). $\delta_C$ (acetone-$d_6$): 77.16 (complexed ArC); 80.57 (CpC); 87.86 (complexed ArC); 105.06 (q, complexed ArC); 124.43 (ArC); 134.03 (q, complexed ArC); 151.96 (q, ArC).

**5b**: Yield: 86%. $\delta_H$ (acetone-$d_6$): 2.15 (3H, s, $CH_3$); 5.38 (10H, s, CpH); 6.56 (4H, d, $J = 6.7$, complexed ArH); 6.80 (4H, d, $J = 6.7$, complexed ArH); 7.33 (2H, d, $J = 7.7$, ArH); 7.53 (1H, t, $J = 5.0$, ArH). $\delta_C$ (acetone-$d_6$): 9.89 ($CH_3$); 77.33 (complexed ArC); 80.48 (CpC); 87.74 (complexed ArC); 104.93 (q, complexed ArC); 119.26 (ArC); 123.62 (q, ArC); 130.05 (ArC), 133.24 (q, complexed ArC); 153.85 (q, ArC).

**5c**: Yield: 91%. $\delta_H$ (acetone-$d_6$): 0.85 (3H, t, $J = 6.3$, $CH_3$); 1.29 (6H, br. s, $CH_2$); 1.64 (2H, m, $CH_2$); 2.67 (2H, t, $J = 7.7$, $CH_2$); 5.35 (5H, s, CpH); 5.37 (5H, s, CpH); 6.60 (4H, m, complexed ArH); 6.81 (4H, m, complexed ArH); 7.32 (2H, m, ArH); 7.63 (1H, m, ArH). $\delta_C$ (acetone-$d_6$): 14.21 ($CH_3$); 23.03, 29.50, 29.88, 30.44, 32.09 ($CH_2$); 77.34, 77.63 (complexed ArC); 80.38, 80.45 (CpC); 87.65, 87.79 (complexed ArC); 104.93, 105.13 (q, complexed ArC); 113.35, 119.40 (ArC); 133.30 (q, complexed ArC); 133.42 (q, ArC); 134.03 (ArC); 153.11, 153.39 (q, ArC).

**5d**: Yield: 92%. IR: 1770 cm$^{-1}$ (CO). $\delta_H$ (acetone-$d_6$): 5.26 (10H, s, CpH); 6.25 (4H, d, $J = 6.3$, complexed ArH); 6.80 (4H, d, $J = 6.9$, complexed ArH); 7.41 (4H, d, $J = 8.9$, ArH); 7.61 (4H, d, $J = 8.8$, ArH); 7.91−8.02 (4H, m, ArH). $\delta_C$ (acetone-$d_6$): 77.30 (complexed ArC); 80.45 (CpC); 87.71 (complexed ArC); 90.96 (q); 104.89 (q, complexed ArC); 121.74 (ArC); 125.64 (q, complexed ArC); 126.56, 130.45, 131.03 (ArC); 133.23 (q, ArC); 136.00 (ArC); 139.94, 152.11, 154.06 (q, ArC); 169.41 (CO).

**5e**: Yield: 93%. IR: 1103, 1266 cm$^{-1}$ ($SO_2$). $\delta_H$ (acetone-$d_6$): 5.42 (10H, s, CpH); 6.68 (4H, d, $J = 6.9$, complexed ArH); 6.87 (4H, d, $J = 6.8$, complexed ArH); 7.56 (4H, d, $J = 8.9$, ArH); 8.15 (4H, d, $J = 8.8$, ArH). $\delta_C$ (acetone-$d_6$): 78.81 (complexed ArC); 80.56 (CpC); 87.69 (complexed ArC); 105.23 (q, complexed ArC); 121.46, 131.21 (ArC); 131.59 (q, complexed ArC); 139.22, 158.42 (q, ArC).

**c. Preparation of Complexes 6a−e.** Complexes **5a−e** (1.0 mmol), 1-naphthol (360 mg, 2.5 mmol), and potassium carbonate (346 mg, 2.5 mmol) were stirred in 10 mL of DMF under a nitrogen atmosphere at room temperature for 16 h. Using the same workup procedure as for complex **2** allowed for the isolation of metalated monomers **6a−e**.

**6a**: Yield: 90%. $\delta_H$ (DMSO-$d_6$): 5.37 (10H, s, CpH); 6.36 (8H, s, complexed ArH); 7.41−7.49 (6H, m, ArH); 7.58−7.66 (6H, m, ArH); 7.93−7.81 (6H, m, ArH). $\delta_C$ (DMSO-$d_6$): 75.08, 75.47 (complexed ArC); 78.18 (CpC); 116.08, 120.93, 122.96 (ArC); 125.50 (q, complexed ArC); 126.18, 126.30, 127.38, 127.45, 128.47 (ArC); 130.35 (q, complexed ArC); 130.57, 134.85, 149.56, 151.08 (q, ArC).

**6b**: Yield: 93%. $\delta_H$ (acetone-$d_6$): 2.24 (3H, s, $CH_3$); 5.36 (10H, s, CpH); 6.47 (8H, s, complexed ArH); 7.25 (2H, d, $J = 7.8$, ArH); 7.44−7.66 (9H, m, ArH); 7.93 (2H, d, $J = 8.0$, ArH); 8.05−8.09 (4H, m, ArH). $\delta_C$ (acetone-$d_6$): 10.08 ($CH_3$); 76.59 (complexed ArC); 79.29 (CpC); 116.64, 118.42, 121.76 (ArC); 123.36 (q, complexed ArC); 126.75 (q, ArC); 126.84, 126.99, 127.97, 128.10, 129.76 (ArC); 131.42, 131.99 (q, ArC); 136.08 (q, complexed ArC); 150.70, 154.70 (q, ArC).

**6c**: Yield: 76%. $\delta_H$ (acetone-$d_6$): 0.85 (3H, br. s, $CH_3$); 1.31 (6H, br. s, $CH_2$); 1.65 (2H, br. s., $CH_2$); 2.67 (2H, br. s, $CH_2$); 5.32 (5H, s, CpH); 5.35 (5H, s, CpH); 6.45 (8H, br.s., complexed ArH); 7.26−7.59 (11H, m, ArH); 7.94−8.07 (6H, m, ArH). $\delta_C$ (acetone-$d_6$): 14.31 ($CH_3$); 23.12, 29.67, 30.09, 30.70, 32.25 ($CH_2$); 76.42, 76.55, 76.65, 76.98 (complexed ArC); 79.21, 79.31 (CpC); 113.16, 116.77, 119.01, 121.76 (ArC); 126.65 (q, complexed ArC); 126.84, 127.02, 127.99, 128.05, 129.14 (ArC); 131.49, 131.70, 132.01, 132.20, 132.96 (q, ArC); 133.92 (ArC); 136.01 (q, complexed ArC); 150.55, 150.61, 153.65, 154.18 (q, ArC).

**6d**: Yield: 88%. IR: 1768 cm$^{-1}$ (CO). $\delta_H$ (acetone-$d_6$): 5.36 (10H, s, CpH); 6.45 (8H, s, complexed ArH); 7.37−7.45 (6H, m, ArH); 7.56−7.65 (10H, m, ArH); 7.91−8.05 (10H, m, ArH). $\delta_C$ (acetone-$d_6$): 76.35 (complexed ArC), 79.14 (CpC); 90.93 (q), 116.69, 121.42, 121.67 (ArC); 125.68 (q, complexed ArC); 126.48 (ArC); 126.61 (q, ArC), 126.79, 126.81, 126.84, 126.95, 127.94, 128.03, 129.10, 130.32, 130.92 (ArC); 131.21, 131.90 (q, ArC); 135.94 (q, complexed ArC); 139.53, 150.50, 152.16, 154.72 (q, ArC); 169.30 (CO).

**6e**: Yield: 87%. IR: 1106, 1266 cm$^{-1}$ ($SO_2$). $\delta_H$ (acetone-$d_6$): 5.37 (10H, s, CpH); 6.47−6.54 (8H, br. s, complexed ArH); 7.44−7.47 (6H, m, ArH); 7.62−7.65 (6H, m, ArH); 7.93 (2H, d, $J = 7.7$, ArH); 8.02−8.08 (8H, m, ArH). $\delta_C$ (acetone-$d_6$): 75.56, 78.38 (complexed ArC); 79.54 (CpC); 116.52, 121.25, 121.71 (ArC); 126.60 (q, complexed ArC); 126.85, 127.07, 128.05, 129.12, (ArC); 129.26 (q, ArC); 131.40 (ArC) 135.93 (q, complexed ArC); 132.49, 139.06, 150.33, 159.36 (q, ArC).

**d. Photolytic Demetalation of 2 and 6a−e.** The metalated monomers were decomplexed photolytically by dissolving the monomer (1 mmol) in a 3:1 mixture of dichloromethane:acetonitrile in a 50 mL Pyrex tube. This solution was then irradiated with a xenon lamp for 4 h, after which time the solvents were removed and the product was placed on a silica gel column. Elution with hexane followed by chloroform resulted in isolation of organic monomers **3** and **7a−e** in good yields.

**3**: Yield: 75%. CH analysis for $C_{26}H_{18}O_2$: Found: C, 86.29%, H, 4.98%; Calculated: C, 86.17%, H, 5.01%. $\delta_H$ ($CDCl_3$): 6.93 (2H, d, $J = 7.6$, ArH); 7.06 (4H, s, ArH); 7.37 (2H, t, $J = 7.9$, ArH); 7.49−7.62 (6H, m, ArH); 7.84−7.89 (2H, m, ArH); 8.24−8.29 (2H, m, ArH). $\delta_C$ ($CDCl_3$): 112.37, 120.23, 121.96, 122.96, 125.70, 125.86, 126.57, 127.67 (ArC); 134.82, 153.09, 153.58 (q, ArC).

**7a**: Yield: 78%. CH analysis for $C_{38}H_{26}O_4$: Found: C, 83.67%, H, 4.88%; Calculated: C, 83.50%, H, 4.79%. $\delta_{H}$ ($CDCl_3$): 6.88 (2H, d, $J = 7.5$); 6.96−7.06 (12H, m, ArH); 7.35 (2H, t, $J = 7.9$, ArH); 7.48−7.60 (6H, m, ArH); 7.83−7.88 (2H, m, ArH); 8.21−8.26 (2H, m, ArH). $\delta_{C}$ ($CDCl_3$): 112.42, 119.91, 120.26, 122.03, 123.05, 125.77, 125.93, 126.66, 127.76 (ArC), 134.93, 153.06, 153.12, 153.30, 153.70 (q, ArC).

**7b**: Yield: 80%. CH analysis for $C_{39}H_{28}O_4$: Found: C, 83.56%, H, 5.10%; Calculated: C, 83.55%, H, 5.04%. $\delta_{H}$ ($CDCl_3$): 2.23 (3H, s, $CH_3$); 6.69 (2H, d, $J = 7.9$, ArH); 6.87−7.06 (11H, m, ArH); 7.36 (2H, t, $J = 7.8$, ArH); 7.49−7.61 (6H, m, ArH); 7.84−7.87 (2H, m, ArH); 8.24−8.28 (2H, m, ArH). $\delta_{C}$ ($CDCl_3$): 9.34 ($CH_3$); 112.21, 113.92, 119.28, 120.31 (ArC); 121.36 (q, ArC); 122.00, 122.92, 125.74, 125.87 (ArC); 126.60 (q, ArC); 126.62, 126.74, 127.71 (ArC); 134.86, 152.73, 153.25, 153.77, 156.45 (q, ArC).

**7c**: Yield: 77%. CH analysis for $C_{44}H_{38}O_4$: Found: C, 83.74%, H, 6.09%; Calculated: C, 83.78%, H, 6.07%. $\delta_{H}$ ($CDCl_3$): 0.84 (3H, t, $J = 6.6$, $CH_3$); 1.30 (6H, s, $CH_2$); 1.60 (2H, t, $J = 7.9$, $CH_2$), 2.62 (2H, t, $J = 7.6$, $CH_2$); 6.57 (1H, d, $J = 2.3$, ArH); 6.68 (1H, dd, $J = 8.2, 2.3$, ArH); 6.86−7.05 (9H, m, ArH); 7.15−7.24 (2H, m, ArH); 7.35 (2H, t, $J = 7.9$, ArH); 7.49−7.60 (6H, m, ArH); 7.84−7.88 (2H, m, ArH); 8.22−8.28 (2H, m, ArH). $\delta_{C}$ ($CDCl_3$): 14.10 ($CH_3$); 22.59, 29.11, 29.60, 30.21, 31.66 ($CH_2$); 109.12, 112.18, 112.33, 113.09, 119.52, 120.18, 120.31, 121.98, 122.90, 122.98, 125.73, 125.87 (ArC); 126.59, 127.69 (ArC); 128.57 (q, ArC); 131.05 (ArC); 134.85, 152.65, 152.80, 153.10, 153.63, 153.74, 155.87, 156.50 (q, ArC).

**7d**: Yield: 66%. CH analysis for $C_{52}H_{34}O_6$: Found: C, 82.62%, H, 4.48%; Calculated: C, 82.74%, H, 4.54%. IR: 1762 $cm^{-1}$ (CO). $\delta_{H}$ ($CDCl_3$): 6.87−6.97 (8H, m, ArH); 7.00 (8H, s, ArH); 7.29−7.39 (4H, m, ArH); 7.47−7.61 (10H, m, ArH); 7.83−7.91 (2H, m, ArH); 8.18−8.23 (2H, m. ArH). $\delta_{C}$ ($CDCl_3$): 91.23 (q), 112.69, 117.54, 120.79, 121.03, 121.90, 123.20, 123.94 (ArC); 125.45 (q, ArC); 125.70, 125.91, 125.95, 126.61, 127.73, 128.68, 129.36, 134.17 (ArC); 134.85, 135.00, 151.65, 152.10, 153.33, 153.76, 158.25 (q, ArC), 169.64 (CO).

**7e**: Yield: 86%. CH analysis for $C_{44}H_{30}O_6S$: Found: C, 76.82%, H, 4.34%; Calculated: C, 76.95%, H, 4.40%. IR: 1105, 1258 $cm^{-1}$ ($SO_2$). $\delta_{H}$ ($CDCl_3$): 6.74−7.38 (14H, m, ArH); 7.38 (2H, t, $J = 7.8$, ArH); 7.48−7.54 (4H, m, ArH); 7.61−7.65 (2H, d, $J = 7.2$, ArH); 7.83−7.87 (6H, m, ArH); 8.16−8.21 (2H, m, ArH).__$\delta_{C}$ ($CDCl_3$): 113.34, 117.29, 120.00, 121.06, 123.63, 125.74, 126.06, 126.70, 127.82, 128.71 (ArC), 134.93, 135.24, 150.06, 152.92, 154.90, 162.17 (q, ArC).

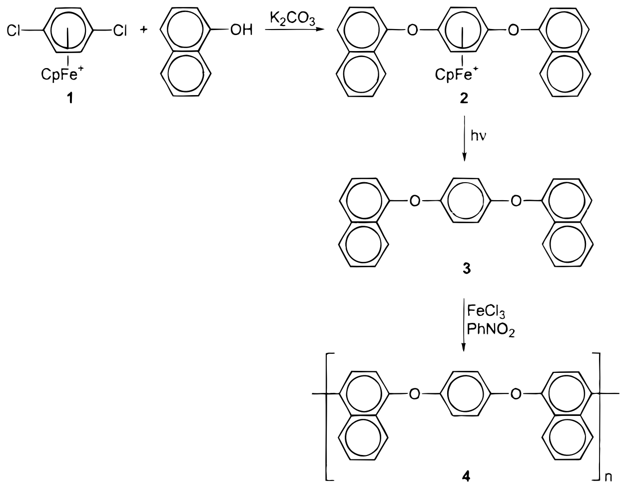
**B. Polymerization.** A representative polymerization was carried out using monomer **7a** with the following experimental conditions. The monomer (109 mg, 0.2 mmol) was dissolved in 1 mL of freshly distilled nitrobenzene in a 10 mL round-bottom flask. Ferric chloride (130 mg, 0.8 mmol) was dissolved in 0.5 mL of nitrobenzene and then added dropwise with stirring to the monomer solution under nitrogen. The solution was stirred at room temperature for 6 h and then precipitated into 250 mL of methanol containing 2 vol % HCl. Following filtration, the precipitate was washed with methanol and allowed to dry. Dissolution of the solid in a minimal amount of chloroform followed by reprecipitation in acetone acidified with 2% HCl allowed for isolation of the polymer.

**4**: $\delta_{H}$ ($CDCl_3$): 6.93−7.05 (2H, m, ArH); 7.12−7.15 (2H, m, ArH); 7.32−7.58 (10H, m, ArH); 8.41 (2H, d, $J = 8.1$, ArH). $\delta_{C}$ ($CDCl_3$): 111.62, 120.72, 122.17, 125.85 (ArC); 126.46 (q, ArC); 126.66, 126.73, 127.94 (ArC); 133.19, 134.31, 153.20, 153.58 (q, ArC).

**8a**: $\delta_{H}$ ($CDCl_3$): 6.93−7.16 (14H, m, ArH); 7.32−7.49 (8H, m, ArH); 8.37 (2H, d, $J = 8.1$, ArH). $\delta_{C}$ ($CDCl_3$): 111.37, 119.90, 120.01, 120.67, 122.15, 125.82 (ArC); 126.37 (q, ArC); 126.64, 126.72, 127.91 (ArC); 133.06, 134.26, 152.71, 153.07, 153.53, 153.64 (q, ArC).

**8b**: $\delta_{H}$ ($CDCl_3$): 2.23 (3H, s, $CH_3$); 6.71 (2H, d, $J = 8.3$, ArH); 6.93−7.16 (11H, m, ArH); 7.33−7.52 (8H, m, ArH); 8.38 (2H, d, $J = 8.4$, ArH). $\delta_{C}$ ($CDCl_3$): 9.39 ($CH_3$); 111.21, 114.05, 119.29, 121.00 (ArC); 121.17 (q, ArC); 122.10, 123.16, 125.72 (ArC); 126.31 (q, ArC); 126.96, 127.99, 129.95 (ArC); 132.95, 134.22, 152.42, 153.46, 153.59, 156.39 (q, ArC).

**Scheme 1**



**8c**: $\delta_{H}$ ($CDCl_3$): 0.85 (3H, br. s, $CH_3$); 1.29 (6H, br. s, $CH_2$); 1.56 (2H, m, $CH_2$); 2.62 (2H, m, $CH_2$); 6.61−6.71 (2H, m, ArH); 6.84−7.45 (19H, m, ArH); 8.32−8.36 (2H, m, ArH). $\delta_{C}$ ($CDCl_3$): 14.11 ($CH_3$); 22.61, 29.13, 29.63, 30.24, 31.68 ($CH_2$); 109.34, 111.27, 111.30, 111.41, 113.24, 119.58, 120.28, 120.58, 120.71, 122.13, 125.79 (ArC); 126.36 (q, ArC); 126.68, 127.90 (ArC); 128.73 (q, ArC); 131.13 (ArC); 133.01, 134.25, 152.0.57, 152.90, 153.37, 153.57, 153.68, 155.87, 156.51 (q, ArC).

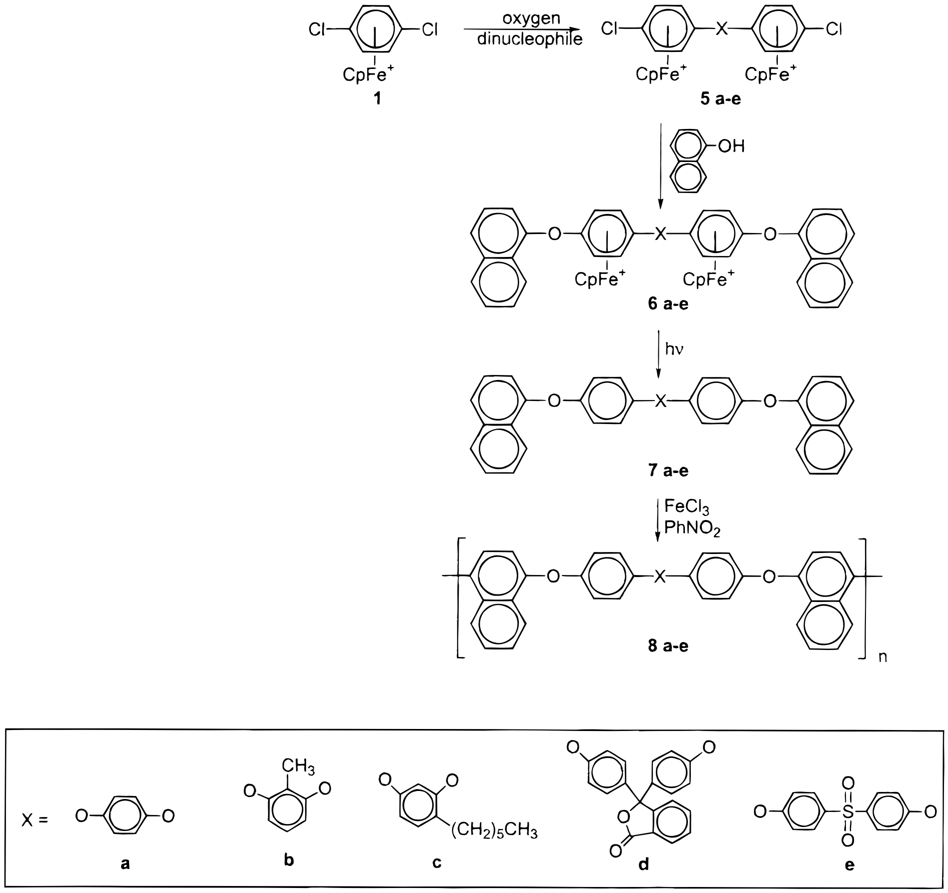
**8d**: IR: 1773 $cm^{-1}$ (CO). $\delta_{H}$ ($CDCl_3$): 6.78−7.68 (28H, m, ArH); 7.92 (2H, m, ArH); 8.33 (2H, d, $J = 8.0$, ArH). $\delta_{C}$ ($CDCl_3$): 91.17 (q); 111.64, 112.65, 117.62, 120.04, 120.49, 121.02 (ArC); 125.46 (q, ArC); 126.04 (ArC); 126.36 (q, ArC); 126.56, 126.58, 126.67, 127.81, 128.68, 129.36, 134.14 (ArC); 134.20, 134.97, 151.92, 152.07, 153.31, 153.43, 158.16 (q, ArC); 169.56 (CO).

**8e**: IR: 1100, 1261 $cm^{-1}$ ($SO_2$). $\delta_{H}$ ($CDCl_3$): 6.94−7.22 (16H, m, ArH); 7.32−7.52 (6H, m, ArH); 7.86 (4H, d, $J = 7.3$, ArH); 8.31 (2H, d, $J = 7.9$, ArH). $\delta_{C}$ ($CDCl_3$): 112.27, 117.37, 120.00, 120.49, 121.91, 125.99 (ArC); 126.53 (q, ArC); 126.62, 126.80, 127.86, 129.75 (ArC) 133.54, 134.29 135.39, 150.39, 153.00, 154.57, 162.32 (q, ArC).

## Results and Discussion

Complexation of transition metal moieties to aromatic rings has long been known to increase the electrophilicity of arenes.[11a−e] The cyclopentadienyliron moiety is particularly attractive due to its strong electron-withdrawing ability and the ease in which a variety of arenes can be complexed and decomplexed.[11d] For the preparation of complexed monomer **2**, the 1,4-dichlorobenzene complex (**1**) was reacted with an excess of 1-naphthol (Scheme 1). Photolytic demetalation of this complex resulted in the isolation of the purely organic monomer (**3**) in 75% yield. For monomers **7a**−**e**, the bimetallic complexes (**5a**−**e**) were first prepared by the reaction of the 1,4-dichlorobenzene complex (**1**) with the appropriate diphenoxy nucleophile (Scheme 2). Reaction of these diiron complexes with 1-naphthol in the presence of $K_2CO_3$ gave the aryl ether complexes with terminal naphthoxy groups (**6a**−**e**) in 76−93% yield. These complexed monomers were subjected to photolytic demetalation as described in the Experimental Section, giving rise to the organic monomers (**7a**−**e**) in good yields. The efficiency of this methodology stems from the ease in which aromatic ether bridges can be introduced into the monomers using cyclopentadienyliron complexes, as well as from the high yields that are associated with their preparation.

**Scheme 2**



Through analysis of the $^{1}H$ and $^{13}C$ NMR spectra of the complexes, monomers, and polymers, the position of the aryl carbon−carbon bond formation could be identified upon polymerization. Percec and co-workers have demonstrated that NMR spectroscopy is a very useful technique in the structural determination of this class of polymers and that coupling occurs selectively at C4 of the naphthyl groups of the monomers.[10] The most obvious change in the $^{1}H$ NMR spectra of the polymeric materials is a downfield shift of the resonances attributed to H8 relative to their positions in the spectra of the monomers. For example, in monomer **7a**, the resonance of H8 appeared from 8.21 to 8.26 ppm and shifted to 8.37 ppm following polymerization to **8a**. It is important to note that comparison of the $^{13}C$ NMR spectra of the monomeric and polymeric materials is also very useful for following the progress of the polymerization reactions. For example, the $^{13}C$ NMR spectrum of metalated monomer **6a** showed that the cyclopentadienyl carbons appeared as a single peak at 78.18 ppm and the complexed aromatics resonated at 75.08 and 75.47 ppm. Upon demetalation, these aromatics were shifted downfield. The resonance at 112.42 ppm in **7a** was assigned to C2 and shifted upfield to 111.37 ppm following the preparation of polymer **8a**. One of the most distinguishable peaks that was used as an indicator of successful polymerization was the appearance of a new quaternary carbon at 133.06 ppm in the polymer spectrum and a concurrent loss of a methine resonance that appeared at 123.05 ppm in the monomer spectrum. This pattern is representative of the aryl−aryl carbon formation at C4.[10]

A desire to control the molecular weights of the polymers led to the study of the affects of reaction time, concentration, and monomer-to-catalyst ratio on the degree of polymerization. The number-average molecular weights ($M_n$) and weight-average molecular weights ($M_w$) of the polymers were determined using gel permeation chromatography (GPC). The effects of these variables on the molecular weights were studied for monomers **3**, **7a**, and **7b** and are summarized in Table 1. It was observed that increasing the reaction time resulted in an increase in the molecular weights of the polymers. Increasing the concentration of the reaction solution or the catalyst-to-monomer ratio also resulted in increased molecular weights. In some cases these increases were dramatic, such as for monomer **7b**, which yielded a polymer (**8b**) with a $M_w$ = 6000 g/mol when a monomer-to-catalyst ratio of 1 to 2 was used and a $M_w$ = 98 200 g/mol when the ratio was adjusted to 1 to 4. The molecular weight for the poly(aryl ether) with the hexyl side chain (**8c**) was measured after 0.5 h rather than the 6 h used for the other monomers. This is due to the monomer yielding high molecular weight material very rapidly, and after 6 h of reaction, the resulting polymer was completely insoluble. The measured $M_w$ and $M_n$ for the soluble portion of **8c** were 33 500 and 9900 g/mol, respectively.

It was found that the molecular weights of the polymers were highly dependent on the structures of the monomers. Monomers **3**, **7a**, and **7b** gave rise to polymers with weight-average molecular weights ranging from 84 000 to 139 900 g/mol as can be seen in Table 2. In contrast, monomers **7c**, **7d**, and **7e** yielded polymers with significantly lower molecular weights, ranging from 10 500 to 33 500 g/mol. However, it is important to note that the molecular weights reported

**Table 1. Molecular Weights and Yields for Polymerization under Various Conditions**

| monomer | | | $FeCl_3$ | | polymer | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| no. | mmol | $PhNO_2$ (mL) | mmol | $PhNO_2$ (mL) | no. | time (h) | yield (%) | $M_w$ (g/mol) | $M_n$ (g/mol) | PDI[a] |
| **3** | 0.2 | 1.0 | 0.8 | 0.5 | **4** | 3.0 | 80 | 87 700 | 34 600 | 2.5 |
| | 0.2 | 1.0 | 0.8 | 0.5 | | 6.0 | 90 | 105 600 | 37 600 | 2.8 |
| | 0.2 | 1.0 | 0.8 | 0.5 | | 20.0 | 83 | 124 100 | 38 300 | 3.2 |
| **7a** | 0.5 | 2.0 | 1.0 | 1.0 | **8a** | 6.0 | 79 | 8 800 | 5 000 | 1.8 |
| | 0.5 | 1.5 | 1.0 | 1.0 | | 6.0 | 78 | 9 400 | 5 500 | 1.7 |
| | 0.5 | 1.0 | 1.0 | 1.0 | | 6.0 | 77 | 11 600 | 6 400 | 1.8 |
| | 0.2 | 1.0 | 0.8 | 0.5 | | 3.0 | 72 | 51 800 | 18 800 | 2.8 |
| | 0.2 | 1.0 | 0.8 | 0.5 | | 6.0 | 81 | 84 000 | 37 500 | 2.2 |
| | 0.2 | 1.0 | 0.8 | 0.5 | | 20.0 | 80 | 89 100 | 40 800 | 2.2 |
| **7b** | 0.5 | 1.0 | 1.0 | 1.0 | **8b** | 0.5 | 74 | 6 000 | 2 600 | 2.3 |
| | 0.5 | 1.0 | 1.0 | 1.0 | | 3.0 | 70 | 7 500 | 3 600 | 2.1 |
| | 0.5 | 1.0 | 1.0 | 1.0 | | 6.0 | 78 | 11 000 | 4 900 | 2.2 |
| | 0.5 | 1.0 | 1.0 | 1.0 | | 18.0 | 75 | 15 000 | 6 400 | 2.3 |
| | 0.5 | 2.0 | 2.0 | 1.25 | | 0.5 | 84 | 15 200 | 6 500 | 2.3 |
| | 0.5 | 1.5 | 2.0 | 1.25 | | 0.5 | 79 | 28 100 | 12 100 | 2.3 |
| | 0.5 | 1.0 | 2.0 | 1.25 | | 0.5 | 87 | 98 200 | 28 700 | 3.4 |

[a] PDI = Polydispersity index, $M_w/M_n$.

**Table 2. Molecular Weights and Thermal Analysis Data for Polymers 4 and 8 a−e**

| no. | $M_w$[a] (g/mol) | $M_n$ (g/mol) | PDI | $T_g$ (°C)[d] | onset of major weight loss (°C)[e] | percent remaining at 1000 °C |
|---|---|---|---|---|---|---|
| **4** | 105 600 | 37 600 | 2.8 | 226 | 539 | 61 |
| **8a** | 84 000[c] | 37 500 | 2.2 | 147 | 490 | 53 |
| **8b** | 139 900 | 42 000 | 3.3 | 156 | 458 | 58 |
| **8c** | 33 500[b,c] | 9 900 | 3.4 | 150 | 472 | 43 |
| **8d** | 11 700[c] | 6 300 | 1.9 | 198 | 462 | 57 |
| **8e** | 10 500[c] | 5 100 | 2.1 | 214 | 575 | 60 |

[a] Time of polymerization = 6 h. [b] Time of polymerization = 0.5 h. [c] Molecular weights of soluble portions. [d] Glass transitions were measured at a heating rate of 20 °C/min for the second heating. [e] Weight losses were measured at a heating rate of 30 °C/min under $N_2$.

for polymers **8a** and **8c−e** are for the soluble portions only.

Thermal analysis results for the poly(aryl ethers) are summarized in Table 2. Thermogravimetric analysis of the polymers was obtained under a nitrogen atmosphere at a heating rate of 30 °C/min. These results showed onsets for the major weight losses ranging from 458 to 575 °C. Polymer **8e**, containing the sulfone bridge, showed exceptional thermal stability with negligible weight loss until 575 °C; even at 1000 °C, it retained approximately 60% of its weight. The methyl- and hexyl-bridged polymers had slightly lower thermal stabilities (458 and 472 °C, respectively) due to the presence of the weaker C−H bonds in the aliphatic substituents. Differential scanning calorimetry was also used to determine the thermal properties of the poly(aryl ethers). The glass transition temperatures ($T_g$) of these polymers are reported in Table 2 for their second heating at a heating rate of 20 °C/min and ranged from 147 to 226 °C. Polymer **4**, with alternating phenoxy and naphthoxy subunits, had the highest $T_g$ at 226 °C, which was followed by polymer **8e**, with a $T_g$ at 214 °C. The high glass transition temperatures and minimal weight losses at high temperatures suggest that these materials may find uses in high-temperature applications.

In conclusion, six different etheric monomers with terminal naphthoxy groups were prepared using cyclopentadienyliron-mediated nucleophilic aromatic substitution reactions. This methodology has allowed for the incorporation of a number of different types of etheric bridges into the polymers under very mild experimental conditions. Polymerization of these monomers using ferric chloride as the oxidant gave rise to their corresponding poly(aryl ethers). Some of the polymers that were prepared had limited solubility, and the molecular weights were therefore measured for the soluble portions only. These polymers showed high thermal stability with weight losses starting from 458 to 575 °C and had glass transition temperatures up to 226 °C.

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