Heteroatom Chemistry
Volume 16, Number 7, 2005

Synthesis of a New Sulfonated Monomer for Poly(aryl Ether)s

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Received 2 August 2004; revised 19 April 2005

ABSTRACT: *A new sulfonated monomer suitable for polyarylether synthesis was made. 1,1′-(p-Phenylenedioxy)bis[4-(4-fluorobenzoyl)]benzene was prepared from phosphorus pentoxide/methanesulfonic acid (PPMA), 1,4-diphenoxybenzene, and p-fluorobenzoic acid in good yield. This compound was selectively monosulfonated on the most activated ring with fuming sulfuric acid and isolated as the sodium salt. Poly(aryl ethers) made from this monomer may find use as proton exchange membranes.* Heteroatom Chem 16:553–556, 2005; DOI 10.1002/hc.20137

INTRODUCTION

Fuel cells have the potential to help combat both the environmental and the energy source problems associated with fossil fuels. The fuel cell technology receiving the most attention contains a solid proton-exchange membrane (PEM) as its electrolyte material. These fuel cells use oxygen from the air and hydrogen to produce energy, with water as the only by-product [1].

The key functional unit in PEM fuel cells is the membrane-electrode assembly (MEA). This consists of catalysts, electrodes, and the proton exchange membrane. PEM's are polymers containing acidic functional groups which impart proton conductivity to the material. Most often these acidic groups are sulfonic acids. High performance polymers have been examined as PEM candidates because they offer the potential of better performance at higher temperatures. Examples of sulfonated, high-performance polymers that have been investigated include polyimides [2], poly(ether sulfones) [3,4], and poly(aryl ether ether nitrile)s [5].

We are synthesizing a series of sulfonated monomers (potential PEM materials) in order to study substituent effects on proton conductivity. Varying the substituents on the sulfonic acid-bearing ring will affect the acidity of the acid and should therefore influence the conductivity of the resulting polymers.

RESULTS

The synthesis of 1,1′-(*p*−phenylenedioxy)bis[4-(4-chlorobenzoyl)]benzene (**3a**) (see Fig. 1) served as a model for the synthesis of 1,1′-(*p*-phenylenedioxy)-bis[4-(4-fluorobenzoyl)]benzene (**3b**). Compound **3a** was synthesized by treating 1,4-diphenoxy benzene (**1**) and *p*-chlorobenzoic acid (**2a**) with P_2O_5 in methanesulfonic acid (PPMA) [6] by the method of Ueda and Ichikawa [7]. The fluorinated monomer **3b** was synthesized in similar fashion using *p*-fluorobenzoic acid (**2b**) in 82% yield.

Sulfonation of **3b** was expected to provide sodium 2,5-bis[(*p*-fluorobenzoyl)phenoxy]benzenesulfonate (**4**). Sulfonation of activated aromatic rings

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Contract grant sponsor: Petroleum Research Fund administered by the ACS.

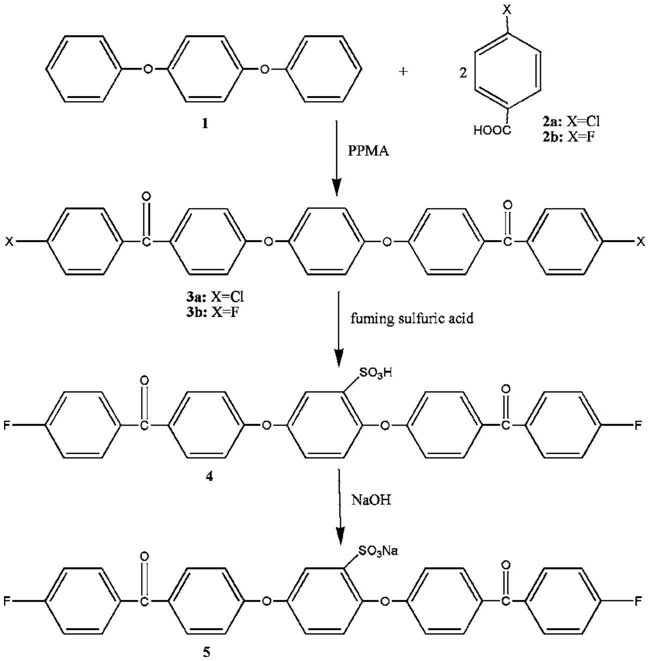

FIGURE 1 Synthetic scheme of sodium 2,5-bis[(*p*-fluorobenzoyl)phenoxy]benzene sulfonate.

can be accomplished with the use of aqueous sulfuric acid [8–11]. This method is reversible and is often driven to completion by removal of water [12]. The rate of sulfonation using aqueous sulfuric acid is reduced with increasing water concentration [9]. Sulfonation was therefore initially attempted on **3b** using concentrated sulfuric acid, but only poor yields were obtained.

Sulfonation of aromatic compounds can also be achieved under more forcing conditions, using liquid or gaseous sulfur trioxide (SO_3) [9,13,14]. Sulfonation with liquid sulfur trioxide is often rapid [9]. Sulfur trioxide can be dissolved in a solvent, slurried, or introduced in the gas phase [13,14]. The sulfonation of **3b** was accomplished using oleum (20% free SO_3) in methylene chloride. The sulfonation was selective to the most activated ring, and **4** was isolated as the sodium salt in 44% yield [15].

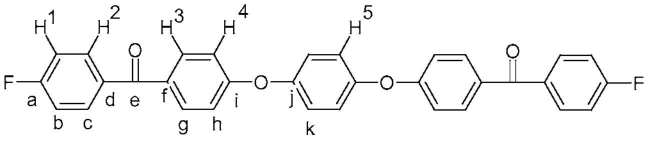

FIGURE 2 ^{13}C and ^{1}H assignments of 1,1′-(*p*-phenylenedioxy)bis[4-(4-fluorobenzoyl)]benzene.

The ^{1}H and ^{13}C assignments (Tables 1 and 3; Fig. 2) for the unsulfonated monomer were readily determined based on a combination of one-dimensional (^{1}H, ^{13}C, and DEPT-135) and two-dimensional (COSY, HMQC, and HMBC) methods. The assignments were aided by comparison to literature data [16]. For example, all of the carbons on the fluorine-bearing ring yielded ^{13}C-^{19}F coupling constants that were consistent with literature values (see Table 2). Assignments (Tables 3 and 4; Fig. 3) for the sulfonated analogue were determined using identical methods. The sulfonic acid salt caused all of the ^{1}H and ^{13}C signals on the outer four rings to be nonequivalent, but it was not possible to distinguish between these signals (e.g. proton 1 and 1′, carbon a and a′).

Sulfonation occurred on the expected electron-rich diether-bearing ring [17]. The singlet at 7.14 ppm from the central ring of the unsulfonated monomer was gone and was replaced by three signals at 7.60, 6.86, and 6.71 ppm that formed an isolated spin system as determined by the COSY spectrum (Table 3). The HMBC spectrum did not show any correlations between these resonances and the carbonyl carbons, which would be present if the spin system was located on any of the other rings. Instead, resonances from the other four spin systems (COSY) showed the expected three-bond correlations between signals 2, 2′, 3, and 3′ and the carbonyl carbons (HMBC). The carbon assignments for the sulfonic acid bearing ring are in agreement with previous, tentative assignments made for sulfonated poly(ether)ether ketone polymers sulfonated on the diether-bearing ring [17].

TABLE 1 Proton Data Including Correlations from 2D Experiments of **3b** (see Fig. 2)

Proton	*δ*	*Multiplicity*	*COSY*	*HMQC*	*HMBC (Selected)*
1	7.16	Mult[a] (overlap)	7.82	115.5	134.2
2	7.82	Mult[a] (overlap)	7.16	132.5(doublet)	132.5
3	7.81	d (8.6)	7.06	132.5	161.8
4	7.06	d (8.9)	7.81	117.1	132.1
5	7.14	Singlet	None	121.9	

[a] Proton is a multiplet due to H-F coupling.

TABLE 2 Carbon and DEPT-135 Experiments of **3b** (see Fig. 2)

δ	*Type/Assignment/Comments*
194.1	Quat./e/ carbonyl carbon
167.0 and 163.7	Quat./a/ $J = 253.7$ C-F coupling
161.8	Quat./i
152.1	Quat./j
134.2	Quat/d/ actually fine doublet $J \sim 3$ Hz
132.5	Methine/c/also doublet overlapped w/132.5, $J \sim 7$ Hz
132.5	Methine/g
132.1	Quat./f
121.9	Methine/k
117.1	Methine/h
115.7 and 115.4	Methine/b/ $J = 21.7$

EXPERIMENTAL

Melting points were obtained with a Mel-Temp capillary apparatus and are uncorrected. NMR spectra were collected on a JEOL-300 instrument, operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C. FTIR spectra were collected on a Perkin Elmer FT-IR 1725x spectrometer; absorptions are reported in cm^{-1}. Microanalysis was obtained by Galbraith Laboratories, Inc., Knoxville, TN.

Diphosphorus pentoxide (Fischer laboratory grade), solvents (Fischer ACS grade), fuming sulfuric acid (20% free SO$_3$ Acros), drying agents (Aldrich), 4-fluorobenzoic acid (Aldrich 98%), 4-chlorobenzoic acid (Aldrich 99%), and 1,4-diphenoxybenzene (Avocado 98%) were commercially available and were used without further purification. CDCl$_3$ (Aldrich) was stored over 3 Å sieves and used without further purification. Thin-layer chromatography (TLC) was performed on Selecto Scientific 60 F$_{254}$ silica gel plates and was visualized by irradiation with UV light.

TABLE 4 Carbon and DEPT-135 Experiments of **4** (see Fig. 3)

δ	*Type/Assignment/Comments*
194.1	Quat./e and e′/ carbonyl carbon
167.0 and 163.7	Quat./a and a′/ $J = 252$ C-F coupling
161.0	Quat./i or i′
160.7	Quat/i or i′
151.2	Quat./j
149.1	Quat./m
136.0	Quat./l
133.54 and 133.36	Quat/d and d′/ each actually fine doublet $J = 2.8$ Hz
132.7	Methine/c or c′
132.6	Methine/g or g′
132.4	Methine/c or c′
132.2	Methine/g′ or g (overlapped with below)
132.2	Quat/f and f′ (overlapped with above)
123.5	Methine/o
122.6	Methine/n
121.0	Methine/k
118.1	Methine/h or h′
117.3	Methine/h or h′
115.70/115.41, 115.61/115.32	Methine/b and b′/ $J = 21.7$

1,1′-(p-Phenylenedioxy)bis[4-(4-chlorobenzoyl)]benzene (**3a**)

General Method. A slurry of *p*-chlorobenzoic acid (1.27 g, 8.11 mmol) and 1,4-diphenoxybenzene (1.08 g, 4.11 mmol) in PPMA (25 mL) under a calcium chloride drying tube was stirred at 25°C for 60 h [7]. After 24 h the slurry became clear. The resulting solution was washed with deionized water (100 mL) and neutralized with solid sodium carbonate. Filtration, followed by drying of the solid product under high vacuum for 24 h, afforded crude **3a** as a pink powder (1.86 g, 84%). Recrystallization from tetrahydrofuran afforded white crystals, mp 260–261°C (lit.

TABLE 3 Proton Data Including Correlations from 2D Experiments of **4** (see Fig. 3)

Proton	δ	*Multiplicity*	*COSY*	*HMQC*	*HMBC*
1 or 1′	7.03	Mult[a] (overlap)	7.67	115.70/115.41	133.54
2 or 2′	7.67	Mult[a] (overlap)	7.03	132.7	167.0/163.7, 194.1
3 or 3′	7.54	d (overlapped)	6.78	132.6	194.1, 160.7
4 or 4′	6.78	d (8.6)	7.54	117.3	132.2
5	7.60	d (overlapped)	6.86	121.0	149.1
6	6.86	dd	7.60, 6.71	123.5	149.1
7	6.71	d	6.86	122.6	151.2, 136.0
4 or 4′	6.89	d (8.6)	7.40	118.1	132.2
3 or 3′	7.40	d (8.6)	6.89	132.2	194.1, 161.0
2 or 2′	~7.57	Mult	6.95	132.4	167.0/163.7, 194.1
1 or 1′	6.95	Mult	7.57	115.61/115.32	133.36

[a] Proton is a multiplet due to H-F coupling.

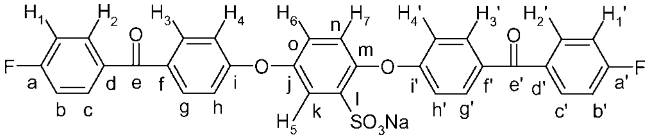

FIGURE 3 ^{13}C and ^{1}H assignments of 2,5-bis[(*p*-fluorobenzoyl)phenoxy]benzene sulfonate.

[7] 264°C). R_f (60:40 CH_2Cl_2/hexane) 0.89. Proton NMR and IR spectra were consistent with the literature data [7].

*1,1′-(p-Phenylenedioxy)bis[4-(4-fluorobenzoyl)]benzene (**3b**)*

By the general method, *p*−fluorobenzoic acid (1.14 g, 8.14 mmol) and 1,4-diphenoxybenzene (1.08 g, 4.11 mmol) in PPMA (28 mL) gave crude **3b** as a light pink powder after vacuum drying (1.69 g, 82.0%). Recrystallization from 1,2-dichloroethane afforded 1.32 g (64.0%) of white crystals, mp 232.4–233.7°C. R_f ($CHCl_3$) 0.32. IR: 3100 (wk), 1646 (vs), 1600 (vs), 1499 (vs), 1406 (m), 1305 (s), 1235 (vs), 1192 (vs), 1052 (s), 928 (m), 839 (s), 765 (s). Anal. ($C_{32}H_{20}F_2O_4$) calcd. C, 75.88; H, 3.98. Found: C, 75.77; H, 4.07. NMR: see Tables 1 and 2.

*Sodium 2,5-bis[(p-fluorobenzoyl)phenoxy]-benzenesulfonate (**4**)*

To a solution of **3b** (206.5 mg, 407.7 μmol) in methylene chloride (75 mL) was added 0.4 mL of oleum (20% free SO_3); the resulting solution was stirred at 25°C for 1 h. Methylene chloride was removed in vacuo affording a yellow oil, which was washed with deionized water (100 mL) and neutralized with 6 M NaOH to pH 7.4. The water was removed under 25 Torr vacuum at 85°C affording 223.1 mg of a mixture of **4** and sodium sulfate. The off-white solid was dried under high vacuum for 24 h. The product was extracted with ethanol which was removed in vacuo affording 150.7 mg of white powder. Column chromatography (90:10 $CHCl_3$:CH_3OH) on silica afforded **4** as a white solid (90.8 mg, 44.0%), mp 220–221.3°C. R_f (90:10 $CHCl_3$:CH_3OH) 0.46. IR: 3100 (wk), 1656 (vs), 1595 (wk), 1471 (wk), 1250 (vs), 1100 (vs), 1052; NMR. See Tables 3 and 4.

CONCLUSION

1,1′-(*p*-Phenylenedioxy)bis[4-(4-fluorobenzoyl)]benzene was synthesized and sulfonated efficiently to prepare a monomer for use in proton exchange membranes. Sulfonated monomers with varied substitutents are being currently being prepared. These monomers will then be polymerized and tested as proton exchange membranes.

ACKNOWLEDGMENT

We would also like to thank Dr. Alan Brown for his helpful comments.

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