



## Synthesis of highly sulfonated polyarylene ethers containing alternating aromatic units



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### ABSTRACT

Sulfonated, sterically-encumbered, alternating copolymers based on poly(arylene ether) are reported. The polymers were prepared by polymerization of 9,9-bis(4-hydroxyphenyl) fluorene with a novel monomer, 4,4''-difluoro-3,3''-bistrifluoromethyl-2'',3'',5'',6''-tetraphenyl-[1,1';4',1'';4'',1''';4''',1'''']-pentaphenyl. Subsequent sulfonation and solution casting provided membranes possessing ion exchange capacities ranging from 0.5 to 2.7 mmol/g. Proton conductivities of membranes increased with IEC and temperature to values >260 mS/cm (at 80 °C, 95% RH). The membranes exhibited good dimensional stability upon water sorption and a resistance to swelling. Dry membranes comprised of isolated spherical aggregates of ions, which upon hydration formed highly conductive pathways, as visualized by AFM analysis. We infer that introducing a high free volume into the polymer by way of incorporating highly sulfonated, multi-phenylated moieties provides mechanically-robust and dimensionally-stable proton exchange membranes.

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### 1. Introduction

The proton exchange membrane is a key component of a polymer electrolyte membrane fuel cell (PEMFC) [1–4]. The membrane must exhibit high proton conductivity, chemical and thermal stability, high dimensional stability when exposed to high and low humidity environments, and low gas permeability. Perfluorinated sulfonic acid (PFSA) ionomer membranes, such as Nafion (Dupont) are preferred materials due to their superior chemical and electrochemical stability and high proton conductivity at moderate temperature [5]. However, PFSA ionomer membranes are highly permeable to gas, costly, and lose many desirable properties under elevated temperature (>80 °C) [6]. These limitations have stimulated efforts to examine alternative PEM materials, particularly those based on hydrocarbon solid polymer electrolytes [7–9].

For the purpose of seeking alternatives to PFSA ionomer several classes of sulfonated aromatic polymer have been investigated, including poly(ether ether ketone)s [10–15], poly(ether sulfone)s [16–20], poly(arylene ether)s [21–25], polyimides and poly

(p-phenylene)s [26–32]. These classes of sulfonated polymer usually achieve conductivity comparable to PFSA only when their IEC is large. Unfortunately, a large IEC leads to excessively swelling and a commensurate loss in dimension stability and a deterioration of mechanical properties [9].

A strategy for designing proton exchange membranes able to uptake water without excessive swelling is to induce phase segregation of the hydrophilic/hydrophobic regions in order to promote hydrophobic–hydrophobic interactions of the polymer chains by localizing the sulfonic acid groups on the main chain, and to introduce free volume into the solid polymer for water to occupy. For example, Pang et al. report novel ionomers based on a fully aromatic poly(arylene ether) possessing pentasulfonated pendent groups. These random copolymers exhibited enhanced conductivity over the temperature range 20–100 °C compared to Nafion 117 [21]. Ueda and co-workers report random copolymers based on locally and densely sulfonated poly(ether sulfone)s in which the pendant phenyl rings were selectively sulfonated to yield phase-separated morphologies that purportedly contributed to its high proton conductivity [33,34]. Hay et al. described poly(arylene ether ketone)s containing a highly sulfonated hydrophilic domains and long hydrophobic chains in order to facilitate phase separation [35]. Miyatake et al. studied several linear and branched sulfonated polyimides and poly(arylene ether)s copolymer membranes containing rigid and bulky fluorene moiety, and reported ionomers

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that yielded high glass transition temperatures, high mechanical strength, transparency, high refraction index, and low dielectric constant, and excellent fuel cell performance [36]. Jannasch and coworkers developed two distinct sulfonated poly(arylene ether sulfone)s, and poly(arylene sulfone)s – varying the positions and number density of the sulfonic acid functionality [37,38]. The tetra-sulfonated copolymers provided densely located sulfonic acid groups and provided high proton conductivity due to distinct phase separation of the ionic domains.

In this article, 4,4'-(9-fluorenylidene) diphenol was chosen as a co-monomer in the preparation of poly(arylene ether ketone)s as it is easily copolymerized [39,40], and ionic groups can be readily attached to the fluorene group by simple electrophilic substitution [36]. We report on a novel class of poly(arylene ether)s having densely sulfonated acid groups with proton conductivity up to 260 mS/cm. These polymers possess low thickness swelling ratios, high proton conductivity and strong mechanical properties.

## 2. Experimental

### 2.1. Materials

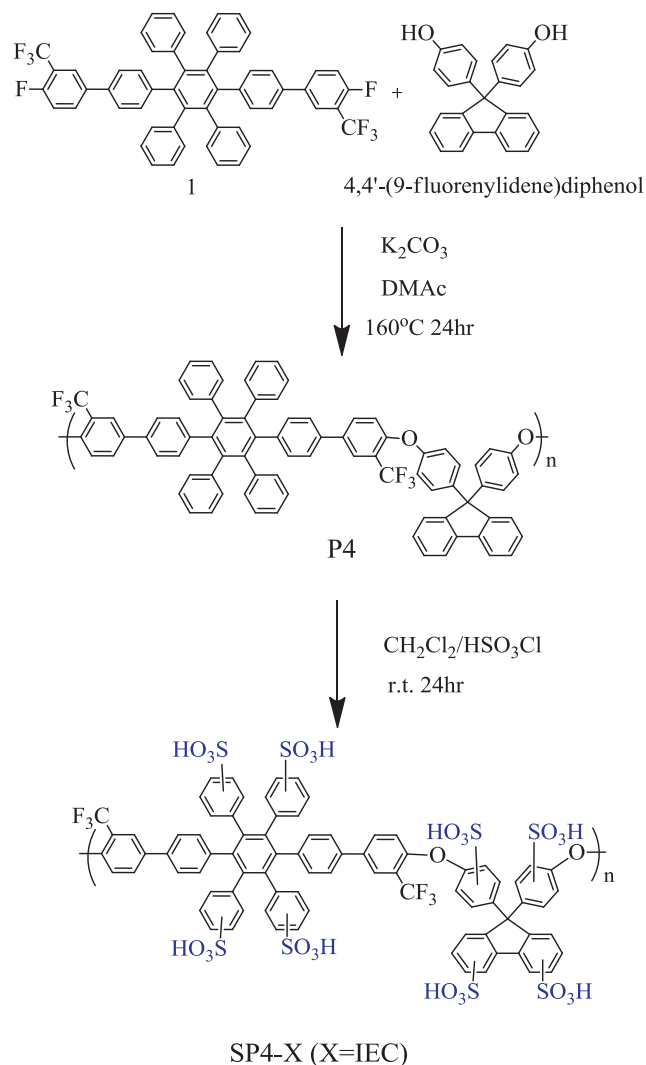
All reagents and solvents were purchased from Aldrich Chemical Co., Merck, Lancaster, Fluoko, or Fisher. *N,N'*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), toluene,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , methanol,  $\text{ClSO}_3\text{H}$ , HCl, NaOH, anhydrous  $\text{K}_2\text{CO}_3$  and aqueous  $\text{H}_2\text{O}_2$  (30%) were obtained from commercial sources. Toluene was dried over CaH and distilled under argon atmosphere and deoxygenated by purging with argon for 30 min prior to use. 9,9-Bis(4-hydroxyphenyl)fluorene and  $\text{Pd}(\text{PPh}_3)_4$  were purchased from Aldrich Chemical Co. and used without further purification. The polymerization was conducted using standard vacuum-line techniques. In order to remove water produced by the reaction, a slow stream of argon was passed through the reaction vessel during polymerization.

### 2.2. 4,4''-Difluoro-3,3''-bistrifluoromethyl-2'',3'',5'',6''-tetraphenyl-[1,1';4',1'';4'',1''']-pentaphenyl (1)

Monomer **1** was prepared according to our previously reported procedure [41]. 4,4''-Dibromo-2',3'-5'-6'-tetraphenyl-[1,1';4',1'']-terphenyl (5 g, 7.22 mmol), 4-fluoro-3-trifluoromethyl phenyl boronic acid (4.5 g, 21 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.05 g, 0.432 mmol),  $\text{K}_2\text{CO}_3$  (4 g, 28.9 mmol),  $\text{H}_2\text{O}$  (13 mL), and toluene (200 mL) was placed in a flame-dried flask and refluxed for 48 h under a nitrogen atmosphere. The solution was cooled and extracted twice using toluene and (1 M) NaCl. The combined organic extracts were washed, dried over  $\text{Na}_2\text{SO}_4$  and concentrated to give **1** as a yellow solid. The crude monomer was purified by recrystallization to obtain pure **1** in 92% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  = ppm): 6.79–7.70 (m, 34H, ArH).

#### 2.2.1. General procedure for polymerization

Polymers were synthesized according to Scheme 1. The condensation reaction followed our previously reported procedure [41], and was carried out in a 50 mL, three-necked round-bottom flask equipped with a stir bar, a Dean-Stark apparatus fitted with a condenser, and a nitrogen inlet. The flask was charged with monomer **1** (2 g, 2.33 mol), 9,9'-bis(4-hydroxyphenyl)fluorene bisphenol monomer (0.816 g, 2.33 mol), potassium carbonate (0.7 g, 5.12 mol), DMAc (20 mL), and toluene (15 mL). The solution mixture was stirred at 130–150 °C for several hours, and during the course of reaction, a slow stream of nitrogen was passed through the reaction vessel to remove water produced by the reaction. After complete removal of the water, the reaction solution was stirred



Scheme 1. Synthesis of SP4-X.

under reflux (160 °C) for 24 h. The crude solution was diluted with 10–15 mL of THF and poured into stirred methanol (250 mL) with stirring to precipitate a fibrous polymer, **P4**, which was collected by filtration, washed and vacuum-dried for 24 h at 120 °C.

To a solution of **P4** (0.4 g) in dichloromethane (30 mL) at room temperature, 0.125 M chlorosulfonic acid solution in dichloromethane was added dropwise. The reaction mixture was stirred for 24 h, then poured into water. The polymer precipitate was filtered, washed thoroughly with deionized water until pH neutral, and dried in vacuum at room temperature overnight to provide the sulfonated polymer, **SP4**. **P4** was sulfonated to different extents according to the above procedure by adding 0.5 mL (7.5 mmol), 0.75 mL (11.2 mmol) and 1 mL (14.9 mmol) of chlorosulfonic acid, respectively. **SP4** polymers were readily soluble in polar aprotic solvents such as DMF, DMAc, DMSO and NMP.

#### 2.2.2. Measurements

NMR spectroscopy was carried out on a 500 MHz  $^1\text{H}$  NMR Varian UNITY INOVA-500 spectrometer using  $\text{DMSO-d}_6$  and  $\text{CDCl}_3$  as solvents. Molecular weights were measured by GPC (Viscotek 270max) with a refractive index detector (Viscotek model 270) calibrated using polystyrene standards. THF was used as the eluent (flow rate of 1 mL/min). FT-IR spectroscopy of dry membrane samples was recorded using a BRUKER Vector 70 spectrometer at a resolution of  $4\text{ cm}^{-1}\text{ min}^{-1}$  between 4000

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