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# Facile synthesis of fluorinated poly(arylene ether)s with pendant sulfonic acid groups for proton exchange membranes

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## ABSTRACT

Linear fluorinated poly(arylene ether)s with and without pendent allyl groups (CFPAE and FPAE) were successfully polymerized from decafluorobiphenyl at room temperature. The subsequent SN<sub>2</sub> nucleophilic substitution of the remaining F atom on CFPAE and FPAE with sodium 4-hydroxybenzenesulfonate yielded SCFPAE and SFPAEs in one simple step under mild conditions. The chemical structures of the polymers were confirmed by <sup>1</sup>H NMR and FT-IR. The ion exchange capacity (IEC), inherent viscosity, water uptake, swelling ratio, proton conductivity, mechanical property, thermal stability, and oxidative stability of the SFPAEs were characterized. The experimental results revealed that the IEC of the SFPAEs can be facilely controlled by the loading amount of sodium 4-hydroxybenzenesulfonate in the reaction mixture. The SFPAE-20 with an IEC of 2.0 mmol g<sup>-1</sup> exhibited an in-plane proton conductivity of 106 mS cm<sup>-1</sup> at 30 °C, higher than that of Nafion N212. More importantly, the SFPAEs showed significantly enhanced oxidative stabilities compared to sulfonated non-fluorinated analogs in literature. While there was still a trade-off between proton conductivity and mechanical strength as often seen for homogeneous systems, the SFPAEs were demonstrated to be promising candidates for proton exchange membranes.

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## Introduction

Proton exchange membrane fuel cells (PEMFCs) have received lots of attention as clean and highly efficient power devices for automotive and stationary applications [1–6]. One of the key materials for PEMFCs is the proton exchange membrane (PEM), which separates anode and cathode from direct contact while allow the transport of proton to complete the inner

circuit for power generation. The state-of-the-art PEM is the perfluorosulfonic acid polymer Nafion (DuPont), which has excellent oxidative stability and proton conductivity. It has been employed in many prototype PEMFCs as the separator to demonstrate the usefulness of the devices. However, the high production cost, poor thermomechanical property and large fuel crossover limit its wide spread application in PEMFCs [7,8]. Therefore, lots of efforts have been focused on the

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exploration of partially fluorinated and non-fluorinated alternatives for PEMFCs [9–11].

Sulfonated poly(arylene ether)s are the most reported chemical categories for PEMs because of their ease-of-synthesis, low cost, good thermal stability, robust mechanical properties, tunable ion exchange capacity etc [12–15]. They usually contain ketone, sulfone, fluorine, or nitrile moieties because of the need for electron-deficient dihalide monomer in the conventional condensation polymerization. The membrane properties are, to a large extent, determined by the polymers' elemental composition and chain structure. Non-crosslinked sulfonated poly(arylene ether)s are usually soluble in polar aprotic solvents such as dimethyl sulfoxide, *N,N'*-dimethylacetamide, *N,N'*-dimethylformamide, and *N*-methyl pyrrolidone, enabling the use of facile solution-casting method to prepare the membranes, while the post-crosslinking processes facilitated by heat or irradiation can further increase the mechanical strength and solvent resistance properties of the membranes.

Generally, sulfonated polymers can be synthesized by either direct polymerization of sulfonate-containing monomers or post-sulfonation of pre-synthesized high-molecular-weight polymers [16–19]. The former method requires extremely pure and stable monomer to achieve enough molecular weight for the preparation of flexible membranes, while the latter method doesn't have too much concern over molecular weight. Therefore, the latter method receives a broad interest in the synthesis of PEMs [20–22], with the fact that various sulfonation agents have been reported, including concentrated sulfonic acid [23,24], chlorosulfonic acid [25], trimethylsilyl chlorosulfonate [26,27], acetyl sulfate [28], and sulfur trioxide [29,30]. One of the issues of these post-sulfonation protocols is that the chain degradation may occur when high functionalization degree is targeted [31]. Therefore, the development of mild post-sulfonation methods for PEM synthesis is highly desirable.

Herein, we report the synthesis of a series of sulfonated fluorinated poly(arylene ether)s with and without unsaturated allyl groups for chemically stable and mechanically robust PEMs. A  $\text{SN}_2$  nucleophilic substitution protocol with sodium 4-hydroxybenzenesulfonate as nucleophile is employed to post-sulfonate these fluorinated poly(arylene ether) precursors to achieve sulfonated polymers with controlled ion exchange capacities. The chemical structure, water uptake, swelling ratio, proton conductivity, thermal stability, oxidative stability, and mechanical properties of the products are characterized. It is proven that the  $\text{SN}_2$  protocol is a facile and highly efficient strategy for the attachment of pendant sulfonic acid groups for high performance PEMs.

## Experimental

### Materials

Sodium 4-hydroxybenzenesulfonate, *N*-methyl pyrrolidone (NMP), *N,N'*-dimethylacetamide (DMAc), decafluorobiphenyl, bisphenol A, ferrous sulfate, calcium hydride, anhydrous cesium fluoride, anhydrous potassium carbonate, hydrogen peroxide (30 wt%), dichloromethane, methanol, sulfuric acid,

sodium hydroxide, sodium sulfate, phenolphthalein, deuterated chloroform, and deuterated dimethyl sulfoxide were purchased from Aladdin Co, Shanghai, China. All chemicals were used as received. 4,4'-(Propane-2,2-diyl)bis(2-allylphenol) was synthesized according to the literature report [32].

### Synthesis of sulfonated fluorinated poly(arylene ether)s (SFPAEs)

Firstly, a fluorinated poly(arylene ether) (FPAE) was synthesized by the condensation polymerization of decafluorobiphenyl and bisphenol A (Scheme 1), according to a previous report [26]. Specifically, to a 100 mL three-necked round-bottom flask equipped with a magnetic stirrer, a thermometer, and a pair of Ar inlet/outlet, 3.3745 g (10.1 mmol) of decafluorobiphenyl, 2.2829 g (10.0 mmol) of bisphenol A, 4.5570 g (15.0 mmol) of anhydrous cesium fluoride, 0.1 g of calcium hydride, and 50 mL of NMP were charged. The mixture was stirred at room temperature for 24 h under Ar atmosphere, and then poured into 500 mL of deionized water to precipitate out the product. The product was collected by filtration, purified by re-dissolving in dichloromethane and precipitating in methanol. The final product was dried under vacuum at 80 °C for 24 h. Yield: 98%.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ , ppm)  $\delta$  1.60 (s, 6H), 7.09 (s, 4H), 7.22 (s, 4H); FT-IR ( $\text{cm}^{-1}$ )  $\nu$  2970, 1649, 1600, 1503, 1485, 1206, 1173, 1124, 1068, 1034, 1004, 981, 828, 723, 564.

Secondly, the FPAE was reacted with various amounts of sodium 4-hydroxybenzenesulfonate in the presence of  $\text{K}_2\text{CO}_3$  to yield SFPAEs with different contents of sulfonate group, as also depicted in Scheme 1. The reaction procedure was similar to a previously reported one [33]. The feeding ratios of sodium 4-hydroxybenzenesulfonate to the repeat unit of FPAE were set to be 0.5, 1.0, 1.5, and 2.0, which gave the product of SFPAE-05, SFPAE-10, SFPAE-15, and SFPAE-20, respectively. A typical procedure for synthesizing SFPAEs was described as followed. To a 25 mL three-necked round-bottom flask equipped with a magnetic stirrer, a condenser, a thermometer, and a pair of Ar inlet/outlet, 0.52 g (1 mmol) of FPAE, 0.39 g (2 mmol) of sodium 4-hydroxybenzenesulfonate, 0.41 g (3 mmol) of  $\text{K}_2\text{CO}_3$ , and 10 mL of NMP were charged. The reaction mixture was stirred at 150 °C under  $\text{Ar}_2$  atmosphere for 6 h. After that, the reaction mixture was cooled down to room temperature and transferred into a dialysis bag (cut-off molecular weight: 8000 Da) to remove all small molecules. The dialysis process was carried in water bath for 3 days, with water being renewed three times a day. A solid product SFPAE-20 was obtained after the evaporation of water and vacuum dried at 80 °C for 24 h. For SFPAE-05, 10, 15, and 20, the yields were 85–90%;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ , ppm)  $\delta$  1.60 (d, 6H), 6.88–7.28 (m, Ar-H);  $^{19}\text{F}$  NMR (400 MHz,  $\text{DMSO-d}_6$ , ppm)  $\delta$  -154.34, -154.16, -153.83, -153.46, -152.99, -152.59, -145.37, -144.86, -144.34, -143.54, -138.36, -136.72; FT-IR ( $\text{cm}^{-1}$ )  $\nu$  2975, 1636, 1600, 1500, 1483, 1209, 1173, 1124, 1066, 1034, 1007, 981, 833, 725, 564.

### Synthesis of sulfonated cross-linkable fluorinated poly(arylene ether)s (SCFPAEs)

Firstly, a cross-linkable fluorinated poly(arylene ether) (CFPAE) with unsaturated double bonds was synthesized

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