



# Partially fluorinated poly(arylene ether)s bearing long alkyl sulfonate side chains for stable and highly conductive proton exchange membranes



Xialin Chen, Haixia Lü, Qilang Lin, Xiang Zhang, Dongyang Chen\*, Yuying Zheng\*

College of Materials Science and Engineering, Fuzhou University, Fuzhou 350116, PR China

## ARTICLE INFO

### Keywords:

Fluorinated ionomers  
Condensation polymerization  
Thiol-ene reaction  
Phase separation

## ABSTRACT

Condensation polymerization of two diallyl-containing bisphenol monomers with decafluorobiphenyl catalyzed by CsF at low temperatures yielded quantitatively the diallyl-containing fluorinated poly(arylene ether)s, which after the thiol-ene click reaction with sodium 3-mercaptopropanesulfonate yielded sulfonated fluorinated poly(arylene ether)s (SFPAEs) with long alkyl sulfonate side-chains. The sulfonate groups were spaced by 7 atoms away from the aromatic backbone, in stark contrast to the previous reports where only 6 spacing atoms could be achieved using a similar chemistry but rather harsh reaction conditions. Two series of SFPAEs based on bisphenol A and bisphenol S units, respectively, were both found to exhibit distinct phase separation and enhanced proton conductivity. Specifically, the SFPAE-A-70 with an ion exchange capacity (IEC) of 1.62 mmol g<sup>-1</sup> exhibited an in-plane proton conductivity of 90 mS cm<sup>-1</sup> at room temperature, which was slightly higher than that of Nafion 212. Furthermore, all of the SFPAEs showed significantly improved oxidative stability in Fenton's reagent when comparing to non-fluorinated analogs. This study offered a new strategy for the synthesis of highly branched ionomers with long and flexible aliphatic side-chains for high performance PEMs.

## 1. Introduction

Proton exchange membranes (PEMs) are becoming increasingly important for a wide range of applications, such as chlor-alkali plants [1,2], polymer electrolyte membrane fuel cells [3–5], vanadium redox flow batteries [6–8], transducers [9], and water purifications [10]. Generally, PEMs are consisted of polymeric backbones and acidic groups which are linked by covalent bonds. Different applications require different properties for PEMs because of their different operational conditions. Nevertheless, the desirable PEMs are expected to be chemically stable, mechanically robust, highly proton conductive, highly ion selective, and low cost. It should be noted that lots of PEMs can be used for not only the original targeted application but also several related others [11,12]. Therefore, the development of high performance PEMs is never a single progress for one technology. More attention should be paid to this fundamental area to support the upgrading the current technologies and the emerging of new ones.

The state-of-the-art PEMs are the perfluorosulfonic acid membranes with trademarks such as Nafion, Flemion, and Aquivion. While they possess high proton conductivity and excellent chemical stability [13], there have limited performance at high temperatures, and their manufacturing cost is high. Accordingly, sulfonated aromatic polymers with high thermal stability and robust mechanical strength have attracted

lots of attention as alternative high performance PEMs [14–16]. The reported aromatic backbones include poly(arylene ether sulfone)s [17,18], poly(arylene ether ketone)s [19,20], poly(phenylene)s [21], polyimides [22,23], polybenzimidazoles [24], and their derivatives. The functionalization of these aromatic backbones with sulfonic acid groups usually endows them with good solubility and considerable proton conductivity. However, their proton conductivity is hard to surpass Nafion even with higher ion exchange capacities (IECs), mainly because of the lack of distinct hydrophilic-hydrophobic phase separation as observed in Nafion [25].

Several strategies have been developed to enhance the phase separation of sulfonated aromatic polymers [5,26]. One of the straightforward approaches is to engineer the sulfonic acid groups on flexible side chains just as Nafion, so that the sulfonic acid groups can easily aggregate into hydrophilic phases while the polymer backbones constitute the hydrophobic phases. For instance, Lee and Guiver et al. reported fluorene-based poly(arylene ether sulfone)s containing locally and densely populated flexible butylsulfonic acid pendant units. Distinct phase separation (ionic domain size: 2–5 nm by TEM) and enhanced proton conductivity (61–209 mS cm<sup>-1</sup> at 30 °C under hydrated conditions) were achieved by this unique molecular design [27]. Higashihara and Ueda et al. also observed distinct phase separation (phase distance: 2.33 nm by WAXD) in novel poly(phenylene)s with flexible

\* Corresponding authors.

E-mail addresses: [dongyang.chen@fzu.edu.cn](mailto:dongyang.chen@fzu.edu.cn) (D. Chen), [yyzheng@fzu.edu.cn](mailto:yyzheng@fzu.edu.cn) (Y. Zheng).

alkyl sulfonated side chains. The c-SPMP8-2 membrane with an IEC of  $2.93 \text{ mmol g}^{-1}$  showed a proton conductivity of  $9.1 \text{ mS cm}^{-1}$  at  $80^\circ\text{C}$  and 30% RH, which was higher than that of Nafion under the same condition [28]. Iojoiu et al. prepared partially fluorinated poly(arylene ether sulfone) copolymers bearing perfluorosulfonic side chains, which showed well-separated morphology as visualized by AFM, and remarkable proton conductivities close to that of Nafion at similar IECs [29]. These previous works validated the concept of promoting phase separations in PEMs by engineering the sulfonic acid groups at the end of long side chains of the polymers.

Following these findings, herein, we develop a new chemistry to synthesize aromatic polymers with long and flexible alkyl sulfonate side chains for high performance PEMs. Specifically, we use the polymerization of diallyl-containing bisphenol monomers with decafluorobiphenyl at low temperatures to yield diallyl-containing fluorinated poly(arylene ether)s, which after the thiol-ene click reaction with sodium 3-mercapto-1-propanesulfonate yields alkyl side chains with the sulfonate groups being spaced by 7 atoms away from the aromatic backbones. This chemistry is modified from a previous one in which the diallyl-containing bisphenol monomers were polymerized at  $165\text{--}170^\circ\text{C}$  in the presence of  $\text{K}_2\text{CO}_3$ , causing the double bond to be rearranged away from the end of the side chains. As a result, only 6 spacing atoms for the sulfonate groups could be achieved after the thiol-ene reaction based on those polymer precursors [30]. The extended side chains reporting herein are beneficial for the hydrophilic-hydrophobic phase separation based on the assumption that the pendant sulfonate groups have excellent tendency to aggregate into ion clusters during membrane preparation [16]. The chemical structure, microscopic morphology, proton conductivity, water affinity, thermal stability, oxidative stability, and mechanical property of the products are characterized in detail. Moreover, the demonstration of a selected membrane as the separator of a vanadium redox flow battery is attempted.

## 2. Experimental

### 2.1. Materials

Decafluorobiphenyl, bisphenol A, bisphenol S, anhydrous cesium fluoride, calcium hydride, sodium 3-mercapto-1-propanesulfonate, 2,2'-azobis(2-methylpropionitrile) (AIBN), 1-methyl-2-pyrrolidinone (NMP), *N,N'*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), allyl bromide, ferrous sulfate, anhydrous potassium carbonate, hydrogen peroxide (30 wt%), 18-crown-6, dichloromethane, ethyl acetate, toluene, *n*-heptane, methanol, sulfuric acid, sodium hydroxide, vanadyl sulfate, and sodium sulfate were purchased from commercial sources. All chemicals were used as received.

### 2.2. Synthesis of diallyl-containing monomers DABPA and DABPS

Diallyl-containing monomers based on bisphenol A (DABPA) and S (DABPS) were synthesized by the reaction of allyl bromide with bisphenol A and S respectively, followed by Claisen Rearrangement, as depicted in Scheme 1. The reaction procedure was similar to the literature report [31]. A representative procedure for the synthesis of DABPS was shown as follows. To a 1 L three-necked round-bottom flask equipped with a condenser, a magnetic stirrer and a gas inlet and outlet were charged 100 g of bisphenol S (0.4 mol), 102 mL of allyl bromide (1.2 mol), 83 g of anhydrous potassium carbonate (0.6 mol) and 300 mL of DMAc. The reaction mixture was heated at  $70^\circ\text{C}$  for 48 h under argon atmosphere. Then, the mixture was cooled down and poured into 2 L of deionized water. The product was precipitated out as white powder, which was collected by filtration and recrystallized from a mixed solvent of toluene and *n*-heptane (yield 92%). The product was then subjected to thermal rearrangement (Claisen Rearrangement) at  $240^\circ\text{C}$  for 1 h under the protection of Ar atmosphere. The final product DABPS was obtained with a yield of 60% after purification by column

chromatography using silica gel (eluent: dichloromethane/ethyl acetate = 20/1).

### 2.3. Synthesis of fluorinated poly(arylene ether)s (FPAEs)

As shown in Scheme 2, the above diallyl-containing monomers DABPA and DABPS were copolymerized with bisphenol A and S, respectively, to yield fluorinated poly(arylene ether)s FPAE-A-x and FPAE-S-x, where A/S represents the type of bisphenol unit, and x represents the molar content of DABPA and DABPS in the total loading of bisphenol monomers. The polymerizations were carried out at low temperatures ( $25^\circ\text{C}$  for FPAE-A-x and  $40^\circ\text{C}$  for FPAE-S-x) according to a previously reported procedure [32]. A typical procedure for the synthesis of FPAE-S-50 was given as follows: to a dry three-necked round-bottom flask were introduced 0.4956 g of DABPS (1.5 mmol), 0.3754 g of bisphenol S (1.5 mmol), 1.0124 g of decafluorobiphenyl (3.03 mmol), 2.3 g of anhydrous cesium fluoride (15 mmol), 0.3 g of calcium hydride, and 6 mL of NMP. The mixtures were magnetically stirred at  $40^\circ\text{C}$  for 24 h under argon atmosphere. The obtained viscous solution was poured into 500 mL of deionized water to precipitate out a fibrous solid, which was collected by filtration. Pure FPAE-S-50 was obtained by re-dissolved the fibrous solid in dichloromethane, precipitating in methanol, and drying under vacuum at  $60^\circ\text{C}$  for 24 h. Yield: 95%.

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

Sulfonate groups were introduced into FPAEs by thiol-ene click reaction, as depicted in Scheme 2. A typical procedure for the synthesis of SFPAE-S-50 was given as follows: to a 25 mL three-necked round-bottom flask equipped with an argon inlet/outlet, a condenser, and a mechanical stirrer were charged with 0.5 g of FPAE-S-50 (0.86 mmol), 0.61 g of sodium 3-mercapto-1-propanesulfonate (3.44 mmol), 0.91 g of 18-crown-6 (3.44 mmol), and 12 mL of a mixed NMP/DMSO solution (vol:vol = 2:1). The reaction temperature was raised to  $80^\circ\text{C}$ , and 5 mL of DMSO containing 0.07 g of AIBN (0.43 mmol) was added dropwise into the flask. The reaction was continued at  $80^\circ\text{C}$  for another 48 h to complete the thiol-ene addition. After that, the reaction mixture was cooled to room temperature, purified by dialysis for 3 days, and finally dried at  $80^\circ\text{C}$  under vacuum overnight to give 0.57 g of SFPAE-S-50. Yield: 88%.

### 2.5. Membrane preparation

Flexible membranes were prepared by a solution-casting method. SFPAEs were dissolved in DMAc to form 5 wt/vol% solutions, which were filtered, cast onto leveled glass plates, dried at  $80^\circ\text{C}$  for 12 h, peeled from the glass by soaking in water, and then dried under vacuum at  $120^\circ\text{C}$  to remove the residue solvents. The membranes were acidified by immersing in 1 M  $\text{H}_2\text{SO}_4$  solution at  $80^\circ\text{C}$  for 1 h, rinsing with deionized water, immersing in deionized water at  $80^\circ\text{C}$  for another 1 h with changing fresh water three times. All membranes were stored in deionized water at room temperature prior to use.

### 2.6. Characterizations

FT-IR spectra were measured on a Thermo Nicolet 5700 FTIR spectrometer.  $^1\text{H}$  NMR spectra were collected on a Bruker AVANCE 400 spectrometer using  $\text{DMSO-}d_6$  or  $\text{CDCl}_3$  as solvents and tetramethylsilane (TMS) as the inner standard. The thermal stability was evaluated by thermogravimetric analysis (TGA) using a NETZSCH STA449C analyzer. The temperature was increased from  $30^\circ\text{C}$  to  $600^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$  under  $\text{N}_2$  atmosphere ( $100 \text{ mL min}^{-1}$ ). The tensile properties were evaluated by a Suns universal testing instrument UTM 6502X. Strain-stress curves were obtained at room temperature at a stretching rate of  $5 \text{ mm min}^{-1}$ . The inherent viscosities of polymers

Download English Version:

<https://daneshyari.com/en/article/7020180>

Download Persian Version:

<https://daneshyari.com/article/7020180>

[Daneshyari.com](https://daneshyari.com)