



# Synthesis of multi-block poly(arylene ether sulfone) copolymer membrane with pendant quaternary ammonium groups for alkaline fuel cell

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## ABSTRACT

A series of multi-block poly(arylene ether sulfone)s are synthesized via the copolymerization of bis(4-hydroxyphenol) sulfone, 3,3', 5,5'-tetramethylbiphenol and 4,4'-difluorodiphenyl sulfone. The resulting multi-block copolymers are brominated by using N-bromosuccinimide (NBS) as bromination reagent. The bromomethylated copolymer is solution cast to form clear, creasable films, and subsequent soaking of these films in aqueous trimethylamine to give benzyltrimethylammonium groups. The anion exchange membranes obtained by the solution hydroxide exchange with aqueous sodium hydroxide show varying degrees of ionic conductivity depending on their ion exchange capacity. The highest hydroxide conductivity  $0.029 \text{ S cm}^{-1}$  is achieved with the QBPEs-40 membrane having IEC value of  $1.62 \text{ mequiv g}^{-1}$  at room temperature and 100% RH. The obtained anion exchange membranes also have good mechanical properties and dimensional stability, which greatly facilitates the preparation of a MEA and the cell operation.

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## 1. Introduction

Anion exchange membrane fuel cells (AEMFCs) have been attracting extensive attention, for it can combine the advantage of proton exchange membrane fuel cells and traditional alkaline fuel cells [1]. They have the potential to solve the problems of catalyst cost and stability while obtaining high power and energy density by changing acidic medium into a basic one [2]. In basic condition, the cathode oxygen reduction over-potential will reduce substantially, resulting in high fuel cell efficiency. Non-noble metal catalysts can be used in AEMFCs because of the facile cathode kinetics, thus the cost of the fuel cell can be reduced significantly [3–6]. The polymer electrolyte membrane is an important part of fuel cells. It serves as the partition that separates the fuel from the oxidant and the support of the catalyst. However, there are no commercially available anion exchange membranes (AEMs) as Nafion does in the field of proton exchange membranes. For AEMFCs applications, AEMs need necessary conductivity, mechanical strength and chemical stability. At present, most commercial AEMs are based on cross-linked polystyrene, and they often blend with some other inert polymer or fabric supports to enhance mechanical properties. The cross-linked polystyrene is not very stable in basic environment and the inert

polymer or fabric supports cannot contribute to the conductivities, these drawbacks limit their further application in AEMFCs [7].

Many efforts have been direct to develop new AEMs materials. Partially or completely fluorinated polymers such as poly(ethylene-co-tetrafluoroethylene) (ETFE), poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), poly(vinylidene fluoride) (PVDF) [8–10], poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [11–14], poly(phenylene) [15] poly(vinyl alcohol) [16,17], and poly(arylene ether sulfone) [18–21] have been investigated as candidates for AEM materials. Among these materials, poly(arylene ether sulfone) was considered as a promising material for AEMFCs application for their excellent mechanical, thermal and chemical stability [22,23]. The traditional synthetic route of poly(arylene ether sulfone) based AEMs typically included a chloromethylation reaction and quaternization step [18]. But the chloromethylation reaction needs toxic chloromethylation reagent, and gelation often occurs during the reaction. Hickner et al synthesized poly(arylene ether sulfone) with bromomethyl function group via bromination route, and prepared AEMs based on brominated poly(ether sulfone) [24]. This route avoided using toxic reagent, and got improved conductivities.

The conductivity is a key factor of AEMs. In the research of proton exchange membranes, it had been found that ionomers with ordered microphase structure could form better ionic transport tunnels and have higher conductivities [25]. There are two main methods to obtain proton exchange membranes with ordered microphase structure. First, synthesizing block copolymer membrane materials [26–30]. Second, making the ionic groups distribute densely on the polymer backbone [31–34]. Most of the

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previous research of AEMs dealt with random copolymers, and there have no report on block copolymers. In this article, we prepared AEMs based on multi-block poly(arylene ether sulfone). To investigate the effect of copolymers structure on conductivity, AEMs based random copolymers and sequence copolymers with similar ionic exchange capacity were prepared, and we found that AEMs based on block copolymer show the highest conductivity among the three kind AEMs.

## 2. Materials and methods

### 2.1. Materials

Bis(4-hydroxyphenyl) sulfone (BPS), 3,3',5,5'-tetramethyl-4,4'-biphenol (TMBP) and 4,4'-difluorodiphenyl sulfone were purchased from Aldrich. N-Bromosuccinimide (NBS) and azodiisobutyronitrile (AIBN) were purchased from Institute of Chemical Engineering of Beijing (China). N-Methyl-2-pyrrolidinone (NMP) was stirred over CaH<sub>2</sub> for 24 h, then distilled under reduced pressure, and stored over 4 Å molecular sieves. All other reagents were obtained from commercial sources and used as received.

### 2.2. Synthesis of multi-block poly(arylene ether sulfone)s containing tetramethyl groups (BPES-y)

The block copolymers were synthesized via a typical procedure. Firstly, the F-terminated oligomers and the phenol-terminated oligomers were synthesized independently. Then the oligomers were mixed and block copolymer was prepared via nucleophilic substitution reaction. Taking the synthesis procedure of BPES-40, where 40 refers to the feed percent of TMBP, as an example: to a 100 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a Dean-Stark trap with a condenser were added TMBP (0.9692 g, 4 mmol), 4,4'-difluorodiphenyl sulfone (0.9153 g, 3.6 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (1.3821 g, 10 mmol), NMP 10 mL, and toluene 15 mL. The mixture was kept at room temperature with stirring to make the monomers dissolve in NMP adequately. After that the mixture was allowed to reflux for 4 h, and then the toluene was removed. The reaction mixture was heated to 170 °C for 16 h. To another 100 mL three-necked flask with same equipment, were added BPS (1.5016 g, 6 mmol), 4,4'-difluorodiphenyl sulfone (1.6272 g, 6.4 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (1.3821 g, 10 mmol), NMP 10 mL, and toluene 15 mL. The procedure was the same as previous. Then the two kind oligomers were mixed after cooled to room temperature. The polymerization was carried out at 180 °C for 16 h. After cooling to room temperature, the mixture was diluted with 15 mL NMP and filtered to remove the salt byproduct. The copolymer was isolated by precipitation in deionized water and washed with hot water three times. The fiber-like copolymer was dried under vacuum before used. Yield: 98%.

### 2.3. Synthesis of sequence poly(arylene ether sulfone)s containing tetramethyl groups (SPES-y)

The sequence copolymers were synthesized as follows: firstly, the TMBP unit oligomers were prepared. After that, BPS and 4,4'-difluorodiphenyl sulfone were added to the reaction mixture, and sequence copolymers were prepared. Taking the synthesis procedure of SPES-40 as an example: to a 100 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a Dean-Stark trap with a condenser were added TMBP (0.9692 g, 4 mmol), 4,4'-difluorodiphenyl sulfone (0.9153 g, 3.6 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (1.3821 g, 10 mmol), NMP 20 mL, and toluene 15 mL. The mixture was heated to reflux for 4 h, and then toluene was removed. The mixture was heated to 180 °C for 16 h. After that, the mixture was cooled to room temperature, and BPS (1.5016 g,

6 mmol), 4,4'-difluorodiphenyl sulfone (1.6272 g, 6.4 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (1.3821 g, 10 mmol), NMP 10 mL were added into it. The following step was similar as the foregoing. The sequence copolymer was isolated by precipitated in deionic water. The copolymer was washed with hot water several times and dried under vacuum before used.

### 2.4. Synthesis of random poly(arylene ether sulfone)s containing tetramethyl groups (RPES-y)

The random copolymers with different molar ratio of TMBP to BPS were synthesized via nucleophilic substitution reaction. Taking the synthesis procedure of RPES-40 as an example: To a 100 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a Dean-Stark trap with a condenser were added TMBP (0.9372 g, 4 mmol), BPS (1.5016 g, 6 mmol), 4,4'-difluorodiphenyl sulfone (2.5425 g, 10 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (2.7642 g, 20 mmol), NMP 10 mL, and toluene 15 mL. The mixture was kept at room temperature with stirring to make the monomers dissolve in NMP adequately. After that the mixture was allowed to reflux for 4 h, and then the toluene was removed. The reaction mixture was heated to 170 °C for 8 h. After cooling to room temperature, the mixture was diluted with 15 mL NMP and filtered to remove the salt byproduct. The copolymer was isolated by precipitation in deionized water and washed with hot water three times and dried under vacuum before used.

### 2.5. Synthesis of bromomethylated poly(arylene ether sulfone)s

A typical procedure for preparing random bromomethylated copolymer RPES-40 (RPESBr-40) was as follows. To a three-necked flask equipped with mechanical stirrer, nitrogen inlet and condenser were added RPES-40 (2.0 g) and 40 mL 1,2-dichloroethane. The mixture was stirred adequately to form homogeneous solution. Then NBS (1.66 g, 9 mmol) and AIBN (0.1 g) were added to the solution. The solution was heated to 80 °C for 8 h, after the NBS and AIBN dissolved. The mixture was cooled to room temperature and coagulated in ethanol with vigorous stirring. The resulting polymer was washed with ethanol several times and dried under vacuum for 24 h at 40 °C. The sequence and block bromomethylated copolymers were prepared in the same procedure.

### 2.6. Preparation of the anion exchange membranes

The bromomethylated copolymer (0.6 g) was dissolved in 10 mL N,N-dimethylacetamide (DMAc). The solution was filtrated and cast onto a flat glass plate. The membrane was dried at 80 °C for 12 h, and at 100 °C under vacuum for 24 h to remove the casting solvent. Then it was peeled off and immersed in 33% trimethylamine aqueous solution for 48 h at 30 °C to make the membrane quaternary-aminated. After that the membrane was kept in 1 mol L<sup>-1</sup> NaOH aqueous solution for 48 h to obtain OH<sup>-1</sup> form membrane. Finally, the membrane was wash thoroughly and immersed in deionized water for 48 h to remove residual NaOH. The quaternary-aminated membrane was kept in deionized water before used.

### 2.7. Measurement

<sup>1</sup>H NMR spectra were measured at 300 MHz on an AV300 spectrometer. The reduced viscosities were determined with an Ubbelohde capillary viscometer at 30 ± 0.1 °C on 0.5 g dL<sup>-1</sup> concentrations of polymer in NMP. Thermogravimetric analysis (TGA) was performed in nitrogen or air atmosphere with a Perkin-Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C min<sup>-1</sup>. Molecular weights of brominated poly(arylene ether sulfone)s

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