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## Journal of Membrane Science

journal homepage: [www.elsevier.com/locate/memsci](http://www.elsevier.com/locate/memsci)

## Block sulfonated poly(arylene ether ketone) containing flexible side-chain groups for direct methanol fuel cells usage

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## ARTICLE INFO

## Article history:

Received 23 March 2012

Received in revised form

7 June 2012

Accepted 8 June 2012

Available online 21 June 2012

## Keywords:

Fuel cells

Proton exchange membranes

Block polymers

Side chain structures

## ABSTRACT

A series of novel block sulfonated poly(arylene ether ketone)s containing side-chain groups were synthesized by condensation polymerization and grafting reactions. The structures of the oligomer and the polymers were investigated by <sup>1</sup>H NMR after each step. The synthetic process was simple and efficient, and the phase separation of the block polymers between the hydrophobic and the hydrophilic components became more apparent. The thermal stability of the membranes was studied by TGA. The proton conductivity of the Block-15 membrane reached up to 0.246 S cm<sup>-1</sup> at 80 °C, which was high enough for practical use. Furthermore, the block membranes showed very strong mechanical properties, water uptake, and resistance to methanol permeability. This study shows that a combination of side chain and block structures are a simple and effective approach to increase the nanophase separation and improve the performance of the proton exchange membranes in fuel cells.

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### 1. Introduction

Direct methanol fuel cells (DMFCs) are considered to be one of the next generation power supplies due to their high energy conversion efficiency and near-zero emissions, especially in vehicles and portable power sources [1–3]. Polymer electrolyte membrane (PEM) is one of the key components in DMFCs. Perfluorosulfonic acid membranes, such as Nafion, are currently widely used as PEMs materials, because of their excellent chemical stability and high proton conductivity. However, several limitations have hampered their widespread commercialization, such as high cost and unstable proton conductivity at high temperature [4,5].

Acid-functionalized aromatic hydrocarbons have been studied intensively in the past decade due to their low cost, high proton conductivity, and thermal and mechanical stabilities [6–8]. There must be enough sulfonic acid groups in these sulfonated polymers to achieve sufficient proton conductivity. However, a high degree of sulfonation induces high methanol permeability and reduces dimensional stabilities [9]. Compared with the sulfonated aromatic polymers, Nafion has a structure consisting of the perfluorinated backbone (hydrophobic) and the flexible pendant

side-chains with sulfonic acid groups (hydrophilic), which shows clear nanophase separation between the hydrophobic and hydrophilic segments [10]. The properties of PEMs are closely related to several chemical characteristics, such as the main chain and side chain structures, degree of sulfonation, number and position of the acid groups, composition of the hydrophilic and hydrophobic components, and the membrane morphology [11]. Furthermore, the phase separation directly determines the properties of PEMs, such as water uptake, proton conductivity, and methanol crossover. It has been reported that the sulfonated aromatic polymers are unable to form defined hydrophilic domains, as the rigid aromatic backbone prevents the formation of continuous conducting channels and ionic clustering [12–14]. Several approaches have attempted to design and synthesize sulfonated aromatic polymers that simulate the structure of Nafion, while maintaining similar performance [15].

Sulfonated block copolymers have been developed as PEMs and have shown better properties (e.g., high IEC and high mechanical strength), which are normally hard to achieve with random copolymer systems [16–20]. In the block copolymers, the nanophase separation of the hydrophobic and the hydrophilic segments could increase and maintain better dimensional stability. McGrath and co-workers synthesized a series of block copolymers based on sulfonated poly(aryl ether sulfone) (SPAES) and sulfonated poly(arylene ether ketone)s (SPAEEKs) [21–23], and they studied the relationship between the structure and the

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membrane performance. Watanabe and co-workers reported a novel structure block poly(arylene ether) used for alkaline fuel cells, which showed higher conductivity than the random polymers at the same IEC level [24]. In our previous work, we also designed and synthesized PEMs based on block-SPEEK polymers, which showed better performances than the random polymers [25–27].

Another effective approach to design the structure of sulfonated aromatic polymers is to add sulfonic acid groups on side chains grafted onto the polymer main chain [28,29]. Lee et al. recently reported a side-chain poly(ether sulfone)s with a very well-designed structure that showed excellent performance at low humidity [30]. Watanabe et al. synthesized sulfonated polyimide with pendant groups that had higher durability and proton conductivity than Nafion at high temperature or low humidity [31]. In our previous work, we synthesized a side-chain-type sulfonated aromatic polymer with reduced water uptake and improved methanol resistance [32]. Because of the naphthalene structures in the polymer chains, the interaction between polymer chains increases, which induce phase separation of the membranes [33].

Research on block SPAEK mainly focuses on the main-chain-type sulfonated polymers instead of the side-chain type copolymers. To the best of our knowledge, there is very little literature which combines the advantages of block polymers and side-chain-type polymers. In this study, we synthesized a series of block SPAEKs with flexible side chain groups attached to the main chain.  $^1\text{H}$  NMR was used to confirm the chemical structures of the polymers after each step. The thermal stability of the block polymers was characterized by thermogravimetric analysis (TGA) and compared with the random polymers. Other properties, such as the mechanical strength, water uptake behavior, and proton conductivity, have been investigated in detail. The results show that our membrane is a promising candidate material for DMFCs.

## 2. Experimental section

### 2.1. Materials

*N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), boron tribromide ( $\text{BBr}_3$ ) and 4,4'-difluoro-benzophenone (DFB) (from Beijing Chemical Reagents) were vacuum-distilled before use. The monomer, 1,5-bis(4-fluorobenzoyl)-2,6-dimethoxy-naphthalene (DMNF), was obtained following the procedure in our previous study [34]. Hydroquinone (HQ) and other chemicals were purchased from Sigma-Aldrich and used without further purification.

### 2.2. Characterization

The  $^1\text{H}$  NMR spectrum was measured on a 500 MHz Bruker Avance 510 spectrometer at 298 K with deuterated dimethyl sulfoxide ( $\text{DMSO-d}_6$ ) as the solvent and tetramethylsilane (TMS) as the standard. The intrinsic viscosities of the polymers were measured at  $0.5 \text{ g L}^{-1}$  in DMF at  $25 \text{ }^\circ\text{C}$  ( $\pm 1$ ) using an Ubbelohde viscometer. The thermal stability was measured using a Pyris 1 TGA (Perkin-Elmer) system. All the membranes were heated from  $100 \text{ }^\circ\text{C}$  to  $700 \text{ }^\circ\text{C}$  at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  in flowing nitrogen.

### 2.3. Random and block polymer preparation

We chose a random polymer with a relatively higher IEC (IEC=1.82) than the comparative sample. It was synthesized and studied in our previous report [34].

#### 2.3.1. Synthesis and characterization of oligomer

Taking the oligomer-9 as an example, the number of repeating units ( $n$ ) is 8. The molar content of hydroquinone and DMNF is 8/9. We used a 250 mL three-necked flask equipped with a mechanical stirrer, a Dean-Stark trap, and a nitrogen inlet. 6.912 g 1,5-bis(4-fluorobenzoyl)-2,6-dimethoxy-naphthalene (DMNF), 1.566 g hydroquinone, 2.2 g anhydrous potassium carbonate, 60 mL DMSO, and 40 mL toluene were added to a flask and stirred at  $140 \text{ }^\circ\text{C}$  for 3 h and then  $180 \text{ }^\circ\text{C}$  for 8 h to remove the water by azeotropic distillation with toluene. The obtained products were poured into DI water. The resulting oligomers were washed with DI water and methanol several times to remove the salts and solvents. Finally, the oligomers were vacuum dried at  $100 \text{ }^\circ\text{C}$  for 24 h.

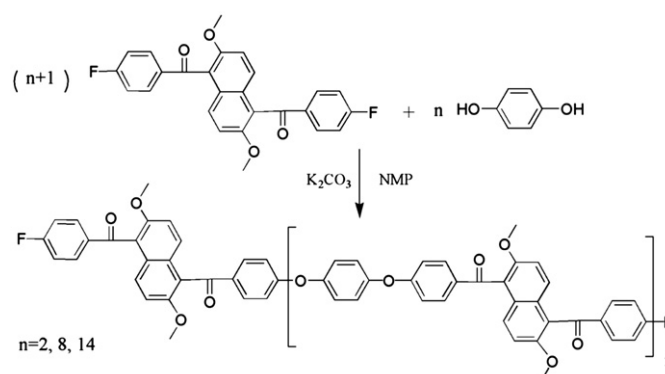
#### 2.3.2. Synthesis and characterization of Block-M polymers

Using the Block-M-3 as an example, the reaction temperature was cooled down to  $120 \text{ }^\circ\text{C}$  after the oligomer-3 was synthesized. Then, DFB and BPA (with a ratio  $k:k+1$ ) were added. DMSO, toluene, and anhydrous potassium carbonate were also added. The system was heated to  $140 \text{ }^\circ\text{C}$  for 3 h, and then  $180 \text{ }^\circ\text{C}$  for 4 h. The resulting solution was poured into DI water, washed with boiling DI water six to eight times, and subsequently dried at  $80 \text{ }^\circ\text{C}$  to obtain the Block-M-3.

#### 2.3.3. Synthesis and characterization of Block-H-x and Block-x polymers

The preparation of the Block-H-x polymers was similar to the work performed in our previous studies [34]. In this conversion, boron tribromide was used to demethylate Block-M-x polymers to Block-H-x polymers. Briefly, using Block-H-3 as an example, 2 g Block-M-3 was dissolved in 10 mL dichloromethane. Then, 20 mL dichloromethane solution (10 wt% boron tribromide) was added drop-wise at  $0 \text{ }^\circ\text{C}$  under a  $\text{N}_2$  atmosphere. The reaction then proceeded for 18 h at room temperature and was subsequently refluxed for 6 h. After washing with boiling DI water and methanol several times to remove excess solvent, a yellow solid resulted. The Block-H-3 product was then dried in a vacuum oven at  $100 \text{ }^\circ\text{C}$  for 48 h (Scheme 2).

The Block-x polymers were synthesized by a single-step in a similar manner to our previous work [26,27]. Using Block-3 as an example, 2 g Block-3 was dissolved in 40 mL DMSO, and this mixture was added to a 250 mL flask equipped with a mechanical stirrer. 0.4 g sodium hydroxide was then added, and the mixture reacted at room temperature for over 6 h. Excess 1,4-butyl sulfone was then added and heated at  $160 \text{ }^\circ\text{C}$  for 18 h. Block-3 resulted after pouring the solution into acetone and washing with acetone and boiled water (Scheme 2). The resulting sulfonated polymers with side chain were named Block-x. For example,



Scheme 1. Synthesis of the oligomer.

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