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Block poly(arylene ether sulfone) copolymers bearing quaterinized aromatic pendants: Synthesis, property and stability

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ABSTRACT

Block poly(arylene ether sulfone) copolymers bearing pendent benzyl-quaternary ammonium groups were prepared through multiple-step reaction pathways that involve pre-polycondensation, block copolycondensation, bromomethylation and Menshutkin reactions. The copolymer ionomer based anion exchange membranes (AEMs) with ion exchange capacity (IEC) from 0.75 to 1.10 mequiv g⁻¹ display relatively large hydroxide conductivities of 45.9–66.1 mS cm⁻¹ at 80 °C, which are ascribed to the distinct hydrophobic/hydrophilic microphase separation resulted from the block copolymer structures and side-chain type hydrophilic segments. Compared to the corresponding random copolymer based AEM, the block ones have obviously higher stability and larger hydroxide conductivity due to the well-connected ionic nanochannels. Among the AEMs, bQPAE-x7y32 with IEC of 1.10 mequiv g⁻¹ gives the best performance with high hydroxide conductivity of 66.1 mS cm⁻¹, low methanol permeability of 4.9 × 10⁻⁷ cm² s⁻¹, large ϕ of 4.6 × 10⁴ Scm⁻³ s, as well as good alkaline stability, respectively.

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Introduction

Spurred by the permission of the nonprecious metallic catalysts (e.g. silver, cobalt, nickel) in anion exchange membrane (AEM) fuel cell (AEMFC) [1], researches on the AEMs have rapidly grown in recent years. The AEMs are composed of copolymer matrix and ionic moiety, and responsible for preventing fuel/oxidant crossover and transporting hydroxide ions from cathode to anode. Among kinds of the ionic

moieties (quaternary ammonium [2], imidazolium [3], phosphonium [4] and guanidinium [5]), quaternary ammonium is the most studied group due to easy preparation. Meanwhile, many aromatic polymers, such as poly(arylene ether) [6,7], poly(phenylene) [8,9], poly(phenylene oxide) [10,11], have high chemical resistance and are employed to prepare ionomer membranes. There are some requirements for developing new AEMs, such as large hydroxide conductivity, good mechanical property, and high alkaline stability. Although many

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AEMs with good performance have been developed up to now, some obstacles to improve the hydroxide conductivity and stability are needed to overcome. To achieve good stability of AEMs, some methods are developed, such as covalent cross-linking [12,13], ring-opening metathesis polymerization [14,15], and choosing benzyltrimethyl ammonium as ionic groups [16,17].

Increasing ion exchange capacity (IEC) is a common method to obtain good hydroxide conductivity of the AEMs, but too large IEC will make membrane absorb much more water, and thus result in an excessive membrane swelling. For example, imidazolium functionalized poly(arylene ether sulfone) membranes have been reported to achieve high hydroxide conductivity via enhancing IEC from 1.61 to 2.10 mequiv g^{-1} , whereas large IEC leads to a high water uptake of 280% and large membrane swelling of 150% at 60 °C [18]. It is known that excessive membrane swelling will cause a decrease in membrane durability and a mismatch between fuel cell and AEM. Besides, choosing proper copolymer structures, such as microporous copolymer, side-chain type or block copolymer, have also been reported to obtain high hydroxide conductivity. McKeown, Guiver and Xu et al. developed microporous copolymer ionomer AEM that exhibited high hydroxide conductivity of 164.4 mS cm^{-1} at 80 °C, which was attributed to the effective ion transportation resulted from the intrinsic microporosity of the charged copolymer matrix [19]. A side-chain type poly(arylene ether sulfone) ionomer AEM was reported to have distinct hydrophobic/hydrophilic phase separation, and thus lead to a large hydroxide conductivity of 93 mS cm^{-1} at 80 °C [20]. In addition, quaternary ammonium functionalized multiblock poly(arylene ether) membrane was reported to display hydroxide conductivity (144 mS cm^{-1} at 80 °C) due to the multiblock structure induced microphase separation [21]. These prove that the side-chain or block copolymer ionomer structures are effective to achieve large hydroxide conductivity because of their distinct hydrophobic/hydrophilic microphase separation. However, few side-chain type monomers are reported to develop the corresponding block copolymers [22–24].

Recently, We have developed two side-chain type difluoro monomers and prepared the corresponding poly(arylene ether) copolymers, the copolymer based AEMs show acceptable high hydroxide conductivity and good alkaline stability [25,26]. It is found that hydroxide conductivity of the copolymer increases with increasing the length of the aromatic spacer between the main-chain and quaternary ammonium groups, the possible reason is that the longer hydrophilic side-chain facilitates the formation of hydrophobic/hydrophilic phase separation and ion transport pathway. Here, to further investigate the effects of block and side-chain structures on the performance of AEMs, series of new poly(arylene ether sulfone) copolymers composed of block structure and pendent benzyl-type quaternary ammonium groups were synthesized, and the corresponding ionomer membranes were prepared. The hydroxide conductivity, water absorption, membrane swelling, methanol permeability, and alkaline stability of the AEMs were investigated and compared with the corresponding random poly(arylene ether sulfone) copolymer ionomer membranes.

Experimental

Materials and reagents

2,6-Difluorophenyl [3,5-bis[(3,5-dimethylphenyl) methyl] phenyl] methanone (DFBDM) was prepared according to our previous procedure [25]. 4,4'-Difluorodiphenyl sulfone (DFDPS) was purchased from Zhejiang Shouferfu Chemical Co. Ltd. 4,4'-Biphenol (BP) was obtained from Aladdin Reagent and sublimated for purification before use. Dimethyl sulfoxide (DMSO) was used after dehydration with 4 Å molecular sieve. Other solvents and reagents were purchased from Sinopharm Chemical Reagent and used as received.

Preparation of fluorine-terminated hydrophobic oligomer (PES-Fx)

The hydrophobic oligomer PES-Fx was prepared according to procedure in Fig. 1(a), where x represents theoretical oligomer lengths of 4 and 7. The preparation procedure of PES-F7 is described below as an example. To a dried 50 mL three-necked flask equipped with a Dean-Stark trap, a condenser and a nitrogen inlet, BP (0.1063 g, 0.571 mmol), DFDPS (0.1659 g, 0.652 mmol), anhydrous potassium carbonate (0.0947 g, 0.685 mmol), 1.2 mL of DMSO and 3.0 mL of toluene were added. The mixture was heated to 140 °C for 4 h with stirring, and then slowly heated to 170 °C to remove the azeotrope of toluene and the produced water under nitrogen flow. The reaction system was kept at 170 °C for another 4 h to form oligomer. After reaction, the resulting solution was poured into water to obtain crude product. The precipitate (PES-F7) was washed several times with water and methanol, respectively, and then dried at 100 °C in vacuum for 24 h.

Preparation of hydroxyl-terminated hydrophilic oligomer (PE-OHy)

The oligomer PE-OHy was synthesized according to procedure in Fig. 1(b), where y represents the theoretical hydrophilic oligomer lengths of 15, 20, 24, and 32. The preparation procedure of PE-OH32 is described below as an example. To a dried 100 mL three-necked flask equipped with a Dean-Stark trap, a condenser and a nitrogen inlet, BP (0.5580 g, 2.997 mmol), DFBDM (1.3196 g, 2.903 mmol), anhydrous potassium carbonate (0.4969 g, 3.596 mmol), 9.4 mL of DMSO and 9.4 mL of toluene were added. The mixture was heated to 140 °C for 4 h with stirring, and then slowly heated to 170 °C to remove the azeotrope of toluene and the produced water under nitrogen flow. The reaction system was kept at 170 °C for another 4 h. After reaction, the resulting solution was poured into water to obtain crude product. The precipitate (PE-OH32) was washed several times with water and methanol, respectively, and then dried at 100 °C in vacuum for 24 h.

Preparation of the block copolymer (bPAE)

The block copolymers (bPAEs) were prepared via block copolycondensation shown in Fig. 1(c). After the oligomers

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