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Synthesis and properties of anion conductive multiblock copolymers containing tetraphenyl methane moieties for fuel cell application

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ABSTRACT

Novel anion conductive multiblock copolymers containing quaternary ammonium basic groups functionalized tetraphenyl methane moieties with sequential hydrophobic/hydrophilic structure were synthesized via prepolycondensation, block copolycondensation, chloromethylation, quaternization, and alkalization. The quaternary ammonium groups were selectively introduced onto the tetraphenyl methane moieties in hydrophilic blocks. The multiblock QPAEs membranes showed well-defined phase segregations. At similar IEC values, hydroxide ion conductivities and mechanical properties strongly depended on the oligomer lengths of hydrophobic blocks and hydrophilic blocks. Hydroxide ion conductivities increased with increasing oligomer length of hydrophilic blocks. Mechanical properties of the QPAE membranes were strengthened by the increase of block length of the hydrophobic segments. The multiblock QPAEs membranes with the IEC values lower than 1.91 meq g^{-1} showed high stabilities under strong basic conditions even with the concentration of NaOH up to 8 M, and retained high conductivities and acceptable mechanical properties after being conditioned with 1 M NaOH at 60 °C for 336 h. The obtained QPAE-X15Y15 membranes with matched hydrophobic/hydrophilic block structure demonstrated the best comprehensive properties. These properties of the multiblock copolymer membranes show their potential as an anion exchange membrane of alkaline fuel cells.

1. Introduction

Fuel cells have been recognized as a promising alternative energy generation technique for stationary, automotive, and mobile applications, due to their high energy efficiency and low pollution levels [1–3]. Among the several kinds of fuel cells, proton exchange fuel cells (PEMFCs) using proton exchange membranes (PEMs) have been well developed [4]. Perfluorinated acid polymers (e.g. Nafion) are state-of-the-art electrolyte membranes used in PEMFCs owing to their high proton conductivity, good mechanical properties and excellent stability. However, there are still some scientific and technological hurdles that should be overcome before large scale commercialization. These hurdles include slow electrode kinetics, the dependence of platinum (Pt) catalysts, CO poisoning of Pt and Pt-based electrocatalysts at low temperatures, high costs of the membranes and catalysts, high fuel permeability and environmental problems with regard to recycling and the disposal of fluorinated polymers [5,6]. To overcome the limitations of PEMFCs, anion exchange membrane fuel cells (AEMFCs) based on anion exchange membranes (AEMs) have attracted enormous interest recently. AEMFCs have better reaction kinetics and more options to use non-precious metals such as Co and Ni as electrocatalysts [5,7,8], thus drastically enhancing fuel cell performance and reducing the cost of fuel cells. Furthermore, the direction of hydroxide anion motion is opposite to that of the fuel flux through the membrane, and this can reduce the fuel permeation greatly [9].

Since the existing AEMs are not ion conductive and stable as the state-of-the-art PEMs, many efforts have been devoted to developing better AEM materials. A variety of AEMs based on poly(ether ketone)s [10–12], poly(ether imide)s [13], poly(phenylene oxide) [14], polystyrene(ethylene butylene)s [15], poly(phthalazion ether sulfone ketons)s [16], poly(arylene ether)s [17–22] and organic–inorganic hybrid composites [23–27] have been fabricated and extensively investigated. Among these materials, poly(arylene ether)s, a class of aromatic polymers demonstrating excellent thermal and chemical stability, good solubility in organic solvents, and outstanding membrane characteristics, are promising materials for AEMs. We have synthesized a series of poly(arylene ether)s containing quaternary ammonium groups functionalized tetraphenyl methane moieties through chloromethylation and quaternization, and showed high hydroxide ion conductivity (20 mS cm^{-1} at 20 °C and 75 mS cm^{-1} at 80 °C respectively) and good chemical and thermal stability [28]. The high hydroxide ion conductivity was attributed to the tetraphenyl

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methane moieties, which were loaded up to 1.78 ionic groups per unit, to give high ion-exchange capacity (IEC). However the maximum ionic groups per unit of the tetraphenyl methane moieties can be four. In the cases of the random ionomers, the ionic groups per unit must be controlled lower than 1.78 to guarantee the balance of the membranes dimension stability and hydroxide ion conductivity. The higher ionic group density per unit resulted in excessive swelling and uncontrollable deformation of the membranes.

In the research of alternative aromatic PEMs, it had been found that multiblock copolymers ionomers with sequential hydrophobic/hydrophilic structure and sulfonic acid groups distributed densely in the hydrophilic segments demonstrate unique phase-separated morphology with well interconnected ion transport channels. The sulfonated multiblock copolymers membranes are highly proton conductive and show fuel cell performance comparable to that of Nafion under severe conditions [29–33]. However, most of the reported research of AEMs based on homopolymers and/or random copolymers and there have been a few reports on AEMs based on block copolymers [8,18,34]. The objective of this research is to produce and evaluate multiblock copoly(arylene ether)s containing dense quaternary ammonium groups functionalized tetraphenyl methane moieties. The synthesis procedure has taken careful consideration to introduce ionic groups selectively at specific segments and to give as high ionic density as possible in the hydrophilic segments. Both are crucial to make the multiblock ionomers membranes architecture. By prepolycondensation, block copolycondensation, chloromethylation, quaternization, and alkalization, the title multiblock copolymers, with well-controlled oligomers lengths and IECs were successfully synthesized. Their water uptake, swelling behavior, hydroxide ion conductivity, thermal and mechanical properties, and chemical stability were investigated.

2. Experimental section

2.1. Materials

All the chemicals are reagent grade and purified by standard methods. Bis(4-fluorophenyl)sulfone (FPS) and 4,4′-sulfonylbis(2,6-dimethylphenol) (SBDMP) were purchased from TCI Inc. Bis(4-hydroxylphenyl)diphenyl methane (HPDPM) was synthesized according to our previous work [35]. Sulfolane, N,N′-dimethylacetamide (DMAc), potassium carbonate, toluene, chloromethyl methyl ether (CMME), 1,1,2,2-tetrachloroethane(TCE), zinc chloride, chloroform, trimethylamine aqueous solution (33 wt%), sodium hydroxide, methanol were obtained from commercial sources.

2.2. Synthesis of fluorine-terminated hydrophobic oligomer

The fluorine-terminated hydrophobic oligomers are synthesized via polycondensation of SBDMP and FPS with controlled monomer composition ratios (e.g., SBDMP/FPS=15/16 composition ratio for the X15 oligomer, numbers after X represent the degree of polymerization of the hydrophobic blocks) in the presence of potassium carbonate in anhydrous sulfolane following the synthesis procedure as shown in Scheme 1. A typical polymerization procedure was as follows (X15). A 50-mL three neck round-bottomed flask was equipped with Dean–Stark trap and a mechanical stirrer under nitrogen flow, and then charged with SBDMP (6.1276 g, 20.00 mmol), FPS (5.4239 g, 21.333 mmol), potassium carbonate (4.1457 g, 30 mmol), sulfolane (22 mL), and toluene (20 mL). The reaction ran at 150 °C for 4 h, and then toluene was removed. The temperature was elevated to 180 °C, and kept for 24 h to obtain a light yellow, viscous mixture. A small amount of FPS (0.2711 g, 1.0666 mmol) was added to the mixture to ensure end-capping the oligomer with fluorine-containing terminal groups and the mixture was maintained at 180 °C for 3 h. After cooling down, the mixture was poured into 100 mL of methanol containing 3 mL of concentrated HCl. The precipitated crude oligomer was washed with deionized water several times and dried at 80 °C. The dried crude oligomer then was dissolved in 50 mL chloroform and filtered with diatomite to remove inorganic salts. The filtrate was poured into 100 mL of methanol. The precipitated oligomer was dried at 80 °C under vacuum. The average degree of the polymerization of the fluorine-terminated hydrophobic oligomer was determined to be 15 from the integral ratio in the ^{1}H NMR spectrum. This gave a fluorine-terminated hydrophobic oligomer X15.

2.3. Synthesis of hydroxyl-terminated hydrophilic oligomer

The synthesis procedure of the hydroxyl-terminated hydrophilic precursor oligomers is shown in Scheme 1 which is similar to the synthesis procedure of the fluorine-terminated hydrophobic oligomers. A typical polycondensation procedure was as follows (Y15, numbers after *Y* represent the degree of polymerization of the hydrophilic precursor blocks). A 50-mL three neck round-bottomed flask was equipped with Dean–Stark trap and a mechanical stirrer under nitrogen flow, and then charged with HPDPM (7.5183 g, 21.333 mmol), FPS (5.0850 g, 20.00 mmol), potassium carbonate (4.4417 g, 32.142 mmol), DMAc (30 mL), and toluene (20 mL). The reaction ran at 150 °C for 4 h, and then toluene was removed. The temperature was elevated to 180 °C, and kept for 24 h to obtain a white, viscous mixture. A small amount of HPDPM (0.3759 g, 1.0666 mmol) was added to the mixture to ensure end capping the oligomer with hydroxyl-containing terminal groups and the mixture was maintained at 180 °C for 3 h. After cooling down, the mixture was poured into 100 mL of methanol containing 3 mL of concentrated HCl. The precipitated crude oligomer was washed with deionized water several times and dried at 80 °C. The dried crude oligomer was dissolved in 50 mL chloroform and filtered with diatomite to remove inorganic salts. The filtrate was poured into 100 mL of methanol with stirring to precipitate out the oligomer. The filtered oligomer was dried at 80 °C under vacuum. The average degree of the polymerization of the hydroxyl-terminated hydrophilic precursor oligomer was determined to be 15 from the integral ratio in the ^{1}H NMR spectrum. This gave a hydroxyl-terminated hydrophilic precursor oligomer Y15.

2.4. Block copolycondensation

The above obtained hydrophobic oligomer X15 (8.0445 g, [–F]=20 mmol) and hydrophilic precursor oligomer Y15 (8.8345 g, [–OH]=20 mmol), potassium carbonate (4.1457 g, 30 mmol), DMAc (25 mL), and toluene (30 mL) were mixed in a 100-mL three neck round-bottomed flask equipped with Dean–Stark trap and a mechanical stirrer under nitrogen flow. The mixture was heated at 150 °C for 4 h before the Dean–Stark trap was removed. Then the polymerization ran at 180 °C for 24 h. After cooling down, the mixture was poured into 200 mL of methanol containing 6 mL of concentrated HCl with strong stirring. The precipitated crude multiblock copolymer was washed with deionized water several times and dried at 80 °C. The dried crude multiblock copolymer was dissolved in 100 mL chloroform and filtered with diatomite to remove inorganic salts. The filtrate was poured into 200 mL of methanol, and then the precipitated polymer was filtered and dried at 80 °C under vacuum to obtain the white block copolymer PAE-X15Y15. The