



Synthesis and characterization of poly(ether sulfone) block copolymers containing pendent quaternary ammonium- and imidazolium groups as anion exchange membranes

Aruna Kumar Mohanty^a, Subramani Devaraju^a, Nowon Kim^{b,*}, Hyun-jong Paik^{a,*}

^a Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Republic of Korea

^b Department of Environmental Engineering, Dong-eui University, Busan 614-714, Republic of Korea



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ABSTRACT

A class of poly(ether sulfone) (FPES) block copolymers containing pendent quaternary ammonium (QA) and imidazolium (IM) groups were prepared as anion exchange membranes by reaction involving nucleophilic substitution, benzylic bromination, quaternization and anion exchange with hydroxide ions. Highly reactive hexafluorobenzene (HFB) was utilized as a linkage group for relatively low temperature (e.g., 105 °C) coupling between hydrophobic and precursor hydrophilic oligomer blocks. The phase separated morphology, water uptake, swelling ratio, conductivity, and chemical stability of the resultant copolymer membranes were also investigated. The hydroxide conductivity of the ionomer membranes (IEC ~ 2.0 mequiv./g) was 21–22 mS/cm and 56–63 mS/cm at 30 °C and 80 °C respectively. The FPES-IM membrane showed relatively very good dimensional integrity in high pH solution, whereas under the similar condition the FPES-QA membrane broke into pieces. However, the degradation of the imidazolium cations in FPES-IM was relatively faster in comparison to the ammonium cations in FPES-QA.

1. Introduction

In recent years, anion exchange membrane fuel cells (AEMFCs) have drawn considerable interest because of their significant advantages over proton exchange membrane fuel cells (PEMFCs) such as fuel flexibility (e.g., methanol, ethanol, ethylene glycol, etc.) [1], high fuel efficiency (low fuel cross-over) [2,3], and low corrosive [1]. In addition, use of non-noble metal catalysts (such as Ni and Co) due to low cathode oxygen reduction over-potential and facile reaction kinetics, and their enhanced durability in the basic environment can reduce the cost drastically for AEMFCs [1–3]. However, there are still some challenges with AEMFCs in terms of performance as the anion exchange membranes (AEMs) for application as electrolyte in AEMFCs have been generally reported with low ionic conductivity in comparison to the acidic proton exchange membranes (PEMs) (the conductivity ratio of H⁺/OH⁻ is about 1.76 in extremely dilute solution) [4]. The ionic conductivity of an ion exchange membrane is generally dependent upon ion exchange capacity (IEC) and water uptake. However, enhancement in the ion conductivity by increasing the IEC of the ion exchange membrane generally results with concurrent repercussions of high water uptake and poor mechanical properties. Therefore, the development of AEMs for high performance of AEMFCs has been a challenge to

meet the comprehensive requirements of high hydroxide conductivity, good dimensional stability and good chemical stability in basic environment.

Various AEMs with main chain structures such as poly(ether sulfone) (PES) [5–9], poly(ether ketone) [10], poly(ether sulfone ketone) [11], poly(ether imide) [12], Poly(phthalazinone ether) [13], poly(phenylene oxide) [14], and polymerized ionic liquid [15] have been reported over the years. Poly(ether sulfone)s have been proposed as interesting AEMs due to their good solubility, high thermal stability, excellent mechanical properties and ability to be modified with different functional groups such as quaternized ammonium [5,6,16], imidazolium [9,17], guanidinium [18], morpholinium [19] and piperazinium [20] salts. While some of these AEMs demonstrated reasonable properties, conductivity improvement and alkaline stability enhancement are still the major challenges for a AEM to be used in AEMFCs. Pan et al. [21] studied the ion aggregating ability of different structures (o-AEM, p-AEM, t-AEM, a-AEM) and showed that the OH⁻ conductivity could be enhanced due to formation of bigger ionic clusters and interconnected broad ionic channels by inducing the aggregation of smaller ionic clusters with strategic introduction of hydrophobic side chain in to the original polymer structure. An important characteristic is that these membranes exhibited higher or comparable hydroxide

* Corresponding authors.

E-mail addresses: knwon@deu.ac.kr (N. Kim), hpaik@pusan.ac.kr (H.-j. Paik).

conductivity with respect to many QA-AEMs with low water uptake which can be attributed to well-defined nanophase-separated morphology. Similar concept of reformation of morphology with multiblock structure in AEMs appear to be comparatively very effective with well-defined phase-separated nano-channels for improvement of ionic conductivity without sacrificing other essential properties such as mechanical and dimensional stability [6,9,11]. The easier aggregation of hydrophilic domains in a hydrophilic/hydrophobic sequenced multiblock AEMs transforms into wide interconnected hydrophilic ionic channels which could increase the local ion concentration and enhanced the hopping conduction of OH⁻. However, multiblock copolymers synthesis is more difficult than random copolymer as they require careful oligomer preparation with proper end-group chemistry essential for a successful coupling reaction. Moreover, conventional approaches to synthesize multiblock copolymers are highly limited since their high reaction temperatures can randomize the hydrophilic/hydrophobic sequences in the final functionalized polymers due to possible transesterification. Fortunately, these issues were addressed to an extent in the PEMs recently reported by McGrath and coworkers where decafluorobiphenyl (DFBP) and hexafluorobenzene (HFB) were used as linkage groups between the hydrophilic and hydrophobic oligomer blocks [22]. The highly reactive nature of HFB (and DFBP) in nucleophilic aromatic substitution reactions can permit the reaction to proceed at significantly lower temperatures which prevents side-reactions including the trans-etherification reaction.

We report here the synthesis of poly(ether sulfone) block copolymers containing pendent quaternary ammonium- and imidazolium groups as novel AEM materials. The synthesis of ionomers involves benzylic bromination of the precursor block copolymer followed by quaternization and anion exchange with hydroxide ions. Before that the precursor block copolymer containing benzylmethyl groups was synthesized using highly reactive hexafluorobenzene as a linkage group for relatively low temperature (e.g., 105 °C) coupling reaction between 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane and 4,4'-hexafluoroisopropylidene diphenol based oligomer blocks. The monomer with benzylmethyl groups in the synthesis of precursor hydrophilic block is used to avoid use of carcinogenic chloromethylation reagents for halomethylation, while the semi-fluorinated hydrophobic block is expected to promote phase separation with the hydrophilic segment, resulting in improved anion transport properties. In the halomethylation with generally used carcinogenic chloromethyl methyl ether (or in situ generated) reagent, high reactivity of the reagent often results in functionalization at only one site on a backbone aromatic ring before side reactions and cross-linking occur ultimately limiting the ionic functionality of the polymer [16,23]. On the other hand, *N*-bromosuccinimide (NBS) is much safer to handle and can introduce benzyl bromide moieties at benzyl positions along the polymer backbone, giving an opportunity to synthesize multifunctionalized aromatic ring in a PES. A good hydrophilic/hydrophobic phase-separated morphology induced from the block copolymer structure is expected to result in enhanced conductivity for the membranes. The structure of the FPES-QA and FPES-IM copolymers is characterized by NMR and FTIR spectroscopy. The membrane properties like water uptake, thermal and aqueous alkaline stability, and anion conductivity of the membranes are also investigated.

2. Experimental

2.1. Materials

4,4'-Hexafluoroisopropylidene diphenol (6FBPA), 4,4'-difluorodiphenylsulfone (DFDPS), 4,4'-dichlorodiphenylsulfone (DCDPS), hexafluorobenzene (HFB) were obtained from Alfa Aesar and used as received. 2,2-Bis(4-hydroxy-3,5-dimethylphenyl)propane (TMBPA) was purchased from TCI and used as received. DCDPS DFDPS, 6FBPA, TMBPA were dried under vacuum at 60 °C for 24 h prior to the polymerization. Anhydrous potassium carbonate (Merck) was dried at 100 °C for 10 h in a vacuum oven. NMP (Daejung) was purified by

stirring with NaOH and distilled from P₂O₅ under reduced pressure. Toluene (Merck) was refluxed over Na metal to remove water and was freshly distilled before use. All other chemicals were obtained from commercial sources and used without further purification.

2.2. Preparation of anion exchange membranes

2.2.1. Synthesis of the OH-terminated oligomer, PES-1

The OH-terminated oligomer PES-1 was synthesized with a target number average molecular weight of 5 kDa in a typical process as follows: DFDPS (5.537 g, 21.7 mmol), TMBPA (6.844 g, 24.0 mmol), potassium carbonate (7.5 g, 54.4 mmol), NMP (80 mL) and toluene (40 mL) were charged in a two-neck 250 mL round bottom flask equipped with Dean-Stark trap and condenser, magnetic stirrer, and gas inlet and outlet. The mixture was heated to 150 °C under nitrogen atmosphere. The toluene and residual water from the reaction mixture were removed from the system as an azeotrope by distillation over 3–4 h. The temperature was then raised to 170 °C, and the reaction proceeded for another 20 h. After cooling to room temperature, the mixture was poured into acidified methanol. The oligomer was collected by filtration, thoroughly washed with deionized water and drying at 100 °C in vacuum for 24 h as white powder (11.3 g, 94% yield).

2.2.2. Synthesis of the F-terminated oligomer, FPES-3

First, the OH-terminated terminated oligomer, FPES-2 with a target number average molecular weight of 8 kDa was synthesized as follows: DCDPS (7.304 g, 25.4 mmol), 6FBPA (9.162 g, 27.2 mmol), potassium carbonate (9.4 g, 68.1 mmol), NMP (110 mL) and toluene (60 mL) were added into a two-neck 250 mL round bottom flask equipped with Dean-Stark trap and condenser, magnetic stirrer, and gas inlet and outlet. The mixture was initially heated at 160 °C for 4 h and then at 185 °C for 24 h. Finally, the mixture was precipitated in acidified methanol. The product was filtered, washed several times with deionized water and dried at 100 °C in vacuum for 24 h (13.8 g, 92% yield).

Reactive F-end groups were obtained by end-capping the synthesized FPES-2 with hexafluorobenzene in DMAc at 80 °C via a nucleophilic aromatic substitution reaction. The end-capping reaction was as follows: FPES-2 (12 g, 1.5 mmol) and potassium carbonate (0.62 g, 4.5 mmol) were charged to a three-necked 250 mL round bottom flask equipped with a Dean-Stark trap and condenser, magnetic stirrer and a nitrogen inlet and outlet. Distilled DMAc (120 mL) and cyclohexane (40 mL) were added to the flask. The solution was allowed to reflux at 110 °C to azeotropically remove the water in the system with cyclohexane over 3 h. The reaction temperature was lowered to 80 °C and the nitrogen purge was stopped. Then, HFB (2.79 g, 15 mmol) was added and the reaction was allowed to proceed for 12 h. The solution was then cooled and precipitated in methanol containing few drops of HCl. The product was collected by filtration, thoroughly washed with deionized water and dried at 60 °C in vacuum for 24 h.

2.2.3. Synthesis of the block copolymer, FPES

The block copolymer was synthesized by coupling between the HFB end-capped 6FBPA based poly(ether sulfone) oligomer, FPES-3 and OH-terminated TMBPA based poly(ether sulfone) oligomer, PES-1. A typical coupling reaction is as follows: PES-1 (8 g, 1.18 mmol), potassium carbonate (0.65 g, 4.72 mmol), DMAc (145 mL), and cyclohexane (50 mL) were added to a three-necked 250 mL round bottom flask equipped with a Dean-Stark trap and condenser, magnetic stirrer and a nitrogen inlet, and outlet. The reaction mixture was heated at 100 °C for 4 h to azeotropically remove the water in the system with cyclohexane. After removal of cyclohexane, the vacuum dried FPES-3 oligomer (9.583 g 1.18 mmol) was added. The coupling reaction was allowed to proceed at 105–110 °C up to 48 h. The viscous reaction solution was precipitated in 1:1 ratio of methanol and water. The copolymer was filtered and dried at 120 °C in vacuum for 24 h.

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