



Synthesis and characterization of poly(arylene ether sulfone)-*b*-polybenzimidazole copolymers for high temperature low humidity proton exchange membrane fuel cells

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ABSTRACT

Multiblock copolymers based on poly(arylene ether sulfone) and polybenzimidazole (PBI) with different block lengths were synthesized by coupling carboxyl functional aromatic poly(arylene ethers) with ortho diamino functional PBI oligomers in NMP, selectively doped with phosphoric acid, and evaluated as a high temperature proton exchange membrane (PEM). Transparent and ductile membranes were produced by solvent casting from DMAc. From dynamic mechanical analysis (DMA), the neat copolymer membranes showed two distinct glass transition temperatures which implies the existence of a nanostructured morphology in the membranes. These two nanophases became more distinct with increasing block length. The membranes were immersed in various concentrations of phosphoric acid solution to produce the proton conductivity. The doping level increased with increasing concentration of the acid solution and a maximum doping level of 12 was achieved when 14.6 M phosphoric acid solution was used. The acid doped membranes showed significantly reduced swelling behavior compared to a control conventional phosphoric acid doped PBI homopolymer system which appears to be related to the selective sorption into the PBI phase. The ionic conductivity of the doped samples at 200 °C afforded up to 47 mS/cm without external humidification. The protonic conductivity was found to increase with block length at a given doping level, reflecting the sharpness of the nanophase separation and the effect was even more prominent at a low doping level of 6–7. It is suggested that the phosphoric acid doped multiblock copolymer system would be a strong candidate for high temperature and low relative humidity PEM applications such as those required for stationary power.

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1. Introduction

The fuel cell is well known to be an energy conversion device which transforms chemical energy directly into electrical energy [1]. Its high energy efficiency and environmentally friendly nature have attracted much attention, making the fuel cell an alternative to conventional energy sources. Among several types of fuel cells, polymer electrolyte membrane fuel cells (PEMFCs) have been most intensively explored for past decades due to their promise for mobile, automotive, and stationary applications [2]. The state-of-the-art PEMs are perfluorinated sulfonic acid containing ionomers (PFSA) which have demonstrated excellent performances including high proton conductivity and excellent chemical stability [3,4]. However, their mechanical and electrochemical properties deteriorate [5] at higher operating temperatures and low relative humidity (RH)

conditions since the proton transport of sulfonic acid based PEMs strongly depends on water in the membranes. It has been proposed that the proton conduction of the sulfonic acid containing PEMs is governed by a vehicle mechanism, where water acts as the vehicle for proton transport [6]. Hence at high temperature and at very low RH, the proton transport is restricted due to insufficient water. Consequently, various approaches have been made to develop PEMs which are suitable for high temperature under low RH conditions.

One of the successful high temperature, low RH PEMs is well recognized to be an inorganic acid doped polymer membrane system [7–10]. The inorganic acids act as ion conducting materials while polymers, which typically possess basic moieties, can immobilize the acid. Among various inorganic acids, phosphoric acid (H₃PO₄) has been widely studied due to its excellent thermal stability, low vapor pressure, and high ionic conductivity even under anhydrous conditions [11–15]. For the matrix polymer, the polybenzimidazole (PBI) family, especially poly(2,2'-*m*-(phenylene)-5,5'-bibenzimidazole), has been intensively studied due to the ease of synthesis and commercial availability [16,17]. Phosphoric

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acid doped PBI membranes can be easily fabricated by immersing solvent cast PBI membranes in phosphoric acid solution. The doping level which can be defined as the number of moles of phosphoric acid per one repeat unit of PBI is controlled by using different concentrations of the doping solution [18]. More recently, Benicewicz et al. have elegantly shown that one can directly polymerize and cast from polyphosphoric acid (PPA). The controlled hydrolysis of PPA in the film affords very large doping levels and excellent performance [19].

In contrast to sulfonic acid based PEMs, the ion transport in phosphoric acid doped systems under anhydrous conditions is thought to follow a proton hopping or Grotthus mechanism [20,21]. The mechanism is reported to depend strongly on acid doping level, water content and temperature. At low doping levels, the proton transport has been suggested to take place between the N–H sites of the polymer and phosphate anion. At higher doping levels, the presence of “free” acid facilitates the enhanced transport from the more rapid diffusion of additional phosphate anions [22]. In the presence of water, ions such as H_3O^+ also can be involved as an additional proton carrier. At high temperatures in the condensed phosphoric acid state, ion transport involving protonic diffusion via the vehicle mechanism is also proposed [23].

Generally, the ionic conductivity of phosphoric acid doped PBI homopolymers increases along with doping level and temperature. However, doping levels higher than 5 may not be desirable in current commercial PBI due to high swelling and deterioration of mechanical properties [24]. Although several approaches have been attempted to address this problem, such as crosslinking of the matrix polymer [25,26], and introducing inorganic fillers to reinforce the membrane [27], highly doped membranes still suffer from mechanical property deterioration, a perceived and perhaps actual problem with electrode performance.

Similar trade-off behaviors between proton conductivity and dimensional stability have been observed in sulfonic acid containing PEM systems. Although an increased degree of sulfonation in the system enhances proton conductivity, beyond a certain concentration a percolated hydrophilic phase develops resulting in excessive water swelling, and a hydrogel which is impractical as a PEM [28,29]. Recently, these problems have been successfully addressed by utilizing multiblock copolymers based on ion conducting hydrophilic blocks and mechanically robust hydrophobic blocks [30–34]. Once the block copolymers are cast into membranes, they can exhibit unique phase separated morphologies and each phase governs independent properties. The ionic groups of the hydrophilic blocks act as proton conducting sites while the nonionic hydrophobic component provides dimensional stability.

In the present work, multiblock copolymers were produced by a homogeneous coupling reaction in NMP between highly reactive *o*-diamino functional PBI oligomers and carboxylic acid-terminated poly(arylene ether sulfone) oligomers [35]. The latter was prepared by using *m*-hydroxybenzoic acid as an efficient end-capper during the nucleophilic step polymerization. The carboxylate formed is unreactive but the phenoxy anion is quite reactive with the activated aromatic halide. The PBI segments in the system facilitate ionic conduction by providing a selective site for absorption of H_3PO_4 while poly(arylene ether sulfone) segments are unaffected and maintain the dimensional and mechanical stability. Ionic transport measurements on the copolymers have been investigated in the absence and in the presence of water as a function of doping level, temperature and morphology.

2. Experimental

2.1. Materials

N,N-Dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidinone (NMP), and toluene were purchased from Aldrich and distilled from

calcium hydride before use. Monomer grade 4,4'-dichlorodiphenyl sulfone (DCDPS) and 4,4'-biphenol (BP) were provided by Solvay Advanced Polymers and Eastman Chemical Company, respectively, and vacuum dried at 110 °C prior to use. Potassium carbonate, 3-hydroxybenzoic acid (99%) (3-HBA), isophthalic acid (99%), 3,3'-diaminobenzidine (99%) (DAB), phosphoric acid (85%) and polyphosphoric acid (115%) were purchased from Aldrich and used without further purification.

2.2. Synthesis of controlled molecular weight poly(arylene ether sulfone)s with telechelic benzoic acid functionality

Benzoic acid-terminated poly(arylene ether sulfone) oligomers (BPS) with molecular weights of 5, 10, and 15 kg/mol were synthesized. An example of the synthesis of 5 kg/mol BPS is as follows: 10.6730 g (57.3 mmol) of BP, 17.9209 g (62.4 mmol) of DCDPS, 1.4061 g (10.2 mmol) of 3-HBA and 11.1900 g (81.0 mmol) of potassium carbonate were added to a three-neck 250-mL flask equipped with a condenser, a Dean Stark trap, a nitrogen inlet/outlet, and a mechanical stirrer. Distilled DMAc (120 mL) and toluene (60 mL) were added to the flask. The solution was allowed to reflux at 155 °C while the toluene azeotropically removed the water from the system. After 4 h, the toluene was completely removed from the system and the reaction temperature was increased to 180 °C. The reaction was allowed to proceed for another 48 h. The resulting viscous solution was filtered to remove the salts and coagulated in methanol. The telechelic benzoic acid functionality of the oligomer was recovered from its potassium salt form by stirring the coagulated polymer in 0.1 M aqueous sulfuric acid solution for 24 h. The polymer was dried at 110 °C *in vacuo* for at least 24 h.

2.3. Synthesis of controlled molecular weight diamine-terminated polybenzimidazole

Diamine-terminated polybenzimidazole blocks with molecular weight 5, 10, and 15 kg/mol were synthesized. A typical coupling reaction was performed as follows: 5.8977 g (35.5 mmol) of isophthalic acid and 8.0995 g (37.8 mmol) of DAB were mixed with 126 g of polyphosphoric acid in a three-neck 250-mL flask equipped with a nitrogen inlet/outlet and a mechanical stirrer. The mixture was heated at 200 °C for 24 h. The resulting dark brown polymer solution was coagulated in deionized water and stirred for 24 h. The telechelic oligomer was filtered and washed with deionized water several times. The residual acid in the polymer was neutralized with 1 M NaOH solution. It was dried at 120 °C *in vacuo* for at least 24 h.

2.4. Synthesis of poly(arylene ether sulfone)-*b*-polybenzimidazole multiblock copolymers

Multiblock copolymers were synthesized via a coupling reaction between the benzoic acid and *o*-diamino end groups on the poly(arylene ether sulfone) and polybenzimidazole oligomers, respectively. A typical coupling reaction was performed as follows: 3.0000 g (0.6 mmol) of poly(arylene ether sulfone) oligomer ($\bar{M}_n = 5$ kg/mol), 3.0000 g (0.6 mmol) of polybenzimidazole oligomer ($\bar{M}_n = 5$ kg/mol) and 60 mL of NMP were added to a three-neck 100-mL flask equipped with a mechanical stirrer, and a nitrogen inlet/outlet. The reaction mixture was heated at 200 °C and allowed to proceed for 48 h. The resulting dark brown viscous copolymer solution was precipitated in methanol and filtered. The polymer was dried at 120 °C *in vacuo* for at least 24 h.

2.5. Characterization of copolymers

^1H NMR analyses were conducted on a Varian INOVA 400 MHz spectrometer with $\text{DMSO-}d_6$ or $\text{DMAc-}d_9$ to confirm the chemical

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