



Macromolecular cross-linked polybenzimidazole based on bromomethylated poly (aryl ether ketone) with enhanced stability for high temperature fuel cell applications



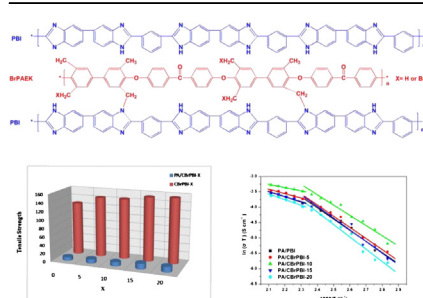
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HIGHLIGHTS

- A series of macromolecular cross-linked polybenzimidazole membranes were prepared.
- The macromolecule BrPAEK was first used as a cross-linker in PBI-based system.
- The CBrPBI-X membranes were prepared by an easy facile heating method.
- The chemical stability, oxidative stability and mechanical properties were improved.
- The results indicated that CBrPBI-10 was a promising candidate as HT-PEM.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of macromolecular cross-linked polybenzimidazole (PBI) membranes have been successfully prepared for the high temperature proton exchange membrane fuel cell (HT-PEMFC) applications. Bromomethylated poly (aryl ether ketone) (BrPAEK) is synthesized and used as a macromolecular cross-linker, the cross-linking reaction can be accomplished at 160 °C using an easy facial heating treatment. The resulting cross-linked membranes CBrPBI-X (X is the weight fraction of the cross-linker) display excellent mechanical strength. After phosphoric acid (PA) doping, the mechanical strength and proton conductivity of the PA/CBrPBI-X membranes are both enhanced comparing with the pristine PA/PBI. Considering the tradeoff of the mechanical strength and proton conductivity, 10 wt% BrPAEK is demonstrated to be an optimum content in the matrix. For instance, the proton conductivity of PA/CBrPBI-10 is 0.038 S cm⁻¹ at 200 °C, which is higher than that of pristine PA/PBI with the proton conductivity of 0.029 S cm⁻¹ at the same temperature. Other properties of the cross-linked membranes are also investigated in detail, including the oxidative stability, solubility and thermal stability. All the results indicate that the PA/CBrPBI-10 membrane has the potential application in HT-PEMFCs.

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1. Introduction

Polybenzimidazole (PBI) is a kind of heterocyclic high-performance polymer with high glass transition temperature, high thermal stability, excellent chemical resistance and mechanical properties [1–3].

Phosphoric acid-doped polybenzimidazoles (PA-PBIs) are supposed to be the most appealing polymers electrolyte membranes for high temperature proton exchange membrane fuel cells (HT-PEMFCs) [4–6]. Proton exchange membranes (PEMs) are the core material of PEMFCs and need to offer an attractive combination of chemical, physical, mechanical, and electrochemical properties [7–9]. As a commercially available PEM, Nafion has been widely studied due to its high proton conductivity, excellent chemical and mechanical

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properties [10,11]. However, the high cost and overly dependent on humidity, poor methanol crossover, as well as other problems limit the large-scale commercialization of PEMFCs [12–15]. Thus, there are numerous efforts to develop alternatives to Nafion, PEMs based on PA–PBI are extensively studied for they can work above 130 °C which is preferable from the point of water and heat management [16–20]. However, the conductivity of PA–PBI is affected by the doping levels and relative humidity. Higher doping levels lead to higher proton conductivity but poorer mechanical properties, so there is a tradeoff between doping levels and mechanical properties [5,21].

To overcome the deficiencies, several methods have been explored. An efficient way is to prepare cross-linked membranes. Li *et al.* reported a kind of cross-linked polybenzimidazole membrane using *p*-xylene dibromide as a cross-linker [22]. Epoxy based cross-linked polybenzimidazole was prepared by Han *et al.*, which displayed enhanced mechanical and chemical stability [23]. The structures of cross-linkers greatly affect the properties of cross-linked membranes. For instance, in our previous work, we have prepared two kinds of epoxy-based cross-linked polybenzimidazoles, one cross-linker was 4,4'-diglycidyl(3,3',5,5'-tetramethylbiphenyl) epoxy resin (TMBP), the other was 1,3-bis(2,3-epoxypropoxy)-2,2-dimethylpropane (NGDE) [23,24]. The most obvious difference between these two cross-linkers was the chemical structure, the former was rigid aromatic ring structure and the latter was totally flexible alkyl chain structure. The results indicated that cross-linked PBI membranes using rigid structure cross-linker displayed better combination properties of mechanical strength, oxidative stabilities, high doping levels and proton conductivity. What's more, several researchers have prepared cross-linked polymer membranes using macromolecular cross-linkers, which resulted in high cross-linking density and excellent mechanical properties and chemical stabilities [25–27].

Herein, we prepared a series of novel cross-linked polybenzimidazole using a macromolecular cross-linker with rigid aromatic ring structure, which is bromomethylated poly (aryl ether ketone) (BrPAEK). For the BrPAEK, we can quantitatively control the contents of the bromine tethered to the benzyl groups. To our best knowledge, there is no report about the BrPAEK being used as the cross-linker in the PBI-based systems. The cross-linked membranes were prepared through a gentle and facile heating method. In order to optimize the resulting cross-linked membranes' performance, we blended various amounts of BrPAEK into PBI matrix. The mechanical properties, oxidative and chemical stability of the cross-linked membranes were significantly improved. All the cross-linked membranes were doped with the phosphoric acid (PA) and the proton conductivity of PA/CBrPBI-*X* (*X* is the weight fraction of the cross-linker) was elevated comparing with the pristine PA/PBI. Other properties were assessed as high-temperature PEMs in detail. All the results showed that BrPAEK was a suitable macromolecular cross-linker and the cross-linked membranes would be potentially used in HT-PEMFCs.

2. Experimental section

2.1. Materials

Monomers 3,3'-diaminobenzidine (DAB), diphenyl-*m*-phthalate (DPIP), 3,3',5,5'-tetramethyl-4,4'-biphenol (TMbP) and *N*-bromosuccinimide (NBS) were purchased from Shanghai Jiachen Chemical Co. 4,4'-Difluorobenzophenone (DFBP) was obtained from Yanbian Longjing Chemical Co., and benzoyl peroxide (BPO) used as initiator was provided from Lanzhou Aokai Chemical Co. and used without further purification. All the other reagents were obtained were of commercially available and treated by a standard method before use.

2.2. Synthesis of PAEK

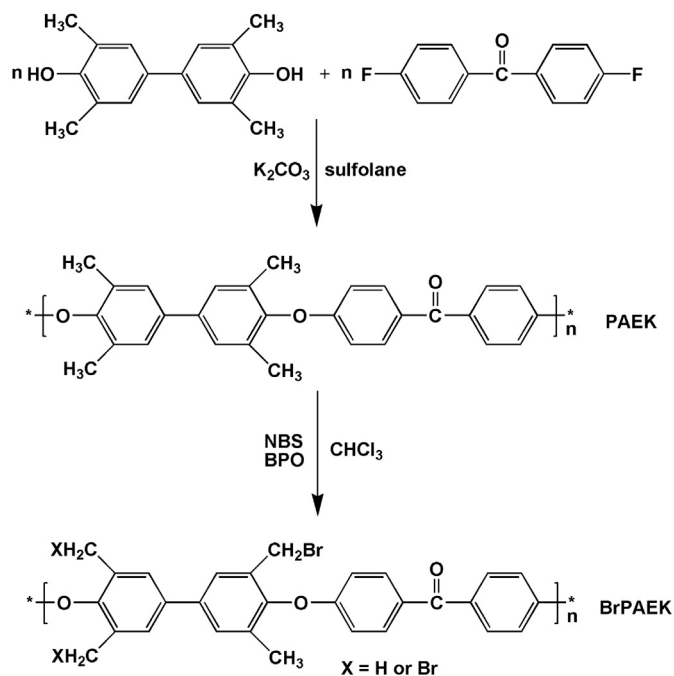
As shown in Scheme 1, poly (aryl ether ketone) (PAEK) was synthesized as follows: (i) DFBP (50 mmol), TMbP (50 mmol), anhydrous potassium carbonate (K_2CO_3) (55 mmol), sulfolane (51 mL) and toluene (30 mL) were added to a 500 mL three-necked flask equipped with a mechanical stirrer, a Dean–Stark trap, and a nitrogen inlet; (ii) The reaction mixture was heated and stirred slowly until the toluene began to reflux at about 140 °C, kept at this temperature for about 3 h and then removed the toluene; (iii) raising the reaction temperature to 210 °C and holding at this temperature until the viscosity of the mixture was high enough; (iv) pouring the viscous solution into cold water; (v) the obtained polymer was thoroughly washed with deionized water and dried in a vacuum oven at 120 °C for 24 h.

2.3. Synthesis of bromomethylated poly (aryl ether ketone) (BrPAEK)

BrPAEK was synthesized by a one-step method, which was clarified in Scheme 1. The bromination process was carried out in chloroform, NBS acted as the bromination reagent and BPO initiated the radical reaction. The specific procedure was as follows: PAEK (5 mmol), NBS (45 mmol), BPO (0.05 g), and chloroform (50 mL) were added to a 250 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, and a condenser. The mixture was slowly heated to 84 °C to reflux and the mixture turned to blood red. After the system was cooled, it was poured into a mixture of ethanol and water. A yellow precipitate was obtained and thoroughly washed with ethanol for several times. The resulting BrPAEK was dried in a vacuum oven at 60 °C for 24 h.

2.4. Synthesis of polybenzimidazole (PBI)

Scheme 2 shows the synthesis process of PBI. A typical two-step melting polymerization was performed as follows: (i) DAB (25 mmol) and DPIP (25 mmol) were added to a 500 mL three-necked flask equipped with a mechanical stirrer and a nitrogen



Scheme 1. The synthesis process of PAEK and BrPAEK.

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