



1,2,4-Triazole functionalized poly(arylene ether ketone) for high temperature proton exchange membrane with enhanced oxidative stability



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ABSTRACT

A series of novel 1,2,4-triazole grafted poly(arylene ether ketone) membranes were prepared to absorb phosphoric acid and used as high temperature proton exchange membranes. Poly(arylene ether ketone) is firstly bromomethylated, followed by nucleophilic substitution of bromomethylated poly(arylene ether ketone) with 3-mercapto-1,2,4-triazole. The structure and the degree of substitution were confirmed by their ¹H NMR spectra. 1,2,4-Triazole functionalized poly(arylene ether ketone) membranes exhibited high thermal decomposition temperature ($T_{d(5\%)}$ higher than 271 °C) and tensile strengths (higher than 78 MPa). After doping with phosphoric acid, these membranes showed enhanced abilities to phosphoric acid absorption with increasing the amount of triazole groups on the side chains. Phosphoric acid doped MTZPAEK(2.15) showed the highest W_{doping} value of 142% and the proton conductivity of 51 mS cm⁻¹ at 190 °C. Remarkably, all the membranes exhibited great oxidative stabilities and could retain their shapes for more than 50 h in Fenton's reagent (3 wt% H₂O₂, 4 ppm Fe²⁺) at 80 °C. This advantage could be ascribed to the unique sulfide groups, which were introduced by nucleophilic substitution reaction and acted as free radical scavengers. The supposed mechanism of enhancing oxidative stability by sulfide groups was confirmed via FT-IR.

1. Introduction

High temperature proton exchange membrane fuel cells (HT-PEMFCs), which usually operate at temperature greater than 100 °C, have drawn much more attention in recent years. HT-PEMFCs not only have the characteristics of high energy conversion efficiency, high energy density and low environment impact, but also offer the significant advantages such as higher tolerance to CO poisoning, enhanced electrode kinetics, less demand for humidification and heat management as well as simplified system design compared to conventional low temperature PEMFCs. Proton exchange membrane is the key component in HT-PEMFCs, which supplies pathways for proton conduction while separating fuels and oxygen gas. A significant work by Wainright et al. investigated polybenzimidazole (PBI) doped with phosphoric acid (PA) as a potential high temperature proton exchange membrane (HTPEM) [1]. The resulting PA doped PBI showed many attractive properties and had a great impact on subsequent research work. In that system, PBI containing *N*-heterocycles not only provided the mechanical strength and thermal stability of the entire membrane, but also provided acid-

base complexation sites for PA due to its basic character. The non-volatile dopant PA formed a continuous hydrogen bond network, in which protons can transport easily by breaking and forming hydrogen bonds. This acid-base complex system had become a typical model and been developed successfully. However, it has been observed that PBI is not a faultless basic matrix. PBI with high molecular weight exhibits proper mechanical properties after doping with PA, but its insolubility in common solvents leads to poor fabricability. On the other hand, the solvent-soluble PBI with relatively low molecular weight has a moderate PA doping level, but its proton conductivity is fairly low [2–4]. Therefore, alternative polymers containing *N*-heterocycles such as pyridine [5], imidazole [6,7], 1,4-diazabicyclo-[2.2.2]-octane [8] and tetrazole [9,10], have been developed as potential candidates to substitute PBI. Among these polymers, poly(arylene ether)s containing *N*-heterocycles are a kind of potential material, owing to their great thermal stability, high mechanical strength and good processibility. For example, Henkensmeier et al. synthesized two tetrazole-modified poly(arylene ether)s, which were doped with phosphate acid and tested for fuel cell relevant properties. The membrane achieved a proton

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conductivity of 25 mS cm^{-1} and a peak power density of 287 mW cm^{-2} at 160°C [10]. Geormezi et al. immersed poly(aryl ether sulfone) membrane containing pyridine structure on the main chain in 85 wt% PA solution at different temperatures for different treating time to obtain HTPEM [11]. The results showed that the conductivity of PA-doped membrane is only 0.014 S/cm at 160°C . Tigelaar's group synthesized a series of poly(aryl ether)s using different contents of monomers containing *N*-heterocycles [12]. The resulting polymer had great thermal and mechanical properties; Nevertheless, *N*-heterocycles were all located on the polymer main chain with rather low content, thereby resulting in low PA doping levels and declined proton conductivities. It has been reported that the acid doping ability is affected by the structure, the location and the content of basic groups. Therefore, the molecular design of *N*-heterocyclic poly(arylene ether) is still a big challenge for HTPEMs with optimized performances.

1, 2, 4-Triazole has a similar structure to imidazole and strong intermolecular hydrogen bonds, but lower pK_a values ($\text{pK}_{a1} = 2.39$, $\text{pK}_{a2} = 9.97$) [13]. *N* (*N* and *N*-H) atoms in the triazole rings can act as proton acceptors and interact with strong acid to form acid-base ion pairs. Therefore, some researchers have mixed 1H-1, 2, 4-triazole with acidic polymers to achieve high proton conductivity at elevated temperature [13,14]. The major weakness of these composite systems is the leakage problem due to the solubility of triazole, which might gradually deteriorate the performance of HT-PEMFCs for long-term operation. To overcome this problem, various strategies have been proposed and carried out by several groups. One typical strategy is to immobilize triazole into monomers. Yan et al. tethered 3-amino-1, 2, 4-triazole onto 3-(glycidylxypropyl)-trimethoxysilane by a ring-opening reaction. Then 1, 2, 4-triazole grafted polysiloxane was achieved through a hydrolysis reaction of the resulting monomers. After doping with PA, it was used as a proton conducting membrane for HT-PEMFCs [15]. The PA-doped polysiloxane membrane exhibited thermal stability up to 250°C and a maximum conductivity of 14.3 mS cm^{-1} at 200°C . Using 1-vinyl-1, 2, 4-triazole to synthesize poly(1-vinyl-1,2,4-triazole) (PVT) via a free-radical polymerization is another effective method. Hazarika and Jana then blended PVT with PBI via a solution blending method. After doping with PA, the blend membrane PBI/PVT(50/50) showed the maximum proton conductivity of 110 mS cm^{-1} at 160°C , which was much higher than that of PBI (39 mS cm^{-1} at 160°C) [16]. Another strategy is to graft triazole groups directly onto polymer side chains. Campagne and co-workers used a two-step reaction (including Finkelstein reaction and nucleophilic substitution reaction) to graft 1H-1,2,4-triazole-3-thiol onto partially fluorinated copolymer [17]. Then the grafted copolymer was blended with sulfonated poly(ether ether ketone) in order to achieve blended membranes for applications in HT-PEMFCs. However, they showed the maximum proton conductivity of only 8 mS cm^{-1} at 140°C under low relative humidity ($\text{RH} < 25\%$), which was much lower than PBI system. Wang and co-workers tethered 3-amino-1, 2, 4-triazole onto sulfonated poly(arylene ether ketone sulfone)s (SPAEEKS) containing carboxylic acid groups via an amide-coupling reaction. The proton conductivities of the triazole groups functionalized SPAEEKS were improved at 120°C under low relative humidity [18]. However, amide bonds on the polymer side chains are probably unstable due to the hydrolysis under strong acid circumstance.

In this study, a facile method of tethering 1, 2, 4-triazole groups onto poly(arylene ether ketone) (PAEK) was successfully achieved via a nucleophilic substitution reaction between bromomethylated PAEK (BrPAEK) and 3-mercapto-1,2,4-triazole (MTZ). BrPAEK with different degrees of bromine substitution (DS) was prepared by a facile and controllable free-radical substitution reaction using *N*-bromosuccinimide (NBS) and benzoyl peroxide (BPO) [19]. Although the reaction of mercapto groups with aryl halides has been reported before [20,21], using mercapto groups to react with benzyl bromide groups as a strategy to modify polymer is firstly reported to the best of our knowledge. Another advantage of the method is that the thioether groups formed by nucleophilic substitution locate on the polymer side

chains, which could significantly enhance the oxidative stabilities of the resulting triazole functionalized PAEKs. After doping with PA, the acid-base composite membranes were comprehensively characterized in terms of mechanical property, thermal stability, PA doping level, dimensional stability and proton conductivity. Moreover, the influences of the amount of triazole groups in PAEK membranes on those properties mentioned above were systematically investigated.

2. Experimental

2.1. Materials

3,3',5,5'-Tetramethyl-4,4'-bisphenol (TMBP) and 4,4'-difluorobenzophenone (DFBP) were purchased from Shanghai Jiachen Chemical Company. NBS, BPO and potassium carbonate were obtained from Sinopharm Chemical Reagent Co., Ltd. MTZ was purchased from Tokyo Chemical Industry Co., Ltd. *N*-methyl-2-pyrrolidone (NMP), toluene, dimethyl sulfoxide (DMSO), 1,1',2,2'-tetrachloroethane and PA solution (85 wt%) were obtained from Tianjin Guangfu Fine Chemical Research Institute. All the reagents and chemicals were used as received without further purification.

2.2. Synthesis and bromomethylation of poly(arylene ether ketone)

TMPAEK containing tetramethyl groups was prepared as follows. TMBP (9.68 g, 0.04 mol), DFBP (8.72 g, 0.04 mol), potassium carbonate (5.52 g, 0.04 mol), DMSO (60 mL) and toluene (20 mL) were added into a 250 mL four-necked flask equipped with a nitrogen inlet, a mechanical stirrer, a thermometer and a Dean-Stark apparatus with a reflux condenser. The whole reactor was filled with nitrogen gas before heating. Then the mixture was heated to 140°C and maintained at this temperature for 4 h until the water was totally separated. The temperature was raised to 180°C and held for another 8 h. After that the viscous mixture was precipitated in distilled water. The precipitation was then collected and washed with boiling water for several times. The yield was 16.2 g (96%). The bromomethylation of TMPAEK was carried out via a free-radical substitution reaction, using NBS and BPO as the brominating reagent and the initiator reagent, respectively. The DS of BrPAEK was determined by the addition amount of the brominating reagent. The preparation procedure was described as follows. NBS (11.56 g, 0.065 mol) and BPO (1.45 g, 0.006 mol) were added into the 1,1',2,2'-tetrachloroethane solution (160 mL) of TMPAEK (16.0 g) with a mechanical agitator. The mixture was heated to the refluxing temperature of 1,1',2,2'-tetrachloroethane and kept for 10 h to form a claret-red solution. The yellow precipitation was got by pouring the reaction mixture into ethanol, and then filtrated and crushed into powder. After washing with ethanol for three times and dried in vacuum oven at 60°C for 12 h, BrPAEK with a DS of 1.53 was obtained to afford a yield of 19.94 g (95%).

2.3. Grafting of 3-mercapto-1,2,4-triazole onto BrPAEK by nucleophilic substitution

The grafting of 1,2,4-triazole onto BrPAEK was taken according to the reaction as shown in Fig. 1. MTZ (1.52 g, 0.015 mol), potassium carbonate (2.07 g, 0.015 mol) and NMP (30 mL) were added in a three-neck flask with a mechanical stirrer. The mixture was heated to 80°C and kept for 3 h under the protection of nitrogen gas. Then the solution was cooled to 40°C . BrPAEK (2.75 g) dissolved in NMP (30 mL) was added to the flask and the reaction was carried out at 40°C for 6 h. The grafted polymer was precipitated in water and washed for several times to remove unreacted MTZ and potassium carbonate. The resulting polymer termed MTZPAEK was collected by filtration and then dried in a vacuum oven at 60°C . The yield was 3.24 g (86%).

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