



Astonishing synergetic effect of proton conducting between phosphonic acid groups and triazolyl groups tethered simultaneously on poly(ether sulfone) backbone

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ABSTRACT

A novel phosphonic acid and triazolyl functionalized poly(ether sulfone) (PES-TriPA) containing simultaneously phosphonic acid and triazolyl side groups is synthesized. The PES-TriPA is prepared by polycondensation of phosphonated bisphenol (PBP) and 3,3'-diethynyl-4,4'-difluorodiphenylsulfone, followed by click reaction to introduce triazolyl groups and hydrolysis to free phosphonic acid groups. Phosphonic acid functionalized poly(ether sulfone) (PES-PA) and triazolyl functionalized poly(ether sulfone) (PES-Tri) are also synthesized for comparison with PES-TriPA. The proton conducting polymers are hot-pressed into proton exchange membranes, and the membrane morphologies, proton conductivities, oxidation and thermal stabilities, water uptakes and methanol permeabilities are characterized. PES-TriPA exhibits more excellent comprehensive properties in comparison with PES-PA and PES-Tri. At 100 °C and 90% relative humidity (RH), the proton conductivity of PES-TriPA reaches 113.0 mS cm⁻¹, in comparison with 55.7 mS cm⁻¹ for PES-PA and 4.3 mS cm⁻¹ for PES-Tri. PES-TriPA also shows better oxidation stability with 95.7% weight left after Fenton's test at 80 °C for 120 h, while only 68.7% left for PES-PA and 75.7% left for PES-Tri. In addition, PES-TriPA exhibits favorable thermal stability and water uptake compared with PES-PA and PES-Tri. Moreover, the methanol permeability of PES-TriPA is only 0.24 × 10⁻⁸ cm² s⁻¹, which is lower than these of PES-PA and PES-Tri with 0.77 × 10⁻⁸ cm² s⁻¹ and 1.20 × 10⁻⁸ cm² s⁻¹, respectively. These superior characteristics are attributed to the synergetic effect between the phosphonic acid groups and triazolyl groups caused by the intermolecular hydrogen bonding interaction throughout the PES-TriPA acid-base amphoteric polymer.

1. Introduction

As the fossil fuel reserves are being depleted rapidly, the exploitation of sustainable energies and the development of new efficient energy conversion technologies have drawn more and more attention from both industrial sectors and academic institutes [1]. Fuel cells are energy conversion devices which convert chemical energy released from chemical reaction directly into electric energy without combustion [2,3]. Among the various designs of fuel cells, proton exchange membrane fuel cells (PEMFCs) have stood out as one of the most competitive fuel cell types and attracted most research attentions. The advantages of PEMFCs include the high energy conversion efficiency, high power and energy density, low pollutant emission, satisfactory safety performance [4]. However, the high materials cost of PEMFCs, and the lack of technologies and infrastructures to economically produce, distribute, and store hydrogen have hampered the large scale

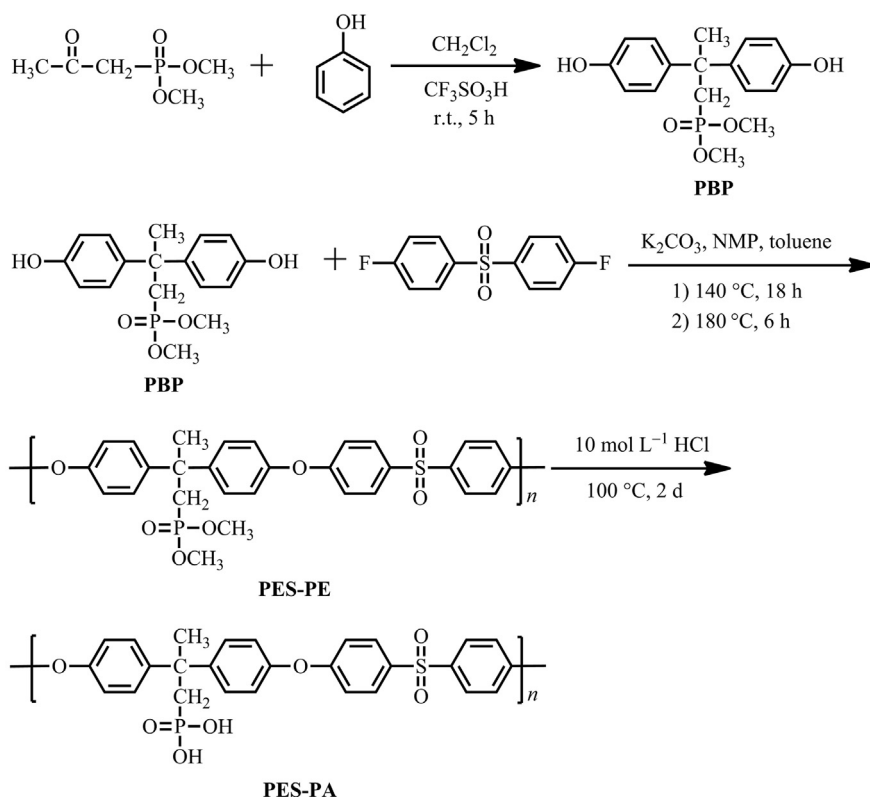
commercialization of PEMFCs [5–7].

Among the few issues hindering the large scale commercial application of PEMFCs, the high costs and inferior properties of proton exchange membranes (PEMs) and electrocatalysts are the most obstinate obstacles [8–10]. The PEMs are made of proton conducting materials to transport proton from anode to cathode in PEMFCs and thus to close the electric circuit. Nowadays, the most accepted proton conducting material is poly(perfluorosulfonic acid) (PFSA), such as NAFION, which has been commercialized long before and dominates the application in the chlor-alkali industry. However, the low proton conductivity under high temperature and low relative humidity (RH), high methanol crossover and high cost have hindered the wide commercial application for PEMFCs [11–13].

In order to overcome the disadvantages of PFSA, PEMs containing phosphoric acids have attracted great research interests [14–17]. These PEMs can be obtained by doping phosphoric acid [18–20]. For example,

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Scheme 1. Synthesis of PES-PA.

Seo et al. doped phosphoric acid into sulfonated poly(tetra phenyl phthalazine ether sulfone) (SPTPPES) [21], while Yue et al. prepared phosphoric acid-doped organic-inorganic cross-linked sulfonated poly (imide-benzimidazole) (CSiSPIBI) [22]. However, phosphoric acid is an extremely hydrophilic material and prone to leakage during the operation of PEMFCs, thus increasing the difficulties of fuel cell administration. The leakage of phosphoric acid can be overcome by grafting phosphonic acid groups onto existing polymers [23–25]. For example, Lafitte et al. prepared phosphonated polysulfone (PSU) by lithiation, phosphonation and hydrolysis [26,27]. The other method to synthesize phosphonated polymers is to directly polymerize or condense phosphonic acid functionalized monomers, such as vinylphosphonic acid (VPA) [28–30]. Abouzari-Lotf et al. synthesized phosphonated poly (arylene ether)s by polycondensation of phosphonate ester functionalized bisphenol and decafluorobiphenyl [29].

Compared with sulfonated polymers, the phosphonated polymers possess relatively low proton conductivity at low temperature and under well hydrated states [31,32]. For instance, Abu-Thabit et al. synthesized phosphonated polysulfone with DS (degree of substitution) of 1.5, while its proton conductivity only reached 12 mS cm^{-1} at 100°C under fully hydrated conditions [33]. Therefore, it is necessary to introduce new functional groups to promote proton conducting for the phosphonated polymers [34]. Among the few possible functional groups, 1*H*-1,2,3-triazolyl group is one of such functional group promoting the proton conducting attributing to the abundant hydrogen-bonding possibility with phosphonic acid groups and multifold intra- and intermolecular proton transport pathways [35,36]. It can also strengthen the thermal, oxidative and chemical stabilities of the phosphonated polymers [37–42]. Moreover, we observed the synergetic proton transport effect, the orders of magnitude increase in proton conductivity, in the acid-base composites composed of phosphonic acid groups and triazolyl groups [43]. In one example, the acid-base composite composed of phosphonic acid functionalized polystyrene (PS-PA) and triazolyl functionalized polystyrene (PS-Tri) achieved about three

folds improvement in comparison with pristine PS-PA [44].

In this work, we are going to synthesize an amphoteric polymeric material, PES-TriPA, by polycondensation instead of composite or other methods above [43–47]. The uniqueness of current work is that both acidic phosphonic acid groups and basic 1,2,3-triazolyl groups are tethered on same polymer backbone, even on the same repeat unit. Such design will certainly increase the hydrogen bonding interaction between phosphonic acid groups and 1,2,3-triazolyl groups and thus is supposed to strengthen the synergetic proton transport effect to the maximum content. Polycondensation not only increases the DS compared with grafting, but also promotes polycondensation due to its relatively low steric hindrance in comparison with phosphonic acid groups tethered directly on benzene ring. In addition, PES-PA and PES-Tri are also synthesized for comparison with PES-TriPA about properties as mono-functionalized polymers.

2. Experiment

2.1. Materials

Dimethyl 2-oxopropylphosphonate (95%), phenol ($\geq 99\%$), trifluoromethanesulfonic acid (98%), sodium ascorbate (NaAsc, 99%), calcium hydride (98.5%), 1-methyl-2-pyrrolidinone (NMP, 99.5%) and bis(triphenylphosphine)palladium (II) chloride ($(\text{PdCl}_2(\text{PPh}_3)_2)$, 15.2% Pd) are purchased from Aladdin Reagent Inc. Bisphenol A (BPA, AR), potassium hydroxide (AR), potassium carbonate (AR), copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, AR), anhydrous sodium sulfate (AR), anhydrous magnesium sulfate (AR), phosphorus pentoxide (P_2O_5 , AR), *N,N*-dimethylformamide (DMF, 99.5%), methanol (AR), copper (I) iodide (CuI, AR), triethylamine (Et_3N , AR), tetrahydrofuran (THF, AR), toluene (AR), dichloromethane (AR), hydrogen peroxide (H_2O_2 , 30%), hydrochloric acid (36–38%) and sulfuric acid (AR) are purchased from Sinopharm Chemical Reagent Co., Ltd. Trimethylsilylthyne (97%) is purchased from Accela ChemBio (Shanghai) Co., Ltd. Chloromethyl

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