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Intermolecular ionic cross-linked proton conducting electrolyte membranes derived from branched sulfonated poly(ether ether ketone)s with benzoxazole pendants

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ABSTRACT

A series of novel branched sulfonated poly(ether ether ketone)s containing intermolecular ionic cross-linkable groups, benzoxazole groups, have been prepared for direct methanol fuel cells. The benzoxazole groups are grafted onto the polymer chain via a thiol-ene click chemistry reaction. The expected structures of the copolymers are confirmed by ^{1}H NMR and Fourier transform infrared spectroscopy. Compared with the unmodified polymer membrane, the ionic cross-linked membranes show enhanced thermal and mechanical properties. We also investigate the changes in water uptake, proton conductivity and chemical stability. The dense membrane structures formed by branching and the interactions between sulfonic acid and benzoxazole groups make a great contribution to the improvements of dimensional stability and methanol resistance property. Although the proton conductivities of the ionic cross-linked membranes are lower than the pristine membrane, the selectivities are much higher. The results show that the novel copolymers in this study are possible potential candidate materials for proton electrolyte membrane.

1. Introduction

Proton electrolyte membrane (PEM), from which protons transfer the anode to cathode, is one of the key elements in solid typed fuel cells such as polymer electrolyte fuel cells and direct methanol fuel cells (DMFCs) [1]. Nafion®, a commercially available perfluorinated sulfonic acid ionomer (PFSA), possesses high proton conductivity, excellent mechanical property and good chemical stability [2]. However, its high cost, high methanol crossover and low conductivity at low humidity or high-temperature operating condition encourage the development of alternative proton conductive polymers [3,4]. Some acid functionalized aryl type hydrocarbon polymers have been widely studied to replace PFSA as potential substitute membrane materials [5]. Therefore, alternative materials such as sulfonated polyimides [6,7], sulfonated poly(ether ether ketone)s [8,9], sulfonated poly(arylene ether sulfone)s [10,11] and acid doped poly(benzimidazole)s [12,13] fall into this category for their remarkable mechanical, thermal and chemical stabilities.

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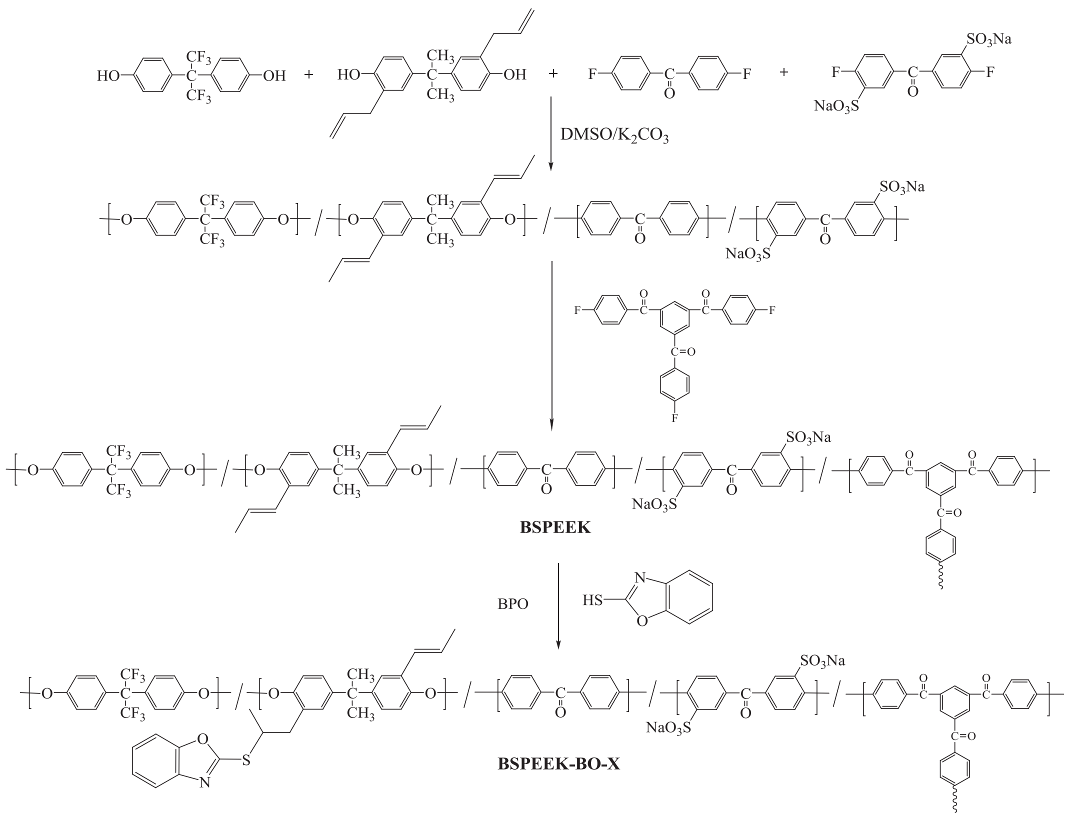

Scheme 1 – Synthesis of BSPEEK and BSPEEK-BO copolymers.

Sulfonated poly(ether ether ketone)s (SPEEK) have been singled out because of their excellent mechanical properties, acceptable cost and high proton conductivities for highly sulfonated membranes [14,15]. Generally, the proton conductivities of SPEEK increase with the sulfonation degree values (SD). However, when the SD reaches a high level, the membranes swell dramatically in hydrated states and become very brittle in the dry state, leading to a decrease of mechanical properties. The highly swollen state also results in a high crossover of fuel along the large hydrophilic channels, particularly methanol [16,17]. From the point of view of polymer structure design, the modification of the basal polymer backbone is a strategy to overcome this compromise of properties [18,19]. Hay et al. reported branched poly(ether ketone)s bearing 6 sulfonic acid groups on each hexaphenylbenzene end group, and their proton conductivities were comparable to that of Nafion® at the same IEC level [20]. Wang et al. reported the preparation of branched sulfonated poly(arylene ether ketone sulfone)s with 1,1,1-tris-p-hydroxy-phenylethane as the branching agent. This research indicated that the branching had a positive effect on the oxidative stability and mechanical strength [21]. Recently, our group reported the preparation of branched sulfonated poly(ether ether ketone)s containing 1,3,5-tris(4-fluorobenzoyl)benzene as the branching agent. Compared with the membrane formed by linear polymers, the branched membranes showed improved mechanical strength, excellent dimensional stabilities and low methanol permeabilities with similar proton conductivities [22].

Cross-linking is a simple and powerful approach to overcome the limitations of the intrinsic properties of sulfonated aromatic polymers. Many researches revealed that the cross-linking could significantly hinder the excess swelling and limited methanol diffusion of the sulfonated polymer [23–25]. Na et al. reported a series of acid–base composite membranes by blending SPEEK and Polybenzimidazole (PBI), and the membranes presented reduced water uptake and methanol permeability [26]. However, it would be hard to get a homogeneous membrane due to the poor solubility of PBI in some cases. Manthiram et al. prepared the composite membranes based on sulfonated poly(ether ether ketone) and basic small molecules containing benzimidazole groups, and the resulted membranes exhibited enhanced proton conductivities and reduced methanol permeabilities [27]. However, the small molecules might leach out during usage in fuel cells.

In the present study, branched sulfonated poly(ether ether ketone)s containing propenyl groups (BSPEEK) were synthesized via a two-step process. As shown in Scheme 1, the benzoxazole groups were grafted onto the BSPEEK backbone by the thiol-ene click reaction between propenyl and thiol groups. Due to the self-combination at the intermolecular level, the ionic cross-linking of the resulting functionalized polymer avoided the basic small molecules leaching out from the membranes, as well as the incompatibility behavior among the various components. With the addition of the branching structure and the ionic cross-linked structure formed between benzoxazole and sulfonic acid groups, the membranes were expected to possess excellent thermal stabilities, mechanical properties and low methanol permeabilities. Moreover, other chemical and physical properties of the ionic cross-linked membranes were studied in detail.