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Preparation, characterization, and properties of poly(styrene-b-sulfonated isoprene)s membranes for proton exchange membrane fuel cells (PEMFCs)

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ABSTRACT

A series of poly(styrene-b-isoprene) block copolymers (PSI) were synthesized by sequential anionic polymerization of styrene and isoprene. Poly(styrene-b-sulfonated isoprene) block copolymers (PSsI) were prepared via reacting the double bonds of the isoprene block with 1,4-dioxane/sulfur trioxide. The spherical-shaped ionic clusters within the PSsI membranes produce a comparable proton conductivity (10^{-1} S/cm above 60 °C) but benefits from approximately 50% lower methanol permeability than that of Nafion-117. Properties, such as proton conductivity and water content values, of PSsI membranes correlate highly to the content of the sulfonated isoprene block in PSsI samples even in the cases of similar IEC. As the hydrophilic block length is increased, the water content and proton conductivity also increased.

1. Introduction

There have been extensive studies into polymer electrolyte membrane fuel cells (PEMFCs) that utilize an ionomer electrolyte membrane. PEMFCs have a wide array of applications, such as utilization in residential power sources, portable electronics, and electric vehicles [1–3]. While serving as a solid, ionic conductor that transports electrochemically generated protons from anode to cathode, the electrolyte membrane also acts as barrier that prevents undesired mixing of reactant gasses [4]. Performance of the fuel cell is largely determined by mechanical strength, chemical stability and proton conductivity of the membrane [5]. Currently, Nafion-117 is the most widely used proton exchange membrane (PEM) [6–8] due to its high chemical and mechanical stability along with its high proton conductivity; however, due to its high cost and difficulties encountered during synthesis and processing [9–11], efforts have been made to provide a more economical and usable alternative [12–14].

While originally developed for use in PEMFC applications [14,15], these membranes are commonly utilized in direct methanol fuel cells (DMFCs). The phase-separated membrane is composed of a hydrophobic matrix and ionic channels [16]: interconnected hydrophilic clusters that transport ions inside the membrane [17]. Formation of these channels is caused by micro- or nano-phase separations between the hydrophilic proton exchange sites and the hydrophobic domain. A recent literature has investigated proton conductivity, morphology and physical properties of polystyrene-containing block copolymers. These include partially sulfonated poly(styrene-b-(ethylene-co-butylene)-b-styrene) (S-SEBS) [18–21], sulfonated poly(styrene-b-isobutylene-b-styrene) (S-SIBS) [22,23], sulfonated hydrogenated poly(butadiene-b-styrene) (S-HPBS) [24,25], poly(styrene-b-ethylene/propylene-b-styrene) (S-SEPS) copolymer [26] and sulfonated poly(styrene-b-ethylene-alt-propylene) (S-SEP) [26,27]. Studies have also indicated that the orientation of ionic domains in the PEM could have a significant effect on proton conductivity. The composition of the copolymer and preparation conditions of the membrane is critically important. For an example, Park et al. [28] studied a series of poly(methyl butylene) (PMB)-b-SPS diblock polymers and showed that the bicontinuous morphologies, such as gyroid or perforated lamellae, improved proton conductivity.

In the present study, we report the synthesis and characterization of proton-conducting membranes. Poly(styrene-b-sulfonated isoprene) (PSsI) is composed of a hydrophobic polymer block of polystyrene and a hydrophilic polymer block of sulfonated polyisoprene as shown in Scheme 1. There are some interesting phenomena to investigate in these particular diblock copolymers. To begin, the two segments of hydrophilic–hydrophobic block copolymers (PSsI) are immiscible. This ensures self-assembly and ionic aggregation. In addition, through utilization of controlled anionic polymerization to grow the polystyrene and polyisoprene chains, length and ionicity of the hydrophilic block can be controlled through the modification of sulfonated polyisoprene chain length or degree of sulfonation. By investigating the relationships among composition, structure,

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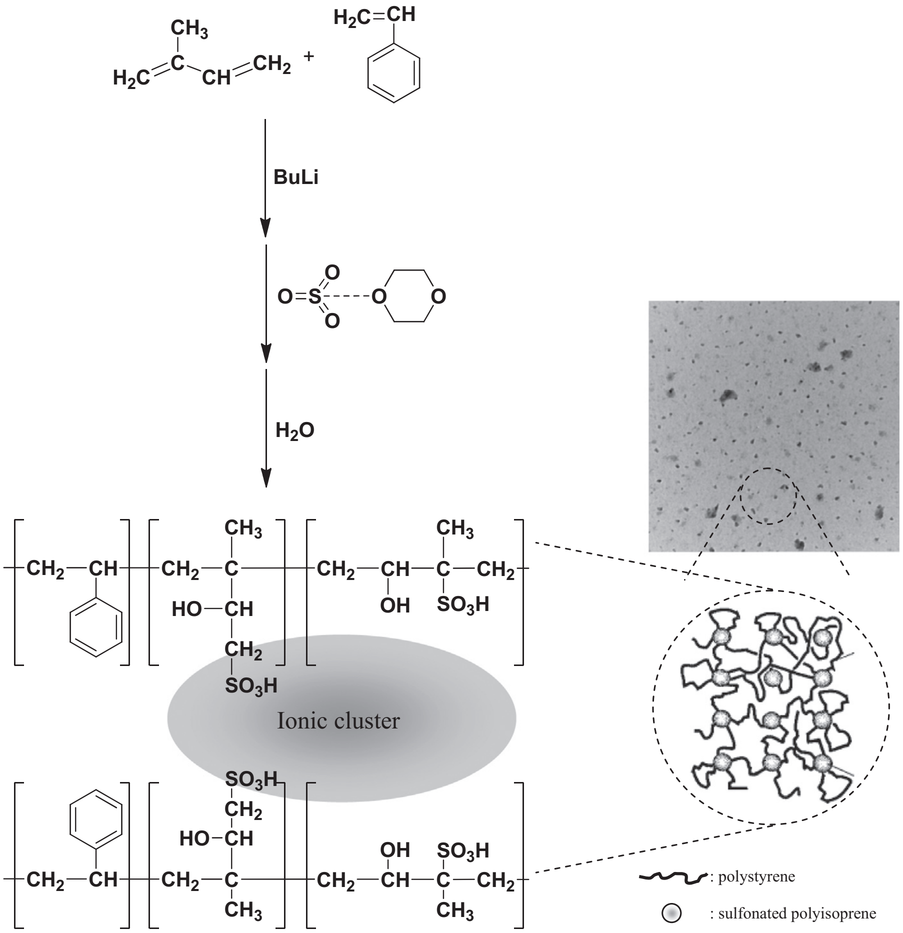

Scheme 1. Schematic representation of synthesis of sulfonation reactions of poly(styrene-b-isoprene).

morphology, and proton conductivity, the general properties of PSsI membranes were ascertained.

2. Experimental

2.1. Materials

Styrene monomer (99%) was purchased from ACROS. Isoprene monomers (99%) were purchased from Alfa. N-butyllithium (1.6 M) was purchased from Chemetall. 1,4-dioxane (99.9%) was purchased from J.T. Baker and purified by distillation. Chlorosulfonic acid was purchased from Fluka. Cyclohexane (100%) was purchased from TEDIA.

2.2. Synthesis of poly(styrene-b-isoprene) (PSI) copolymers

The styrene–isoprene block copolymers, for example PSI(25/75), were prepared by living anionic polymerization as follows: 0.17 g n-butyllithium (1.6 M) was added to 45 ml of dried cyclohexane and 2.54 g (24.42 mmol) styrene, and the mixture was stirred for 3 h. After the 7.44 g (109.41 mmol) isoprene was added to the polystyrene living anion solution for block copolymerization. The polymerization was terminated by addition of a 5% (v/v) methanol/water solution. The PSI(25/75) diblock copolymer was precipitated by pouring the solution slowly into methanol, dried in vacuum at room temperature. With different feeding ratios of monomers, these PSIs are labeled as PSI(25/75), PSI(50/50), and PSI(75/25), where the associated digits denote the weight ratio of styrene/isoprene.

2.3. Synthesis of poly(styrene-b-sulfonated isoprene) (PSsI) copolymers

The poly(styrene-b-sulfonated isoprene) copolymers, for example PSI(25/75)-1.0, were prepared below. A solution of sulfur trioxide/1,4-dioxane complex was first prepared by adding chlorosulfonic acid(1.8 g) drop-wise to 1,4-dioxane(18 g) with stirring. The solution was stirred and kept at room temperature for 2 h. With stirring, a predetermined amount of the prepared sulfur trioxide/1,4-dioxane complex solution was added drop-wise to a 25 g 1,4-dioxane solution containing 1.5 g of the PSI block copolymer. The solution was kept below 25 °C during the reaction by water-cooling for 2 h, then 20 g of distilled water was added to neutralize the solution. The mixture was heated to 80 °C for 4 h with stirring. Aqueous solutions of sulfonated block copolymers were obtained after removing organic solvents through evaporation under reduced pressure. The aqueous solutions of the polymers were dialyzed against deionized water. Dry PSsI samples were recovered by freeze-drying.

2.4. Characterization

The ion exchange capacity (IEC) was determined through classical titration. Following immersion in a saturated sodium chloride solution, the subsequent release of protons in solution was titrated using 0.05 N sodium hydroxide aqueous solution.

Differential scanning calorimetry (DSC) measurements for dry membranes were conducted on a DuPont TA2010 analyzer over the temperature range of 40–140 °C at a heating rate of 20 °C/min while being subjected to a dry nitrogen atmosphere. In the fully