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1,6-Bis(4-vinylphenyl)hexane as a crosslinking agent for the preparation of crosslinked sulfonated poly(ether ether ketone) membranes by EB irradiation

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HIGHLIGHTS

- 1,6-Bis(4-vinylphenyl)hexane (BVPH) was prepared as a crosslinking agent.
- Sulfonated poly(ether ether ketone) was crosslinked using BVPH via EB irradiation.
- The crosslinked membranes showed greatly improved dimensional and chemical stability.
- The crosslinking process only slightly decreased the proton conductivity.
- The crosslinked membranes exhibited substantially reduced methanol permeability.

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ABSTRACT

In order to mitigate problems associated with highly sulfonated aromatic hydrocarbon membranes, such as dimensional stability, mechanical strength, and methanol crossover, sulfonated poly(ether ether ketone) (SPEEK) membranes containing 1,6-bis(4-vinylphenyl)hexane (BVPH) were crosslinked by EB irradiation. Compared to the pristine SPEEK membrane, the crosslinked membranes exhibited significantly improved dimensional stability, chemical stability, and mechanical strength. The crosslinking procedure slightly reduced the proton conductivity of the membranes. The crosslinking of SPEEK with BVPH was also found to slightly reduce the proton conductivity of the membranes, but significantly reduced the methanol permeability.

1. Introduction

Perfluorinated polymer membranes with sulfonic acid groups such as DuPont™ Nafion® are commonly employed as proton-conducting membranes of polymer electrolyte membrane fuel cells, due to their good mechanical and chemical properties, excellent proton conductivity, and long-term durability (Mauritz and Moore, 2004). However, because of drawbacks of high cost and low performance at high temperature, alternative membranes such as sulfonated poly(ether sulfone)s, poly(ether ketone)s, poly(phenylene)s, polyimides, and polybenzimidazoles have been actively investigated (Park et al., 2011; Iojoiu et al., 2006; Smitha et al., 2005; Hickner et al., 2004; Li et al., 2003). However, the highly sulfonated membranes can have problems in dimensional stability and mechanical strength due to their excess water uptake.

One simple approach to overcome such problems associated with excessive water uptake is to crosslink the polymer membranes. Various crosslinking methods have been employed for aromatic hydrocarbon membranes. For example, polymer membranes were crosslinked via esterification (Lee et al., 2006), UV irradiation (Zhong et al., 2007, 2009; Park et al., 2012), Freidel–Craft reaction (Rhoden et al., 2011; Han et al., 2010, 2011; Phu et al., 2009), and electron beam irradiation (Song et al., 2011, 2013). Most of the crosslinked membranes exhibited improved

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dimensional stability, though each method can have some advantages and disadvantages. Among the several different methods, the electron beam-induced crosslinking method seems to be the most convenient due to the fast process, deep penetration of the electron beam, and the lack of need for an initiator and high reaction temperature.

Shin et al. developed an electron beam (EB)-induced crosslinking method of sulfonated poly(ether ether ketone) (SPEEK) (Song et al., 2011, 2013). Briefly, SPEEK membranes containing polyester acrylate, triacrylate. diacrylate, and monoacrylate were irradiated by EB at room temperature. With increasing crosslinker content from 10 to 50%, the gel fraction increased, but both ion exchange capacity (IEC) and proton conductivity decreased. They also found that the crosslinked SPEEK (c-SPEEK) membranes had well-developed ionic aggregation in the cluster region since the ionic aggregation is not largely affected by the EB irradiation. However, the crosslinkers used for their study have ester bonds that can be hydrolyzed under acidic and high temperature conditions, which are similar to the operational conditions of fuel cells.

Divinylbenzene (DVB) is a commercially available crosslinker of p- and m-isomer, and is not hydrolysable under acidic conditions. DVB, especially p-isomer, is highly reactive to undergo inhomogeneous and inefficient crosslinking with other comonomers such as styrene, due to the conjugation of the vinyl groups over the aromatic ring of p-isomer (Sundell et al., 1993). One approach to reduce the high reactivity of DVB is to incorporate a hydrocarbon chain between two styrene molecules such that the two vinyl groups are insulated from each other. In this study, 1,6-bis(4-vinylphenyl)hexane (BVPH), an unhydrolyzable crosslinker, was prepared and used to crosslink SPEEK membranes by EB irradiation at room temperature. This paper describes the synthesis and characterization of the c-SPEEK membranes.

2. Experimental

2.1. Materials

PEEK powder (Victrex®) was dried in a vacuum at 130 °C for at least 12 h prior to sulfonation. 4-Bromostyrene,1,6-diboromhexane, $CuBr_2$, sulfuric acid, and N,N-dimethyl acetamide (DMAc) were purchased from Sigma–Aldrich and used without further purification.

2.2. Sulfonation of PEEK

PEEK was sulfonated following a reported method (Song et al., 2011). Briefly, PEEK powder (35 g) was added slowly to sulfuric acid (98 wt%, 500 mL) at room temperature under a nitrogen atmosphere. After the PEEK was dissolved completely, the resulting solution was stirred at 60 °C for 2 h. The polymer solution was then cooled to 5 °C in an ice-water bath to terminate the reaction and poured into a large amount of ice water (ca. 5 times the volume) with stirring using a glass rod. The isolated polymer was washed with deionized water until a neutral pH was achieved. The prepared SPEEK was dried at 25 °C for 12 h and then 50 °C for 5 h in a vacuum oven. The degree of sulfonation (DS) of the SPEEK was determined to be 0.55 based on its ^{1}H NMR spectrum (Song et al., 2013).

2.3. Synthesis of 1,6-bis(4-vinylphenyl)hexane(BVPH)

Magnesium ribbons (0.334 g, 13.8 mmol) and a few small grains of iodine were placed into a three-necked round-bottomed flask equipped with a reflux condenser, which was placed in an ultrasonic apparatus. A solution of 4-bromostyrene (1.63 mL, 12.5 mmol) in dry THF (15 mL) was added dropwise, and the resulting mixture was subjected to ultrasonic radiation for 1 h min until the magnesium ribbon disappeared, followed by the addition of a mixture of 1,6-dibromphexane (0.96 mL, 6.25 mmol) and $CuBr_2$ (2 mol% in dry THF, 10 mL) at 5 °C. The resulting mixture was continuously subjected to ultrasonic radiation again for 1 h, and quenched by the addition of a dilute aqueous HCl solution. The reaction mixture was washed with water and extracted with ether. The organic fractions were combined and dried over $MgSO_4$. The solvent was removed by a rotary evaporator, and the concentrated crude product was purified by silica column chromatography using hexane as an eluent to give a colorless oil product (yield: 56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.31 (d, 4H), 7.13–7.12 (d, 4H), 6.72–6.65 (m, 2H), 5.72–5.67 (d, 2H), 5.20–5.17 (d, 2H), 2.61–2.57 (t, 4H), 1.66–1.60 (m, 4H), 1.38–1.32 (m, 4H); FT-IR (KBr, cm^{-1}): 3084, 3005, 2932, 2853, 1632, 1605, 1408, 990, 904.

2.4. Preparation of membranes

The SPEEK was dissolved in DMAc to form a 10 wt% solution, followed by the addition of BVPH, so that the BVPH content was 5, 10, and 15 wt% with respect to SPEEK. The resulting solutions were cast onto glass plates. The cast membranes were dried in an oven at 70 °C for 40 min, and then irradiated with EB at a dose of 100–400 kGy with a dose rate of 6 kGy/min at room temperature (Korea Atomic Energy Research Institute, Advanced Radiation Technology Institute, Jeongup, Korea). The irradiated membranes were dried at 110 °C for 4 h in an oven.

2.5. Gel fraction

The gel fraction was estimated from the weight change of the irradiated SPEEK membrane before and after the dissolution of the membrane in DMAc. The gel fraction value was calculated using

$$\text{gel fraction}\ (\%) = (W/W_o) \times 100,$$

where W_o is the weight of the initial membrane and W is the weight of the remaining membrane after dissolution.

2.6. Ion exchange capacity (IEC)

The IEC of polymer membranes was measured using a titration method. Dry membranes were immersed in an aqueous 1.0 M NaCl solution for 24 h, and the resulting solution was subsequently back titrated with a 0.01 M NaOH solution using a titration buret and phenolphthalene as an indicator. The IEC was calculated using the following equation:

$$\text{IEC}\ (\text{mmol}/g) = [C_{\text{NaOH}} \times V_{\text{NaOH}}]/W_{\text{dry}}$$

where C_{NaOH} is the NaOH solution concentration, V_{NaOH} is the volume of the 0.01 M NaOH aqueous solution consumed in the volumetric titration, and W_{dry} is the weight of the dry membranes.

2.7. Water uptake

The samples were dried in a vacuum oven at 120 °C for 1 day, and then immersed and maintained in deionized water for 1 day to obtain water uptake equilibrium. The water uptake was calculated using the following equation:

$$\text{water uptake}\ (\%) = (W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \times 100$$

where W_{wet} and W_{dry} are the weight of wet and dry membranes, respectively.