

새로운 연료전지용 술폰화된 PES계 가교 고분자 전해질 막의 개발

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Development of Crosslinked Sulfonated Poly(ether sulfone)s as Novel Polymer Electrolyte Membranes

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요 약. 새로운 연료전지용 고분자 전해질 막으로서 알릴기로 터미네이션된 술폰화된 PES계 고분자를 비스아자이드와의 열적 가교 반응을 이용하여 합성하였다. 공중합체의 조성은 $^1\text{H NMR}$ 에 의해 확인되었다. 전도성 부분인 친수성 영역의 균일한 분포와 견고한 에터 술폰계 고분자 주골격의 끝부분에만 가교기를 도입하여 소수성 영역을 최소화 하는 전략으로 얻어진 가교 고분자 막은 높은 온도에서 우수한 수소이온 전도도와 열적 안정성을 나타내었으며 또한, 나피온에 비해 3배 이상의 수소이온 선택성을 나타내었다.

주제어: 고분자 전해질 막, 술폰화된 에터 술폰계 고분자, 가교화, 수소이온 전도도, 선택성

ABSTRACT. Sulfonated poly(ether sulfone)s (PESs) with a network structure were prepared by heat-induced crosslinking of the allyl-terminated telechelic sulfone polymers using a bisazide and their structure was analyzed by $^1\text{H NMR}$. Having both uniform distribution of the hydrophilic conductive sites and controlled hydrophobic nature by minimized crosslinking, the crosslinked polymer (PES-60) membrane offered excellent proton conductivity at high temperature with a good thermal stability. In addition, selectivity of the crosslinked membrane (PES-60) was more than three times than that of Nafion[®].

Keywords: Polymer electrolyte membrane, Sulfonated poly(ether sulfone)s, Crosslinking, Proton conductivity, Selectivity

INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) have been extensively studied as clean and efficient power sources for applications in electronic vehicles, residential power sources, and portable electronic devices.¹⁻³ Perfluorosulfonic acid (PFSA) membranes, such as Nafion[®], is widely used as the proton exchange membrane in low-temperature fuel cells due to its excellent chemical, mechanical

and oxidative stabilities, as well as its high proton conductivity when fully hydrated.^{4,5} However, the high cost and relatively low performance at higher operating temperatures demand a search for alternative polymer membranes. At elevated temperatures, perfluorosulfonic acid polymers suffer from lowered conductivity due to the loss of water, and significant deterioration in the mechanical strength is accompanied. In addition, methanol fuel readily migrates from the anode, through the PFSA membranes, to the cathode, reducing the open-circuit

potential and poisoning the electrocatalysts at the cathode for the case of DMFCs.⁶ Since methanol crossover seriously retards the commercial viability of DMFCs, there have been extensive research activities to reduce the methanol permeability of Nafion[®] membranes.

Significant efforts have been made to develop new proton exchange membranes,⁷⁻¹⁷ and in some cases, either high proton conductivity^{18,19} or low methanol crossover²⁰⁻²⁴ was achieved. Nevertheless, few membranes have satisfied both high conductivity at elevated temperatures and low methanol permeability.

Sulfonated aromatic polymers, including poly(ether sulfone)s, have been investigated as one of the alternatives to Nafion[®] due to their good physical properties and high proton conductivity.^{6,7,25-29} These properties have been shown to depend on the degree of sulfonation of the aromatic polymer: a high degree of sulfonation degrades physical properties of the humidified polymers, together with an increase in methanol diffusion, whereas an improved proton conductivity under high humidity conditions was obtained. The presence of high sulfonate content was also known to make the membranes soluble in water, and films were hardly maintained or rather prepared.

Crosslinking has often been used as an efficient means to limit methanol crossover and also to enhance physical properties of the highly sulfonated polymers, together with the mechanical stabilities of the membranes. Although a significant reduction in methanol permeability was achieved for the network structure, an inherently lower proton conductivity was accompanied due to an increased hydrophobicity and/or a significant alteration of the membrane microstructure by crosslinking. It has been generally known that these highly hydrophobic films had conductivity usually below 0.1 S cm⁻¹ even at high temperature above 100 °C.

We have recently introduced the highly proton conductive polymers without loss of the structural integrity,³⁰ and report herein a mechanism of crosslinking and a detailed description of the cross-linked sulfonated poly(ether sulfone)s (PESs) having

not only low methanol diffusion coefficient but also high proton conductivity at an increased temperature. Our approach to solve the typical limitations of the sulfonated aromatic polymer electrolyte membrane (good conductivity by high degree of sulfonation at the expense of structural integrity) and the crosslinked system (significant loss of conductivity due to an increased hydrophobicity), was to introduce a crosslinkable site only at the terminus to bring a balanced hydrophobic nature by so-called 'controlled crosslinking'.

EXPERIMENTAL

Materials

4-Fluorophenyl sulfone (FPS), hydroquinone 2-potassium sulfonate (HPS), and bisphenol A (BPA) were obtained from Aldrich chemical Co. and HPS was recrystallized from deionized water. Potassium carbonate, FPS and HPS were dried at 60 °C under vacuum for at least 24 h before polymerization. All other chemicals were obtained from commercial sources and were used without further purification. Nafion[®] membrane (112, 50 μm) was obtained from DuPont, which was treated according to the standard procedure of 30 min in a 5 wt.% H₂O₂ solution at 80 °C, 30 min in Milli-Q water at 80 °C, and 30 min in an 8 wt.% H₂SO₄ solution at 80 °C. After each treatment, the membrane was rinsed with Milli-Q water three times to remove traces of H₂O₂ and H₂SO₄. The membrane was stored in Milli-Q water before use.

Synthesis of the sulfonated poly(ether sulfone) copolymers with a terminal-crosslinkable group

Synthesis of the hydroxy-terminated sulfonated PES-70 (1). A typical process for synthesizing poly(ether sulfone)s (PESs) is as follows. 4-Fluorophenyl sulfone (5 g, 19.6 mmol), bisphenol A (1.12 g, 4.8 mmol), hydroquinone 2-potassium sulfonate (3.59 g, 15.8 mmol) and potassium carbonate (5.57 g, 40.3 mmol) were added to a mixture of dimethyl acetamide (25 mL) and toluene (40 mL) in a 100 mL round bottom flask which was equipped with a Dean-stark apparatus.

The reaction mixture was heated at 150 °C for 4 h. After the water was essentially removed from the reaction mixture by azeotropic distillation, toluene was distilled out. The temperature of the reaction mixture was then raised to 180 °C and allowed to stir at this temperature overnight under a nitrogen atmosphere. After this time, the mixture was cooled to room temperature and dissolved in DMF (30 mL), followed by pouring into methanol (500 mL). The product was collected by filtration and the residual inorganic materials in the polymer were extracted by treatment with deionized water several times. This was repeated twice, and the residue was dried at 60 °C under vacuum for at least 48 h to give the hydroxy-terminated sulfonated PES-70 **1** as a white powder (6.38 g, 64%); δ_{H} (300 MHz, DMSO- d_6) 7.8-8.0 (15H, m, ArH), 7.3-7.5 (3H, m, ArH^d), 6.9-7.3 (29H, m, ArH) and 1.6 (6H, s, CH₃^b); ν_{max} (KBr)/cm⁻¹ 3454, 3100, 2971, 1590, 1473, 1301, 1156, 1028, 872 and 836.

Synthesis of the hydroxy-terminated sulfonated PES-60 (1). This was prepared essentially in the same manner as described for the PES-70 using 4-fluorophenyl sulfone (5 g, 19.6 mmol), bisphenol A (1.57 g, 6.8 mmol), hydroquinone 2-potassium sulfonate (3.13 g, 13.7 mmol) and potassium carbonate (5.57 g, 40.3 mmol) in dimethyl acetamide (25 ml) and toluene (40 ml): white powder (9.05 g, 93%); δ_{H} (300 MHz, DMSO- d_6) 7.8-8.0 (10H, m, ArH), 7.3-7.5 (1.5H, m, ArH^d), 6.9-7.3 (21H, m, ArH) and 1.6 (6H, s, CH₃^b); ν_{max} (KBr)/cm⁻¹ 3454, 3104, 2970, 1590, 1473, 1301, 1156, 1028, 872 and 839.

The hydroxy-terminated sulfonated PES-50 (1)

This was prepared essentially in the same manner as described for the PES-70 using 4-fluorophenyl sulfone (5 g, 19.6 mmol), bisphenol A (2.01 g, 8.82 mmol), hydroquinone 2-potassium sulfonate (2.68 g, 11.76 mmol) and potassium carbonate (5.57 g, 40.3 mmol) in dimethyl acetamide (25 ml) and toluene (40 ml): white powder (9.1 g, 93%); δ_{H} (300 MHz, DMSO- d_6) 7.8-7.9 (9H, m, ArH), 7.3-7.4 (1.1H, m, ArH^d), 6.9-7.3 (19H, m, ArH) and 1.6

(6H, s, CH₃^b); ν_{max} (KBr)/cm⁻¹ 3448, 3106, 2982, 1585, 1473, 1307, 1156, 1023, 871 and 840.

The hydroxy-terminated sulfonated PES-40 (1).

This was prepared essentially in the same manner as described for the PES-70 using 4-fluorophenyl sulfone (5 g, 19.6 mmol), bisphenol A (2.46 g, 10.78 mmol), hydroquinone 2-potassium sulfonate (2.24 g, 9.8 mmol) and potassium carbonate (5.57 g, 40.3 mmol) in dimethyl acetamide (25 ml) and toluene (40 ml): white powder (9.0 g, 91%); δ_{H} (300 MHz, DMSO- d_6) 7.8-7.9 (7H, m, ArH), 7.3-7.4 (0.7H, m, ArH^d), 6.9-7.3 (16H, m, ArH) and 1.6 (6H, s, CH₃^b); ν_{max} (KBr)/cm⁻¹ 3437, 3112, 2978, 1586, 1470, 1305, 1155, 1022, 873 and 842.

Synthesis of the allyl-terminated sulfonated PES-70 (2).

Sodium hydride (0.77 g, 19.98 mmol) was added in a DMF (50 mL) solution of the hydroxy-terminated PES-70 **1** (9 g, 9.9 mmol) at 0 °C under nitrogen. This was left to stir for 1 h at this temperature before allyl bromide (0.43 mL, 5 mmol) was added. The reaction mixture was stirred at room temperature for 12 h under nitrogen and then precipitated into 500 mL of methanol. The filtrate was collected, washed with deionized water several times and dried at 60 °C under vacuum to give the allyl-terminated PES-70 **2** as a white powder (4.9 g, 43%); δ_{H} (300 MHz, DMSO- d_6) 7.8-8.0 (15H, m, ArH), 7.3-7.5 (3H, m, ArH), 6.9-7.3 (29H, m, ArH), 5.9-6.0 (0.4H, m, CH), 5.5-5.6 (0.8H, m, CH₂), 3.8-3.8 (0.4H, m, CH₂) and 1.65 (6H, s, CH₃); ν_{max} (KBr)/cm⁻¹ 3465, 3098, 2979, 1594, 1474, 1408, 1301, 1259, 1110, 1080, 970, 920 and 841.

Synthesis of the allyl-terminated sulfonated PES-60 (2).

This was prepared essentially in the same manner as described for the allyl-terminated PES-70 using PES-60 **1** (9.0 g, 9.9 mmol), sodium hydride (0.77 g, 19.9 mmol) and allyl bromide (0.43 ml, 5 mmol): white powder (8.8 g, 84%); δ_{H} (300 MHz, DMSO- d_6) 7.8-8.0 (10H, m, ArH), 7.3-7.5 (1.5H, m, ArH), 6.9-7.3 (21H, m, ArH), 5.9-6.0 (0.2H, m, CH), 5.5-5.6 (0.4H, m, CH₂),

3.8-3.8 (0.4H, m, CH_2) and 1.65 (6H, s, CH_3); ν_{\max} (KBr)/ cm^{-1} 3465, 3098, 2979, 1594, 1474, 1408, 1301, 1259, 1110, 1080, 970, 920 and 841.

Synthesis of the allyl-terminated sulfonated PES-50 (2). This was prepared essentially in the same manner as described for the allyl-terminated PES-70 using PES-50 (1) (9.0 g, 9.9 mmol), sodium hydride (0.77 g, 19.9 mmol) and allyl bromide (0.43 ml, 5 mmol): white powder (8.5 g, 94%); δ_H (300 MHz, DMSO- d_6) 7.8-7.9 (9H, m, ArH), 7.3-7.4 (1.1H, m, ArH^d), 6.9-7.3 (19H, m, ArH), 5.9-6.0 (0.2H, m, CH), 5.5-5.6 (0.4H, m, CH_2), 3.8-3.8 (0.4H, m, CH_2) and 1.6 (6H, s, CH_3^b); ν_{\max} (KBr)/ cm^{-1} 3468, 3095, 2983, 1601, 1470, 1408, 1301, 1261, 1109, 1083, 976, 919 and 839.

Synthesis of the allyl-terminated sulfonated PES-40 (2). This was prepared essentially in the same manner as described for the allyl-terminated PES-70 using PES-40 (1) (9.0 g, 9.9 mmol), sodium hydride (0.77 g, 19.9 mmol) and allyl bromide (0.43 ml, 5 mmol): white powder (8.6 g, 95%); δ_H (300 MHz, DMSO- d_6) 7.8-7.9 (7H, m, ArH), 7.3-7.4 (0.7H, m, ArH^d), 6.9-7.3 (16H, m, ArH), 5.9-6.0 (0.2H, m, CH), 5.5-5.6 (0.4H, m, CH_2), 3.8-3.8 (0.4H, m, CH_2) and 1.6 (6H, s, CH_3^b); ν_{\max} (KBr)/ cm^{-1} 3462, 3104, 2979, 1596, 1472, 1407, 1301, 1258, 1110, 1080, 973, 917 and 839.

Characterization of the sulfonated copolymer

FT-IR spectra were recorded using a Nicolet MAGNA 560-FTIR spectrometer. ¹H NMR spectra were recorded on a Bruker Advance DPX-300 instrument using DMSO- d_6 as a solvent. The chemical shift data for each signal are given in units of δ (ppm) relative to tetramethylsilane (TMS) where δ (TMS) = 0, and referenced to the solvent residual.

Fabrication of the crosslinked membranes and acidification

All membranes were prepared in a DMF solution of the corresponding polymers using the solution-casting method, and the film thickness was controlled by a doctor blade. DMF solutions of the

allyl-terminated poly(ether sulfone)s **2** (20%, w/v) were cast onto films in the presence of the 2,6-bis(4-azidobenzylidene)-4-methyl-cyclohexanone **3** (30 wt.% compared to polymers **2**). Thermal curing was accomplished during the drying process. The cast films were then dried in a vacuum oven at 180 °C for 18 h to complete crosslinking. The membranes on the glass plate were soaked into water at room temperature to remove the residual solvent, and the films were peeled off by immersion in deionized water. For acidification, the thermally-cured membranes were immersed in NaOH solution (15% in water) at 80 °C for 4 h, followed by HCl (10% in water) at 80 °C for 3 h, and deionized water at 80 °C for 3 h. Finally, the membranes were washed repeatedly with deionized water.

For comparison, partially crosslinked membranes were fabricated in the same method except the addition of the crosslinking agent **3**, and all the data were compared with those measured using the commercially available Nafion[®]-112 under the same conditions.

Water uptake and ion exchange capacities

Total water uptake (%) was measured as follows: after soaking the membranes in distilled water for more than 24 h, they were wiped with a filter paper and weighed immediately (W_{wet}). The membranes were then dried under a vacuum condition until a constant weight was obtained (W_{dry}). The water uptake (%) by weight is the ratio of the hydrated membrane to the dried membrane.

Ion exchange capacities (IEC) of the membranes were determined by the titration method. A membrane in a H⁺-form was first equilibrated in 2.0 M NaCl solution for 24 h to fully exchange the protons with sodium cations. The membrane was then rinsed with deionized water. The acidity in the NaCl solution was titrated by 0.01 M NaOH. The membrane was then re-acidified, washed and dried to measure the dry weight (W_{dry} , g). IEC (in mequiv./g) was calculated as the moles of exchangeable protons per gram of the dry weight according to Eq. 1.

$$X = \frac{V_{\text{NaOH}} C_{\text{NaOH}}}{m_{\text{dry}}} \left[\frac{\text{meq}}{\text{g}_{\text{dry}}} \right]$$

Equation 1. X: IEC; m_{dry} : weight of the dried membrane; V_{NaOH} : volume of the NaOH solution used; C_{NaOH} : concentration of the NaOH solution.

Thermal properties of the membranes

The thermal stability of the acid form membranes was analyzed by the thermogravimetric analysis measurements on a TGA-2950 instrument at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in a nitrogen flow. Differential scanning calorimetry thermograms were recorded on a Perkin-Elmer Pyris 1 DSC at a scanning rate of $5\text{ }^{\circ}\text{C min}^{-1}$ and indium metal was used as a standard.

Measurements of proton conductivity and methanol diffusion coefficient

Proton conductivity (σ) of each membrane coupon (size: $1\text{ cm} \times 4\text{ cm}$) was obtained using $\sigma = l/RS$ (l : distance between reference electrodes, S : cross-sectional area of a membrane coupon). Here, ohmic resistance (R) was measured by four-point probe alternating current (ac) impedance spectroscopy using an electrode systems connected with an impedance/gain-phase analyzer (SI-1260) and an electrochemical interface (SI-1287) over the frequency range from 10 to 200 kHz. The proton conductivity value was obtained by the average of at least 2 different tests.

Methanol permeability of the membranes was measured at room temperature using a liquid permeability cell. The cell consisted of two reservoirs, which were separated by a vertical membrane coupon with a diameter of 2.5 cm. 5% of methanol solution in water was placed on one side of the cell ($V_A = 15\text{ mL}$) and deionized water was filled on the other side ($V_B = 15\text{ mL}$). The magnetic stirrers were used continuously during the measurements. The concentration-driven diffusion of methanol from compartment A to B across the membrane was monitored as a function of time, by a differential refractive index using a RI-750F

refractometer.

Under conditions of $C_A \gg C_B$ (where C_A and C_B are the methanol concentrations in the A and B compartments), there is a pseudo-steady-state condition prevailing in the two compartments during the initial part of the experiment. Accordingly, the flux of methanol is constant and the relationship of the methanol concentration in the B compartment with time is given by the following Eq. 2.

$$P = a \frac{VL}{AC}$$

Equation 2. P: methanol permeability; a: obtained graph slope/calibration graph slope; A: area of the membrane; V: volume of the one side cell; L: thickness of the membrane; C: concentration of methanol

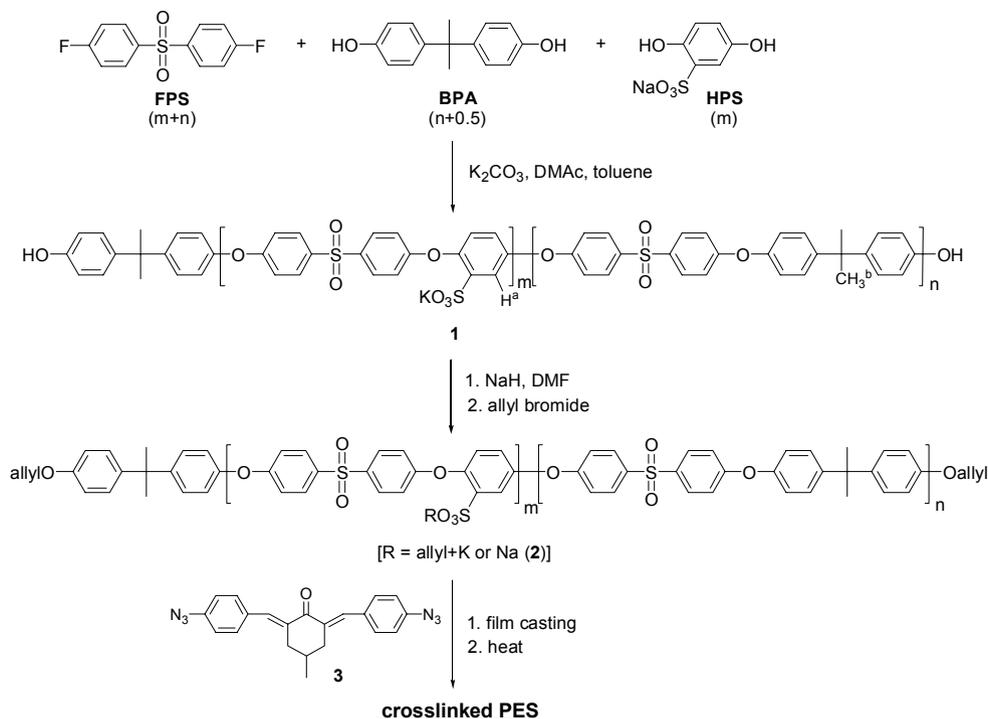
Prior testing, all membrane samples were fully hydrated by immersing in deionized water for 24 h at room temperature.

RESULTS AND DISCUSSION

Synthesis and characterization of the sulfonated poly(ether sulfone)s

The crosslinkable sulfonated poly(ether sulfone)s (PESs) with allyl groups were prepared in two step. The sulfonated poly(ether sulfone)s (PESs) with hydroxy terminal groups (**1**) were first synthesized by the addition-elimination-type polycondensation of hydroquinone 2-potassium sulfonate (HPS, m mole) and bisphenol A (BPA, n mole) with fluorophenyl sulfone [FPS, $(m+n)$ mole]. This was followed by allylation of the terminal hydroxy groups by reacting polymer **1** with NaH and allyl bromide in a DMF solution to produce the allyl-terminated telechelic sulfonated sulfone polymers **2** (Scheme 1). A slight excess of BPA ($n + 0.5$ mole) was used to obtain the sulfonated PESs **1** with terminal hydroxyls, which were then end-capped with allyl groups.

The PESs with different mole% of hydrophilic sulfonate group (PES-40, PES-50, PES-60 and



Scheme 1. Schematic representation for preparing the crosslinked poly(ether sulfone)s

PES-70) were prepared by changing the molar ratios of HPS for the polymerization reaction. The copolymer composition (m:n) was confirmed by comparing the relative ^1H NMR absorption peak areas between H^{a} (7.3 ppm) and H^{b} (1.6 ppm) as

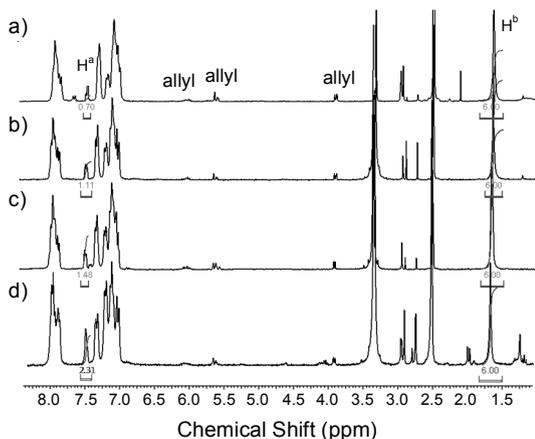


Fig. 1. ^1H NMR spectra of the allyl-terminated PES-40 (a), PES-50 (b), PES-60 (c) and PES-70 (d)

shown in Figure 1. In addition, integration of the allyl protons was compared with those of the aromatic protons, and showed that the degrees of polymerization (D.P.) for the sulfonated PES were in the range of 10 to 18. The polymerization results of the copolymers **2** with different monomer compositions are listed in Table 1.

The films prepared from polymers **2** with acid content from 40 to 60 mole% (PES-40, PES-50 and PES-60) offered uniformity and toughness,

Table 1. Polymerization results of the copolymers **2**

Polymer	D.P. ^a	M.W. ^b	m-K (mol%) ^c
PES-40	17	15,000	42
PES-50	18	16,000	53
PES-60	13	12,000	60
PES-70	10	8,600	69

^aDegree of polymerization. ^bMolecular weight. ^cHPS-SO₃Na unit content in the PES copolymers **2** confirmed by ^1H NMR.

whilst PES-70 having almost 70 mole% of HPS-SO₃H unit in the PES copolymer gave very poor film. Too much hydrophilic nature is ascribed to the inferior film formation for PES-70.

We also hoped that the interaction among the polymer chains could be enhanced by means of crosslinking, leading to an enforced mechanical strength and an increased hydrophobicity for the prepared membranes.

Preparation and characterization of the cross-linked poly(ether sulfone) membranes

To achieve the network structure, DMF solutions of the allyl-terminated poly(ether sulfone)s **2** were cast into films in the presence of bis(aryl azide) (30 wt.% compared to polymer **2**) onto the glass plates, and dried under vacuum at 180 °C for 18 h. During the drying process, the reactive terminal allyl groups in polymers **2** reacted with the bis(aryl azide) to form the polymer network by thermal irradiation (*Scheme 1*). An azide **3** was known to cause a nitrogen loss to produce a nitrene intermediate **4**, which was then reacted with the double bonds to form a mainly aziridine-based polymer network (*Scheme 2*).^{31,32} It is important that oxygen must be excluded as the reaction of a nitrene with molecular oxygen to give a nitroso compound is an extremely facile process.

The crosslinked structure was confirmed by comparing the FT-IR spectra of the sulfonated polymers **2** before and after thermal curing. The absorption peak at 2100 cm⁻¹ corresponding to the azide disappeared and the allyl peaks at 920 cm⁻¹ were reduced in intensity after the thermal process, indicating that the bisazide **3** was effectively incorporated into the allyl-terminated poly(ether sulfone)s

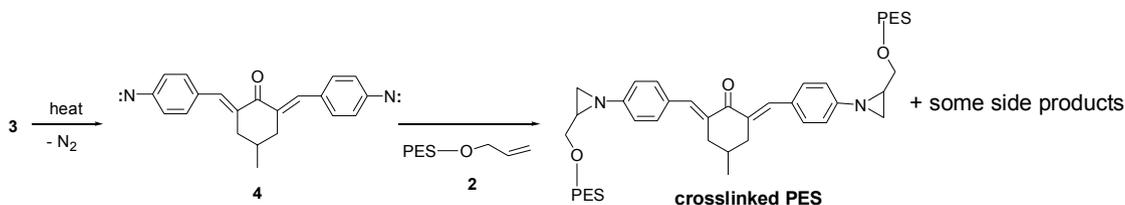
2 to form the crosslinked network.

For comparison, sulfonated PESn membranes (PESn-40, PESn-50 and PESn-60) were also prepared in the same method except the addition of the bis(aryl azide) as a crosslinker during the film casting.

Physical properties of the membranes

Chemical resistance of the prepared membranes was measured by testing membrane solubility in various common organic solvents including DMF and DMSO. The membranes prepared from the azide-assisted thermally cured PESs in all compositions (PES-40, PES-50 and PES-60) were not soluble, whereas the azide-free films (PESn) were slowly dissolved under the same conditions.

The hydrolytic stability was also evaluated by treating the membranes at 100 °C and 100% RH for 24 h for an accelerated testing. The azide-free PESn membranes withstand the condition up to 12 h, after this time it started to decompose, whereas the crosslinked PES membranes did not display any changes in appearance during the evaluation time. Only partial swelling was observed for the crosslinked PES-50 and PES-60 during measurement. The hydrolytic stability of the crosslinked PES-60 membrane, having as high as 60 mole% of hydrophilic unit in the polymer backbone, is particularly beneficial for the PEMFC operation at high temperature. Furthermore, sulfonic acid groups were believed to be intact during the treatment as no changes were observed in the IR spectra of the all crosslinked membranes (PES-40, PES-50 and PES-60). The above results indicate that the azide-assisted crosslinking has successfully improved the chemical resistance and hydrolytic



Scheme 2. Mechanistic representation for the preparation of the crosslinked PES using a bis(aryl azide) as a crosslinker

stability of the sulfonated poly(ether sulfone) membranes.

Water uptake and ion exchange capacities

Water uptake and ion exchange capacities (IEC) are important factors which directly affect proton transportation in proton conducting membranes. In Table 2, the water uptake and IEC data for both crosslinked membranes and their non-crosslinked counterparts were summarized. As expected, water uptake and IEC increase with an increased acid content, and the crosslinking caused a decrease in both values possibly due to an enhanced hydrophobic nature.

Proton conductivity and thermal properties of the membranes

Proton conductivity measurements of the mem-

Table 2. Water uptake and ion exchange capacities of the crosslinked membranes, their azide-free counterparts and Nafion[®]-112 membranes at 25 °C

Membrane	ratio(m:n)	water uptake(%)	IEC (meq/g)
PESn-40	[4:6]	12.89	0.73
Pes-40		10.50	0.72
PESn-50	[5:5]	21.65	0.97
PES-50		16.21	0.83
PESn-60	[6:4]	47.97	1.43
PES-60		24.62	1.18
Nafion [®]		34.91	1.12

branes were performed by means of complex impedance analyses from r.t. to 100 °C, and the film samples were placed in a closed cell to keep the relative humidity at 100%. At room temperature, the more hydrophobic crosslinked membranes (PES-40, PES-50 and PES-60) showed lower proton conductivity than the corresponding azide-free membranes (PESn-40, PESn-50 and PESn-60), and the conductivity increased with an increase of the acid content for both crosslinked membranes and their azide-free noncrosslinked counterparts (Table 3 and Figure 2).

Figure 2 represents the effect of temperature on proton conductivity of the membranes. Crosslinking with the addition of bis(aryl azide) resulted in reduction of the proton conductivity for mem-

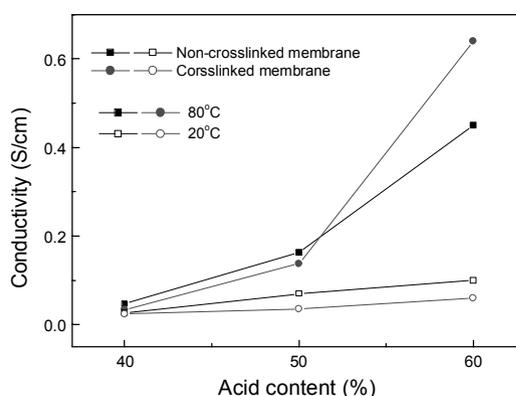


Fig. 2. Effect of the acid content on proton conductivity of the membranes at both 20 and 100 °C

Table 3. Proton conductivity of the crosslinked membranes, their azide-free counterparts and Nafion[®]-112 membrane at various temperature

Polymer	$\sigma(20\text{ }^{\circ}\text{C})$ (S/cm)	$\sigma(40\text{ }^{\circ}\text{C})$ (S/cm)	$\sigma(60\text{ }^{\circ}\text{C})$ (S/cm)	$\sigma(80\text{ }^{\circ}\text{C})$ (S/cm)	$\sigma(100\text{ }^{\circ}\text{C})$ (S/cm)
Crosslinked					
PES-40	0.024	0.028	0.031	0.034	0.043
PESn-40	0.026	0.033	0.044	0.046	0.068
Crosslinked					
PES-50	0.036	0.05	0.108	0.138	0.147
PESn-50	0.07	0.098	0.138	0.162	0.204
Crosslinked					
PES-60	0.06	0.18	0.41	0.64	0.79
PESn-60	0.1	0.21	0.3	0.45	0.52
Nafion [®]	0.13	0.23	0.32	0.41	0.48

branes with an acid content of 40%(PES-40) and 50%(PES-50). In contrast, for PES-60, having an acidic portion of 60%, crosslinking led to an increase in proton conductivity of the membrane at temperature higher than 60 °C.

This unexpected result may be ascribed to the homogeneous distribution of the conductive sites over the well-defined rigid rod PES backbone at increased temperature, and minimized hydrophobic network due to the introduction of crosslinkable site only at the terminus. Further studies including surface analysis for the conductive channel formation are, however, required to assist our assumptions. Nonetheless, crosslinked PES-60 showed excellent proton conductivity above 60 °C. At 100 °C, the fully crosslinked membrane (PES-60) showed conductivity as high as 0.79 S cm⁻¹, which was much higher than that of Nafion[®] (0.49 S cm⁻¹) under the same conditions.

Having the highest conductivity, the crosslinked PES-60 and its azide-free non-crosslinked counterpart, PESn-60, were further investigated for their thermal properties. The thermogravimetric analysis measurements showed a two-step weight loss for both PES-60 and PESn-60 membranes. The first loss from 20 to 170 °C is ascribed to the loss of absorbed water and the second above 265 °C represents decomposition of the polymers, presumably *via* loss of the sulfonic acid groups. The decomposition temperature is almost as high as that of Nafion[®], and an increase in the decomposition temperature was observed for the fully crosslinked membrane, indicating that the acid groups were more tightly held for the PES-60. The more strongly-bound sulfonic acid groups for the PES-60, compared with PESn-60, are thought to be another reason for the higher conductivity at higher temperature (Figure 2). In addition, the PES-60 and PESn-60 were measured by differential scanning calorimeter in the temperature range of 20 °C to 200 °C, but no special features were observed in this region.

Methanol permeability of the membranes

The methanol diffusion coefficient was measured

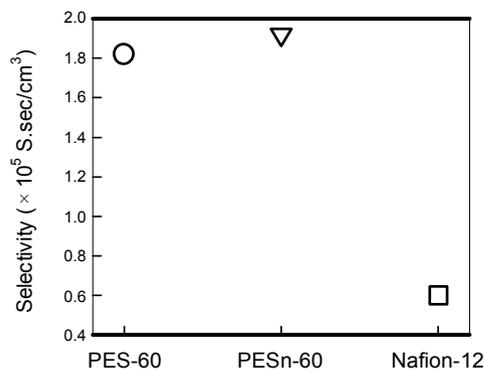


Fig. 3. Selectivity of the crosslinked PES-60, its non-crosslinked counterpart PESn-60, and Nafion[®]-112 membranes

using a glass diffusion cell. The cell consisted of two compartments that were separated by a vertical membrane. Methanol and water were placed on two sides of the diffusion cell, respectively, and the increases of methanol concentration in the water compartment with time were measured using a refractometer at room temperature. The results showed lower methanol diffusion coefficients for both PES-60 and its corresponding azide-free PESn-60 membranes than Nafion[®], with much lower value for the more hydrophobic PES-60, as expected (3.3×10^{-7} cm²/sec for PES-60; 5.2×10^{-7} cm²/sec for PESn-60; and 1.9×10^{-6} cm²/sec for Nafion[®]-112). The methanol permeability of the sulfonated PES-60 is only 17% of that of Nafion[®] under the same conditions.

The high proton conductivity and low methanol permeability of PES-60 resulted in good selectivity as a polymer electrolyte membrane for direct methanol fuel cell. In fact, the selectivity (ϕ) is an effective parameter evaluating the membrane performance in a DMFC system. It is defined as the ratio of proton conductivity (σ) to methanol permeability (P_M). Selectivity for the crosslinked membrane (PES-60) was more than three times than that of Nafion[®] (Figure 3).

CONCLUSIONS

Novel poly(ether sulfone)s (PESs) with terminal

crosslinkable sites were synthesized and their structure was analyzed by ^1H NMR. Thermal irradiation of the prepared polymers in the presence of bisazide as a crosslinker successfully produced the crosslinked polymer network.

Having both the uniform distribution of the hydrophilic conductive sites and controlled hydrophobic nature by minimized crosslinking over the rigid rod poly(ether sulfone) backbone, our crosslinked polymer (PES-60) membrane offered excellent proton conductivity at high temperature with a good thermal stability. In addition, much lower methanol permeability than Nafion[®] was observed.

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