

PS-*b*-PHEA 디블록 공중합체와 폴리비닐알콜을 이용한 수소이온 전도성 가교형 전해질막의 제조

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Preparation of Proton Conducting Crosslinked Membranes From PS-*b*-PHEA Diblock Copolymer and Poly(vinyl alcohol)

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요약: 폴리스티렌-폴리히드록시에틸 아크릴레이트(PS-*b*-PHEA) 디블록 공중합체와 폴리비닐알콜(PVA)을 1:1 무게비로 블렌딩하여 수소 이온 전도성 가교형 고분자 전해질막을 개발하였다. 특히 술포석시닉산(SA)를 사용하여 디블록 공중합체의 PHEA 블록과 PVA와 가교반응을 시켰고, 이를 FT-IR 분광법을 이용하여 분석하였다. 이온교환능(IEC)은 SA 함량이 증가함에 따라 계속하여 증가하여 0.95 meq/g까지 도달하였고, 이는 전해질막에 이온 그룹수가 증가하기 때문이다. 하지만, 흡수율은 SA 함량이 20 wt%까지는 증가하다 그 이상에서는 감소하였다. 또한 수소 이온 전도도도 SA 함량에 따라 증가하여 20 wt% SA 농도에서 0.024 S/cm의 최대값을 나타내었다. 흡수율과 수소이온전도도의 이러한 경향은 SA 함량이 증가함에 따라 이온 그룹의 수가 증가하는 효과와 가교가 증가하는 효과가 서로 경쟁적으로 일어나기 때문으로 생각된다.

Abstract: This work demonstrates the preparation of proton conducting crosslinked polymer electrolyte membranes by blending polystyrene-*b*-poly(hydroxyethyl acrylate) (PS-*b*-PHEA) and poly(vinyl alcohol) (PVA) at 1:1 wt ratio. The PHEA block of the diblock copolymer was crosslinked with PVA using sulfosuccinic acid (SA) via the esterification reaction between -OH of membrane and -COOH of SA, as confirmed by FT-IR spectroscopy. Ion exchange capacity (IEC) continuously increased from 0.14 to 0.91 meq/g with increasing concentrations of SA, due to the increasing portion of charged groups in the membrane. In contrast, the water uptake increased up to 20.0 wt% of SA concentration above which it decreased monotonically. The membrane also exhibited a maximum proton conductivity of 0.024 S/cm at 20.0 wt% of SA concentration. The maximum behavior of water uptake and proton conductivity is considered to be due to competitive effect between the increase of ionic sites and the crosslinking reaction according to the SA concentration.

Keywords: polymer electrolyte membrane, diblock copolymer, crosslinking, proton conductivity, fuel cell

1. Introduction

Polymer electrolytes refer to a material which comprises metal salts dissolved in a polymeric matrix or the polymer backbones with covalently bonded ionizing

groups attached to them. In recent years, polymer electrolytes have been identified as a promising material for the applications to secondary batteries [1,2], dye sensitized solar cells [3] and facilitated olefin transport membranes [4]. In particular, proton conducting polymer electrolytes, which have negatively charged groups attached to the polymer backbone, are extensively used

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in the fuel cell applications [5-12].

The easier transportation of proton ions is one of the most crucial properties in a successful fuel cell membrane. Thus, proton conducting polymer electrolyte membranes usually contain pendant cation exchange sites such as sulfonic acids (SO_3^-). Upon hydration of a membrane, the ionic clusters of sulfonic acid groups are expanded, producing an interconnected network of ionic channels for facile proton transport. Currently, the most commonly used polymer electrolyte membrane is a perfluorinated sulfonic acid membrane, known by its trade name Nafion. All of these membranes possess good thermal, chemical, and mechanical properties because of their perfluorinated polymer backbones. However, a high cost, low proton conductivity and low water uptake at high temperatures are considered the main obstacles for commercialization of polymer electrolyte membranes for fuel cells. Thus significant research efforts have been devoted to the development of alternative polymer electrolytes to perfluorinated membranes over the past years [13-21].

In this work, proton conducting, crosslinked polymer electrolyte membranes were prepared by blending polystyrene-*b*-poly(hydroxyethyl acrylate) (PS-*b*-PHEA) and poly(vinyl alcohol) (PVA) at 1:1 wt ratio. The PHEA block of diblock copolymer was crosslinked with PVA via the esterification reaction using sulfosuccinic acid (SA) as a crosslinking agent. Several characteristics of the resultant polymer electrolyte membranes, e.g. ionic exchange capacity (IEC), water uptake and proton conductivity are reported in this paper.

2. Experimental

2.1. Materials

Styrene (99%), 2-hydroxyethyl acrylate (HEA, 99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 99%), copper(I) chloride (CuCl , 99%), methyl 2-bromo-propionate (MBP) and sulfosuccinic acid (70 wt% in water), poly(vinyl alcohol) (PVA, 99% hydrolyzed, M_n 85,000) were purchased from Aldrich and used as received without further purification.

2.2. Synthesis of PS-*b*-PHEA Diblock Copolymer

First, PS-Br homopolymer was synthesized by atom transfer radical polymerization (ATRP). 20 g of styrene, 0.296 g of CuCl , and 1.24 mL of HMTETA were added in a 250 mL pearshaped flask. This green mixture was stirred until it formed a homogeneous solution. The solution was purged with nitrogen for 30 min, and then 0.22 mL of MBP was added. The mixture was placed in a 110°C oil bath for 5 h. After polymerization, the polymer product was diluted with THF. This solution was passed through an activated Al_2O_3 column to remove the catalyst. The polymer was then precipitated out with methanol. The PS-Br homopolymer was then dried in a vacuum oven overnight at room temperature.

Second, 6 g of as-synthesized PS-Br homopolymer was dissolved in 10 ml of toluene. Then, 6.5 mL of HEA, 0.089 g of CuCl , and 0.372 mL of HMTETA were added to the solution. This green mixture was stirred until a homogeneous solution formed. The solution was purged with nitrogen for 30 min, and then placed in a 50°C oil bath for 7 h. After polymerization, the block copolymer was diluted with THF. This solution was passed through an activated Al_2O_3 column to remove the catalyst. The polymer was then precipitated out with methanol. The PS-*b*-PHEA diblock copolymer was then dried in a vacuum oven overnight at room temperature.

2.3. Preparation of Crosslinked PS-*b*-PHEA/PVA Membranes

1 g of PS-*b*-PHEA diblock copolymer and 1 g of PVA were dissolved together in 20 mL of DMSO with stirring. After making homogeneous solution, different amounts of SA were added into the solution and stirred for more than 2h. The polymer mixtures were then cast on a Teflon-coated glass dish, and dried in an oven at 80°C for two days. The obtained membranes were peeled off from the dishes and then annealed at 120°C for 3 h for crosslinking reaction. The membranes were washed with water several times to remove unreacted SA.

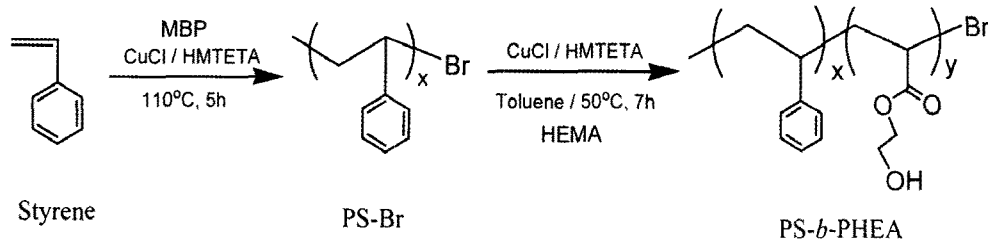


Fig. 1. ATRP synthesis of PS-*b*-PHEA diblock copolymer.

2.4. Ion Exchange Capacity (IEC)

IEC of the membranes was measured by the classical titration method. The membranes were soaked in 1.0 M NaCl solution for 24 h before measuring IEC. The protons released due to the exchange reaction with Na ions were titrated against 0.01 M standardized NaOH solution, using phenolphthalein indicator. The experimental IEC of the membranes was calculated using the following equation.

$$\text{IEC (mEq/g)} = \frac{X \times N_{\text{NaOH}}}{\text{Weight}(\text{polymer})} \quad (1)$$

where *X* is the volume of NaOH consumed and N_{NaOH} is the normality of NaOH.

2.5. Water Uptake

Water uptake was determined by weighing vacuum dried membrane and fully equilibrated membrane with water. The surface of the membrane sample was quickly wiped with an absorbent paper to remove the excess of water adhering to it and the sample was then weighed. The water uptake of the membrane was determined from

$$\text{water uptake (wt\%)} = \frac{W_w - W_d}{W_d} \times 100 \quad (2)$$

where W_w and W_d are the weights of wet and dried membranes, respectively.

2.6. Proton Conductivity

A four-point probe method was used to measure the proton conductivity of the membranes using home

made conductivity cell. Before the measurement of proton conductivity, the prepared membranes were equilibrated with deionized water. Complex impedance measurements were carried out in the frequency range 1 Hz-8 MHz at 25°C, using a ZAHNER IM-6 impedance analyzer. The impedance spectra of the membranes can be used to generate Nyquist plots, and the proton conductivity was calculated from the plots [21,22].

2.7. FT-IR Measurement

FT-IR spectra were recorded Excalibur Series FTIR (DIGLAB Co.) instrument between the frequency range of 4000 to 400 cm^{-1} using ATR facility.

3. Results and Discussion

PS-*b*-PHEA diblock copolymer was synthesized using atomic transfer radical polymerization (ATRP), as illustrated in Fig. 1 [16]. The first step involves the homopolymerization of styrene in bulk initiated by MBP/CuCl/HMTETA at 110°C for 5 h. Secondly, PS-*b*-PHEA diblock copolymer was synthesized at 50°C for 7 h using PSBr and CuCl/HMTETA as a macroinitiator and catalyst/ligand complex, respectively. According to the ^1H NMR spectroscopy [16], the diblock copolymer has a composition of 56:44 wt% PS-*b*-PHEA, and the synthesis of block copolymer via ATRP is successful.

The synthetic procedures for crosslinked PS-*b*-PHEA/PVA membranes are presented in Fig. 2. The PS-*b*-PHEA diblock copolymer and PVA was crosslinked with SA via the esterification between -OH of PHEA (or PVA) and COOH of SA. Because SA contains sul-

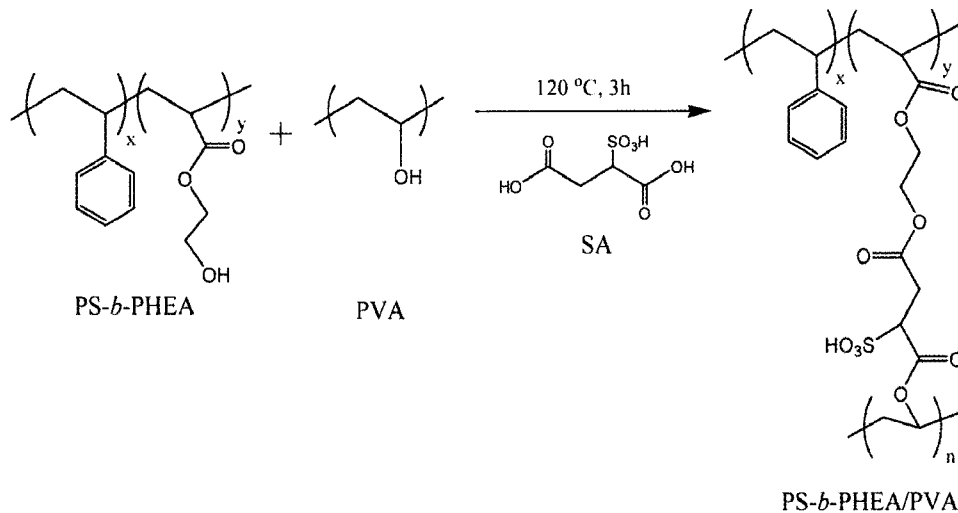


Fig. 2. Synthetic procedures for the crosslinked membranes consisting of PS-*b*-PHEA diblock copolymer and PVA via SA.

ionic acid groups, the crosslinked PHEA/PVA blocks become proton conducting domains. It is thus expected that the crosslinked membranes consist of the hydrophobic nonconducting PS blocks and the crosslinked conducting PHEA/PVA blocks.

Fig. 3 shows the FT-IR spectra of PS-*b*-PHEA, PVA and PS-*b*-PHEA/PVA membrane before and after crosslinking. The pristine PS-*b*-PHEA diblock copolymer exhibited some absorption bands at 3,432, 1,725 and 1,153 cm^{-1} , assigned to -OH, -C=O and C-O of PHEA, respectively. Four absorption bands at 1601, 1,583, 1,494 and 1,451 cm^{-1} are attributable to the aromatic C=C stretching modes of PS [23]. The IR spectrum of PS-*b*-PHEA/PVA membrane before crosslinking is a simple summation of PS-*b*-PHEA, PVA and SA. Upon crosslinking, however, two stretching bands at 1,725 and 1,162 cm^{-1} grew up significantly, attributable to the formation of -C=O and C-O in the membranes, respectively [24]. In addition, the broad absorption band of -OH at 3,317 cm^{-1} shifted to a higher wavenumber at 3,426 cm^{-1} , resulting from the changed strength of hydrogen bonding in the membranes. These FT-IR spectroscopic results are clearly suggestive of a crosslinking reaction by the esterification between -OH of PHEA and -COOH of SA [25,26]. The shoulder peak at 1,230 cm^{-1} is due to the stretching vibrations of the sulfonic acid groups of SA.

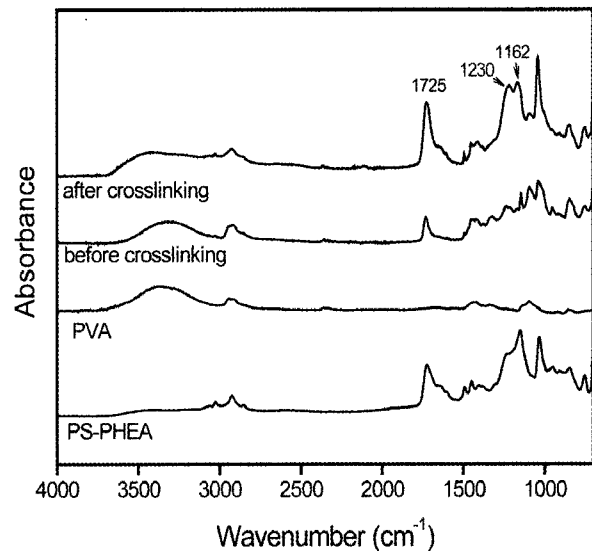


Fig. 3. FT-IR spectra for PS-*b*-PHEA, PVA and PS-*b*-PHEA/PVA membrane before and after crosslinking.

The IEC value represents the quotient of the molar content of sulfonic acid groups to membrane weight. The IEC data of PS-*b*-PHEA/PVA membranes are presented in Fig. 4. The IEC values continuously increased from 0.14 to 0.91 meq/g with increasing amounts of SA, mostly due to the increased portion of charged groups in the membrane. The membrane with 30 wt% of SA exhibited 0.91 meq/g of IEC value, which is close to that of Nafion. High IEC value of the PS-*b*-PHEA/PVA membrane demonstrates that the higher amounts of sulfonic acid groups are contained in the

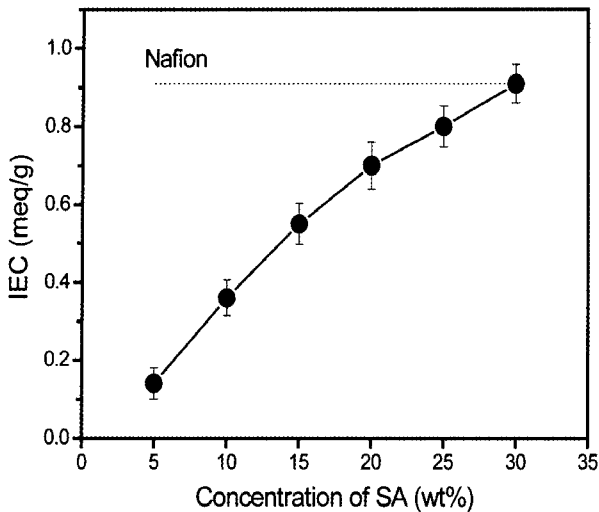


Fig. 4. IEC for the PS-*b*-PHEA/PVA crosslinked membranes with various SA concentrations.

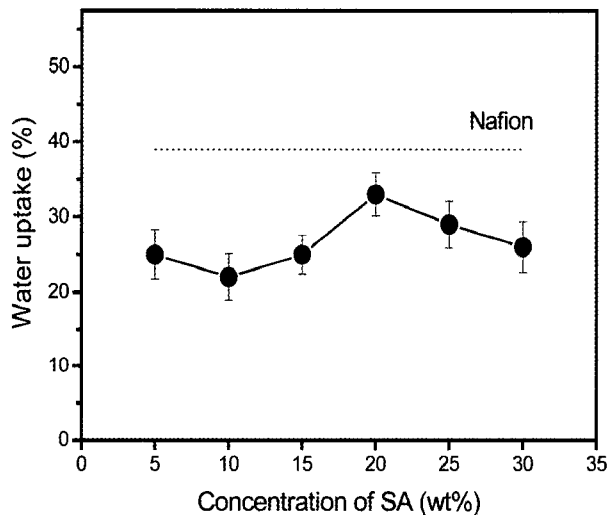


Fig. 5. Water uptake for the PS-*b*-PHEA/PVA crosslinked membranes with various SA concentrations.

membranes.

Fig. 5 shows the water uptake of PS-*b*-PHEMA/PVA membranes crosslinked with the different amounts of SA. Upon the introduction of SA 5 wt%, the water uptake was 25%. Water uptakes slightly increased up to 33% at 20 wt% of SA concentration, after which they decreased monotonically. It is generally accepted that a water uptake is directly related to the concentration of ionic sites, i.e., SO_3^- groups. In this work, however, the water uptake did not follow the behavior of IEC values of the membranes. It is presumably due to the fact that the introduction of SA produces the cross-

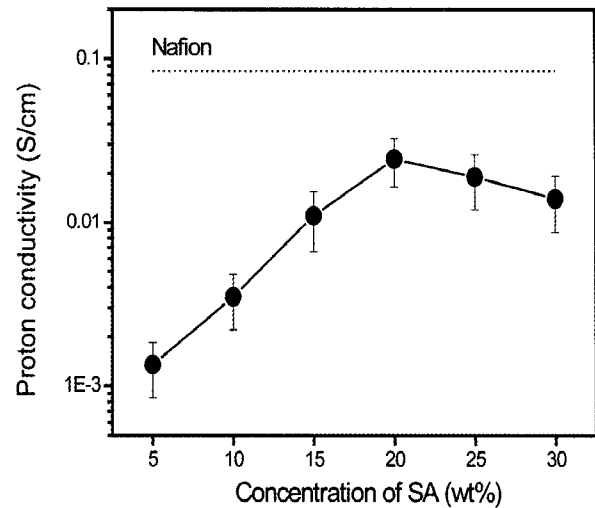


Fig. 6. Proton conductivity for the PS-*b*-PHEA/PVA crosslinked membranes with various SA concentrations.

linking of the membrane, leading to more rigid and compact structure of the membranes.

The proton conductivities of crosslinked PS-*b*-PHEMA/PVA membranes with the different amounts of SA are shown in Fig. 6. As shown in this Fig, proton conductivities were significantly dependent upon the SA concentration, i.e. the contents of acidic SO_3^- groups and the degree of crosslinking. Overall the proton conductivities of crosslinked PS-*b*-PHEMA/PVA membranes were in the order of $10^{-3} \sim 10^{-2}$ S/cm at room temperature. A maximum proton conductivity of 0.024 S/cm was achieved at 20.0 wt% of SA concentration, presumably related to well-developed connectivity of proton conducting domains in the cross-linked PS-*b*-PHEMA/PVA membranes.

4. Conclusion

The proton conducting, crosslinked membranes were developed by blending PS-*b*-PHEA diblock copolymer and PVA, followed by thermal crosslinking reaction between -OH of PHEA block/or PVA and -COOH of SA. The IEC values continuously increased with increasing SA concentrations whereas the water uptake increased up to 20.0 wt% of SA concentration above which it decreased monotonically. Accordingly, the proton conductivity of PS-*b*-PHEA/PVA crosslinked

membrane at room temperature increased up to 20.0 wt% of SA concentration, above which it decreased. A maximum proton conductivity was 0.024 S/cm at 20.0 wt% of SA concentration. These maximum behaviors were elucidated in terms of competitive effect between the increase of ionic sites and the crosslinking reaction with increasing SA concentrations.

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