

Poly(vinyl chloride) 가지형 공중합체를 이용한 수소이온 전도성 가교형 전해질막의 제조와 분석

고 종 관·최 진 규·박 정 태·고 주 환·김 종 학[†]

연세대학교 화공생명공학과

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Preparation and Characterization of Proton Conducting Crosslinked Membranes Based On Poly(vinyl chloride) Graft Copolymer

Jong Kwan Koh, Jin Kyu Choi, Jung Tae Park, Joo Hwan Koh, and Jong Hak Kim[†]

Department of Chemical and Biomolecular Engineering, Yonsei University, 262 Seongsanno, Seodaemun-gu,
Seoul 120-749, Korea

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요 약: Poly(vinyl chloride) (PVC) 주사슬과 poly(hydroxyethyl acrylate) (PHEA) 곁사슬로 구성된 가지형 공중합체를 원자전달라디칼 중합을 통해 합성하였다. PVC의 2차 염소원자의 직접적인 개시반응에 의해 친수성인 PHEA 단량체를 그 래프팅시켰다. 이렇게 합성된 PVC-g-PHEA을 술포석시닉산(SA)를 사용하여 가교시켰으며, 이는 가지형 공중합체의 -OH 그룹과 SA의 -COOH와의 에스테르 반응을 FT-IR 분광법을 이용하여 분석하였다. 이온교환능(IEC)은 SA 함량이 증가함에 따라 계속하여 증가하여 0.87 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 0.025 S/cm의 최대값을 나타내었고, 이는 SA 함량이 증가함에 따라 이온 그룹의 수가 증가하는 효과와 가교가 증가하는 효과가 서로 경쟁적으로 일어나기 때문으로 사료된다.

Abstract: A graft copolymer consisting of poly(vinyl chloride) (PVC) backbone and poly(hydroxyethyl acrylate) (PHEA) side chains was synthesized via atom transfer radical polymerization (ATRP). Direct initiation of the secondary chlorines of PVC facilitates grafting of hydrophilic PHEA monomer. This graft copolymer, i.e. PVC-g-PHEA was cross-linked with sulfosuccinic acid (SA) via the esterification reaction between -OH of the graft copolymer and -COOH of SA, as confirmed by FT-IR spectroscopy. Ion exchange capacity (IEC) continuously increased to 0.87 meq/g with increasing concentrations of SA, due to the increasing portion of charged groups in the membrane. However, 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 0.025 S/cm at 20.0 wt% of SA concentration, which is presumably due to competitive effect between the increase of ionic sites and the crosslinking reaction.

Keywords: polymer electrolyte membrane, graft 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

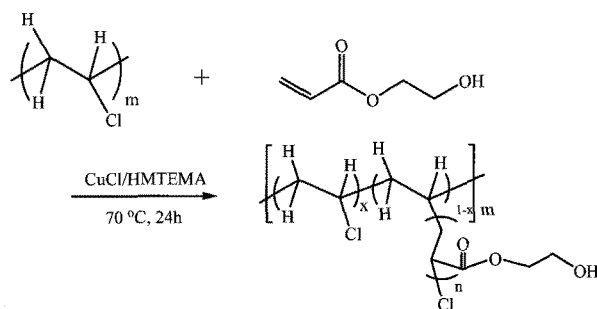
groups attached to them. Because of the unique electrochemical properties, polymer electrolytes have recently been of technological interest for the possible applications to energy conversion units such as batteries, fuel cells, solar cells, electrochromic display devices and facilitated transport membranes [1-4]. In par-

[†]주저자(e-mail : jonghak@yonsei.ac.kr)

ticular, proton conducting polymer electrolytes, which have negatively charged groups attached to the polymer backbone, are extensively used in the fuel cell applications [5-8].

Many investigations have been carried out on proton conducting polymer electrolyte membranes for the applications to fuel cells over the last decade [9-12]. 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. The most common polymer electrolyte membranes used in fuel cells applications are perfluorinated polymer membranes, e.g. DuPont's Nafion[®] membranes. These membranes consist of a hydrophobic fluorocarbon backbone and hydrophilic sulfonic pendant side chains. These structures produce a microphase-separated morphology of membranes and thus they exhibit excellent thermal, mechanical and electrochemical properties. However these membranes have the following disadvantages: 1) high cost, \$600~1200 m^{-2} , 2) high cost per unit power, 300 D kW^{-1} at 240 mWcm^{-2} , 3) high methanol crossover through membranes and 4) low proton conductivity at high temperature/low humidity conditions. Thus significant research efforts have been devoted to the development of alternative polymer electrolytes to perfluorinated membranes over the past years [13-21].

Here, a novel graft copolymer comprised of poly(vinyl chloride) (PVC) backbone and poly(hydroxyethyl acrylate) (PHEA) side chains was synthesized via atom transfer radical polymerization (ATRP). This graft copolymer was solution blended with sulfosuccinic acid (SA) and thermally crosslinked, resulting in proton conducting crosslinked polymer electrolyte membranes. Several characteristics of the resultant polymer electrolyte membranes, e.g. ionic exchange capacity (IEC), water uptake and proton conductivity are reported in



Scheme 1. ATRP for the synthesis of PVC-g-PHEA graft copolymer.

this paper.

2. Experimental

2.1. Materials

PVC ($M_n = 55,000$ g/mol, $M_w = 97,000$ g/mol), 2-hydroxyethyl acrylate (HEA, 99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 99%), copper(I) chloride (CuCl , 99%) and sulfosuccinic acid (70 wt% in water) were purchased from Aldrich. All solvents and chemicals were reagent grade, and were used as received.

2.2. Synthesis of PVC-g-PHEA Graft Copolymer

Schematic procedure for the synthesis of PVC-g-PHEA graft copolymer is presented in Scheme 1. 2.0 g of PVC was dissolved in 18 mL of NMP in a round flask at 70°C. Then, 3.0 mL of HEA, 0.04 g of CuCl and 0.1 mL of HMTETA were added to the solution and the reaction flask was sealed with a rubber septum. After N_2 purging for 30 min, the reaction vessel was immersed in an oil bath at 70°C. The reaction was allowed to proceed for 24 h. After passing the solution through a column with activated Al_2O_3 to remove the catalyst, it was precipitated into methanol. The polymer was purified by redissolving in DMSO and reprecipitating in methanol. Finally, the polymer was dried in a vacuum oven overnight at room temperature. The product was gained as a form of powder and the grafting ratio was 15.0 wt%.

2.3. Preparation of Crosslinked PVC-g-PHEA /SA Membranes

0.5 g of PVC-g-PHEA graft copolymer was dissolved in 10 mL of DMSO with stirring. After making homogeneous solution, the different amounts of SA were added into the solution and stirred for more than 2 h. 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.

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.

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

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

is the normality of NaOH.

2.5. Water Uptake

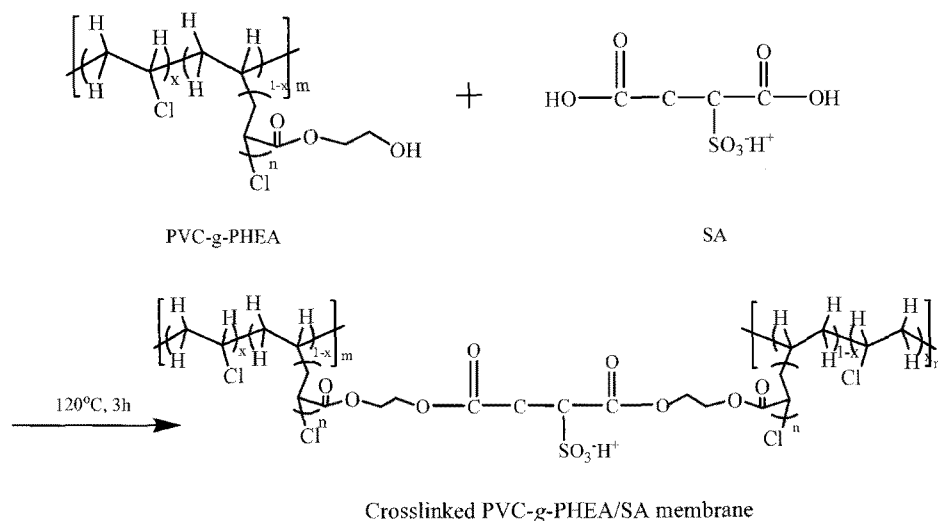
Water uptake was determined by weighing vacuum dried membrane and fully equilibrated membrane with water. The surface of the membrane sample was quickly wiped with an absorbent paper to remove the excess of water adhering to it and the sample was then weighed. The water uptake of the membrane was determined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



Scheme 2. Schematic procedure for the preparation of crosslinked PVC-g-PHEA/SA membranes.

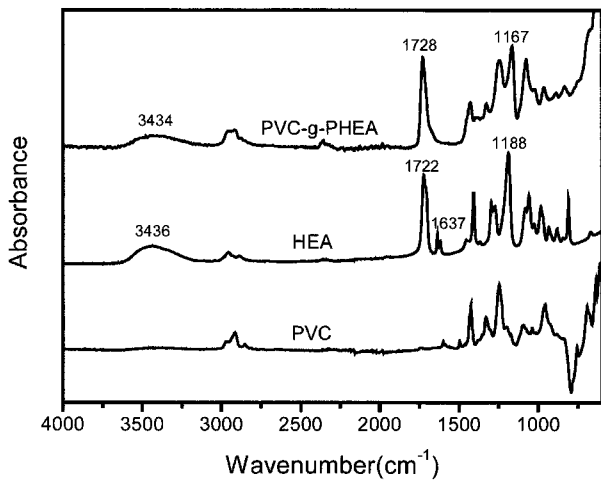


Fig. 1. FT-IR spectra of PVC, HEA and PVC-g-PHEA.

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 4,000 to 400 cm^{-1} using ATR facility.

3. Results and Discussion

The synthetic procedure for crosslinked PVC-g-PHEA/SA membranes is illustrated in Scheme 2. The PVC-g-PHEA graft copolymer was solution blended with SA and thermally crosslinked at 130°C for 2 h via the esterification between the -OH of PHEA and the -COOH of SA. Because SA contains sulfonic acid groups, the crosslinked PVC-g-PHEA/SA membranes possess proton conducting properties. Therefore, the crosslinked membranes consist of the hydrophobic nonconducting PVC mainchain domains and the crosslinked conducting PHEA/SA domains.

Fig. 1 shows FT-IR spectra of pristine PVC, HEA monomer and PVC-g-PHEA graft copolymer. The absorption bands at 1,728 and 1,167 cm^{-1} of PVC-g-PHEA graft copolymer are assigned to the carbonyl stretching vibration of PHEA, implying successful graft copolymerization from PVC. The broad band at 3,434 cm^{-1} is due to the hydroxyl group of PHEA in the graft copoly-

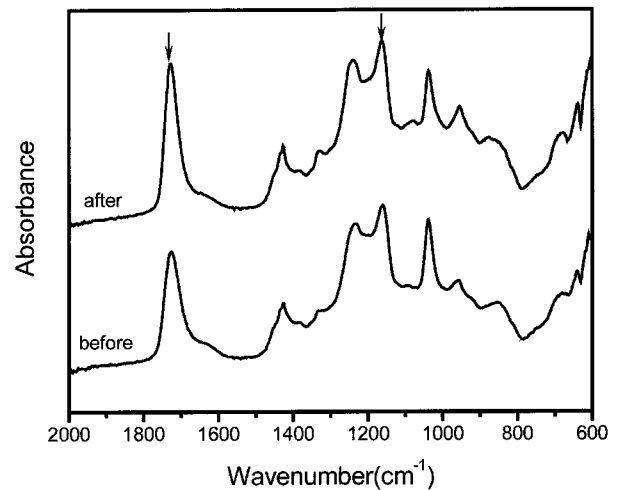


Fig. 2. FT-IR spectra of PVC-g-PHEA/SA membrane before and after crosslinking.

mer.

Fig. 2 shows the FT-IR spectra of PVC-g-PHEA/SA membranes before and after crosslinking at 130°C for 2 h. Upon crosslinking of membranes, two stretching bands at 1,730 and 1,162 cm^{-1} grew up, attributable to the formation of -C=O and C-O in the membranes, respectively [24]. This result supports the crosslinking reaction of the membranes 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 vibration of the sulfonic acid groups of SA.

The IEC values of crosslinked PVC-g-PHEA/SA membranes are presented in Fig. 3 as a function of SA concentration. The IEC values continuously increased from 0.12 to 0.87 meq/g with increasing amounts of SA, resulting from the increased portion of charged groups in the membrane. The membrane with 30 wt% of SA exhibited 0.87 meq/g of IEC value, which is almost close to the IEC of Nafion 117. The high IEC value of the crosslinked PVC-g-PHEA/SA membranes represent that the higher amounts of sulfonic acid groups are contained in the membranes.

Fig. 4 shows the water uptake of crosslinked PVC-g-PHEA/SA membranes with the different amounts of SA. Upon the introduction of SA 5 wt%, the membrane exhibited 22% of water uptake. The water uptake of membranes gradually increased with SA con-

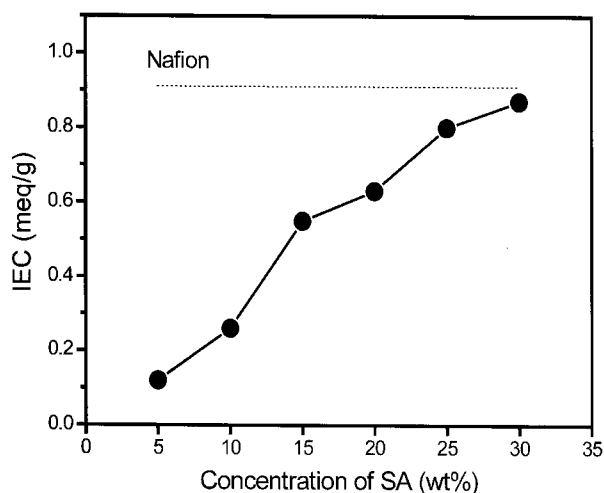


Fig. 3. IEC values of crosslinked PVC-g-PHEA/SA membranes as a function of SA concentration.

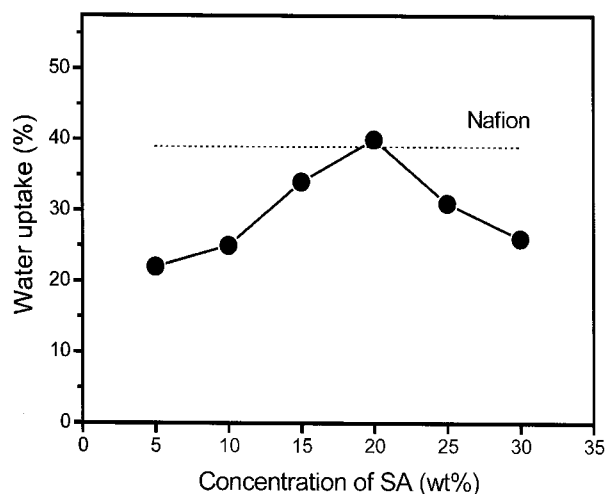


Fig. 4. Water uptake of crosslinked PVC-g-PHEA/SA membranes as a function of SA concentration.

centration up to 20 wt% of SA concentration, after which they decreased monotonically. Generally, a water uptake is linearly proportional to the concentration of ionic SO_3^- groups, i.e. IEC value. In this work, however, the water uptake was not consistent with the behavior of IEC values of the membranes shown in Fig. 3. It may be explained by the fact that the introduction of SA produces the crosslinking of the membranes, resulting in more rigid and compact structures of the membranes. Thus, water uptake of membranes is likely to be decreased at higher crosslinking degree of membranes.

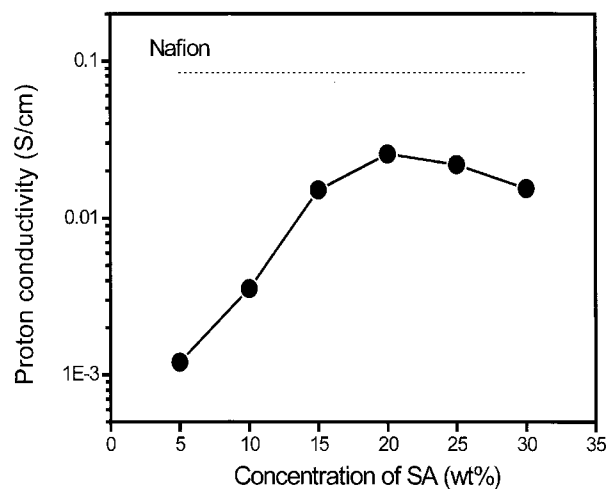


Fig. 5. Proton conductivity of crosslinked PVC-g-PHEA/SA membranes as a function of SA concentration.

Fig. 5 shows the proton conductivities of crosslinked PVC-g-PHEA/SA membranes at room temperature as a function of the concentration of SA. As shown in this figure, proton conductivities were significantly dependent upon the SA concentration, i.e. the contents of acidic SO_3^- groups and the degree of crosslinking. The proton conductivity of membranes was initially increased with SA concentration up to 20 wt%, after which it is gradually decreased. This behavior may be again explained by the competitive effect between the increase of ionic sites and the crosslinking reaction, according to the SA concentration. Overall, the proton conductivities of crosslinked PVC-g-PHEA/SA membranes were in the order of $10^{-3} \sim 10^{-2}$ S/cm at room temperature. A maximum proton conductivity of 0.025 S/cm was achieved at 20.0 wt% of SA concentration, presumably related to well-developed connectivity of proton conducting domains in the crosslinked PVC-g-PHEA/SA membranes.

4. Conclusion

Proton conducting crosslinked polymer electrolyte membranes were prepared based on PVC graft copolymer. PVC-g-PHEA graft copolymer was synthesized via ATRP process using PVC backbone as a macro-initiator. The proton conducting crosslinked membranes

were developed by blending the PVC-g-PHEA graft copolymer and SA, followed by thermal crosslinking reaction between -OH of PHEA in the graft copolymer 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. In accord with water uptake, the proton conductivity of crosslinked PVC-g-PHEA/SA membranes at room temperature increased up to 20.0 wt% of SA concentration, above which it decreased. A maximum proton conductivity of crosslinked PVC-g-PHEA/SA membranes was achieved as 0.025 S/cm at 20.0 wt% of SA concentration. This maximum behavior was elucidated in terms of competitive effect between the increase of ionic sites and the crosslinking reaction with increasing SA concentrations.

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