

Poly(vinyl chloride) 빗살형 공중합체를 이용한 무가습 수소이온 전도성 전해질막의 제조

고 주 환 · 서 진 아 · 안 성 훈 · 증 효 퇴 · 김 종 학[†]

연세대학교 화공생명공학과
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Preparation of Proton Conducting Anhydrous Membranes Using Poly(vinyl chloride) Comb-like Copolymer

Joo Hwan Koh, Jin Ah Seo, Sung Hoon Ahn, Xiaolei Zeng, and Jong Hak Kim[†]

Department of Chemical and Biomolecular Engineering, Yonsei University, 262 Seongsanno, Sudaemun-gu, Seoul 130-749, Korea

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요 약: Poly(vinyl chloride) (PVC) 주사슬과 poly(hydroxyethyl acrylate) (PHEA) 곁사슬로 구성된 빗살모양의 PVC-g-PHEA 공중합체를 원자전달라디칼 중합을 통해 합성하였다. 이렇게 합성된 PVC-g-PHEA의 OH 그룹과 이미다졸 디카르복실산 (IDA)의 COOH 그룹과의 에스테르 반응에 의하여 가교된 전해질막을 제조하였다. 인산(PA)을 도핑하여 이미다졸-인산 착체를 형성한 결과, PA 함량이 증가함에 따라 고분자 전해질막의 수소 이온 전도도가 증가하였다. 특히 100도 비가습 조건에서 수소 이온 전도도는 최대 0.011 S/cm까지 증가하였다. 만능 재료 시험기(UTM) 측정결과, 제조된 PVC-g-PHEA/IDA/PA 전해질막은 575 MPa의 높은 Young 모듈러스 및 기계적 강도를 보여주었다. 열분석 결과(TGA) 전해질막은 200°C까지 열적으로 안정함을 확인하였다.

Abstract: A comb-like copolymer consisting of a poly(vinyl chloride) backbone and poly(hydroxy ethyl acrylate) side chains, *i.e.* PVC-g-PHEA, was synthesized through atom transfer radical polymerization (ATRP). This comb-like copolymer was crosslinked with 4,5-imidazole dicarboxylic acid (IDA) via the esterification of the -OH groups of PHEA in the graft copolymer and the -COOH groups of IDA. Upon doping with phosphoric acid (PA, H₃PO₄) to form imidazole-PA complexes, the proton conductivity of the membranes continuously increased with increasing PA content. A maximum proton conductivity of 0.011 S/cm was achieved at 100°C under anhydrous conditions. The PVC-g-PHEA/IDA/PA complex membranes exhibited good mechanical properties, *i.e.* 575 MPa of Young's modulus, as determined by a universal testing machine (UTM). Thermal gravimetric analysis (TGA) shows that the membranes were thermally stable up to 200°C.

Keywords: atom transfer radical polymerization (ATRP), comb copolymer, crosslink, proton conductivity, anhydrous polymer electrolyte membrane

1. Introduction

A fuel cell is an electrochemical device which combines O₂ and H₂, with the aid of electrocatalysts to produce electricity. Among the many types of fuel cells, polymer electrolyte membrane fuel cell (PEMFC)

is one of the most promising technologies for applications such as portable electronics, distributed generation of energy and vehicles. The important component of PEMFC is a polymer electrolyte membrane [1-8]. The membrane serves to separate the reactant gases as an electrolyte for energy-generating electrochemistry, and to facilitate the selective transport of protons from the

[†]주저자(e-mail : jonghak@yonsei.ac.kr)

anode to the cathode.

Numerous efforts have been dedicated to developing high performance polyelectrolyte membrane [9-11] and, up to now, of a great number of different membranes, Nafion[®] membrane is the most successful one. Nafion[®] was developed by DuPont de Nemours, USA, in the 1960s. The Nafion membrane consists of a perfluorinated backbone with side chains which are terminated by strongly acid SO₃H groups. However, Nafion restricts PEMFC operation at temperatures below 100°C. Such a temperature limitation is associated with a strong dependence of the proton transport on the absorbed water. Therefore, the development of anhydrous polymer electrolyte membranes for high temperature operation has been receiving a great deal of attention [12-15].

In this work, we report on anhydrous proton conducting membranes based on poly(vinyl chloride) (PVC) comb-like copolymer. First, poly(hydroxy ethyl acrylate) (PHEA) was grafted from a PVC backbone via ATRP using chlorine atoms as a macroinitiator [16,17]. This graft copolymer was crosslinked with 4,5-imidazole dicarboxylic acid (IDA) via the esterification of -OH groups of PHEA and -COOH groups of IDA [18,19]. The anhydrous proton conducting membranes were developed by doping with phosphoric acid (PA, H₃PO₄) to form imidazole-PA complexes. Several characteristics of anhydrous PVC graft copolymer electrolyte membranes, such as proton conductivity, mechanical and thermal properties, are reported in this paper.

2. Experimental

2.1. Materials

PVC ($M_n = 55,000$ g/mol, $M_w = 97,000$ g/mol), 2-hydroxy ethyl acrylate (HEA, 99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 99%), copper(I) chloride (CuCl, 99%), 4,5-imidazole dicarboxylic acid (IDA), phosphoric acid (PA, H₃PO₄), and 1-methyl-2-pyrrolidinone (NMP) were purchased from Aldrich. Methanol and dimethyl sulfoxide (DMSO) were purchased from J. T. Baker. All solvents and chemicals were reagent grade and were used as received.

Table 1. Concentrations of PHEA, IDA, and PA in PVC-*g*-PHEA/IDA/PA membranes

	Mole ratio of added [PHEA]:[IDA]:[PA]
Membr1	3 : 1 : 1
Membr2	3 : 2 : 2
Membr3	3 : 3 : 3
Membr4	3 : 4 : 4

2.2. Synthesis of PVC-*g*-PHEA Comb-like Copolymer

5.0 g of PVC was dissolved in 100 mL NMP in a round flask at 80°C. After making a homogeneous polymer solution, 15.0 g of HEA, 0.4 g of CuCl and 1.0 mL of HMTETA were successively added and the reaction flask was sealed with a rubber septum. After N₂ 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 polymerization, the resultant polymer solution was diluted with NMP. After passing the solution through a column with activated Al₂O₃ to remove the catalyst, the polymer solution 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.

2.3. Preparation of PVC-*g*-PHEA/IDA/PA Membranes

1 g of PVC-*g*-PHEA graft copolymer was dissolved in DMSO at 5 wt%. Varying amounts of IDA and PA were added to PVC-*g*-PHEA solutions, as shown in Table 1. Each polymer solution was cast into a Petri dish and dried in an oven at 80°C for 24 h and 100°C for 24 h. Finally, the membranes were crosslinked at 130°C for 3 h.

2.4. Proton Conductivity

A four-point probe method was used to measure the proton conductivity of the membranes using a home made conductivity cell, as illustrated in our recent paper [20]. The impedances of the samples were determined using an AC impedance analyzer (IM6e, ZAHNER, Germany). The impedance analyzer was op-

erated in galvanostatic mode with an AC current amplitude of 0.1 mA over a frequency range of 1 MHz to 1 Hz using the Nyquist method. Proton conductivity was obtained as follows:

$$\sigma = \frac{L}{RS} \quad (1)$$

where σ is the proton conductivity (in S/cm), and L is the distance (in cm) between the electrodes used to measure the potential. R is the impedance of the electrolyte (in Ω) and S is the surface area for ions to penetrate the electrolyte (in cm^2). The impedance of each sample was measured five-times to ensure good data reproducibility. All the measurements in this experiment were carried out under anhydrous conditions (relative humidity < 20%). The average estimated error was $\pm 5\%$.

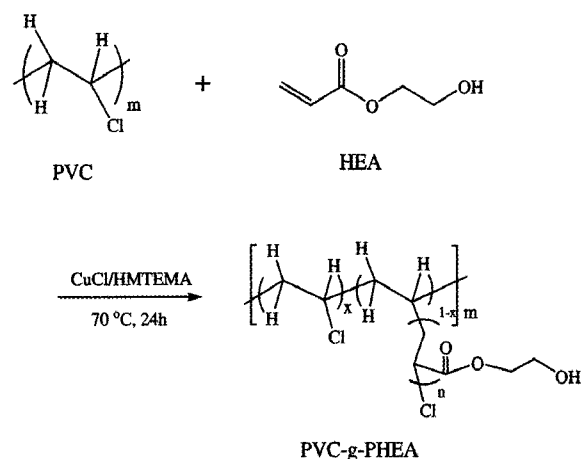
2.5. Characterization of Membranes

FT-IR spectra of the materials were collected using an Excalibur Series FT-IR (DIGLAB Co.) instrument in the frequency range of 4,000 to 400 cm^{-1} in attenuated total reflection (ATR) mode. Tensile evaluation was performed with a universal testing machine (UTM, LR10KPlus Series) at a speed of 5 mm/min. All the measurements in the UTM experiment were carried out at 23°C and 50% RH. All the films were rectangular with a length of 2 cm and a width of 0.7 cm. The average thickness of the films was approximately 80 μm . The thermal properties of the membranes were determined by thermal gravimetric analysis (TGA, Mettler Toledo TGA/SDTA 851e, Columbus, OH). TGA measurements were performed under a nitrogen atmosphere at a rate of 20°C/min. The degradation of the membranes was measured using the weight loss percentage that occurred during the heating process.

3. Results and Discussion

3.1. Synthesis of PVC-g-PHEA Graft Copolymer

The reaction scheme for the synthesis of the PVC comb-like copolymer via ATRP is illustrated in Scheme



Scheme 1. Graft copolymerization of PHEA from PVC via ATRP.

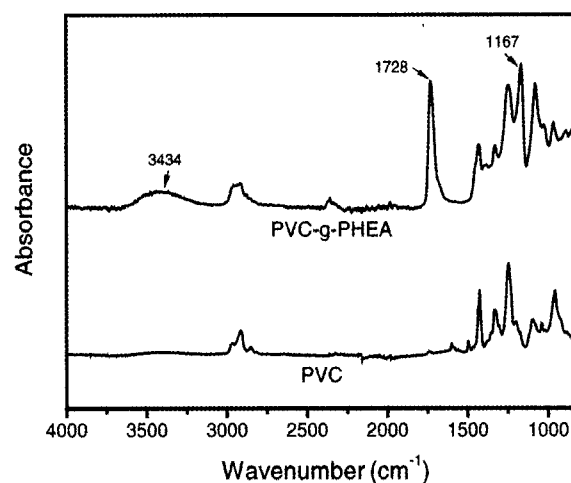
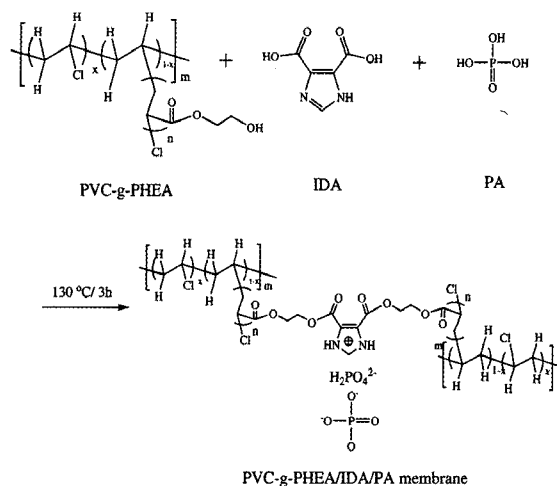


Fig. 1. FT-IR spectra of pristine PVC and PVC-g-PHEA graft copolymer.

1. As shown, the secondary chlorine atoms in PVC were directly initiated to produce graft copolymerization of PHEA from PVC backbones. Graft polymerization was carried out at 70°C for 24 h. This condition was not stringent compared to the cases of cationic and anionic polymerization [21]. As a result, the amphiphilic comb-like copolymer consisting of hydrophobic PVC main chains and hydrophilic crosslinkable PHEA side chains were synthesized. The amphiphilic PVC-g-PHEA graft copolymer is expected to molecularly self-assemble into continuous nanophase domains of semi-crystalline PVC interweaved with hydrophilic domains of PHEA brush-like layers [22].

Fig. 1 shows the FT-IR spectra of pristine PVC and a graft copolymer of PVC with PHEA. Compared to the



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

pristine polymer, the PVC-g-PHEA graft copolymer exhibited strong absorption bands at 1,728 and 1,167 cm^{-1} . These bands are assigned to the stretching vibrations of C=O and C-O of PHEA, respectively. A broad absorption band at 3,434 cm^{-1} was also observed, attributable to the -OH groups of PHEA. The stretching band of C=C in HEA at around 1,637 cm^{-1} was not observed in the PVC-g-PHEA graft copolymer, indicating the successful graft copolymerization of PHEA from secondary chlorine atoms on the PVC backbone via ATRP.

3.2. Preparation of Anhydrous Membranes

Scheme 2 shows the procedure for preparation of the crosslinked membranes consisting of PVC-g-PHEA graft copolymer, IDA and PA (H_3PO_4). The graft copolymer is expected to be crosslinked with IDA via the esterification of the -OH groups of PHEA and the -COOH groups of IDA at high temperatures, e.g. 130°C. Upon doping the membranes with PA, the complexes of imidazole-PA are formed. As shown in Table 1, the mole ratio of added [PHEA]:[IDA]:[PA] was changed from 3:1:1 to 3:4:4. The mole ratio of IDA to PA was always fixed at unity. Then, the mole ratio of the -OH groups of the PHEA units to the -COOH groups of IDA was varied to investigate the effect of IDA and PA concentrations.

The FT-IR spectra of PVC-g-PHEA and PVC-g-PHEA/IDA/PA membrane after crosslinking at 130°C

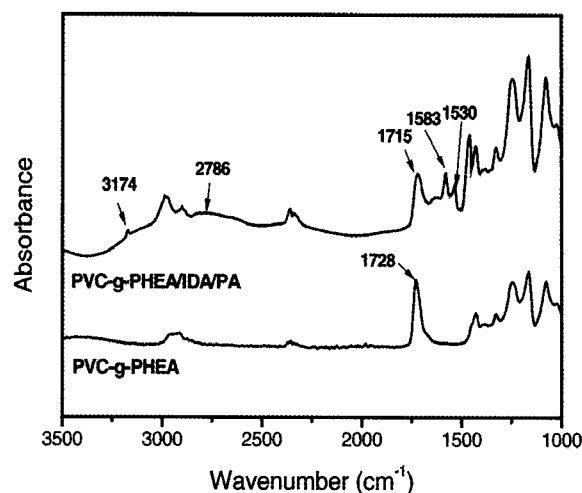


Fig. 2. FT-IR spectra of PVC-g-PHEA and PVC-g-PHEA/IDA/PA crosslinked membranes.

for 3 h are presented in Fig. 2. The membrane sample with a mole ratio of added [PHEA]:[IDA]:[PA] = 3:2:2 was used. The PVC-g-PHEA graft copolymer exhibited strong absorption at 1,728 cm^{-1} , assigned to the carbonyl (-C=O) stretching vibration of PHEA. Upon introduction of IDA/PA and crosslinking, the peak at 1,728 cm^{-1} shifted to the wavenumber at 1,715 cm^{-1} . This peak shift clearly shows that the PVC-g-PHEA graft copolymer is crosslinked with IDA via the esterification of the -OH groups of PHEA and the -COOH groups of IDA [18,19]. The crosslinked PVC-g-PHEA/IDA/PA membrane also exhibited absorption bands at 3,174 and 2,786 cm^{-1} , assigned to -NH and hydrogen bonded -OH groups in the membranes [23,24]. Characteristic peaks of imidazole groups were also observed at 1,583 and 1,530 cm^{-1} [24].

3.3. Conductivity, Mechanical and Thermal Properties

The proton conductivities of PVC-g-PHEA/IDA/PA membranes with different IDA/PA compositions are presented in Fig. 3 as a function of inverse temperature. All the membranes exhibited the increase of the proton conductivities with the elevation of temperature. It is because elevated temperatures favor both the dynamics of proton transport and the structural reorganization of polymeric chains, leading to the increase of proton conductivity at high temperatures. The

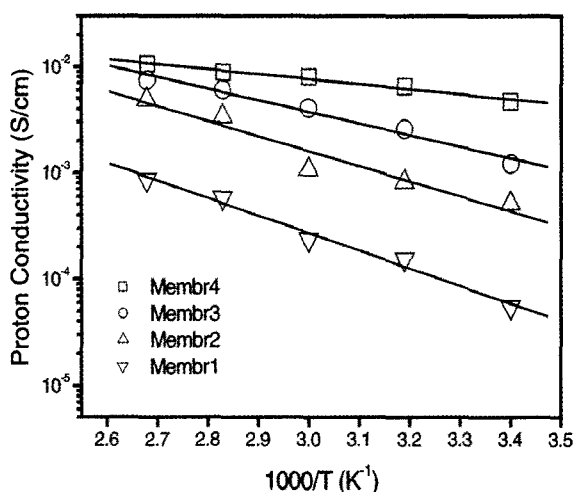


Fig. 3. Temperature dependent proton conductivities of PVC-g-PHEA/IDA/PA membranes with different IDA/PA contents.

temperature dependence of proton conductivity in cross-linked PVC-g-PHEA/IDA/PA membranes fits well with the Arrhenius equation. It was found that the higher PA concentration in the membranes, the higher the proton conductivity obtained. As a result, the PVC-g-PHEA/IDA/PA membrane with [PHEA]:[IDA]:[PA] = 3:4:4 exhibited the maximum conductivity of 0.011 S/cm at 100°C, which is to some degree lower than that of Nafion 117 (0.03 S/cm) at the same experimental conditions.

Tensile evaluation was performed on the membranes using UTM at a speed of 5 mm/min. Tensile strength at break (MPa), elongation at break (%) and Young's modulus (MPa) for the PVC-g-PHEA/IDA/PA membranes with different IDA/PA contents are summarized in Table 2. All the mechanical properties of membranes were enhanced with increasing IDA/PA concentrations due to both the effective crosslinking of the membranes and the formation of imidazole-PA complexes. Interestingly, both the tensile strength at break and the elongation at break were increased simultaneously. This can be explained by the fact that the introduction of IDA leads to effective crosslinking in the membranes and PA makes the membranes more flexible. The maximum mechanical properties were obtained at 3:4:4, i.e. tensile strength at break of 71.3 MPa, elongation at break of 25.6%, and Young's mod-

Table 2. Tensile Strength, Elongation, and Young's Modulus for PVC-g-PHEA/IDA/PA Membranes

	Tensile strength at break (MPa)	Elongation at break (%)	Young's modulus (MPa)
Membr1	10.1	9.7	105
Membr2	21.5	11.7	209
Membr3	46.8	19.3	280
Membr4	71.3	25.6	575

ulus of 575 MPa.

The thermal stabilities of PVC-g-PHEA/IDA/PA membranes were investigated using TGA and presented in Fig. 4. The small weight loss of the PVC-g-PHEA/IDA/PA membrane below 150°C is mainly due to the loss of water adsorbed because of the hygroscopic nature of the membrane. Upon introduction of IDA/PA and crosslinking, the residual amounts of membranes increased, representing that the crosslinked structure of the membranes and the formation of IDA-PA complexes enhance the thermal properties of the polymer electrolyte membranes. The PVC-g-PHEA/IDA/PA crosslinked membranes exhibited thermal stability up to 200°C.

4. Conclusions

In this work, anhydrous proton conducting cross-linked PVC graft copolymer electrolyte membranes were synthesized using a one-pot ATRP process and a crosslinking reaction. A PVC backbone was directly used as a macroinitiator for the synthesis of the PVC-g-PHEA comb-like copolymer. FT-IR spectroscopy confirms 1) the success of the "grafting from" method using ATRP, and 2) crosslinking reaction and complex formation in the membranes. The proton conductivities of PVC-g-PHEA/IDA/PA membranes increased with increasing temperature and increasing contents of IDA/PA in the membranes. A maximum proton conductivity of 0.011 S/cm was observed at 100°C under anhydrous conditions. The characterization of the membranes by UTM and TGA demonstrated their good mechanical properties with up to 575 MPa of Young's modulus and thermal stability up to 200°C.

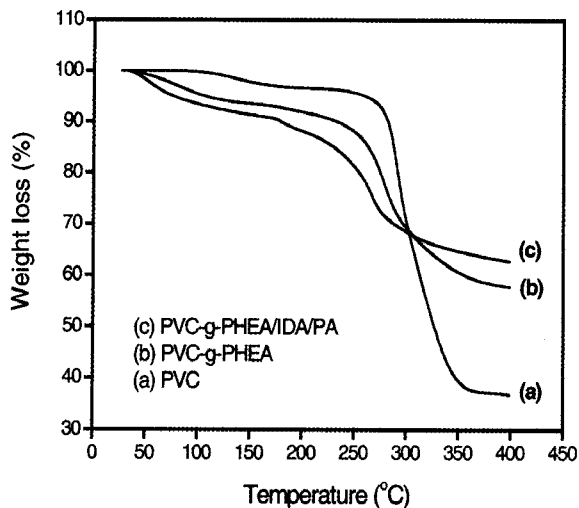


Fig. 4. TGA data for pristine PVC, PVC-g-PHEA graft copolymer and PVC-g-PHEA/IDA/PA membranes.

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