

수소이온 전도성 가교된 P(VDF-co-CTFE)-MAA/SEMA 막 제조 및 분석

라즈쿠마 파텔 · 증 효 퇴 · 허 성 연 · 김 중 학[†]

연세대학교 화학생명공학과

(2013년 8월 8일 접수, 2013년 8월 26일 수정, 2013년 8월 26일 채택)

Preparation and Characterization of Proton Conducting Crosslinked P(VDF-co-CTFE)-MAA/SEMA membranes

Rajkumar Patel, Zeng Xiao Lei, Sung Yeon Heo, and Jong Hak Kim[†]

Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul 120-749, Korea

(Received August 8, 2013, Revised August 26, 2013, Accepted August 26, 2013)

요 약: 촉매 1,8-diazabicyclo[5,4,0]undec-7-ene(DBU)를 이용하여, poly(vinylidene fluoride-co-chlorotrifluoroethylene) P(VDF-co-CTFE) 고분자와 methacrylic acid (MAA)를 반응시켜, P(VDF-co-CTFE)-MAA 공중합체를 제조하였다. 또한 P(VDF-co-CTFE)-MAA와 2-sulfoethyl methacrylate (SEMA) 단량체를 4',4'-azobis(4-cyanovaleric acid) (ACVA) 개시제 하에서 자유 라디칼 중합하여 수소 이온 전도성 막을 제조하였다. SEMA 함량이 많아짐에 따라 술폰산 그룹이 증가하였다. SEMA 함량이 50%일 때 최대 이온교환 용량값이 0.82 meq/g에 도달하였으며 이는 함수량 결과와 일치하였다. 또한, SEMA 함량이 50%일 때 수소이온 전도도가 0.041 S/cm까지 도달하였다. 이러한 결과는 분리막에서 SEMA 함량이 증가할수록 수소 이온을 전달시킬 수 있는 이온그룹이 증가하기 때문이다.

Abstract: Poly(vinylidene fluoride-co-chlorotrifluoroethylene) P(VDF-co-CTFE) polymer was attached to methacrylic acid (MAA) in the presence of 1,8-diazabicyclo[5,4,0]undec-7-ene(DBU) catalyst to prepare P(VDF-co-CTFE)-MAA copolymer. The modified P(VDF-co-CTFE)-MAA was polymerized with 2-sulfoethyl methacrylate (SEMA) monomer in the presence of 4',4'-azobis(4-cyanovaleric acid)(ACVA) initiator by free radical polymerization to form the proton conducting membrane. The ratio of the SEMA was increased in the membrane to increase the presence of the acidic group. The maximum IEC value that was observed at 50% SEMA was around 0.82 meq/g, which is consistent with the water uptake value. The highest proton conductivity achieved by P(VDF-co-CTFE)-MAA/SEMA membrane with 50% SEMA was approximately 0.041 S/cm. This indicates that the available ionic group for the proton conduction increases with the increase in the SEMA in the membrane.

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

1. Introduction

The incorporation of metal salt in the polymer matrix or polymer backbone linked covalently is usually known as polymer electrolytes. Due to the excellent electrochemical properties, solid 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]. Specially proton conducting polymer electrolytes, which have negatively charged groups attached to the polymer backbone, are extensively used in the fuel cell applications such as polymer electrolyte membrane fuel cells (PEMFC) or direct methanol fuel cells (DMFC) [5-8].

[†]교신저자(e-mail: jonghak@yonsei.ac.kr)

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 very important for fuel cell applications. Thus, proton conducting polymer electrolyte membranes usually contain pendant cation exchange sites such as sulfonic acids (SO_3^-). The most commonly used proton conducting polymer electrolyte membranes in fuel cells applications are DuPont's Nafion® membranes consisting of a hydrophobic fluorocarbon backbone and hydrophilic sulfonic pendant side chains. These structures produce a micro-phase-separated morphology of membranes and thus they exhibit excellent thermal, mechanical and electrochemical properties. However these membranes have the following demerits such as high cost, high cost per unit power, high methanol crossover and reduced proton conductivity at high temperature/low humidity conditions. Thus many efforts have been made to the development of alternative polymer electrolytes to perfluorinated membranes[13-21].

In this work, a novel proton conducting membrane consisting of poly(vinylidene fluoride-co-chlorotrifluoroethylene) P(VDF-co-CTFE), methacrylic acid (MAA) and 2-sulfoethyl methacrylate (SEMA) is prepared. The P(VDF-co-CTFE)-MAA/SEMA membranes were developed by linking the P(VDF-co-CTFE) with MAA monomer and in turn polymerizing with SEMA by free radical polymerization. The resulting membrane was characterized by Fourier transform infrared (FTIR) spectroscopy to check the successful polymerization. The electrochemical properties like ion exchange capacity (IEC), water uptake and proton conductivity were reported.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride-co-chlorotrifluoroethylene) (P(VDF-co-CTFE)) was provided from Solvey chemicals. Methacrylic acid (MAA), 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), 2-sulfoethyl methacrylate (SEMA), 4',4'-

azobis(4-cyanovaleric acid (ACVA) and N-methyl-2-pyrrolidone (NMP) are procured from Aldrich chemicals.

2.2. Synthesis of P(VDF-co-CTFE)-MAA

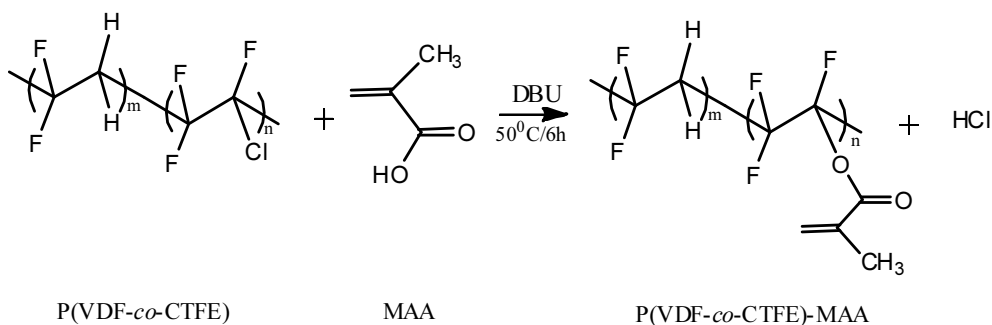
In a 250 mL round flask, 4.0 g P(VDF-co-CTFE) was dissolved in 30 ml NMP at 80°C. When the powders were dissolved completely, the temperature of the reaction flask was lowered to room temperature. And then, 4 mL MAA was added into the solution. After preparing homogeneous solution, 4.0 mL DBU was added into the reaction flask and the colorless reaction solution became black. The reaction flask was sealed with a rubber septum and pure nitrogen was purged for 30 minutes. The flask was immersed in an oil bath at 50°C and the reaction was allowed to proceed for 6 h. After reaction, the resultant polymer was precipitated into a large amount of methanol for 2 times. The aquatic layer was removed and a dark brown liquid was obtained. Finally, the polymer was collected by centrifugation and dried in an oven overnight at 50°C.

2.3. Preparation of P(VDF-co-CTFE)-MAA/SEMA Membranes

To prepare the P(VDF-co-CTFE)-MAA/SEMA membrane, a different amount of P(VDF-co-CTFE)-MAA was dissolved in 3 mL NMP, and then the different amount of SEMA was added with stirring, followed by 0.015 g ACVA. The detailed composition of each component is presented in Table 1. The mixture was stirred for 1 day and poured into a glass dish. Finally, the dish was put into an oven at 80°C for 24 h and the solution became a membrane. Pouring some water into the glass to peel the membrane off and a light brown membrane was obtained. The prepared membranes were stored in water until ready to be used.

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



Scheme 1. Synthesis of P(VDF-*co*-CTFE)-MAA copolymer.

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 homemade conductivity cell. Before the measurement of proton conductivity, the prepared membranes were equilibrated

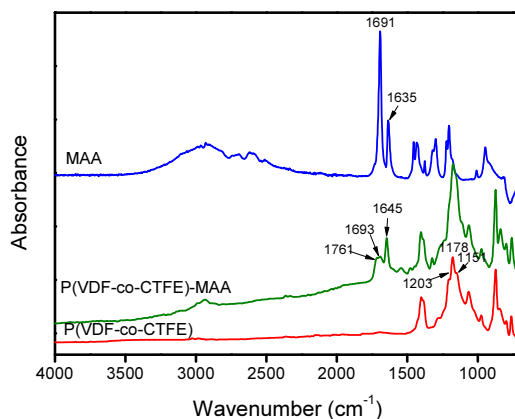


Fig. 1. FT-IR spectra of pristine P(VDF-*co*-CTFE), pristine MAA and P(VDF-*co*-CTFE)-MAA copolymer.

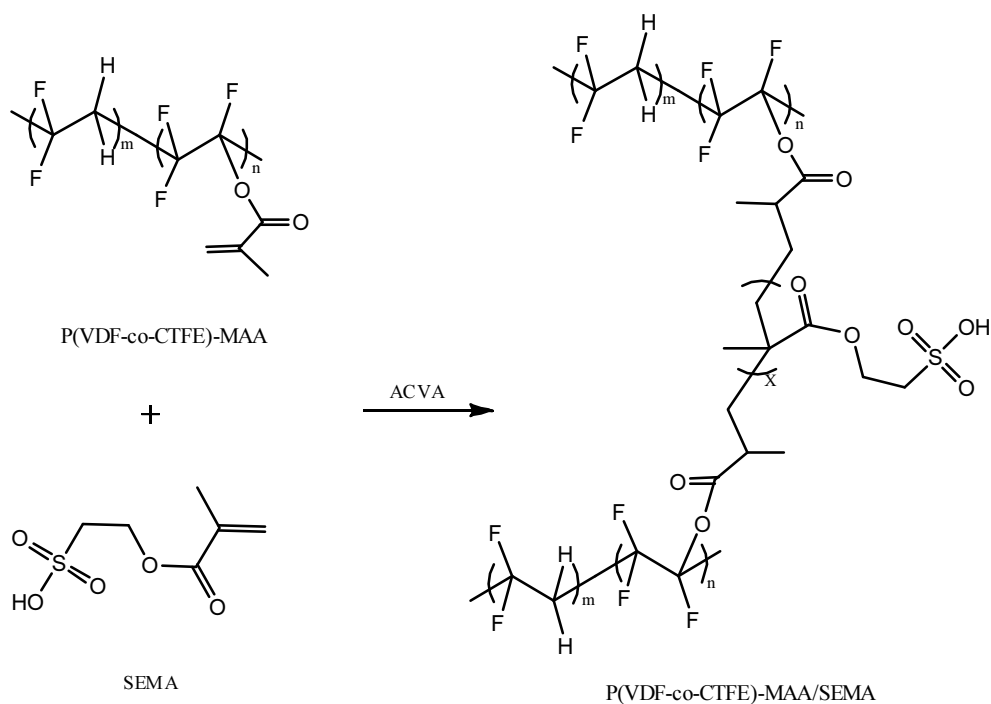
with deionized water. Complex impedance measurements were carried out in the frequency range 1 Hz-8 MHz at 25°C, using a ZAHNER IM-6 impedance analyzer. The impedance spectra of the membranes can be used to generate Nyquist plots, and the proton conductivity was calculated from the plots[21,22].

2.7. FT-IR Measurement

FT-IR spectra were recorded Excalibur Series FTIR (DIGLAB Co.) instrument between the frequency range of 4,000 to 400 cm^{-1} using ATR facility.

3. Results and Discussion

The synthesis process of P(VDF-*co*-CTFE)-MAA copolymer is presented in Scheme 1. The chlorine linked to the P(VDF-*co*-CTFE) is attached to the carboxylic group by condensation reaction in the presence of DBU



Scheme 2. Preparation of P(VDF-co-CTFE)-MAA/SEMA membranes.

catalyst to form an ester link. Fig. 1 shows the FTIR spectra of pristine P(VDF-co-CTFE), pristine MAA and P(VDF-co-CTFE)-MAA copolymer. The pristine P(VDF-co-CTFE) exhibited strong absorption band at around 1,203, 1,178, and 1,151 cm^{-1} , which are attributed to the crystalline chains of P(VDF-co-CTFE). After the formation of the ester linkage in P(VDF-co-CTFE)-MAA, the new absorption bands are observed at 1,693, 1,645 cm^{-1} due to the carbonyl group (C = O) and the C = C double bond of the MAA.

The preparation scheme of P(VDF-co-CTFE)-MAA/SEMA membranes is presented in Scheme 2. The prep-

aration composition of the P(VDF-co-CTFE)-MAA/SEMA membrane is presented in Table 1. Because the membranes with SEMA content above 50% showed poor mechanical properties, the membranes with 0~50% of SEMA were prepared and characterized. The acrylic monomer of the P(VDF-co-CTFE)-MAA polymerized with the acrylic monomer of SEMA by free radical polymerization in the presence of the free radical initiators ACVA. The successful polymerization was confirmed by FTIR study. Fig. 2 represents the FT-IR spectra of P(VDF-co-CTFE)-MAA, pristine SEMA and the composite membranes with different ratio of

Table 1. Composition for the Preparation of P(VDF-co-CTFE)-MAA/SEMA Membranes

SEMA wt%	P(VDF-co-CTFE)-MAA (g)	SEMA (g)	ACVA (g)	NMP (mL)
10%	0.27	0.03	0.015	3.0
20%	0.24	0.06	0.015	3.0
30%	0.21	0.09	0.015	3.0
40%	0.18	0.12	0.015	3.0
50%	0.15	0.15	0.015	3.0

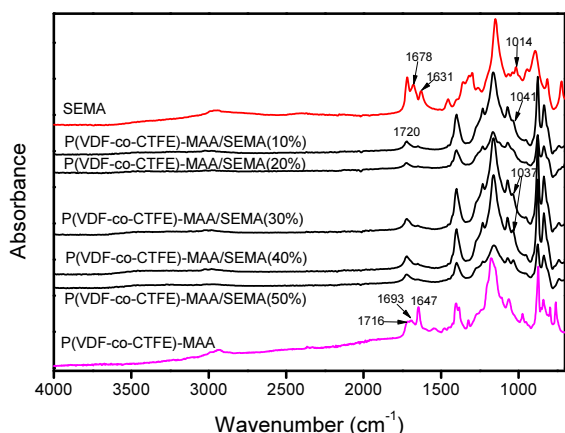


Fig. 2. FT-IR spectra of pristine SEMA, P(VDF-*co*-CTFE)-MAA copolymer and the P(VDF-*co*-CTFE)-MAA/SEMA membranes with different ratios of SEMA.

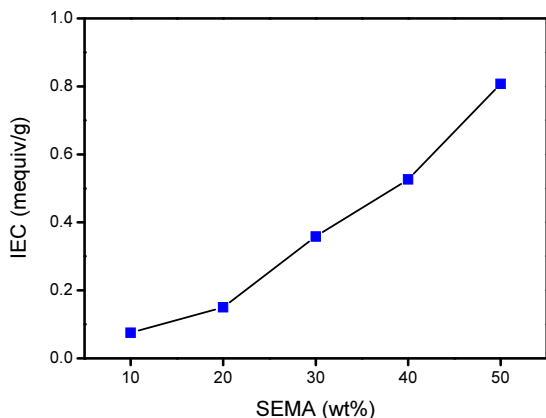


Fig. 3. IEC values of P(VDF-*co*-CTFE)-MAA/SEMA membranes with different ratios of SEMA.

SEMA. The absorption bands at $1,631\text{ cm}^{-1}$ and $1,678\text{ cm}^{-1}$ of the SEMA, $1,647\text{ cm}^{-1}$ and $1,693\text{ cm}^{-1}$ of the P(VDF-*co*-CTFE)-MAA attributed to the C = C double bond disappeared after reaction indicates the successful polymerization between SEMA and P(VDF-*co*-CTFE)-MAA in the presence of ACVA free radical initiators. In addition, with the increase of SEMA amount, the peak at $\sim 1,040\text{ cm}^{-1}$ attributed to O = S = O group became stronger. This implied that the incorporation of the SEMA group increase with the increase in the amount of the SEMA monomer.

Fig. 3 shows the IEC values of the P(VDF-*co*-CTFE)-MAA/SEMA membranes as a function of SEMA concentration. By increasing the amount of the SEMA in

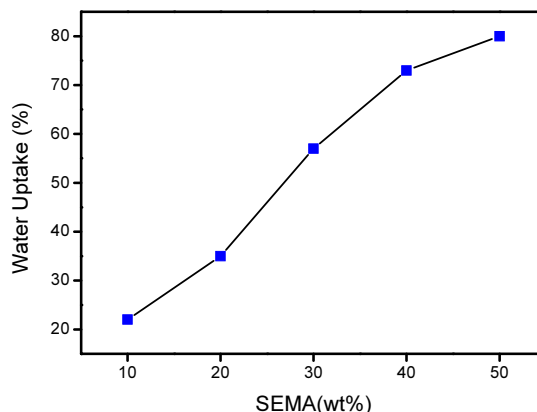


Fig. 4. Water uptake of P(VDF-*co*-CTFE)-MAA/SEMA membranes with different ratios of SEMA.

the P(VDF-*co*-CTFE)-MAA/SEMA membranes from 10 to 50 wt% the IEC value increased from 0.07 to 0.82 meq/g due to the increased in the charged group in the membrane. At 50 wt% of SEMA group in the membrane, it exhibited 0.82 meq/g of IEC value which is close to the IEC value of Nafion 117. The higher value of IEC of the P(VDF-*co*-CTFE)-MAA/SEMA membrane indicates the presence of large amount of sulfonic group in the membrane.

The water uptake of the P(VDF-*co*-CTFE)-MAA/SEMA membrane with different amount of SEMA is represented in Fig. 4. The water uptake value at 10 wt% of SEMA is around 21%. The water uptake increased almost linearly with increase in SEMA concentration up to 50% SEMA with a value of 79%. The water uptake is consistent with the IEC value as presented in Fig. 3. This is mainly due to the fact that water uptake is linearly proportional to the concentration of ionic SO_3^- groups, i.e. IEC value.

The proton conductivities of the P(VDF-*co*-CTFE)-MAA/SEMA membrane at room temperature as a function of the concentration of SEMA is presented in Fig. 5. The proton conductivities are mostly dependent on the presence of the SEMA or acidic SO_3^- group as presented in Fig. 5. The conductivity was around 0.0024 S/cm at concentration of 20 wt% SEMA. The maximum proton conductivity achieved was around 0.0414 S/cm for SEMA concentration of 50%. The

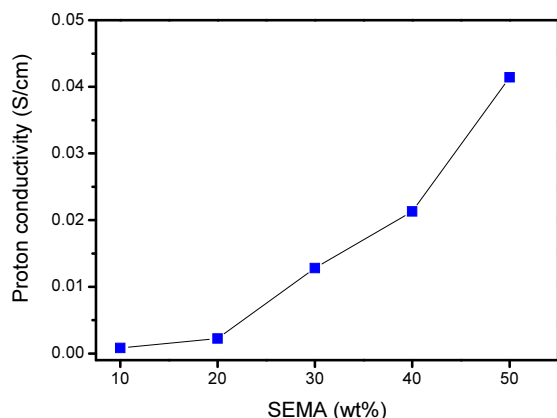


Fig. 5. Proton conductivity of P(VDF-co-CTFE)-MAA/SEMA membranes with different ratios of SEMA.

tendency of the increase in the proton conductivity is similar to the IEC value as presented in Fig. 3, which is due to the increase in the acidic SO_3^- group availability in P(VDF-co-CTFE)-MAA/SEMA membrane.

4. Conclusion

The hydrophobic, mechanically and thermally strong polymer, P(VDF-co-CTFE) was covalently linked to the acrylic monomer MAA through the functional chlorine group in the presence of DBU catalyst. Then P(VDF-co-CTFE)-MAA polymer was converted to proton conducting P(VDF-co-CTFE)-MAA/SEMA polymer electrolyte membrane via linking to SEMA through MAA by free radical polymerization reaction in the presence of ACVA initiator. The IEC value increased continuously with the increase in the SEMA concentration in the membrane. The maximum IEC value was 0.82 meq/g at 50% SEMA, which well correlates with the water uptake results. The highest proton conductivity of P(VDF-co-CTFE)-MAA/SEMA membrane was 0.041 S/cm at 50% SEMA.

Acknowledgement

This work has been supported by the Core Research Program (2012R1A2A2A02011268) and the Low Observable Technology Research Center program of Defense

Acquisition Program Administration and Agency for Defense Development.

References

1. P. E. Trapa, B. Huang, Y.-Y. Won, D. R. Sadoway, and A. M. Mayes, "Block Copolymer Electrolytes Synthesized by Atom Transfer Radical Polymerization for Solid-State, Thin-Film Lithium Batteries, Electrochem", *Solid-State Letters*, **5**, A85 (2002).
2. J. H. Kim, M. S. Kang, Y. J. Kim, J. Won, N. G. Park, and Y. S. Kang, "Dye-Sensitized Nanocrystalline Solar Cells Based on Composite Polymer Electrolytes Containing Fumed Silica Nanoparticles", *Chem. Commun.*, **14**, 1662 (2004).
3. S. W. Kuo, C. H. Wu, and F. C. Chang, "Thermal Properties, Interactions, Morphologies, and Conductivity Behavior in Blends of Poly(vinylpyridine) and Zinc Perchlorate", *Macromolecules*, **37**, 192 (2004).
4. J. H. Kim, B. R. Min, J. Won, S. H. Joo, H. S. Kim, and Y. S. Kang, "Role of Polymer Matrix in Polymer/Silver Complexes for Structure, Interactions, and Facilitated Olefin Transport", *Macromolecules*, **36**, 6183 (2003).
5. J.-H. Choi, P.-H. Kang, Y.-M. Lim, J.-Y. Sohn, J.-H. Shin, C.-H. Jung, J.-P. Jeun, and Y.-C. Nho, "Preparation and Characterization of Poly(styrenesulfonic acid)-grafted Fluoropolymer Membrane for Direct Methanol Fuel Cell", *Korean Membrane Journal*, **9**, 52 (2007).
6. L. Depre, M. Ingram, C. Poinson, and M. Popall, "Proton conducting sulfon/sulfonamide functionalized materials based on inorganic-organic matrices", *Electrochim. Acta*, **45**, 1377 (2000).
7. S. D. Mikhailenko, K. Wang, S. Kaliaguine, P. Xing, G. P. Robertson, and M. D. Guiver, "Proton conducting membranes based on cross-linked sulfonated poly(ether ether ketone) (SPEEK)", *J. Membr. Sci.*, **233**, 93 (2004).
8. C. H. Park, C. H. Lee, Y. S. Chung, and Y. M.

- Lee, "Preparation and Characterization of Cross-linked Block and Random Sulfonated Polyimide Membranes for Fuel Cell", *Membrane Journal*, **16**, 241 (2006).
9. D. J. Kim, B.-J. Chang, C. K. Shin, J.-H. Kim, S.-B. Lee, and H.-J. Joo, "Preparation and Characterization of Fluorenyl Polymer Electrolyte Membranes Containing PFCB Groups", *Membrane Journal*, **16**, 16 (2006).
 10. S.-L. Chen, J. B. Benziger, A. B. Bocarsly, and T. Zhang, "Photo-Cross-Linking of Sulfonated Styrene-Ethylene-Butylene Copolymer Membranes for Fuel Cells", *Ind. Eng. Chem. Res.*, **44**, 7701 (2005).
 11. J. R. Varcoe, R. C. T. Slade, E. L. H. Yee, S. D. Poynton, D. J. Driscoll, and D. C. Apperley, "Poly(ethylene-co-tetrafluoroethylene)-Derived Radiation-Grafted Anion-Exchange Membrane with Properties Specifically Tailored for Application in Metal-Cation-Free Alkaline Polymer Electrolyte Fuel Cells.", *Chem. Mater.*, **19**, 2686 (2007).
 12. Z. Li, J. Ding, G. P. Robertson, and M. D. Guiver, "A Novel Bisphenol Monomer with Grafting Capability and the Resulting Poly(arylene ether sulfone)s", *Macromolecules*, **39**, 6990 (2006).
 13. C. Manea and M. Mulder, "Characterization of polymer blends of polyethersulfone/sulfonated polysulfone and polyethersulfone/sulfonated polyetheretherketone for direct methanol fuel cell applications", *J. Membr. Sci.*, **206**, 443 (2002).
 14. J. H. Choi, C. K. Yeom, J. M. Lee, and D. S. Suh, "Nanofiltration of Electrolytes with Charged Composite Membranes", *Membrane Journal*, **13**, 29 (2003).
 15. C. Heitner-Wirguin, "Recent advances in perfluorinated ionomer membranes: structure, properties and applications", *J. Membr. Sci.*, **120**, 1 (1996).
 16. D. K. Lee, Y. W. Kim, J. K. Choi, B. R. Min, and J. H. Kim, "Preparation and Characterization of Proton Conducting Crosslinked Diblock Copolymer Membranes", *J. Appl. Polym. Sci.*, **107**, 819 (2008).
 17. Y. W. Kim, J. K. Choi, J. T. Park, and J. H. Kim, "Proton Conducting Poly(vinylidene fluoride-co-chlorotrifluoroethylene) Graft Copolymer Electrolyte Membranes", *J. Membr. Sci.*, **313**, 315 (2008).
 18. Z. Wang, H. Ni, C. Zhao, X. Li, T. Fu, and H. Na, "Investigation of sulfonated poly(ether ether ketone sulfone)/heteropolyacid composite membranes for high temperature fuel cell applications", *J. Polym. Sci. B: Polym. Phys.*, **44**, 1967 (2006).
 19. T. Z. Fu, C. J. Zhao, S. L. Zhong, G. Zhang, K. Shao, H. Q. Zhang, J. Wang, and H. Na, "SPEEK/epoxy resin composite membranes *in situ* polymerization for direct methanol fuel cell usages", *J. Power Sources*, **165**, 708 (2007).
 20. Y. S. Kim, F. Wang, M. Hickner, T. A. Zawodzinski, and J. E. McGrath, "Fabrication and characterization of heteropolyacid (H₃PW₁₂O₄₀)/ directly polymerized sulfonated poly(arylene ether sulfone) copolymer composite membranes for higher temperature fuel cell applications", *J. Membr. Sci.*, **212**, 263 (2003).
 21. J. K. Choi, D. K. Lee, Y. W. Kim, B. R. Min, and J. H. Kim, "Composite Polymer Electrolyte Membranes Comprising Triblock Copolymer and Heteropolyacid for Fuel Cell Applications", *J. Polym. Sci. B: Polym. Phys.*, **46**, 691 (2008).
 22. J. T. Park, K. J. Lee, M. S. Kang, Y. S. Kang, and J. H. Kim, "Nanocomposite Polymer Electrolytes Containing Silica Nanoparticles: Comparison between Poly(ethylene glycol) and Poly(ethylene oxide) dimethyl ether", *J. Appl. Polym. Sci.*, **106**, 4083 (2007).