Highly Phosphonated Poly(*N*-phenylacrylamide) for Proton Exchange Membranes

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ABSTRACT: A novel highly phosphonated poly(*N*-phenylacrylamide) (**PDPAA**) with an ion-exchange capacity (IEC) of 6.72 mequiv/g was synthesized by the radical polymerization of *N*-[2,4-bis(diethoxyphosphinoyl)phenyl]acrylamide (**DEPAA**), followed by the hydrolysis with trimethylsilyl bromide. Then, the crosslinked **PDPAA** membrane was successfully prepared by the electrophilic substitution reaction between the aromatic rings of **PDPAA** and the carbocation formed from hexamethoxymethylmelamine (CYMEL) as a crosslinker in the presence of methanesulfonic acid. The crosslinked **PDPAA** membrane had high oxidative stability against Fenton's reagent at room temperature. The proton conductivity of the crosslinked **PDPAA** membrane was 8.8×10^{-2} S/cm at 95% relative humidity (RH) and 80 °C, which was comparable to Nafion 112. Under low RH, the crosslinked **PDPAA** membrane showed the proton conductivity of 1.9×10^{-3} and 4.7×10^{-5} S/cm at 50 and 30% RH, respectively. The proton conductivity of the crosslinked **PDPAA** membrane lied in the highest class among the reported phosphonated polymers, and, consequently, the very high local concentration of the acids of **PDPAA** (IEC = 6.72 mequiv/g) achieved high and effective proton conduction under high RH. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 93–100, 2011

KEYWORDS: crosslinking; crosslinking reaction; high-performance polymers; phosphonated polymers; polyacrylamides; polymer electrolyte fuel cells; polymer electrolyte membranes; proton conductivity; radical polymerization

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INTRODUCTION Polymer electrolyte fuel cells (PEFCs) have attracted considerable attention in recent years because of their potential as future power sources for automotive, stationary, and portable applications. The function of PEFCs is basically to separate the anode and the cathode sides and to conduct protons under a wide range of operation conditions.[1–3] In the case of automotive application, the guideline of proton conductivity is around 1.0×10^{-1} S/cm at 120 °C under 20–30% relative humidity (RH). State-of-the-art PEFC membranes are perfluorinated polymers such as Nafion® and Flemion®, which show high proton conductivity under a wide range of RH at moderate operation temperature because of the well-defined phase separation between the hydrophilic main chains and the hydrophobic side chains.[4] However, they have some drawbacks, such as limited operation temperature (<80 °C) and high cost. Hence, acid-functionalized aromatic hydrocarbon polymers have been widely investigated as alternative nonfluorinated polymeric materials,[5–7] and a number of sulfonated aromatic polymers, such as poly(phenylene)s,[8,9] poly(ether ether ketone)s,[10–12] poly(ether sulfone)s,[13–17] and polyimides,[18–20] have been developed as candidates for PEFC materials. Up to now, intensive effort gave some high-performance PEFC materials based on sulfonated polymers.[9,13,15,17] High proton conduction under high temperature (>90 °C) and low RH conditions, however, is a tough issue for sulfonated polymers to overcome because their proton transportation is dominated by water molecules associated with sulfonic acid groups. Consequently, a drastic decrease in proton conductivity under low water uptake conditions is inevitable.

Recently, phosphonated polymers have been attractive for several applications.[21,22] Especially, in the field of PEFCs, phosphonated polymers are one of the candidates to solve the aforementioned problem because they show the high degree of self-dissociation and hydrogen bonding because of their amphoteric properties, which enables proton conduction even under anhydrous conditions.[23–26] Additionally, as well as for sulfonated polymers, a high concentration of acids is important to form large hydrogen-bonded aggregates, which provide proton transportation channels, according to the previous report.[25]

Recently, Parvole and Jannasch reviewed the synthetic approaches and properties of polymers containing

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phosphonic acid groups and concluded that the concentration of phosphonic acid groups in membranes should be sufficiently high to enable the formation of percolating hydrogen-bonded networks for proton transportation.[25] Based on these findings, membranes with very high local concentrations (ion exchange capacity, IEC, up to 5.3 mequiv/g) of immobilized proton-conducting phosphonic acid by grafting poly(vinylphosphonic acid) side chains on polysulfones were prepared and showed high proton conductivity of 5 mS/cm under nominally dry conditions and up to 93 mS/cm under 100% RH at 120 °C.[26] However, the synthesis of these polymers is not straightforward because phosphonated polymers are prepared by modification of premade polymers. Additionally, the structure of polymers, especially the grafting positions, is not clear, and less repeatability of polymer reactions may also be a matter of concern.

Herein, we report a facile synthesis of highly phosphonated poly(*N*-phenylacrylamide) (**PDPAA**) with a high concentration of phosphoric acids by the radical polymerization of *N*-[2,4-bis(diethoxyphosphinoyl)phenyl]acrylamide (**DEPAA**), followed by the hydrolysis with trimethylsilyl bromide. The crosslinked **PDPAA** membrane was successfully prepared by the electrophilic substitution reaction of the aromatic rings of **PDPAA** and the carbocation formed from hexamethoxymethylmelamine (CYMEL) as the crosslinker in the presence of methanesulfonic acid because **PDPAA** with an IEC of 6.72 mequiv/g was soluble in water. The obtained crosslinked membrane showed high proton conductivity of 8.8×10^{-2} S/cm, comparable to Nafion 112 at 95% RH and 80 °C. Additionally, the properties of the crosslinked **PDPAA** membrane, such as thermal stability, oxidative stability, and water uptake, are also discussed in detail.

EXPERIMENTAL

Materials

Dicyclohexylmethylamine was purchased from Sigma-Aldrich. 2,4-Dibromoaniline, triphenylphosphine, diethyl phosphate, acryloyl chloride, and trimethylsilyl bromide were purchased from TCI. Distilled ethanol, palladium (II) acetate, pyridine, and 2,2′-azobis(isobutyronitrile) (AIBN) were purchased from Wako. *N,N*-Dimethylformamide (DMF) was distilled from calcium hydride before use. Tetrahydrofuran (THF) was refluxed over sodium benzophenone for 12 h and then distilled. Other solvents and reagents were used without further purification.

Monomer Synthesis

Synthesis of 2,4-Bis(diethoxyphosphinoyl)aniline (DEPA)

To a freshly distilled ethanol (120 mL) solution of 2,4-dibromoaniline (5.02 g, 20 mmol), palladium (II) acetate (0.45 g, 2.0 mmol), and triphenylphosphine (1.57 g, 6.0 mmol) were added diethyl phosphite (12.4 mL, 96 mmol) and dicyclohexylmethylamine (12.7 mL, 60 mmol). The mixture was refluxed under nitrogen atmosphere for 48 h. After the evaporation, the residue was dissolved with dichloromethane, washed with 2 M HCl and water, and then dried over $MgSO_4$. After evaporation, the residue was purified by silica gel chromatography (ethyl acetate:hexane = 50:1) to give 2,4-bis(diethoxyphosphinoyl)aniline (**DEPA**; 5.02 g, 68.8%).

^{1}H NMR ($CDCl_3$, δ, ppm): 7.74–7.84 (1H, t), 7.48–7.54 (1H, t), 6.68–6.74 (1H, m), 6.05 (2H, s), 3.89–4.11 (8H, m), 1.20–1.26 (12H, m).

Synthesis of N-[2,4-Bis(diethoxyphosphinoyl)phenyl] acrylamide (DEPAA)

Acryloyl chloride (1.22 mL, 15 mmol) was added in small portions to a THF solution (9.5 mL) of **DEPA** (3.45 g, 9.0 mmol) and pyridine (1.22 mL, 1.5 mmol) at 0 °C. The mixture was stirred at room temperature for 1 h. Water was added into the mixture and extracted with dichloromethane. The organic layer was washed with saturated aqueous $NaHCO_3$ solution and water and then dried over $MgSO_4$. After evaporation, the residue was purified by silica gel column chromatography (ethyl acetate) to give **DEPAA** (1.32 g, 33.3%).

m.p. 142–143 °C. FTIR (KBr, cm^{-1}): 3428.8, 3382.5, 1697.0, 1635.0, 1619.9, 1592.9, 1496.5, 1473.3, 1292.0, 1176.4, 1099.2, 1010.5, 825.4. ^{1}H NMR ($CDCl_3$, δ, ppm): 11.20 (1H, s), 8.84–8.90 (1H, m), 8.02–8.11 (1H, t), 7.89–7.96 (1H, t), 6.44–6.50 (1H, d), 6.26–6.35 (1H, q), 5.81–5.85 (1H, d), 4.03–4.21 (8H, m), 1.31–1.37 (12H, m). ^{13}C NMR (300 MHz, $CDCl_3$, δ, ppm): 164.7, 146.4, 137.5, 137.0, 132.4, 128.4, 120.9, 120.7, 120.6, 63.1, 16.7. Anal. Calcd. for $C_{17}H_{27}NO_7P_2$: C, 48.69%; H, 6.49%; N, 3.34%; Found: C, 48.61%; H, 6.28%; N, 3.24%.

Polymerization of DEPAA (PDEPAA)

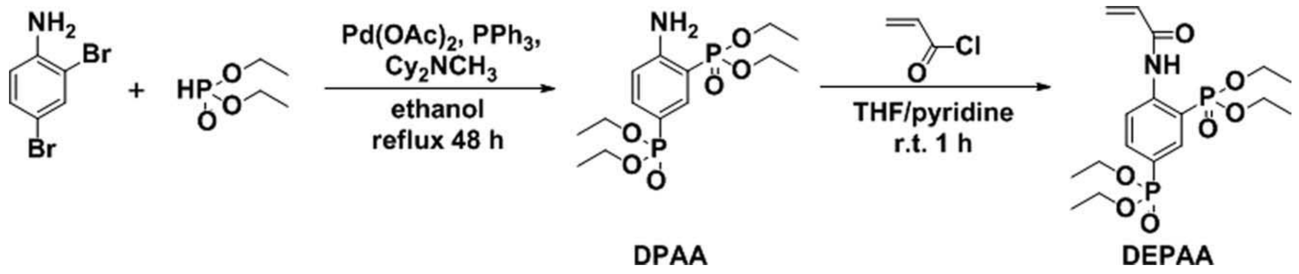
DEPAA (0.63 g, 1.5 mmol), AIBN (0.01 g, 0.06 mmol), and distilled DMF (0.6 mL) were placed in a glass tube using standard freeze-evacuate-thaw procedures. The reaction mixture was heated at 60 °C for 48 h and then cooled to room temperature. The viscous polymer solution was dissolved in DMF and poured in water. The precipitate was collected and dried *in vacuo* at 50 °C for 24 h to give **PDEPAA** (0.49 g, 78.0%).

FTIR (KBr, cm^{-1}): 3401.82, 2985.3, 1708.6, 1299.8, 1253.5, 1049.1, 964.2, 794.2. ^{1}H NMR ($CDCl_3$, δ, ppm): 10.86 (1H, bs), 8.23 (1H, m), 7.87 (1H, t), 7.54 (1H, bs), 4.12–4.03 (8H, m), 2.33–1.05 (15H, m).

Synthesis of PDPAA by Hydrolysis of PDEPAA

PDEPAA (0.42 g, 1.0 mmol) was first dissolved in distilled chloroform (5.0 mL). Then, trimethylsilyl bromide (2.6 mL, 19.7 mmol) was added dropwise at 5 °C, and the mixture was stirred at 40 °C for 24 h. After the evaporation, the alcoholysis of the silylated intermediate was performed by adding an excess of methanol (5.0 mL). The mixture was stirred at room temperature for 6 h, and then the solvent was evaporated. The residue was poured into acetone. The precipitate was collected and dried *in vacuo* at 40 °C for 24 h (0.3 g, 97.8%).

FTIR (KBr, cm^{-1}): 3448.1, 2275.6, 1673.9, 1585.2, 1519.6, 1380.8, 1006.7. ^{1}H NMR (CD_3OD, δ, ppm): 8.02 (2H, bs), 7.50 (1H, bs), 2.54–2.01 (3H, m).



SCHEME 1 Synthesis of **DEPAA**.

Membrane Preparation and IEC

A methanol solution of **PDPAA** was cast onto a flat glass plate. Drying the solution at 80 °C for 12 h under reduced pressure gave a transparent, flexible, and tough membrane. IEC value of the polymer was determined by titration with 0.02 M aq. NaOH. The point of neutralization between the phosphonic acids and 0.02 M aq. NaOH was determined at pH = 8.0.

Preparation of Crosslinked Membrane

The optimized condition to prepare the crosslinked membranes is as follows: methanol solution of **PDPAA** (0.15 g, 0.5 mmol), 7 wt % of CYMEL for **PDPAA**, and 0.07 wt % of methanesulfonic acid for **PDPAA** was casted onto a Teflon sheet. Drying the film at 40, 60, 80, 100, 120, and 150 °C for 6 h (for 1 h at each temperature) under ambient atmosphere gave a transparent membrane.

Water Uptake

The humidity dependence of water uptake was measured by plating the membrane in a thermocontrolled humid chamber for 4 h. Then, the membrane was taken out and quickly weighed on a microbalance. Water uptake was calculated from:

$$\mathrm{WU} = (W_s - W_d)/W_d \times 100 \text{ wt } \%,$$

where W_s and W_d are the weights of wet and dried membrane, respectively.

Proton Conductivity

Proton conductivity in plane direction of the membrane was determined using an electrochemical impedance spectroscopy technique over the frequency from 5 Hz to 1 MHz (Hioki 3532-80). A two-point probe conductivity cell with two platinum plate electrodes was fabricated. The cell was placed under a thermocontrolled humid chamber. Proton conductivity (σ) was calculated from:

$$\sigma = d/(L_s w_s R),$$

where d is the distance between the two electrodes, L_s and w_s are the thickness and width of the membrane, and R is the resistance value measured.

Oxidative Stability

Oxidative stability of the membranes was tested by immersing the films into Fenton's reagent (3% H_2O_2 aqueous solution containing 20 ppm $FeSO_4$) at room temperature. The dissolved time of the membranes into the reagent was used to evaluate their oxidative stability.

Measurement

^{1}H (300 MHz) and ^{13}C spectra (75 MHz) were recorded with a Bruker DPX300S spectrometer. ^{31}P spectrum (162 MHz) was recorded with a JEOL. Fourier transform infrared (FTIR) spectra were obtained with a Horiba FT-120 spectrophotometer. Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 10 °C/min for thermogravimetry (TG) and differential thermal analysis (DTA). Molecular weight measurement was performed via gel permeation chromatography (Waters) with two polystyrene gel columns (shodex KD-806M). *N*-Methyl-2-pyrrolidinone containing 0.01 M LiBr was used as a solvent at a flow rate of 0.5 mL/min. M_n and M_w were calibrated by standard polystyrene samples.

RESULTS AND DISCUSSION

Monomer Synthesis

The monomer **DEPAA** was prepared by a two-step procedure using 2,4-dibromoaniline as the starting material (Scheme 1). 2,4-Dibromoaniline was reacted with diethyl phosphite through Pd-catalyzed phosphorylation[27] to afford **DEPA**, which was further reacted with acryloyl chloride to yield **DEPAA**. The structure of **DEPAA** was characterized by the elemental analysis, FTIR, and ^{1}H NMR spectroscopies. The FTIR spectrum of **DEPAA** showed characteristic absorptions at 1697 and 1635 cm^{-1}, which are assignable to an amide carbonyl group and a carbon–carbon double bond, respectively. Figure 1 shows the ^{1}H NMR spectrum of **DEPAA**. All peaks agree with the assignment to the expected structure of **DEPAA**.

Polymer Synthesis

The synthesis of **PDPAA** was carried out by the radical polymerization of **DEPAA** using AIBN as a radical initiator in DMF, followed by the hydrolysis of the phosphonic acid ester using trimethysilyl bromide (Scheme 2). The polymerization proceeded smoothly and yielded high molecular weight of **PDEPAA**. The number-average and weight-average molecular weights of **PDPAA** were 101,000 and 207,000, respectively, estimated by GPC based on polystyrene standards. **PDPAA** was obtained as white solid and soluble in methanol and water.

The chemical structure of **PDPAA** was confirmed by FTIR, ^{1}H, and ^{31}P NMR spectroscopies. Figure 2 shows the ^{1}H

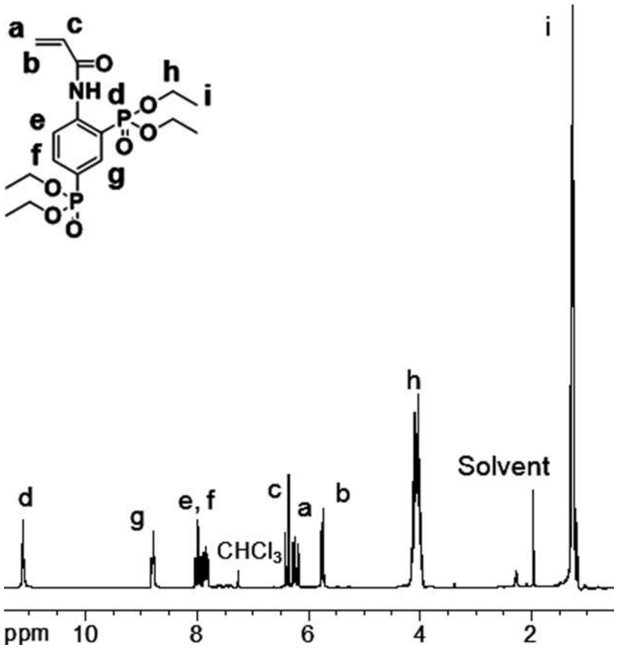


FIGURE 1 ^{1}H NMR spectrum of **DEPAA** in $CDCl_3$.

NMR spectra of **PDEPAA** and **PDPAA**. The signals of the acrylate group (δ = 5.81–6.50) disappear in the ^{1}H NMR spectrum of **PDEPAA**, and the signals corresponding to the phosphonic ethyl ester group can be observed at δ = 4.12–4.03 and 2.33–1.05. This spectrum suggests that the vinyl polymerization proceeded completely without the decomposition of the monomer, and the signals of the phosphonic ethyl ester disappear completely in the ^{1}H NMR spectrum of **PDPAA** after the hydrolysis. Additionally, the ^{31}P NMR spectrum has two peaks corresponding to the characteristic phosphonic acids at δ = 10.0−20.0, which also supports that the whole reaction proceeded without any decomposition and side reaction to give the desired **PDPAA** (Fig. 3). In the FTIR spectra (Fig. 4), the disappearance of the absorption at around 1635 cm^{-1} assignable to the vinyl group was confirmed, and the characteristic absorption at 1253 cm^{-1} corresponding to the phosphonic ester disappears after the hydrolysis, resulting in the appearance of the absorption at 2275 cm^{-1} corresponding to the phosphonic acids. The IEC value of **PDPAA** was determined to be 6.72 mequiv/g (theoretical IEC value = 6.49 mequiv/g) by titration with 0.02 M aq. NaOH, which also indicates the complete hydrolysis.

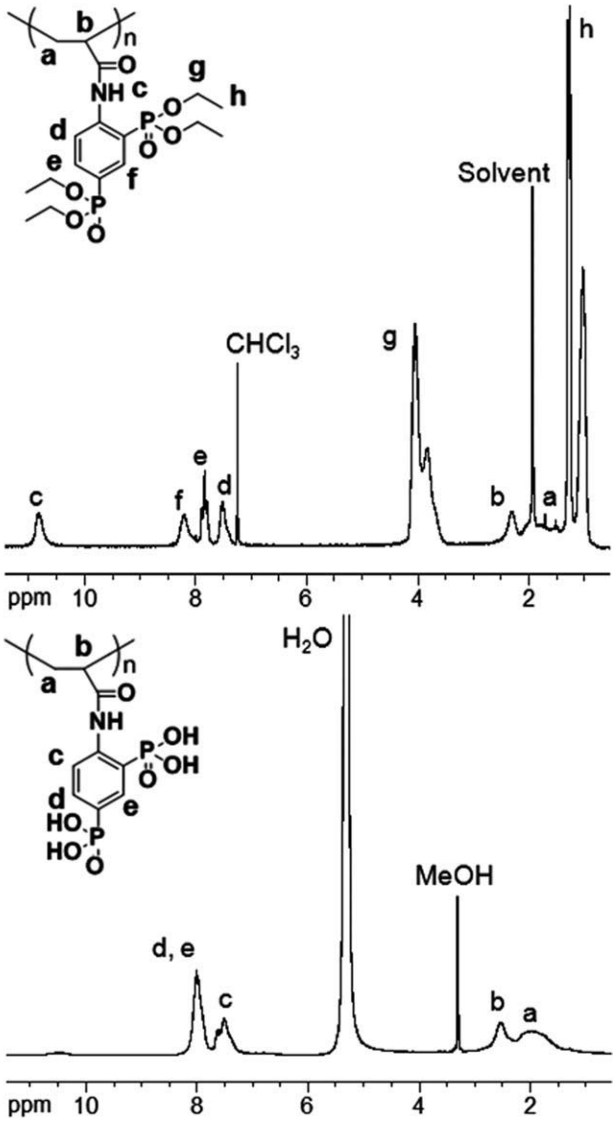
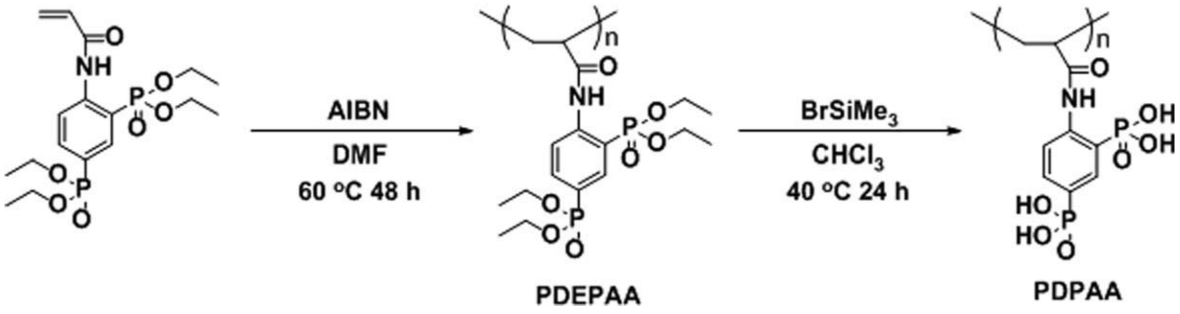


FIGURE 2 ^{1}H NMR spectra of **PDEPAA** (top) in $CDCl_3$ and **PDPAA** (bottom) in CD_3OD.

As **PDPAA** itself was soluble in water, the crosslinked **PDPAA** membrane was prepared by the electrophilic substitution



SCHEME 2 Synthesis of **PDPAA**.

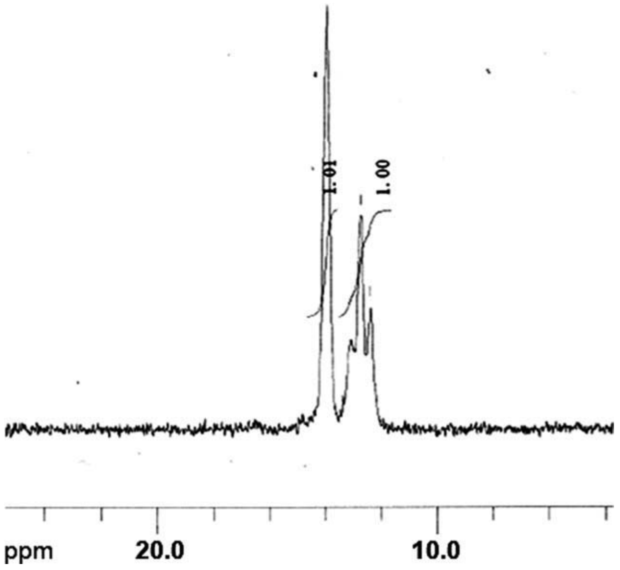


FIGURE 3 ^{31}P NMR spectrum of **PDPAA**.

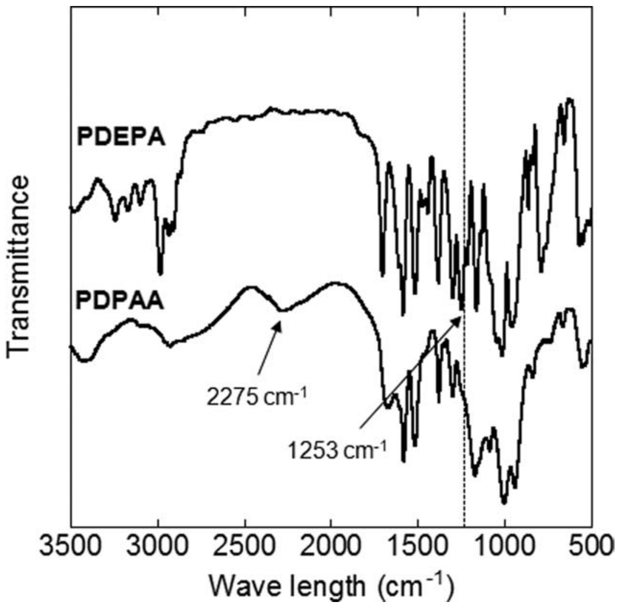


FIGURE 4 FTIR spectra of **PDEPA** and **PDPAA**.

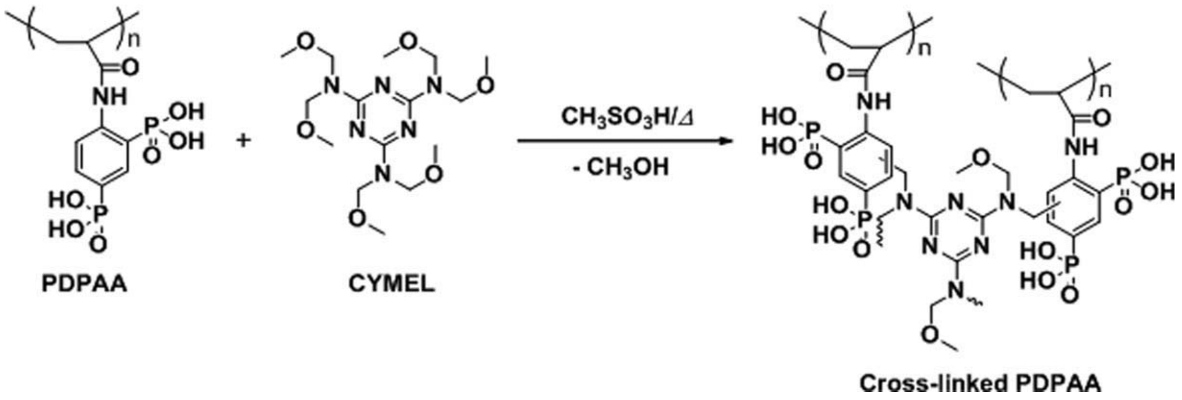
reaction between the aromatic rings of **PDPAA** and the carbocation formed from CYMEL as the crosslinker in the presence of methanesulfonic acid (Scheme 3).[28] Additionally, this crosslinking system, which little affects IEC values, enables to obtain a crosslinked membrane with high IEC value. As a result of optimization of the crosslinking reaction conditions, such as the amount of CYMEL, reaction time, and reaction temperature, a fine crosslinked **PDPAA** membrane could be prepared as follows: a methanol solution of **PDPAA**, 7 wt % of CYMEL for **PDPAA**, and 0.07 wt % of methanesulfonic acid for **PDPAA** were cast onto a Teflon sheet. The film was dried at 40, 60, 80, 100, 120, and 150 °C totally for 6 h (for 1 h at each temperature) under ambient atmosphere to give a fine membrane. After the crosslinking reaction, the obtained crosslinked **PDPAA** membrane became insoluble in water, which indicates that the crosslinking reaction proceeded successfully.

Thermal Properties of PDPAA

The thermal properties of **PDPAA** and crosslinked **PDPAA** were evaluated by TG analysis. Figure 5 shows the TG curves of **PDPAA** and crosslinked **PDPAA** under nitrogen atmosphere. In **PDPAA**, the two-step weight loss of the polymer is observed from 210 to 350 °C and above 350 °C. The first weight loss is due to the elimination of the phosphonic acid groups, and the second is attributed to the degradation of polymer backbones. On the other hand, the similar TG curve was observed in the crosslinked **PDPAA**. The weight loss due to the polymer decomposition starts from around 210 °C, which indicates that the crosslinked **PDPAA** has enough thermal stability for fuel cell operation.

Oxidative Stability

The oxidative stability of the crosslinked **PDPAA** membrane was evaluated in Fenton's reagent (a 3% H_2O_2 aqueous solution containing 20 ppm $FeSO_4$) at room temperature. Generally, sulfonated polymers with high IEC value have been known to demonstrate low oxidative stability against Fenton's reagent.[12,14,17] On the other hand, the crosslinked **PDPAA** membrane kept the shape of the membrane for 24 h, and it took 48 h for complete dissolution, indicating that the



SCHEME 3 Preparation of the crosslinked **PDPAA** membrane.

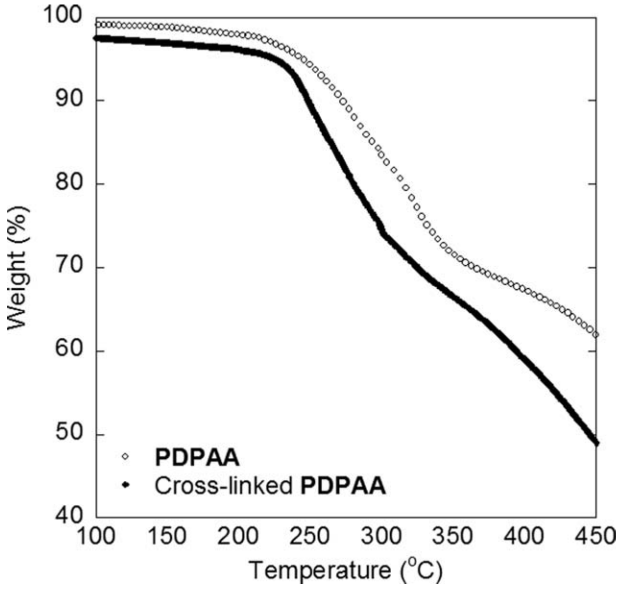


FIGURE 5 TG curves of **PDEPAA** and **PDPAA** under nitrogen atmosphere.

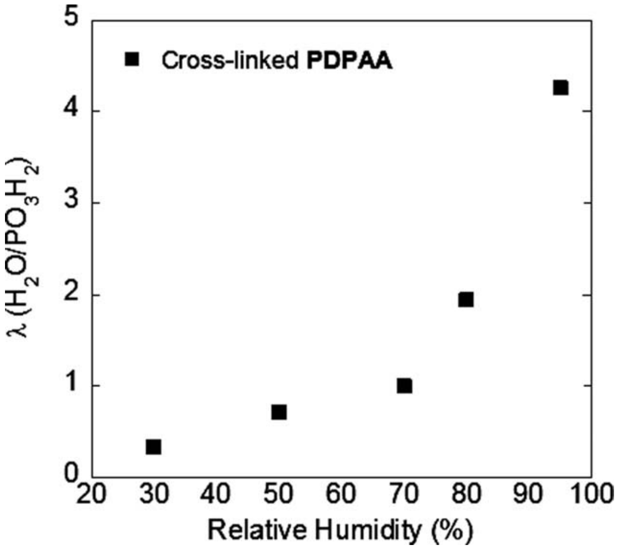


FIGURE 7 Humidity dependence of hydration number (λ) of crosslinked **PDPAA** membrane at 80 °C.

crosslinked **PDPAA** membrane has excellent oxidative stability against Fenton's reagent regardless of quite high IEC value.

Water Uptake

The water uptake behavior of acid-functionalized polymers is a significant factor for proton conductivity. Although the proton conduction of phosphonic acids is considered to be mainly derived from their own self-dissociation and hydrogen bonding, high water uptake can contribute to the enhancement of proton conductivity. Accordingly, even phosphonated polymers need high water uptake to achieve high and effective proton conduction. However, excess water uptake induces unacceptable dimensional changes and a decrease in the mechanical strength. The humidity dependence of water uptake was investigated for the crosslinked **PDPAA** membrane at 80 °C. As shown in Figure 6, the crosslinked **PDPAA** membrane shows moderate water uptake (50.0 wt %) at 95% RH, which corresponds to λ (the number of water molecules per an acid group) = 4.3 (Fig. 7). Decreasing RH, the water uptake decreases to 12.0, 8.3, and 3.8 wt %, which corresponds to λ = 1.0, 0.7, and 0.3 at 70, 50, and 30% RH, respectively. Considering that the crosslinked **PDPAA** membrane has quite high IEC value (6.72 mequiv/g), the water uptake is expected to be higher in a wide range of RH (especially under low RH) as well as

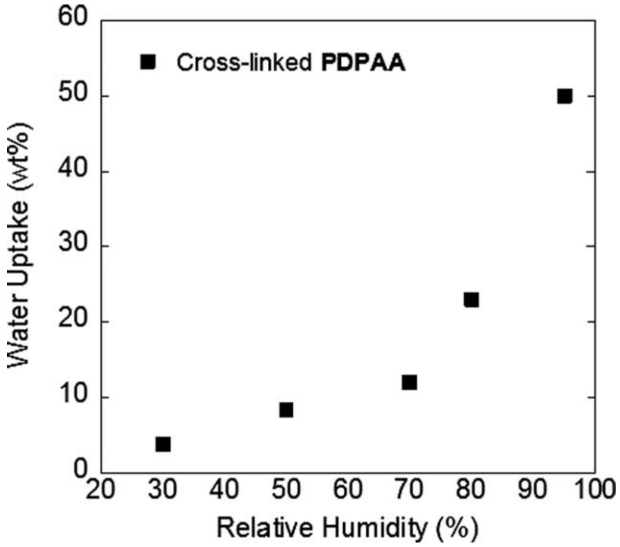


FIGURE 6 Humidity dependence of water uptake of crosslinked **PDPAA** membrane at 80 °C.

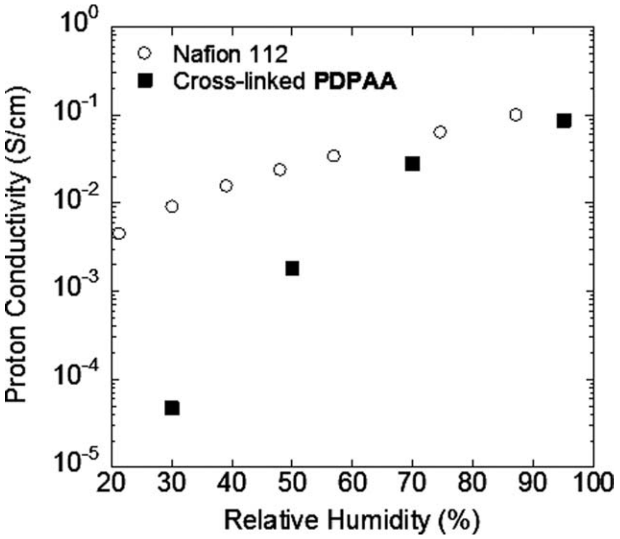


FIGURE 8 Humidity dependence of proton conductivity of crosslinked **PDPAA** and Nafion 112 membranes at 80 °C.

sulfonated polymers with high IEC values.[15,27] This is probably because of its weaker acidity that that of sulfonated polymers, and **PDPAA** is likely not to form the water-swollen phase, which efficiently retains water in the membrane, and the compact crosslinked structure may attribute to this behavior.

Proton Conductivity

The humidity dependence of the proton conductivity of the crosslinked **PDPAA** membrane was measured at 80 °C. Generally, the proton conductivity of the membrane is considered to play a significant role in the performance of fuel cells. As shown in Figure 8, the crosslinked **PDPAA** membrane shows high proton conductivity, comparable to Nafion 112 at 95% RH, and still maintains relatively high proton conductivity of 2.8×10^{-2} S/cm at 70% RH, indicating that the water-assisted proton transportation similar to that in conventional sulfonated polymers can contribute to high proton conductivity under high RH. Under low RH, the proton conductivity of 1.9×10^{-3} and 4.7×10^{-5} S/cm is observed at 50 and 30% RH, respectively. The proton conductivity of the crosslinked **PDPAA** membrane is strongly dependent on RH, which implies that the formation of percolating hydrogen-bonded networks for proton transportation is deficient under low RH. Yet, to the best of our knowledge, the proton conductivity of the crosslinked **PDPAA** membrane still lies in one of the highest class among the reported phosphonated polymers,[26,29–32] which clearly demonstrates that the very high local concentration of the acids of **PDPAA** (IEC = 6.72 mequiv/g) was effective for high proton conduction.

CONCLUSIONS

A novel highly phosphonated **PDPAA** with an IEC of 6.72 mequiv/g was successfully prepared by the radical polymerization of **DEPAA**, followed by the hydrolysis with trimethylsilyl bromide. Then, the crosslinked **PDPAA** membrane was prepared by the reaction of **PDPAA** with CYMEL as the crosslinker in the presence of methanesulfonic acid. The crosslinked **PDPAA** membrane showed high oxidative stability against Fenton's reagent at room temperature and moderate water uptake at 95% RH. However, the water uptake significantly decreased from 12.0 to 3.8 wt % at 70 to 30% RH in spite of quite high IEC value. These results implied that the crosslinked compact structure suppressed water swelling. The crosslinked **PDPAA** membrane showed high proton conductivity of 8.8×10^{-2} S/cm at 95% RH, which was comparable to Nafion 112 under the same conditions. Although the polymer has interesting properties, the proton conductivity of crosslinked PDPAA under low RH is required to improve for fuel cell applications.

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