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1 Introduction

Phosphonated polymers are of current interest as materials for polymer electrolyte membranes (PEMs). Unlike sulfonated polymers which transport protons by water-assisted systems (the vehicle mechanism^{1,2}), such as sulfonated perfluoropolymers (*e.g.*, Nafion® and Flemion®)^{3,4} and sulfonated hydrocarbon polymers,⁵⁻⁹ phosphonated polymers achieve proton transportation from high self-dissociation and hydrogen-bonding networks (the Grotthuss mechanism^{1,2}) even under anhydrous conditions.¹⁰⁻¹³ Thus, the development of PEMs based on phosphonated polymers, which can successfully

Polymer electrolyte membrane based on polyacrylate with phosphonic acid *via* long alkyl side chainst

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A series of novel phosphonated polymers with phosphonic acid groups *via* different lengths of flexible pendant side chains was synthesized. The radical polymerization of the corresponding diethyl esters of acrylate monomers, followed by hydrolysis with trimethylsilyl bromide produced the expected polyacrylates. Among the three polymers, the cross-linked poly[6-(acryloyloxy)hexylphosphonic acid] (PAHPA) membrane prepared by the recombination of polymer radicals with benzoyl peroxide as a radical initiator showed excellent proton conductivity comparable to that of the Nafion 117 membrane in the range of 30–80% relative humidity (RH) at 80 °C, regardless of the significant low water uptake behavior. Furthermore, well-defined phase separation between the hydrophobic and hydrophilic domains was clearly observed by scanning transmission electron microscopy (STEM) and synchrotron X-ray scattering measurements. To the best of our knowledge, the cross-linked PAHPA membrane shows the best proton conductivity performance among phosphonated polymers already reported.

function at high temperature (>100 $^{\circ}$ C) and in nominally dry conditions, has been recently investigated.^{13–20}

In previous work, we focused on a high ion exchange capacity (IEC)²¹ value and prepared phosphonated poly(N-phenylacrylamide) with an IEC value of 6.72 mequiv g^{-1} (PDPAA). Although the cross-linked PDPAA membrane showed high proton conductivity comparable to the Nafion 112 membrane under high RH due to the high IEC value, a drastic decrease in proton conductivity was clearly observed with decreasing RH.22 That is, the proton conductivity behavior depended on not only the hydrogen-bonding network but also on a water-assisted system. The speculation that we obtained from these phenomena is as follows: water-assisted proton transportation like that with sulfonated polymers functioned successfully under high RH in phosphonated polymers with high IEC values. The rigid side chains, however, might hinder the formation of the well-connected hydrogen-bonding networks and result in deficient proton conduction under low RH. Thus, in addition to high IEC values, a flexible polymer structure which can induce the formation of hydrogen-bonding networks is considered to be essential to achieve efficient proton transportation over a wide range of RH. Considering these factors, poly(vinylphosphonic acid) (PVPA) (IEC = 18.5 mequiv g^{-1}) is one of the most promising candidates for PEMs due to the extremely high IEC values.23-26 However, the proton conductivity of PVPA was not as high as expected probably because of the limitation of molecular motion. Although a cyclic oligosiloxane containing phosphonic acid groups via a flexible alkyl spacer was also

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Here, we designed a novel series of phosphonated polymers, which possessed phosphonic acid groups *via* flexible pendant side chains of 2, 4, and 6 methylene units, PAEPA, PABPA, and PAHPA, toward high proton conductivity even under a low RH of 30%. The flexible pendant side chains can hinder the formation of the anhydrides and give rise to promising performance due to the high IEC values and hydrogen-bonding networks derived from the flexible polymer structures.

2 Results and discussion

2.1 Synthesis

PAEPA, PABPA, and PAHPA were synthesized by radical polymerization of diethyl 2-(acryloyloxy)ethylphosphonate (AEPN), diethyl 4-(acryloyloxy)butylphosphonate (ABPN), and diethyl 6-(acryloyloxy)hexylphosphonate (AHPN) using 2,2'-azobis(isobutyronitrile) (AIBN) as a radical initiator in toluene, followed by hydrolysis of the phosphonic acid ester using trimethylsilyl bromide (Scheme 1) (see ESI for details, Fig. S1-S9[†]). The molecular weights of PAEPN, PABPN, PAHPN, were estimated to be $M_{\rm n} = 34\,800$ and $M_{\rm w} = 89\,200$, $M_{\rm n} = 43\,000$ and $M_{\rm w} = 86\,900$, $M_{\rm n} = 40\ 000$ and $M_{\rm w} = 93\ 000$, respectively, by size exclusion chromatography. The structures of PAEPA, PABPA, and PAHPA were characterized from ¹H NMR (Fig. S3, S6 and S9[†]) and FT-IR spectra. After the hydrolysis, the peaks corresponding to the ethyl groups clearly disappeared in all ¹H NMR spectra (Fig. S3, S6 and S9⁺). All the polymers themselves are soluble in water due to the high IEC values, and the cross-linked polymer membranes were thus prepared by radical reaction with benzoyl peroxide as a radical initiator (5 mol% for the polymers). The polymer radicals formed by the α-hydrogen abstraction recombined to form crosslinked polymers. The obtained membranes showed rubbery properties and became insoluble in water, indicating that the cross-linking reactions were successfully carried out to obtain the cross-linked membranes. The occurrence of the cross-linking reaction at the CH or CH2 group of a polyacrylate was further confirmed by comparing the normalized absorbance peak intensity attributed to carboxyl ester (C=O) groups at 1731 cm⁻¹ (a) and that attributed to methine (C-H) groups at 2935 cm⁻¹ (b) of the polyacrylate in the FT-IR spectra, showing the decrease in the peak intensity ratio, a/b, from 0.716 to 0.607 (Fig. S10[†]).

The IEC values of PAEPA, PABPA, and PAHPA determined by titration with a 0.02 M NaOH aqueous solution were 5.44, 4.76, and 4.09 mequiv g^{-1} , respectively, which were in good agreement with the theoretical IEC values of 5.55, 4.80, and 4.23 mequiv g^{-1} .



Scheme 1 Synthesis of PAHPA.

2.2 Thermal stability

The thermal stabilities of the cross-linked membranes were evaluated by thermogravimetry analysis (Fig. S11[†]). A three-step weight loss is observed from 150 to 250, from 250 to 300, and above 300 °C in the cross-linked membranes. Each weight loss corresponds to the dehydration between the phosphonic acid groups (the formation of the anhydrides),^{24,25} the elimination of the phosphonic acid groups, and the decomposition of the polymer backbone, respectively.

2.3 Oxidative stability

The oxidative stabilities of the cross-linked membranes were evaluated in Fenton's reagent at room temperature as an accelerated test. The cross-linked membranes maintained the shape of the membrane over 24 h. Membranes with high IEC values generally show a weak oxidative stability against Fenton's reagent.^{28,29} The cross-linked membranes, in contrast, showed high oxidative stability regardless of the high IEC values and the aliphatic structure. One of the reasons for the high oxidative stability is probably the quite low water uptake especially in the case of PAHPA, as described below, by which the hydroxy radical attack on the membrane could be significantly suppressed.

2.4 Hydrolytic stability

The cross-linked membrane of PAHPA was also subjected to a hydrolytic stability test at 80 °C and 95% RH for 1 week. In the FT-IR spectra (Fig. S12[†]), the absorbance peak intensity attributed to the carbonyl (C=O) stretching of the ester groups at 1731 cm⁻¹ remained unchanged, without appearance of a new peak for the carbonyl (C=O) stretching of the carboxylic acid groups around 1700 cm⁻¹ after testing. The result indicates that the PAHPA membrane has a good stability to hydrolysis, probably because the ester groups are introduced apart from the phosphonic acid groups *via* the long hydrophobic spacer, repulsing the water molecules to be consumed for hydrolysis.

2.5 Water uptake and hydration number

Water uptake of the membranes is closely related to proton conductivity. In sulfonated polymers, the IEC values of the membranes generally dominate the water uptake of the membranes, and high water uptake leads to efficient waterassisted proton transportation.³⁰ In contrast, the high degree of hydrogen bonding and the lower acidity of the phosphonic acid groups can limit the water uptake behavior of the membranes in phosphonated polymers. The humidity dependence of water uptake was investigated for the cross-linked polyacrylate and Nafion 117 membranes at 80 °C (Fig. 1a). The slopes of the plots for the water uptake depending on the RH are quite different with the lengths of the side chains, becoming smaller in the order of PAEPA, PABPA, and PAHPA. Especially, regardless of the high IEC value (4.09 mequiv g^{-1}), the cross-linked PAHPA membrane shows a lower water uptake than that of the Nafion 117 membrane (0.90 mequiv g^{-1}), leading to excellent dimensional stability as well.



Fig. 1 Humidity dependence of (a) water uptake and (b) hydration number (λ) of Nafion 117, cross-linked PAEPA, PABPA and PAHPA membranes at 80 °C.

Further, the hydration number (λ), which is the number of water molecules per acid group, is plotted against RH (Fig. 1b). Compared to Nafion 117 membrane, significantly lower λ values were observed in all the cross-linked membranes over the whole range of RH. Kaltbeitzel *et al.* previously investigated the water sorption of PVPAs and noted that the water uptake strongly decreased with decreasing RH ($\lambda < 1$ at 30% RH and 80 °C). They also mentioned that such water uptake behavior resulted from the dehydration between the phosphonic acid groups (the formation of the anhydrides).^{23,24} Wegner *et al.* demonstrated the formation of the anhydrides in PVPA by NMR spectroscopy as well.²⁵ Thus, the same phenomena can occur in the cross-linked membranes, although the cross-linked structure can affect the water uptake behavior as well.

2.6 Proton conductivity

The humidity dependence of proton conductivity was measured for the cross-linked PAEPA, PABPA, PAHPA and Nafion 117 membranes at 80 °C (Fig. 2). Proton conductivity is generally considered to play an important role in the performance of fuel cells. Thus, higher levels of proton conductivity can provide higher power densities in polymer electrolyte fuel cells (PEFCs). As can be seen in Fig. 2, the slopes of the plots for proton conductivity strongly depend on the length of side chain, becoming smaller in the order of PAEPA, PABPA, PAHPA and finally the cross-linked PAHPA membrane shows excellent proton conductivity comparable to the Nafion 117 membrane in



Fig. 2 Humidity dependence of proton conductivity of cross-linked PAEPA, PABPA, PAHPA and Nafion 117 membranes at 80 °C.

the whole range of RH (30–80%). It should be noted that the proton conductivity increased in the order of PAEPA, PABPA, and PAHPA, despite the IEC values decreasing from 5.44, 4.76, to 4.09 mequiv g⁻¹. Even at 30% RH, the cross-linked PAHPA membrane achieved a high proton conductivity of 8.9×10^{-3} S cm⁻¹. To the best of our knowledge, the cross-linked PAHPA membrane shows the best performance of the proton conductivity among phosphonated polymers already reported.

The phosphonated polymer in our previous work (PDPAA) showed a drastic decrease in proton conductivity with decreasing RH regardless of the high IEC value (6.72 mequiv g^{-1}), which was concluded to result from the formation of the deficient hydrogen-bonding networks due to the rigid side chains, preventing efficient proton transportation.²² In contrast, the flexible pendant side chains of PAHPA should contribute to the formation of the hydrogen-bonding networks, which will lead to excellent proton conductivity over the whole range of RH. The significantly low water uptake of the cross-linked PAHPA membrane also supports the belief that the proton transportation is derived from not only the water-assisted feature but also the hydrogen-bonding network system.

2.7 Morphology

The cross-sectional morphology of the cross-linked PAHPA membrane was investigated by STEM. In the STEM images (Fig. 3), the dark and bright regions were assigned to the hydrophilic domains with phosphonic acid groups and the hydrophobic domains, respectively, since the membrane was stained with lead ions by ion exchange of the phosphonic acid groups in 2 wt% Pb(OCOCH₃)₂ aqueous solution. As can be seen in Fig. 3, a clear phase separation between the hydrophilic and hydrophobic domains is observed. Interestingly, the interdistance of the cylinders is significantly narrow (~ 2 nm) but uniform and well-connected, which suggests that the flexible polymer structure successfully induced the self-arrangement of each molecule to form a well-defined periodic nanostructure. Such well-defined continuous hydrophilic domains (i.e., the hydrogen-bonding networks) must contribute to efficient proton transportation, and excellent proton conductivity derived from the hydrogen-bonding networks was accomplished in the cross-linked PAHPA membrane.



Fig. 3 Cross-sectional STEM image of cross-linked PAHPA membrane, scale bar = 20 nm.

In order to gain more detailed morphology, synchrotron small and wide angle X-ray scattering (SAXS and WAXS) measurements were further performed for the PAHPA films before and after immersion in deionized water for 6 h (*i.e.*, dry and wet PAHPA films) in order to obtain structural details and their changes with water swelling. The polymer films were observed to reveal featureless SAXS patterns before and after water swelling (data not shown). These results indicate that the PAHPA chains in films do not form any microstructure before and after water swelling.

However, the polymer films showed isotropic ring scattering in the WAXS patterns (Fig. 4). The dry film revealed several peaks positioned at q = 3.21, 6.42 and 9.63 nm⁻¹; their relative scattering vector lengths from the beam center were 1, 2 and 3 (Fig. 4a and c). The results indicate that the scattering peak at $q = 3.21 \text{ nm}^{-1}$ is the first order peak and the others are the second and third peaks of the first one respectively. The dspacing of the first order peak was determined to be 1.96 nm. This *d*-spacing value is smaller than twice the length (1.24 nm) of the fully stretched bristle including phosphonic acid estimated by molecular simulation with the Cerius2 software package (Accelrys, San Diego, CA, USA). These results imply structural information on the dry PAHPA film as follows. The PAHPA chains have a cylinder-like structure centered at the polymer backbone (i.e., helical conformation) rather than a sheet-like structure. Such molecular cylinders are laterally assembled together in a certain correlation length but without any regular packing order; such laterally assembled molecular cylinders have a periodic interdistance of 1.96 nm, which is consistent with that observed in the STEM image. The bristles in the laterally assembled molecular cylinders are partially interdigitated via hydrogen bonding formations of the phosphonic acids at the bristle ends.

In addition, another strong, broad peak was observed at $q = 14.03 \text{ nm}^{-1}$. This broad scattering peak was found to consist of



Fig. 4 Representative two-dimensional (2D) WAXS patterns of (a) dry and (b) wet PAHPA films. (c) One-dimensional (1D) scattering profiles extracted from the 2D scattering patterns in (a) and (b). In each 1D scattering profile, the scattering peaks were separated WAXS patterns using a Gaussian function: the circles are the measured data; the black dashed lines are the peaks separated by fitting with the Gaussian function; the red solid line is the sum of the separated peaks.

two sub-peaks (one peak centered at $q = 14.03 \text{ nm}^{-1}$ and the other centered at 17.45 nm⁻¹) by peak separation analysis using a Gaussian function. Their *d*-spacings were determined to be 0.45 nm and 0.36 nm, respectively. The d-spacing value of 0.45 nm is comparable to the mean interdistance of conventional flexible linear polymers such as polyethylene and polypropylene and, thus can be assigned as the mean interdistance between the bristles. In contrast, the d-spacing value of 0.36 nm is relatively shorter than the mean interdistances of conventional flexible linear polymers and the bristles of the PAHPA polymer but larger than the interdistance (0.20 nm) of water molecules displaying hydrogen bonding. Therefore, this d-spacing can be assigned as the mean interdistance between the PAHPA polymers and water molecules. The PAHPA polymer was found to be hygroscopic because of the phosphonic acid groups and thus its film might contain some water molecules which were absorbed when the film was exposed to ambient air even though the air contact time was short.

The wet PAHPA films showed a WAXS pattern similar to that observed for the dry films (Fig. 4b and c). However, the three peaks in the low q region were weakened in intensity, compared to those of the dry films. Moreover, their positions were slightly shifted toward the lower q region: 3.03, 6.07 and 9.10 nm^{-1} (Fig. 4c). From these peaks, the mean interdistance of the helical polymer chains was determined to be 2.07 nm. This value is slightly larger than that of the dry films. Another strong, asymmetric peak additionally appeared around 20 nm⁻¹. This peak was separated into two sub-peaks at q = 14.03 (d-spacing = 0.45 nm) and 19.84 nm⁻¹ (*d*-spacing = 0.32 nm). The first subpeak corresponded to the mean interdistance of the bristles, which is the same as that of the bristles in the dry films. The second sub-peak originated from the mean interdistance between the PAHPA polymers and water molecules, which is slightly shorter than that of the dry films. These results collectively indicate that in the PAHPA film the lateral interdistance of the helical polymer chains was slightly increased by water swelling.

3 Conclusions

A novel series of phosphonated polymers which had phosphonic acid groups via flexible pendant side chains (PAEPA, PABPA, and PAHPA) was synthesized by the radical polymerization of AEPN, ABPN and AHPN, respectively, followed by hydrolysis with trimethylsilyl bromide. Among these three, the cross-linked PAHPA membrane showed excellent proton conductivity comparable to that of the Nafion 117 membrane in the range of 30-80% RH at 80 °C, regardless of the significant low water uptake behavior. Furthermore, well-defined phase separation between the hydrophilic and hydrophobic domains was clearly observed in the cross-section of the cross-linked PAHPA membrane by STEM. WAXS measurements revealed the phase separated structures with d-spacing at 1.96 (dry state) and 2.07 nm (wet state), which correspond to the periodic mean interdistance of laterally assembled cylinder-like structures of the cross-linked PAHPA. These results proved that the sufficiently long flexible pendant side chains (>6 methylene units) induced the aggregation of the hydrophilic domains (*i.e.*, the formation of the hydrogen-bonding networks) to achieve excellent proton transportation derived from the hydrogenbonding networks. Consequently, the strategy in this work, which is the introduction of the flexible pendant side chain into the phosphonated polymer, is truly promising to realize ideal and efficient proton transportation derived from the hydrogenbonding networks, and PAHPA creates a new possibility for the development of PEMs based on phosphonated polymers. Their actual fuel cell fabrication and evaluation are now under investigation.

4 Experimental

4.1 Materials

Diethyl 2-hydroxyethylphosphonate (DEHEP), diethyl 4-bromobutylphosphonate (DEBBP) and diethyl 6-bromohexylphosphonate (DEBHP) were prepared according to a previous report.³¹ Tetrahydrofuran (THF) was refluxed over sodium benzophenone for 12 h and then distilled. Triethylamine was distilled from calcium hydride before use. Other solvents and reagents were used without further purification.

4.2 Characterization

¹H (300 MHz) and ¹³C (75 MHz) spectra were recorded with Bruker DPX300S spectrometers. Number- and weight-average molecular weights $(M_n \text{ and } M_w)$ were measured by gel permeation chromatography (GPC) on a Hitachi LC-7000 system equipped with polystyrene gel columns (TSKgel GMHHR-M) eluted with N,N-dimethylformamide (DMF) containing 0.01 M LiBr at a flow rate of 1.0 mL min⁻¹ calibrated by standard polystyrene samples. Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 10 °C min⁻¹ for thermogravimetry (TG). For scanning transmission electron microscopy (STEM) observations, the membranes were stained with lead ions by ion exchange of the phosphonic acid groups in 2 wt% Pb(OCOCH₃)₂ aqueous solution, rinsed with deionised water for 3 days, and dried at room temperature for 1 day. The strained membranes were embedded in an epoxy resin, sectioned to 90 nm thickness with a microtome Ultracut UCT, and placed on copper grids. Images were taken on a Hitachi H7100FA TEM with an accelerating voltage of 100 kV. Synchrotron X-ray scattering measurements were carried out at the 3C, 4C and 9A beamlines of the Pohang Accelerator Laboratory at the Pohang University of Science and Technology.32-37 The light source from an in-vacuum undulator (1.8 m long; 20 mm period) of the storage ring was monochromatized using a liquid nitrogen cooled double Si(111)/Si(311) crystal monochromator system, giving an X-ray beam of 0.1154 nm (for wide angle scattering measurements) and 0.1240 nm wavelength (for small angle scattering measurements). The beam size was 50 μ m \times 300 μ m. A two-dimensional (2D) charge-coupled detector (CCD) (Rayonix SX165, USA) was employed. Scattering patterns were measured at sample-to-detector distances (SDD) of 230 and 3388 mm. X-ray scattering measurements were performed in transmission mode for PAHPA films before and after

immersion in deionized water for 6 h. The scattering angle was calibrated with pre-calibrated standards (sucrose, silver behenate and polystyrene-*b*-polyethylene-*b*-polybutadiene-*b*-polystyrene (SEBS) block copolymer). All scattering measurements were collected in 60 s and carried out at 25 $^{\circ}$ C.

4.3 Synthesis

Diethyl 2-(acryloyloxy)ethylphosphonate (AEPN). To a dry THF solution (11.0 mL) of DEHEP (2.00 g, 11.0 mmol) and triethylamine (1.84 mL, 13.2 mmol) was added acryloyl chloride (1.07 mL, 13.2 mmol) dropwise at 0 °C under a nitrogen atmosphere. Then the mixture was stirred at room temperature for 1 h. After adding water, the mixture was extracted with diethyl ether, washed with water and saturated NaHCO3 aqueous solution, and then dried over MgSO₄. After removing the solvent, the obtained product was purified by column chromatography (ethyl acetate : hexane = 2:1) to obtain a colorless liquid (1.79 g, 69%). ¹H NMR (CDCl₃, δ, ppm): 6.44 (1H, d), 6.12 (1H, q), 5.86 (1H, d), 4.40 (2H, m), 4.13 (4H, m), 2.21 (2H, m), 1.34 (6H, t). ¹³C NMR (CDCl₃, δ , ppm): 166.1, 131.3, 128.5, 62.2, 59.2, 31.2, 27.5, 25.7 16.8. FT-IR (NaCl, cm⁻¹): 2985, 2908, 1727, 1635, 1446, 1411, 1265, 1191, 1025, 968, 809. Anal. calcd for C₉H₁₇O₅P: C; 45.76%, H; 7.25%; found: C; 44.87%, H; 6.88%.

Poly[diethyl 2-(acryloyloxy)ethylphosphonate] (PAEPN). AEPN (0.14 g, 0.61 mmol), 2,2'-azobis(isobutyronitrile) (AIBN) (0.0040 g, 0.024 mmol), and dry toluene (0.25 mL) were placed in a glass tube using standard freeze–evacuate–thaw procedures. The mixture was stirred at 60 °C for 6 h. After cooling to room temperature, the mixture was diluted with toluene and then poured into hexane. The precipitate was collected and dried *in vacuo* at 50 °C for 24 h to give PAEPN (0.14 g, 98%). ¹H NMR (MeOD, δ , ppm): 4.47 (2H, broad), 4.34 (4H, m), 2.70–1.66 (5H, broad). FT-IR (Si, cm⁻¹): 3451, 2985, 2935, 1735, 1446, 1392, 1249, 1164, 1025, 964.

Poly[4-(acryloyloxy)ethylphosphonic acid] (PAEPA). To a chloroform solution (5.0 mL) of PAEPN (0.24 g, 1.01 mmol) was added trimethylsilyl bromide (0.78 mL, 6.0 mmol) dropwise at 0 °C, and the mixture was stirred at 40 °C for 24 h. After evaporation, the residue was dissolved in methanol and the solution was stirred at room temperature for 6 h. Then methanol was evaporated and the obtained product was then dried *in vacuo* at 40 °C for 24 h to obtain PAEPA (0.17 g, 94%). ¹H NMR (D₂O, δ , ppm): 4.36 (2H, broad), 2.54–1.50 (5H, m). FT-IR (Si, cm⁻¹): 2965, 2287, 1727, 1454, 1164, 1010.

4-(Diethoxyphosphoryl)ethyl acetate (DEPEA). A DMF solution (29 mL) of DEBBP (7.85 g, 28.9 mmol) and sodium acetate (5.68 g, 69.3 mmol) was stirred at 110 °C for 5 h under a nitrogen atmosphere. After removing the solvent, water was added and the mixture was extracted with diethyl ether, then washed with water and saturated NaHCO₃ aqueous solution, and then dried over MgSO₄. A colorless liquid was obtained (3.17 g, 44%). The obtained product was used for the next reaction without any purification. ¹H NMR (CDCl₃, δ , ppm): 4.09 (6H, m), 2.05 (3H, s), 1.84–1.52 (6H, broad), 1.33 (6H, t).

Diethyl 4-hydroxybutylphosphonate (DEHBP). A MeOH solution (14 mL) of DEBHP (8.26 g, 32.7 mmol) and potassium

hydroxide (0.21 g, 3.67 mmol) was stirred at room temperature for 15 h under a nitrogen atmosphere. After removing the solvent, water was added and the mixture was extracted with dichloromethane and then dried over MgSO₄. After removing the solvent, a colorless liquid was obtained (4.61 g, 67%). The obtained product was used for the next reaction without any purification. ¹H NMR (CDCl₃, δ , ppm): 4.10 (4H, m), 3.67 (2H, t), 2.01–1.62 (6H, broad), 1.33 (6H, t).

Diethyl 4-(acryloyloxy)butylphosphonate (ABPN). To a dry THF solution (11.0 mL) of DEHBP (2.25 g, 10.69 mmol) and triethylamine (1.8 mL, 12.8 mmol) was added acryloyl chloride (1.0 mL, 12.8 mmol) dropwise at 0 °C under a nitrogen atmosphere. Then the mixture was stirred at room temperature for 1 h. After adding water, the mixture was extracted with diethyl ether, washed with water and saturated NaHCO₃ aqueous solution, and then dried over MgSO₄. After removing the solvent, the obtained product was purified by column chromatography (ethyl acetate : hexane = 2:1) to obtain a colorless liquid (2.2 g, 80%). ¹H NMR (CDCl₃, δ , ppm): 6.41 (1H, d), 6.12 (1H, q), 5.83 (1H, d), 4.22-4.02 (6H, m), 1.85-1.59 (6H, broad), 1.31 (6H, t). ¹³C NMR (CDCl₃, δ, ppm): 166.2, 130.6, 128.5, 63.9, 61.6, 29.5, 26.4, 24.5, 19.3, 16.6. FT-IR (NaCl, cm⁻¹): 2985, 1724, 1635, 1457, 1411, 1199, 1025. Anal. calcd for C13H25O6P: C; 50.00%, H; 8.01%; found: C; 49.78%, H; 7.98%.

Poly[diethyl 4-(acryloyloxy)butylphosphonate] (PABPN). ABPN (0.16 g, 0.61 mmol), 2,2'-azobis(isobutyronitrile) (AIBN) (0.0040 g, 0.024 mmol), and dry toluene (0.25 mL) were placed in a glass tube using standard freeze–evacuate–thaw procedures. The mixture was stirred at 60 °C for 6 h. After cooling to room temperature, the mixture was diluted with toluene and then poured into hexane. The precipitate was collected and dried *in vacuo* at 50 °C for 24 h to give PAHPN (0.15 g, 95%). ¹H NMR (CDCl₃, δ , ppm): 4.11 (6H, broad), 2.45–2.22 (1H, broad), 2.00–1.60 (8H, broad), 1.34 (6H, t). FT-IR (Si, cm⁻¹): 2985, 1731, 1650, 1446, 1392, 1230, 1025.

Poly[4-(acryloyloxy)butylphosphonic acid] (PABPA). To a chloroform solution (3.0 mL) of PABPN (0.16 g, 0.62 mmol) was added trimethylsilyl bromide (0.48 mL, 3.7 mmol) dropwise at 0 °C, and the mixture was stirred at 40 °C for 24 h. After evaporation, the residue was dissolved in methanol and the solution was stirred at room temperature for 6 h. Then methanol was evaporated and the obtained product was dried *in vacuo* at 40 °C for 24 h to obtain PABPA (0.11 g, 90%). ¹H NMR (CD₃OD, δ , ppm): 4.14 (2H, broad), 2.56–2.14 (1H, broad), 2.13–1.44 (8H, broad). FT-IR (Si, cm⁻¹): 2958, 2283, 1727, 1110, 991.

Diethyl 6-hydroxyhexylphosphonate (DEHHP). A DMF solution (14 mL) of DEBHP (4.31 g, 14.3 mmol), sodium acetate (1.41 g, 17.2 mmol), and tetrabutylammonium bromide (0.10 g, 0.32 mmol) was stirred at 120 °C for 2 h under a nitrogen atmosphere. After cooling to room temperature, NaOH aqueous solution (50 wt%, 20 mL) was added dropwise and the mixture stirred at room temperature for 15 h. The mixture was extracted with diethyl ether, washed with water, and then dried over MgSO₄. After removing the solvent, a colorless liquid was obtained (1.61 g, 47%). The obtained product was used for the next reaction without any purification. ¹H NMR (CDCl₃, δ , ppm):

4.13–3.96 (4H, m), 3.61–3.55 (2H, t), 2.21 (1H, s), 1.74–1.48 (6H, m), 1.48–1.33 (4H, m), 1.30–1.25 (6H, t).

Diethyl 6-(acryloyloxy)hexylphosphonate (AHPN). To a dry THF solution (8.0 mL) of DEHHP (1.88 g, 7.89 mmol) and triethylamine (1.3 mL, 9.47 mmol) was added acryloyl chloride (0.76 mL, 9.47 mmol) dropwise at 0 °C under a nitrogen atmosphere. Then the mixture was stirred at room temperature for 1 h. After adding water, the mixture was extracted with diethyl ether, washed with water and saturated NaHCO3 aqueous solution, and then dried over MgSO4. After removing the solvent, the obtained product was purified by column chromatography (ethyl acetate : hexane = 2:1) to obtain a colorless liquid (1.36 g, 59%). ¹H NMR (CDCl₃, δ, ppm): 6.38 (1H, d), 6.08 (1H, q), 5.79 (1H, d), 4.14-3.98 (6H, m), 1.75-1.54 (6H, m), 1.39-1.36 (6H, m), 1.29 (6H, t). ¹³C NMR (CDCl₃, δ , ppm): 166.3, 130.5, 128.5, 77.5, 77.1, 76.6, 64.4, 61.4, 61.3, 30.1, 28.3, 26.5, 25.5, 25.4, 24.6, 22.4, 22.3, 16.5, 16.4. FT-IR (NaCl, cm⁻¹): 2981, 2935, 2912, 1724, 1635, 1246, 1030. Anal. calcd for C₁₃H₂₅O₆P: C; 53.42%, H; 8.62%; found: C; 52.26%, H; 8.44%.

Poly[diethyl 6-(acryloyloxy)hexylphosphonate] (PAHPN). AHPN (0.18 g, 0.61 mmol), 2,2'-azobis(isobutyronitrile) (AIBN) (0.0040 g, 0.024 mmol), and dry toluene (0.25 mL) were placed in a glass tube using standard freeze–evacuate–thaw procedures. The mixture was stirred at 60 °C for 24 h. After cooling to room temperature, the mixture was diluted with toluene and then poured into hexane. The precipitate was collected and dried *in vacuo* at 50 °C for 24 h to give PAHPN (0.17 g, 96%). ¹H NMR (CDCl₃, δ , ppm): 4.15–3.98 (6H, m), 2.22–1.59 (9H, m), 1.37–1.29 (10H, m). FT-IR (Si, cm⁻¹): 2981, 2935, 1732, 1242, 1030.

Poly[6-(acryloyloxy)hexylphosphonic acid] (PAHPA). To a chloroform solution (5.0 mL) of PAHPN (0.28 g, 0.96 mmol) was added trimethylsilyl bromide (0.75 mL, 5.7 mmol) dropwise at 5 °C, and the mixture was stirred at 40 °C for 24 h. After evaporation, the residue was dissolved in methanol and the solution was stirred at room temperature for 6 h. Then methanol was evaporated and the obtained product was dried *in vacuo* at 40 °C for 24 h to obtain PAHPA (0.2 g, 90%). ¹H NMR (CD₃OD, δ , ppm): 4.09 (2H, broad), 2.32–1.47 (13H, m). FT-IR (Si, cm⁻¹): 2939, 2866, 2310, 1732, 1165.

4.4 Preparation of cross-linked membranes and ion exchange capacity (IEC)

2-Methoxyethanol solutions of PAEPA, PABPA and PAHPA (0.31 mmol) and benzoyl peroxide (BPO) (0.0037 g, 0.015 mmol) were cast onto Teflon sheets. Drying at 80, 90, and 100 $^{\circ}$ C for 1 h respectively (totally for 3 h) under a nitrogen atmosphere gave cross-linked membranes. The IEC values of the cross-linked membranes were determined by titration with 0.02 M NaOH aqueous solution.

4.5 Oxidative stability

The oxidative stabilities of the membranes were tested by immersing the membranes into Fenton's reagent $(3\% H_2O_2$ aqueous solution containing 20 ppm FeSO₄) at room Paper

temperature. The dissolution time of the membranes into the reagent was used to evaluate their oxidative stability.

4.6 Water uptake and dimensional change

The humidity dependence of water uptake was measured by plating a membrane in a thermo-controlled humidity chamber for 5 h. Then the membrane was taken out, and quickly weighed on a microbalance. Water uptake was calculated from:

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

where W_s and W_d are the weights of wet and dried membrane, respectively. The average values of statistically collecting data were obtained by repeated experiments.

4.7 Proton conductivity

Proton conductivity in the plane direction of a membrane was determined using an electrochemical impedance spectroscopy technique over the frequency from 5 to 10^5 Hz using a chemical impedance meter (Hioki 3532-80, Nihon Denkei Co., Ltd) in a temperature and humidity chamber (IW 222 type, Yamato Scientific Co., Ltd). A two-point-probe conductivity cell with two platinum plate electrodes was fabricated. The cell was placed in a thermo-controlled humid chamber. Proton conductivity (σ) was calculated from:

$$\sigma = d/(L_{\rm s}w_{\rm s}R)$$

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. The *R* values were determined by exporting the electrochemical impedance plotting line to *X*-intercept. The average σ values of statistically collecting data were obtained by repeated experiments.

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