

Synthesis and characteristics of hyperbranched polymer with phosphonic acid groups for high-temperature fuel cells

Takahito Itoh · Keita Hirai · Masashi Tamura ·
Takahiro Uno · Masataka Kubo · Yuichi Aihara

Received: 23 August 2009 / Revised: 1 October 2009 / Accepted: 5 October 2009 / Published online: 20 October 2009
© Springer-Verlag 2009

Abstract Two different molecular weight hyperbranched polymers (HBP(L)-(PA)₂ and HBP(H)-(PA)₂) with two phosphonic acid groups as a functional group at the periphery and a low molecular weight hyperbranched polymer (HBP(L)-(PA)₂-Ac) with both two phosphonic acid groups and an acryloyl group as a cross-linker at the periphery were successfully synthesized as thermally stable proton-conducting electrolytes. A cross-linked electrolyte membrane (CL-HBP(L)-(PA)₂) was prepared by thermal polymerization of the HBP(L)-(PA)₂-Ac using benzoyl peroxide. Ionic conductivities of the HBP(L)-(PA)₂, the HBP(H)-(PA)₂, and the CL-HBP(L)-(PA)₂ under dry condition and their thermal properties were investigated, and also, the effect of the phosphonic acid group number on them was discussed. Ionic conductivities of the HBP(L)-(PA)₂ and the HBP(H)-(PA)₂ were found to be 1.5×10^{-5} S cm⁻¹ at 150 °C and 3.6×10^{-6} S cm⁻¹ at 143 °C, respectively, under dry condition, and showed the Vogel–Tamman–Fulcher type temperature dependence. The hyperbranched polymers and the cross-linked electrolyte membrane were thermally stable up to 300 °C, and the cross-linked electrolyte membrane (CL-HBP(L)-(PA)₂) had suitable thermal stability as an electrolyte membrane for the high-temperature fuel cells under dry condition. Fuel cell measurement using a single membrane

electrode assembly cell with the cross-linked membrane was performed.

Keywords Hyperbranched polymer ·
Phosphonic acid group · Proton conductivity · Fuel cell

Introduction

Polymer electrolyte fuel cells (PEFCs) are the most promising candidates for electric vehicles and portable electrical power sources because they have high-energy densities and high-conversion efficiency, and they are environmentally benign systems [1–4]. These fuel cells have typically used perfluorinated, modified perfluorinated, partially fluorinated polymer electrolytes as the membranes to separate the electrodes, and the oxygen and hydrogen (or methanol) gas streams [5, 6]. The perfluorsulfonic acid polymer Nafion[®] is one of the most extensively studied proton exchange membrane for PEFC applications. However, it has a number of drawbacks that needs to be overcome, which are the high cost, due to its complicated system construction, the durability, and the poor performance at temperature above 80 °C due to the loss of the water. One of the arguments of the development of the new polymer electrolytes is the necessity to operate the fuel cell at high-temperature conditions. Therefore, there has been a great demand of low-cost and thermally stable electrolyte membranes for the high-temperature PEFCs. Sulfonated aromatic polymers, organic–inorganic composite electrolyte membranes, and blend of different polymers with phosphoric acid have been explored [5–10]. In the first two types of electrolytes, the ionic conductivity depends upon the presence of water. Among the blends with phosphoric acid, poly(benzimidazole) has been successfully tested in the fuel

T. Itoh (✉) · K. Hirai · M. Tamura · T. Uno · M. Kubo
Division of Chemistry for Materials,
Graduate School of Engineering, Mie University,
1577 Kurima Machiya-cho,
Tsu, Mie 514-8507, Japan
e-mail: itoh@chem.mie-u.ac.jp

Y. Aihara
Samsung Yokohama Research Institute,
2-7 Sugasawa-cho, Tsurumi-ku,
Yokohama 230-0027, Japan

cells which were operated at temperatures of up to 200 °C, though long-term durability of these electrolytes have not been published yet [9, 10]. Recently, as new polymeric materials that are capable of fast proton conduction in the absence of any volatile compounds and that are durable at elevated temperatures, fully polymeric proton-conducting membranes based on nitrogen-containing heterocycles such as imidazole, benzimidazole, and pyrazole which have in many respects properties similar to those of water have been prepared and studied [11–16]. These approaches have been studied for applying them to the high-temperature fuel cell systems because the proton conduction strongly depends on the presence of the water for the sulfonated polymer systems [17]. On the other hand, the ion conducting phenomena have been widely investigated in dry polymer systems such as combinations of alkaline metal salts and polyethers [18–20]. Approaches to use dry polymer systems for proton conduction may be required at the temperature higher than 100 °C since the ionic conduction is generally cooperated with polymer chain motion. In addition, single proton type conductors are promising electrolytes for avoiding evaporation and/or migration of low molecular proton media and acids. Previously, we prepared a proton-conducting membrane based on the hyperbranched polymer with a sulfonic acid group at the periphery [21] and a hyperbranched polymer with phosphonic acid group at the periphery [22] and investigated their ionic conductivities under dry conditions and thermal properties. For the case of the hyperbranched polymers with a phosphonic acid group (HBP-PA), though the phosphorous atom has significantly improved the thermal stability of the polymer, phase separation phenomenon took place in the semi-interpenetrated membrane obtained by polymerization of HBP-PA with a hyperbranched polymer with an acryloyl group (HPB-Ac). To suppress the phase separation, we synthesized the hyperbranched polymer (HBP-PA-Ac) containing both a phosphonic acid group and an acryloyl group at the periphery in the same molecule and investigated the ionic conductivity under dry conditions and thermal properties for the cross-linked electrolyte membrane (CL-HBP-PA) obtained by thermal polymerization of the HBP-PA-Ac [23]. However, ionic conductivity of the CL-HBP-PA membrane was still low. An increase in phosphonic acid groups in the electrolytes is expected to improve the ionic conductivity of hyperbranched polymer-based electrolytes, due to an increase in the number of the carriers.

In this work, we synthesized hyperbranched polymers containing two phosphonic acid groups (HBP-(PA)₂ and HBP-(PA)₂-Ac) at the periphery (Scheme 1) and a cross-linked electrolyte membrane (CL-HBP-(PA)₂), obtained by polymerization of the HBP-(PA)₂-Ac and investigated the

ionic conductivity, thermal properties, and fuel cell performance of the cross-linked membrane.

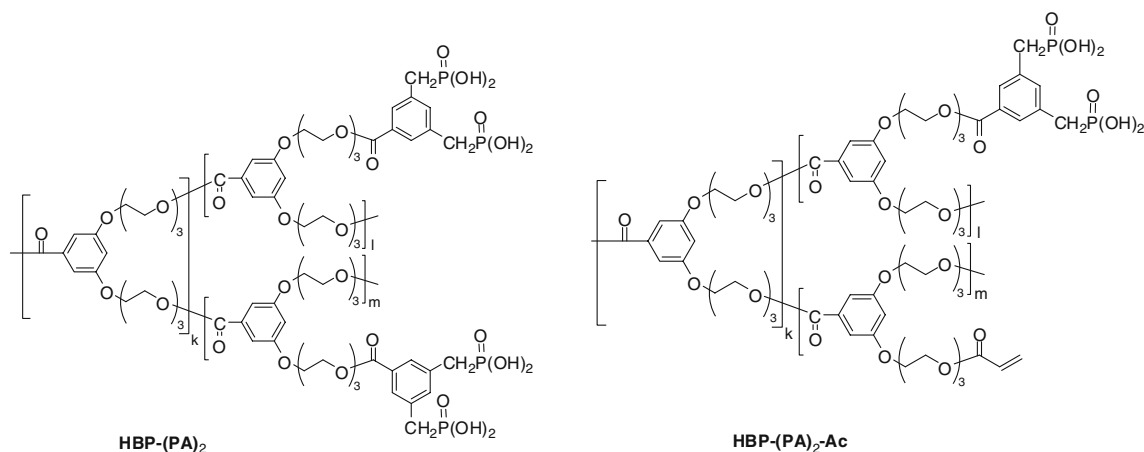
Experimental

Materials

A hyperbranched polymer with a hydroxyl group at the periphery (HBP-OH) was prepared by polymerization of methyl 3,5-bis[(8'-hydroxy-3',5'-dioxaoctyl)oxy]-benzoate and separated into two parts, a low molecular weight hyperbranched polymer (HBP(L)-OH) and a high molecular weight hyperbranched polymer (HBP(H)-OH), according to the method reported previously [22, 24] (HBP(L)-OH: yield 12.76 g (80% yield); number-average molecular weights (M_n)=4,200 and HBP(H)-OH: yield 2.86 g (18% yield); M_n =13,000). The hyperbranched polymer with an acryloyl group at the periphery (HBP-Ac) was prepared by a reaction of the HBP(L)-OH with an acryloyl chloride according to the method reported previously [21]. Benzoyl peroxide (BPO) was purified by recrystallization from chloroform/methanol solution, and an acrylic acid was distilled under reduced pressure under nitrogen. *N,N*-dimethylaminopyridine (DMAP), dicyclohexylcarbodiimide (DCC), bromotrimethylsilane, *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMAc) were used as received.

Hyperbranched polymer with two diethyl phosphate groups at the periphery (HBP-(PE)₂)

HBP(L)-OH (2.64 g, 6.59 mmol, M_n =4,100) and 3,5-(diethoxyphosphorylmethyl)benzoic acid (2.91 g, 6.89 mmol), prepared as white solids (mp 105–106 °C) in 85% yield by reaction of 3,5-bis(bromomethyl)benzoic acid with triethylphosphite in toluene at reflux, were dissolved in 60 ml of dichloromethane and into the solution were added DCC (2.72 g, 13.2 mmol) and DMAP (1.61 g, 13.2 mmol) and then the mixture was stirred at room temperature for 50 h. Insoluble products were filtered off, and the filtrate was poured into a large amount of hexane to deposit the product, which was purified by a dissolution–reprecipitation method (repeatedly three times) using dichloromethane/ethanol as a solvent and hexane as a precipitant and dried under reduced pressure to give a low molecular weight hyperbranched polymer (HBP(L)-(PE)₂) with two ethyl phosphonate groups on the aromatic ring at the periphery as a pale yellow highly viscous oil. The high molecular weight hyperbranched polymer (HBP(H)-(PE)₂) with two ethyl phosphonate groups was also prepared as a pale yellow highly viscous oil from HBP(H)-OH (1.95 g, 4.88 mmol) by the same procedure of synthesizing HBP(L)-(PE)₂.



Scheme 1 Chemical structures of the HBP-(PA)₂ and the HBP-(PA)₂-Ac

HBP(L)-(PE)₂ and HBP(H)-(PE)₂: yield: 4.04 g (76% yield), $M_n=4,200$ for HBP(L)-(PE)₂ and 2.48 g (63% yield), $M_n=13,000$ for HBP(L)-(PE)₂. IR (NaCl): ν_{CH} 2,906, $\nu_{\text{C=O}}$ 1,719, $\nu_{\text{C=C}}$ 1,594, $\nu_{\text{P=O}}$ 1,253, $\nu_{\text{C-O}}$ 1,172, $\nu_{\text{P-O}}$ 1,026 cm^{-1} ; ^1H NMR (CDCl_3): δ 7.86 (br, 2H), 7.46 (br, 1H), 7.19 (br, 2H), 6.68 (br, 1H), 4.45 (br, 4H), 4.11 (br, 4H), 4.03 (m, 8H), 3.83–3.67 (br, 16H), 3.17 (d, $J_{\text{H-P}}=21.8$ Hz, 4H), 1.23 (t, $J=7.26$ Hz, 12H); ^{13}C NMR (CDCl_3): δ 165.7 (C=O), 165.6 (C=O), 159.3 (Ar), 135.2 (Ar, $J_{\text{C-P}}=7.3$ Hz), 132.2 (Ar), 132.1 (Ar, $J_{\text{C-P}}=6.1$ Hz), 130.8 (Ar, $J_{\text{C-P}}=2.8$ Hz), 128.5 (Ar, $J_{\text{C-P}}=4.0$ Hz), 107.7 (Ar), 106.3 (Ar), 70.3 (CH_2), 70.1 (CH_2), 69.4 (CH_2), 69.0 (CH_2), 67.5 (CH_2), 67.1 (CH_2), 63.6 (CH_2), 63.5 (CH_2), 61.8 (CH_2 , $J_{\text{C-P}}=7.4$ Hz), 32.9 (CH_2 , $J_{\text{C-P}}=139.2$ Hz), 16.0 (CH_3 , $J_{\text{C-P}}=6.1$ Hz). Found: C%, 52.22%; H%, 6.80%.

Hyperbranched polymer with two phosphonic acid groups at the periphery (HBP-(PA)₂)

HBP(L)-(PE)₂ (3.27 g, 4.07 mmol, $M_n=4,200$) was dissolved in 60 ml of dichloromethane and into the solution was added slowly bromotrimethylsilane (2.1 mL, 16.3 mmol) by using a syringe and then the mixture was refluxed with stirring under nitrogen for 8 h. After cooling to room temperature, 40 ml of methanol was added into the reaction mixture and then stirred for 15 h. The resulting solution was placed under reduced pressure to remove solvent and give a residue as a pale yellow highly viscous oil, which was dissolved in a small amount of DMF. Insoluble products were filtered off, and the filtrate was poured into a large amount of isopropyl ether to deposit the product, which was purified in three cycles of a dissolution–reprecipitation method. DMF and isopropyl ether were used as a solvent and a precipitant, respectively, and finally washed with isopropyl alcohol and dried under reduced pressure to give a low molecular weight hyperbranched polymer (HBP(L)-(PA)₂) with two phosphonic acid groups as a

pale yellow solid. The high molecular weight hyperbranched polymer (HBP(H)-(PA)₂) with two phosphonic acid groups was also prepared as a pale yellow solid from HBP(H)-(PE)₂ (2.48 g, 3.08 mmol) by the same procedure of synthesizing HBP(L)-(PA)₂.

HBP(L)-(PA)₂ and HBP(H)-(PA)₂: yield: 2.26 g (80% yield; HBP(L)-(PA)₂) and 1.89 g (81% yield; HBP(H)-(PA)₂). IR (NaCl): ν_{OH} 3,423, ν_{CH} 2,280, $\nu_{\text{C=O}}$ 1,718, $\nu_{\text{C=C}}$ 1,599, $\nu_{\text{P=O}}$ 1,278, $\nu_{\text{C-O}}$ 1,174, $\nu_{\text{P-O}}$ 999 cm^{-1} ; ^1H NMR ($\text{DMSO}-d_6$): δ 7.74 (s, 2H), 7.38 (s, 1H), 7.03 (br, 2H), 6.77 (br, 1H), 4.36 (br, 4H), 4.08 (br, 4H), 3.73–3.59 (br, 16H), 3.01 (d, $J_{\text{H-P}}=21.8$ Hz, 2H); ^{13}C NMR ($\text{DMSO}-d_6$): δ 166.2 (C=O), 165.7 (C=O), 160.0 (Ar), 134.9 (Ar, $J_{\text{C-P}}=9.7$ Hz), 131.9 (Ar), 130.3 (Ar), 130.3 (Ar, $J_{\text{C-P}}=9.7$ Hz), 129.8 (Ar, $J_{\text{C-P}}=9.7$ Hz), 128.6 (Ar, $J_{\text{C-P}}=12.2$ Hz), 107.9 (Ar), 107.3 (Ar), 70.2 (CH_2), 69.2 (CH_2), 68.6 (CH_2), 67.9 (CH_2), 67.7 (CH_2), 62.4 (CH_2), 62.3 (CH_2), 36.2 (CH_2 , $J_{\text{C-P}}=139.9$ Hz). Found: C% 47.36%; H%, 5.64%.

Hyperbranched polymer with both two diethyl phosphate groups and an acryloyl group at the periphery (HBP-(PE)₂-Ac)

A low molecular weight hyperbranched polymer (HBP(L)-OH) (3.71 g, 9.26 mmol, $M_n=4,200$), acrylic acid (0.67 g, 9.26 mmol), DMAP (1.47 g, 12.04 mmol), and DCC (2.48 g, 12.04 mmol) were dissolved in 70 ml of dichloromethane at room temperature and then stirred for 48 h under nitrogen. Deposited dicyclohexylurea was filtered off, and the filtrate was placed under reduced pressure to remove volatile materials to give a viscous oil. The viscous oil was purified by a dissolution–reprecipitation method using a mixture of dichloromethane and ethanol as a solvent and isopropyl ether as a precipitant (repeated three times), followed by a mixture of dichloromethane and ethanol as a solvent and hexane as a precipitant (repeated

three times), and dried under reduced pressure to give a hyperbranched polymer (HBP(L)-Ac) with an acryloyl group partially at the periphery. The resulting HBP(L)-Ac, 3,5-(diethoxyphosphorylmethyl)benzoic acid (3.60 g, 8.52 mmol), DMAP (1.47 g, 12.04 mmol), and DCC (2.48 g, 12.04 mmol) were dissolved in 70 ml of dichloromethane at room temperature and then stirred for 60 h under nitrogen. Deposited dicyclohexylurea was filtered off, and the filtrate was placed under reduced pressure to remove volatile materials to give a viscous oil. The viscous oil was purified by a dissolution–reprecipitation method using a mixture of dichloromethane and ethanol as a solvent and isopropyl ether as a precipitant (repeated three times), followed by a mixture of dichloromethane and ethanol as a solvent and hexane as a precipitant (repeated three times), and dried under reduced pressure to give a low molecular weight hyperbranched polymer (HBP(L)-(PE)₂-Ac), with both two diethyl phosphate groups and an acryloyl group at the periphery as a pale yellow viscous oil.

HBP(L)-(PE)₂-Ac: yield 1.96 g (64% yield). $M_n=4,200$. Acryloyl group content: 47% (determined by ¹H NMR measurement). IR (NaCl): ν_{CH} 2,939, $\nu_{\text{C=O}}$ 1,721, $\nu_{\text{C=C}}$ 1,596, $\nu_{\text{P=O}}$ 1,237, $\nu_{\text{C-O}}$ 1,175, $\nu_{\text{P-O}}$ 1,028 cm^{-1} ; ¹H NMR (DMSO-*d*₆): δ 7.78 (s, 1.2H), 7.43 (s, 0.6H), 7.02 (br, 2H), 6.76 (br, 1H), 6.28 (d, $J=17.2$ Hz, 0.4H), 6.16 (dd, $J=9.2, 17.2$ Hz, 0.4H), 5.92 (d, $J=9.2$ Hz, 0.4H), 4.36 (br, 3.2H), 4.19 (br, 0.8H), 4.07 (br, 4H), 3.94 (m, 4.8H), 3.72–3.59 (br, 16H), 3.18 (d, $J_{\text{H-P}}=28.4$ Hz, 1.2H), 1.16 (t, $J=7.25$ Hz, 7.2H); ¹³C NMR (CDCl₃): δ 165.8 (C=O), 165.7 (C=O), 159.4 (Ar), 135.4 (Ar), 132.3 (Ar), 132.2 (Ar, $J_{\text{C-P}}=6.1$ Hz), 131.5 (Ar), 130.3 (CH₂), 129.3 (Ar), 128.5 (CH), 107.8 (Ar), 106.3 (Ar), 70.4 (CH₂), 70.3 (CH₂), 69.3 (CH₂), 68.9 (CH₂), 68.8 (CH₂), 67.4 (CH₂), 64.0 (CH₂), 63.9 (CH₂), 63.3 (CH₂), 61.9 (CH₂, $J_{\text{C-P}}=6.1$ Hz), 33.0 (CH₂, $J_{\text{C-P}}=137.9$ Hz), 16.1 (CH₃, $J_{\text{C-P}}=4.9$ Hz). Found: C%, 54.43%; H%, 6.85%.

Hyperbranched polymer with both two phosphonic acid groups and an acryloyl group at the periphery (HBP-(PA)₂-Ac)

HBP(L)-(PE)₂-Ac (4.73 g, 6.78 mmol, $M_n=4,200$) was dissolved in 70 ml of dichloromethane and into the solution was added slowly bromotrimethylsilane (4.0 ml, 30.0 mmol) by using a syringe and then the mixture was stirred under nitrogen for 19 h. The reaction mixture was placed under reduced pressure to remove solvent to give a viscous residue, to which was added 70 ml of methanol and then stirred for 19 h. The resulting solution was placed under reduced pressure to remove the solvent and give a residue as pale yellow highly viscous oil, which was dissolved in a small amount of DMF. The resulting solution was poured into a large amount of isopropyl ether to deposit the

product, which was purified in three cycles of a dissolution–reprecipitation method. DMF and isopropyl ether were used as a solvent and a precipitant, respectively and finally washed with isopropyl alcohol and dried under reduced pressure to give a low molecular weight hyperbranched polymer (HBP(L)-(PA)₂-Ac) with both two phosphonic acid groups and an acryloyl group at the periphery as pale yellow viscous oil.

HBP(L)-(PA)₂-Ac: yield 3.85 g (95% yield). IR (NaCl): ν_{OH} 3,434, ν_{CH} 2,945, $\nu_{\text{C=O}}$ 1,720, $\nu_{\text{C=C}}$ 1,598, $\nu_{\text{P=O}}$ 1,239, $\nu_{\text{C-O}}$ 1,175, $\nu_{\text{P-O}}$ 999 cm^{-1} ; ¹H NMR (DMSO-*d*₆): δ 7.95 (s, 1.2H), 7.38 (s, 0.6H), 7.01 (br, 2H), 6.76 (br, 1H), 6.28 (d, $J=17.2$ Hz, 0.4H), 6.17 (dd, $J=9.2, 17.2$ Hz, 0.4H), 5.89 (d, $J=9.2$ Hz, 0.4H), 4.35 (br, 3.2H), 4.19 (br, 0.8H), 4.08 (br, 4H), 3.72–3.57 (br, 16H), 3.15 (d, $J_{\text{H-P}}=15.5$ Hz, 2.4H); ¹³C NMR (DMSO-*d*₆): δ 165.8 (C=O), 165.5 (C=O), 165.3 (C=O), 159.6 (Ar), 134.5 (Ar, $J_{\text{C-P}}=9.6$ Hz), 131.9 (Ar), 131.6 (CH₂), 129.8 (Ar), 128.9 (Ar), 129.5 (Ar), 128.5 (Ar), 128.2 (CH), 107.6 (Ar), 107.4 (Ar), 69.9 (CH₂), 68.8 (CH₂), 68.3 (CH₂), 67.9 (CH₂), 67.5 (CH₂), 67.2 (CH₂), 64.5 (CH₂), 63.8 (CH₂), 62.1 (CH₂), 61.5 (CH₂), 36.0 (CH₂, $J_{\text{C-P}}=139.2$ Hz). Found: C%, 50.24%; H%, 6.17%.

Cross-linked electrolyte membrane (CL-HBP(L)-(PA)₂)

A given amount of the HBP(L)-(PA)₂-Ac was dissolved in DMAc to obtain the 50 wt.% HBP(L)-(PA)₂-Ac solution and then to the solution were added a BPO (3 wt.% of the polymer) as a radical initiator and a fumed silica (SiO₂, 10 wt.% of the polymer) as a thickener. The resulting viscous suspension was poured on a parting agent-coated poly(ethylene terephthalate) (PET) sheet, spread with doctor blade to get a constant thickness membrane, and DMAc was evaporated slowly at 100 °C for 24 h to prepare a casting membrane. Finally, the membrane was dried and cross-linked by heating at 120 °C for 48 h. The dried membrane was peeled from the parting agent-coated PET sheet to obtain a film of 50 μm thickness and then stored inside the glove box.

Measurements

The number-average molecular weights (M_n) of the polymers were determined by gel permeation chromatography (Tosoh HLC-803D with two columns of Tosoh TSKgel Multipore H_{XL}-M) with standard polystyrenes as a reference and tetrahydrofuran (THF) as an eluent.

The ionic conductivities were determined by using AC impedance method on an Autolab PGSTAT30 (Eco Chemie) controlled by a personal computer. The polymer electrolyte samples (13 mm in diameter and approximately 95- μm thick) were put into two identical platinum blocking

disk electrodes with a Teflon® spacer for ensuring the membrane thickness. The electrodes were held in a semi-open PTFE cell with stainless steel electrodes. The impedance measurements were carried out from 1 Hz to 1 MHz in a temperature range of 80–150 °C. All cell preparation and the measurements were performed under argon atmosphere (dew point < -85 °C).

The thermal stabilities of hyperbranched polymers (HBP(H, L)-(PA)₂) and a cross-linked electrolyte membrane (CL-HBP(L)-(PA)₂) were investigated using thermogravimetric analysis with a TG/DTA 6200 instrument (Seiko Instruments Inc.). The samples were weighted, loaded in a Pt pan, and heated from 50 to 900 °C at a heating rate of 10 °C min⁻¹ under air (200 mL min⁻¹). Aluminum oxide powder was used as a reference material. The differential scanning calorimetry (DSC) measurement was performed using a DSC 6200 Differential Scanning Calorimeter (Seiko Instruments Inc.). Samples were sealed in Au-coated stainless steel pans under argon atmosphere and scanned from -100 to 100 °C with a scanning rate of 10 °C min⁻¹.

Equivalent weight (E_w) values of phosphonic acid function for the hyperbranched polymers and a cross-linked electrolyte membrane were determined from phosphorous content by using an inductively coupled plasma (ICP) method. The measurement was performed using an Inductively Coupled Plasma SPS-1700HVR (SII Nano-Technology Inc.).

The fuel cell measurement was carried out with a single membrane electrode assembly (MEA) cell. Gas diffusion electrodes with 20 wt.% Pt loading (Pt/Vulcan XC-72, Electrochem Inc., MA) were used to prepare the MEA. The active area for the anode and cathode was 9 cm². A membrane was sandwiched between the two electrodes, and the resulting MEA was pressed at 10 kg cm⁻² at room temperature. Polarization (I–V) performance was determined by a potential scan using a Solartron 1260 electrochemical station with a scanning rate of 20 mV sec⁻¹ under a flow of dry H₂ (100 mL min⁻¹)/O₂ (100 mL min⁻¹).

Results and discussion

Synthesis of the hyperbranched polymer with two phosphonic acid groups at the periphery (HBP-(PA)₂)

The two different molecular weights of hyperbranched polymers with two phosphonic acid groups at the periphery (HBP(L)-(PA)₂ and HBP(H)-(PA)₂) were successfully synthesized according to a synthetic route as shown in Scheme 2.

The hyperbranched polymer with a hydroxyl group at the periphery (HBP-OH) was synthesized from methyl 3,5-bis[(8'-hydroxy-3',6'-dioxaoctyl)oxy]benzoate by the

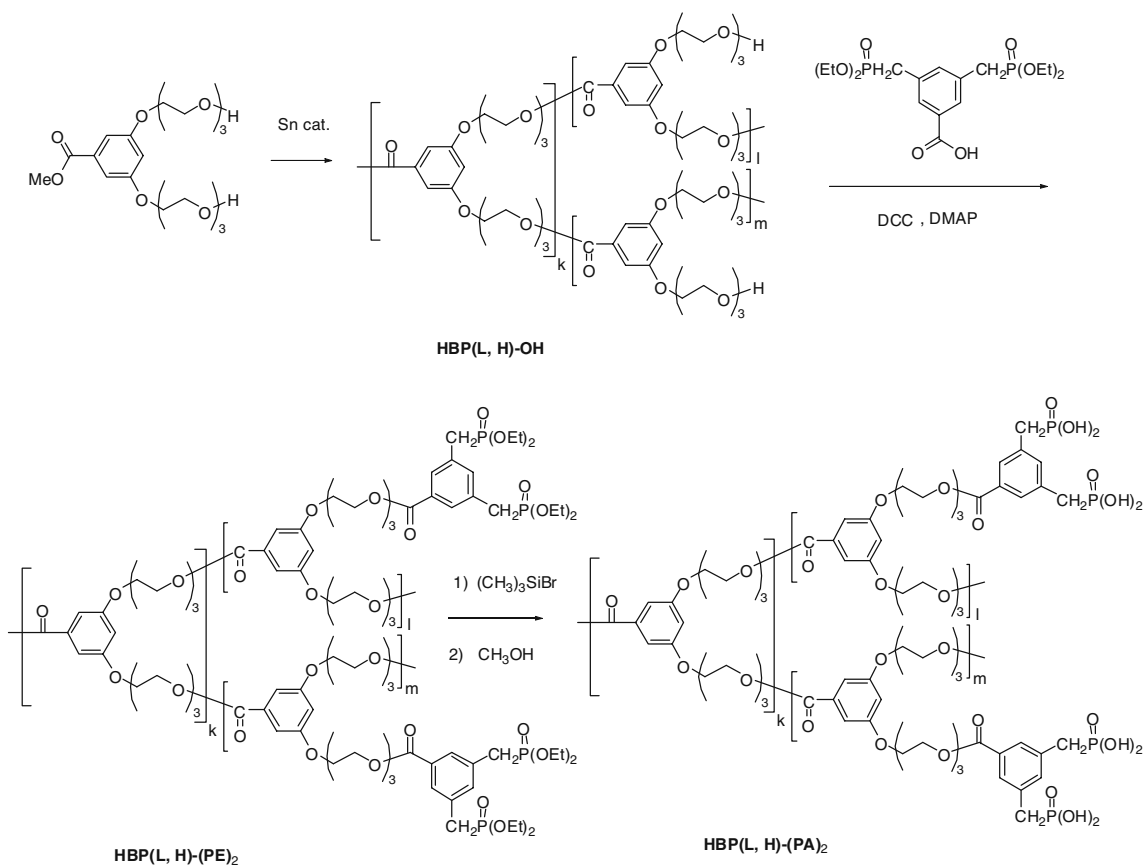
same procedure reported previously [22, 24], and they were separated into two parts, a low molecular weight polymer fraction (HBP(L)-OH, $M_n=4,200$) and a high molecular one (HBP(H)-OH, $M_n=13,000$), by a dissolution–reprecipitation method using THF as a solvent and methanol as a precipitant. The low molecular weight HBP(L)-OH and the high molecular weight HBP(H)-OH were reacted with 3,5-(diethoxyphosphorylmethyl)benzoic acid in the presence of DCC and DMAP at room temperature to give the HBP(L)-(PE)₂ in 76% yield and the HBP(H)-(PE)₂ in 63% yield, respectively, as yellow highly viscous oils. The reaction of HBP(L)-(PE)₂ and HBP(H)-(PE)₂ with bromotrimethylsilane, followed by solvolysis in methanol, afforded the hyperbranched polymers (HBP(L)-(PA)₂ and HBP(H)-(PA)₂) with two phosphonic acid groups at the periphery as pale yellow solids, which were purified by a dissolution–reprecipitation method using DMF as a solvent and isopropyl ether as a precipitant, respectively. Both polymers (HBP(L)-(PA)₂ and HBP(H)-(PA)₂) are soluble in DMF, DMAc, and dimethylsulfoxide but insoluble in benzene, chloroform, THF, isopropyl ether, methanol, ethanol, acetonitrile, and water.

Equivalent weight (E_w) values of the HBP(L)-(PA)₂ and the HBP(H)-(PA)₂ were determined from a phosphorous content by using an ICP method to be 378 for the HBP(L)-(PA)₂ and 382 for the HBP(H)-(PA)₂, respectively.

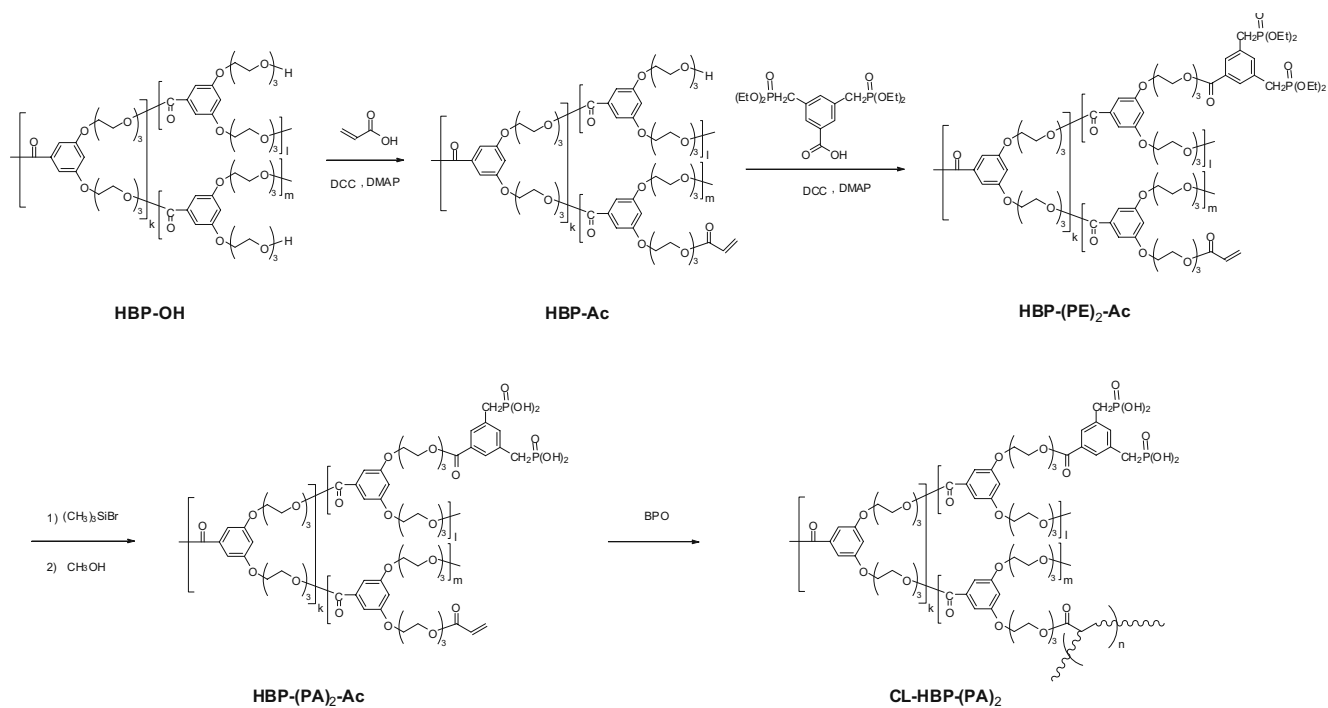
Synthesis of the hyperbranched polymer with both two phosphonic acid groups and an acryloyl group at the periphery (HBP-(PA)₂-Ac)

A low molecular weight hyperbranched polymer with both two phosphonic acid groups and an acryloyl group at the periphery (HBP-(PA)₂-Ac) was successfully synthesized according to a synthetic route as shown in Scheme 3.

The HBP(L)-OH ($M_n=4,200$) was reacted with an acrylic acid in the presence of DCC and DMAP at room temperature to give the HBP(L)-Ac as a yellow highly viscous oil. The reaction of the HBP(L)-Ac with 3,5-bis(diethoxyphosphorylmethyl)benzoic acid in the presence of DCC and DMAP at room temperature gave the HBP(L)-(PE)₂-Ac in 64% yield as a yellow highly viscous oil. The reaction of the HBP(L)-(PE)₂-Ac with bromotrimethylsilane, followed by solvolysis in methanol, afforded a hyperbranched polymer (HBP(L)-(PA)₂-Ac) with both two phosphonic acid groups and an acryloyl group at the periphery as a pale yellow solid, which was purified by a dissolution–reprecipitation method using DMF as a solvent and isopropyl ether as a precipitant, respectively, and finally washed with isopropyl alcohol. An acryloyl group content in the HBP(L)-(PA)₂-Ac was determined by ¹H-NMR measurement to be 47%. Polymer electrolyte (HBP(L)-(PA)₂-Ac) is soluble in DMF, DMAc, and DMSO but



Scheme 2 Synthesis route of the HBP(L, H)-(PA)₂



Scheme 3 Synthesis route of the HBP-(PA)₂-Ac and the CL-HBP-(PA)₂

insoluble in benzene, chloroform, THF, isopropyl ether, methanol, ethanol, acetonitrile, and water.

Synthesis of the semi-interpenetrated electrolyte membrane (HBP-(PA)₂-co-HBP-Ac) and the cross-linked electrolyte membrane (CL-HBP-(PA)₂)

We attempted to prepare a semi-interpenetrated electrolyte membrane (HBP-(PA)₂-co-HPB-Ac) by copolymerization of the HBP(L)-(PA)₂ with the HPB-Ac in vacuo at 130 °C for 48 h. Unfortunately, the polymerization provided the membrane with phase-separated structure as well as the case of the HBP-PA-co-HBP-Ac membrane reported previously [23], which is not suitable for fuel cell measurement.

The cross-linked electrolyte membrane (CL-HBP(L)-(PA)₂) could be formed by solvent casting technique on parting agent-coated PET sheet at room temperature and by the cross-linking reaction using BPO as a radical initiator. On this solvent casting, 10 wt.% fumed silica as a thickener was added to the HBP(L)-(PA)₂-Ac solution in DMAc to obtain a large size homogeneous film with a given thickness. Without addition of fumed silica, we failed to prepare a large size membrane suitable for fuel cell test. Moreover, although the formation of the cross-linked membranes by solvent casting on the glass plate without fumed silica was possible, we failed to peel it without break. During the cross-linked membrane formation, some shrinkage was observed.

Equivalent weight (*E_w*) value of the CL-HBP(L)-(PA)₂ (Ac content=47%) membrane was determined from phosphorous content by a ICP method to be 718.

Ionic conductivities

Hyperbranched polymers with two phosphonic acid groups at the periphery (HBP(H, L)-(PA)₂)

The temperature dependence of the ionic conductivities for the HBP(L)-(PA)₂ and the HBP(H)-(PA)₂ in the temperature range of 80–150 °C is shown in Fig. 1.

Ionic conductivity data of the both electrolytes were typically interpreted using the Vogel–Tamman–Fulcher (VTF) Eq. 1 [25–27]:

$$\sigma(T) = AT^{-\frac{1}{2}} \exp[-B/(T - T_0)] \tag{1}$$

where σ and T are the ionic conductivity and the absolute temperature, respectively. A , B , and T_0 are the fitting parameters and correspond to a carrier ion number, an activation energy, and the temperature where the free volume vanishes, respectively. The VTF parameters obtained by fitting the conductivity data to Eq. 1 were summarized in

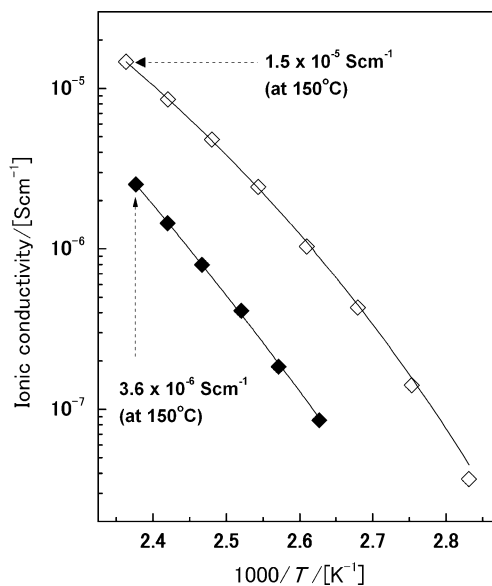


Fig. 1 Arrhenius plots of the ionic conductivity for (empty diamond) the HBP(L)-(PA)₂ (*M_n*=4,200) and (filled diamond) the HBP(H)-(PA)₂ (*M_n*=13,000). The solid lines are the results of fitting the ionic conductivity data on the VTF equation

Table 1. Ionic conductivities of both polymeric materials exhibited VTF type temperature dependence approaching $1.5 \times 10^{-5} \text{ S cm}^{-1}$ for the HBP(L)-(PA)₂ and $3.6 \times 10^{-6} \text{ S cm}^{-1}$ for the HBP(H)-(PA)₂, respectively, at 150 °C under dry condition. Observation of the VTF type behavior indicates that the phosphonic acid group in the polymer might dissociate to produce a proton as a charge carrier, and the resulting proton might be transported by segmental motion of the polymer as in the various polymer electrolytes composed of poly(ethylene oxide) (PEO) and PEO-based derivatives and lithium salts [18, 20].

The HBP(L)-(PA)₂ exhibits higher ionic conductivity than the HBP(H)-(PA)₂, which is due to the smaller free volume for the HBP(H)-(PA)₂ than the HBP(L)-(PA)₂ as shown in the higher glass transition temperature of the HBP(H)-(PA)₂ as described in “Thermal Properties.” Moreover, when the ionic conductivity of the HBP(L)-(PA)₂ was compared with that of the HBP(L)-PA reported previously [22], the former (*M_n*=4,200, $1.5 \times 10^{-5} \text{ S cm}^{-1}$ at 150 °C) showed lower ionic conductivity by one order than the latter (*M_n*=4,200, $1.3 \times 10^{-4} \text{ S cm}^{-1}$ at 150 °C), although the ion exchange capacity (IEC; 2.66 mmol g⁻¹, *E_w*=376)

Table 1 VTF parameters of the HBP(L, H)-(PA)₂ and CL-HBP(L)-(PA)₂ obtained by fitting the ionic conductivity data to Eq. 1

Polymer electrolytes	<i>A</i> [S cm ⁻¹ K ^{-1/2}]	<i>B</i> [K]	<i>T</i> ₀ [K]
HBP(L)-(PA) ₂	3.29	1680	242
HBP(H)-(PA) ₂	2.97	1701	255
CL-HPB(L)-(PA) ₂	7.71	1939	229

of the HBP(L)-(PA)₂ is much larger than that of the HBP(L)-PA ($E_w=720$, $IEC=1.39$ mmol g⁻¹). This is ascribed to higher T_g value (51.5 °C) in the HBP(L)-(PA)₂, which is due to an increase in hydrogen bond between phosphonic acids induced by larger number of functional groups, compared to that (31.7 °C) in the HBP(L)-PA.

Cross-linked electrolyte membrane (CL-HBP(L)-(PA)₂)

The temperature dependence of the ionic conductivity for the CL-HBP(L)-(PA)₂ membrane in the temperature range of 80–150 °C is shown in Fig. 2, together with that of the CL-HBP(H)-PA reported previously for comparison [23].

Ionic conductivity of the cross-linked membrane was found to be 1.7×10^{-5} S cm⁻¹ at 150 °C under dry condition, and it is almost the same to that of the HBP(L)-(PA)₂ (1.5×10^{-5} S cm⁻¹ at 150 °C) with no acryloyl group, though CL-HBP(L)-(PA)₂ has a loss in the carrier number caused by the replacement of phosphonic acid groups with the acryloyl groups in the same molecule. Probably, it is considered that an introduction of an acryloyl group into the HBP-(PA)₂ might reduce the degree of hydrogen bond between the phosphonic acid groups in the HBP-(PA)₂, resulting in similar number of proton carriers for ion conduction in both electrolytes. Ionic conductivity data of the electrolyte membrane was analyzed well with the VTF equation, and VTF parameters are summarized in Table 1. This indicates that the proton conduction in the electrolyte membrane is cooperated by polymer chain motion.

Here, we compared ionic conductivities between the CL-HBP(L)-(PA)₂ ($T_g=41.3$ °C, Ac content=47%) membrane

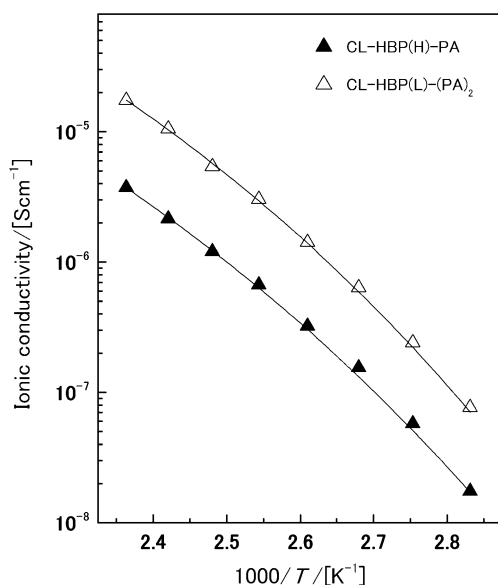


Fig. 2 Arrhenius plots of the ionic conductivity for the CL-HBP(L)-(PA)₂ membrane ($M_n=4,200$; filled triangle) and the CL-HBP(H)-PA membrane ($M_n=11,000$; empty triangle). The *solid lines* are the results of fitting the ionic conductivity data on the VTF equation

and the CL-HBP(H)-PA ($T_g=38.8$ °C, Ac content=27%) membrane, which have almost the same T_g values, though acryloyl contents and their molecular weights ($M_n=4,200$ for the CL-HBP(L)-(PA)₂ membrane and $M_n=11,000$ for the CL-HBP(H)-PA membrane) are different. Ionic conductivity ($\sigma=1.7 \times 10^{-5}$ S cm⁻¹ at 150 °C) of the CL-HBP(L)-(PA)₂ membrane is about seven times higher than that ($\sigma=2.6 \times 10^{-6}$ S cm⁻¹ at 150 °C) of the CL-HBP(H)-PA membrane reported previously [23]. This is due to the difference in carrier number caused by the different phosphonic acid group contents between the CL-HBP(L)-(PA)₂ membrane ($E_w=718$, $IEC=1.39$ mmol g⁻¹) and the CL-HBP(H)-PA membrane ($E_w=1350$, $IEC=0.74$ mmol g⁻¹) [23].

Thermal properties

Hyperbranched polymers with two phosphonic acid groups at the periphery (HBP-(PA)₂)

DSC measurement was carried out in a temperature range of -100–100 °C for the HBP(L)-(PA)₂ and the HBP(H)-(PA)₂ under argon. DSC traces of the HBP(L)-(PA)₂ and the HBP(H)-(PA)₂ are shown in Fig. 3, indicating that they are completely amorphous. The glass transition temperatures (T_g) were found to be 51.5 °C for the HBP(L)-(PA)₂ and 60.8 °C for the HBP(H)-(PA)₂, respectively. Lower ionic conductivity observed for the HBP(H)-(PA)₂ in comparison with the HBP(L)-(PA)₂ might be ascribed to a higher T_g value of the HBP(H)-(PA)₂, that is, the reduction of free volume in the HBP(H)-(PA)₂.

TG measurement was carried out under air to investigate the thermal stability for the HBP(L)-(PA)₂ and the HBP(H)-(PA)₂. The TG traces for both polymers are shown in Fig. 4, where the polymers showed two-stage decomposition and began to decompose at the temperature of about

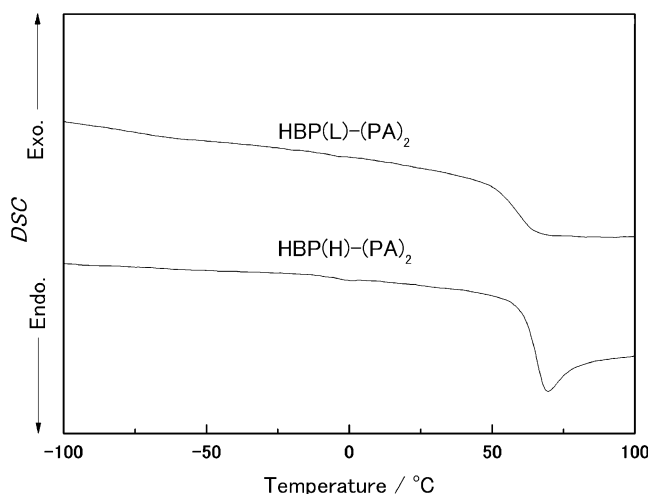


Fig. 3 DSC traces of the HBP(L)-(PA)₂ ($M_n=4,200$) and the HBP(H)-(PA)₂ ($M_n=13,000$) under argon

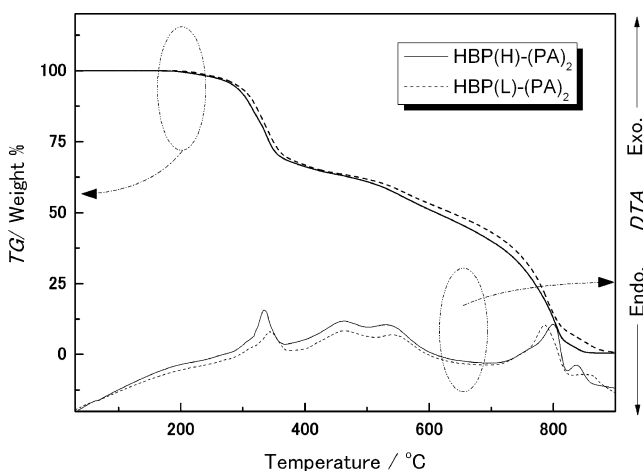


Fig. 4 TG and DTA curves of the HBP(L)-(PA)₂ (*M_n*=4,200) and the HBP(H)-(PA)₂ (*M_n*=13,000) under argon

300 °C. The weight loss in the temperature range of 300–400 °C amounted to about 30%, which corresponds approximately to the weight percent of the ethylene oxide chain unit in the polymers, indicating that the decomposition might take place an ether chain in the polymers. Their thermal stabilities are similar to the hyperbranched polymer with a phosphonic acid group (HBP-PA) reported previously [22], and also, the number of phosphonic acid groups does not affect significantly thermal stability of the polymer electrolytes. Anyway, they have suitable thermal stability as an electrolyte in the polymer electrolyte fuel cell operating under nonhumidified conditions.

Cross-linked electrolyte membrane (CL-HBP(L)-(PA)₂)

DSC measurement was carried out in the temperature range of –100–100 °C for the CL-HBP(L)-(PA)₂ membrane under

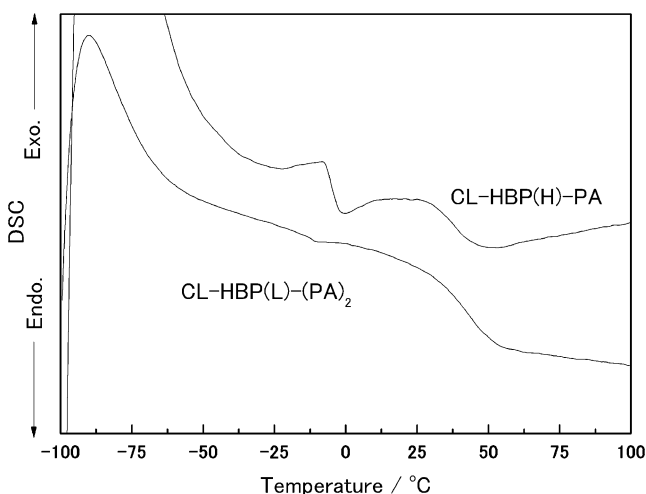


Fig. 5 DSC traces of the CL-HBP(L)-(PA)₂ membrane (*M_n*=4,200) and the CL-HBP(H)-PA membrane (*M_n*=11,000) under argon

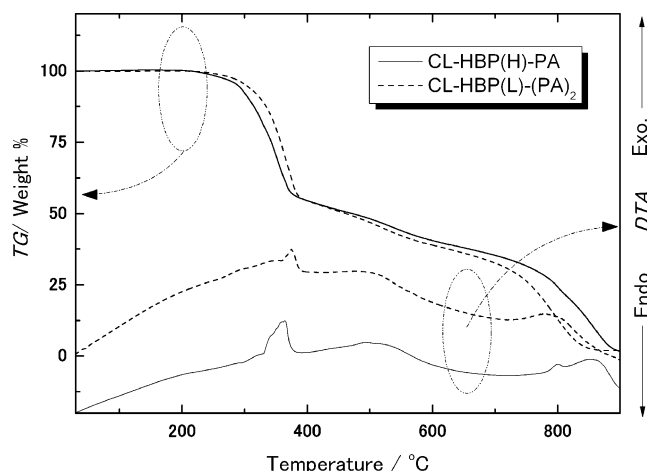


Fig. 6 TG and DTA curves of the CL-HBP(L)-(PA)₂ membrane (*M_n*=4,200) and CL-HBP(H)-PA membrane (*M_n*=11,000) under air

argon. DSC trace of the CL-HBP(L)-(PA)₂ membrane is shown in Fig. 5, together with that of the CL-HBP(H)-PA reported previously for comparison [23].

The *T_g* value was found to be 41.3 °C, and also, *T_g* value of the CL-HBP(H)-PA is reported to be 38.8 °C [23].

TG measurement was carried out under air to investigate the thermal stability for the CL-HBP(L)-(PA)₂ membrane. The TG trace for the membrane is shown in Fig. 6, together with that of the CL-HBP(H)-PA reported previously for comparison [23].

The CL-HBP(L)-(PA)₂ membrane showed two-stage decomposition and began to decompose at the temperature of about 300 °C as well as the CL-HBP(H)-PA membrane. The weight loss in the temperature range of 300–400 °C

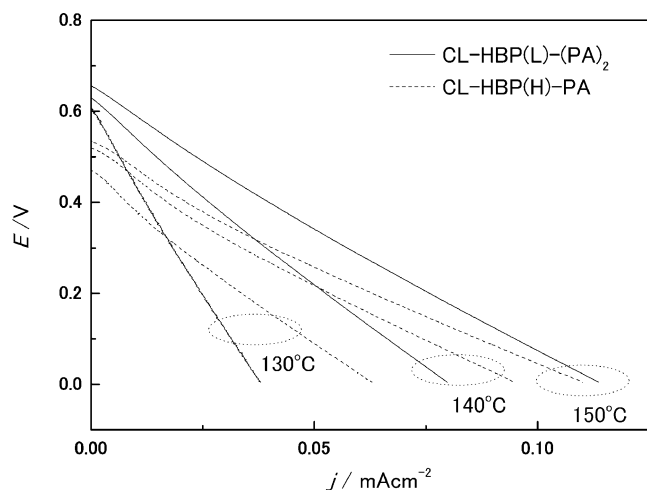


Fig. 7 The current vs voltage characteristic of test fuel cell at various temperatures using the CL-HBP(L)-(PA)₂ (Ac content=47%) membrane and the CL-HBP(H)-PA (Ac content=27%) membrane (*M_n*=11,000) as an electrolyte under nonhumidified conditions. Dry hydrogen gas and dry oxygen gas were used as fuel and oxidation gas, respectively

amounted to about 40%, which corresponds approximately to the weight percent of the ethylene oxide chain unit in the polymers, indicating that the decomposition might take place an ether chain in the polymer. Anyway, it is sure that they have suitable thermal stability as electrolyte membranes for the high-temperature fuel cell under nonhumidified conditions as well as the CL-HBP(L)-PA membrane reported previously [23].

Fuel cell measurement

The polarization (I–V) characteristic of the CL-HBP(L)-(PA)₂ membrane was measured using a test fuel cell. The voltage profiles observed at cell temperatures of 130, 140, and 150 °C under nonhumidified conditions are shown in Fig. 7, together with those of the CL-HBP(H)-PA system reported previously for comparison [23].

Dry hydrogen and dry oxygen gases were used as the fuel and the oxidant, respectively. The open-circuit voltage (OCV) value of 0.66 V was obtained for the CL-HBP(L)-(PA)₂ membrane at 150 °C, which is much lower than the theoretical value of 1.23 V. The I–V characteristic of CL-HBP(L)-(PA)₂ was slightly improved in comparison with the CL-HBP(H)-PA membrane, where the OCV for the CL-HBP(H)-PA membrane is reported to be 0.53 V at 150 °C [23]. The reason for the low OCV might be related to gas crossover or internal micro short circuit due to poor mechanical strength of the membranes. It is necessary to improve and optimize these factors in order to attain the better cell performance. Although IR free polarization should be considered, the activation over potential of these electrolytes might be much larger than that of a typical PEFC. At the temperature range between 130 and 140 °C, the limiting currents (at 0 V) of CL-HBP(H)-PA indicated higher values in comparison with that of CL-HBP(L)-(PA)₂. This may indicate that the cell characteristics are governed by the contact interface between the membrane and catalyst layers. Because of the difference in the degree of cross-linking, CL-HBP(H)-PA behaves as adhesive compound more than CL-HBP(L)-(PA)₂ at low temperatures. As the polarization profiles showed curvature and the scanning rate was sufficiently slow, this might be Faradic capacity related to oxygen reduction reaction at nonhumidified high-temperature conditions. At the low current density, sufficient water flux (i.e., back diffusion water) is not expected for wetting the membrane. Therefore, both kinetics and proton transport are presumed to be different from a typical PEFCs. The proton conductivity of 10^{-3} S cm⁻¹ at least is required to clarify the detail electrochemical reactions since the IR drop is a major resistive component in this cell.

Conclusion

We investigated the anhydrous proton-conducting membranes for use in the polymer electrolyte fuel cells at high temperature. We synthesized the two different molecular weight hyperbranched polymers (HBP(L, H)-(PA)₂) with two phosphonic acid groups as a functional group and a low molecular weight hyperbranched polymer (HBP(L)-(PA)₂-Ac) with both two phosphonic acid groups and an acryloyl group as a cross-linker at the periphery as a thermally stable proton-conducting electrolyte and obtained the cross-linked electrolyte membrane (CL-HBP(L)-(PA)₂) by thermal polymerization of the HBP(L)-(PA)₂-Ac using benzoyl peroxide. The ionic conductivity of the CL-HBP(L)-(PA)₂ membrane was found to be 1.7×10^{-5} S cm⁻¹ at 150 °C under dry condition and showed the VTF type temperature dependence. The membrane was thermally stable up to 300 °C, and it had suitable thermal stability as an electrolyte in the polymer electrolyte fuel cell operating under dry condition. Fuel cell measurements using a single membrane electrode assembly cell with the cross-linked membrane was successfully performed. An increase in the phosphonic acid group in the electrolyte membrane truly improved the ionic conductivity from the comparison between the CL-HBP(L)-(PA)₂ and CL-HBP(H)-PA membranes with same T_g values. Unfortunately, higher ionic conductivity does not contribute significantly to the power generation, although optimization of the measurement conditions is needed.

References

1. Kreuer KD (1996) *Chem Mater* 8:610
2. Srinivasan S, Mosdale R, Stevens P, Yang C (1999) *Annu Rev Energ Environ* 24:281
3. Steele BCH, Heinzel A (2001) *Nature* 414:345
4. Yang C, Costamagna P, Srinivasan S, Benziger J, Bocarsly AB (2001) *J Power Sources* 103:1
5. Savadogo O (1998) *J New Mater Electrochem Syst* 1:47
6. Savadogo O (2004) *J Power Sources* 127:135
7. Karlsson LE, Jannasch P (2004) *J Membr Sci* 230:61
8. Jannasch P (2003) *Curr Opin Colloid Interface Sci* 8:211
9. Wainright JS, Wang J, Weng D, Savinell RF, Litt M (1995) *J Electrochem Soc* 142:L121
10. Wang J, Savinell RF, Wainright JS, Litt M, Yu H (1996) *Electrochem Acta* 41:193
11. Schuster M, Meyer WH, Wagner G, Herz HG, Ise M, Schuster M, Kreuer KD, Maier J (2001) *Solid State Ion* 145:85
12. Schuster MFH, Meyer WH, Schuster M, Kreuer KD (2004) *Chem Mater* 16:329
13. Kreuer KD (2001) *J Membr Sci* 185:29
14. Herz HG, Kreuer KD, Maier J, Scharfenberger G, Schuster MFH, Meyer WH (2003) *Electrochim Acta* 48:2165
15. Persson JC, Jannasch P (2003) *Chem Mater* 15:3044

16. Persson JC, Jannasch P (2005) *Macromolecules* 38:3283
17. Kreuer KD, Schuster M, Paddison SJ, Spohr E (2004) *Chem Rev* 104:4637
18. Gray FM (1991) *Solid polymer electrolytes: fundamentals and technological applications*. VCH Publishers, New York
19. Scrosati B (ed) (2003) *Applications of electroactive polymers*. Chapman and Hall, London
20. Gray FM (1997) *Polymer electrolytes*. The Royal Society of Chemistry, London
21. Itoh T, Hamaguchi Y, Uno T, Kubo M, Aihara Y, Sonai A (2006) *Solid State Ion* 177:185
22. Itoh T, Hamaguchi Y, Hirai K, Uno U, Kubo M, Aihara Y, Sonai A (2006) Synthesis, ionic conductivity, and thermal properties of hyperbranched polymer with phosphonic acid groups at the chain ends for high temperature fuel cell. In: Fuller T, Bock C, Cleghorn S, Gasteiger H, Jarvi T, Mathias M, Murthy M, Nguyen T, Ramani V, Stuve E, Zawodzinski T (eds) *ECS transactions, proton exchange membrane fuel cells 6, vol 3*. The Electrochemical Society, Pennington, pp 113–121
23. Itoh T, Hirai K, Tamura M, Uno U, Kubo K, Aihara A (2008) *J Power Sources* 178:627
24. Itoh T, Ikeda M, Hirata N, Moriya Y, Kubo M, Yamamoto O (1999) *J Power Sources* 81–82:824
25. Vogel H (1921) *Phys Z* 22:645
26. Tamman G, Hesse W (1926) *Anorg Allg Chem* 156:245
27. Fulcher GS (1925) *J Am Ceram Soc* 8:339