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Preparation of Acid-Functionalized Poly(phenylene oxide)s and Poly(phenylene sulfone) and Their Proton Conductivity

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A series of highly acid-functionalized poly(phenylene oxide)s and poly(phenylene sulfone) were prepared and proton conductivity in their membranes is discussed. Phosphorylated poly(phenylene oxide)s were prepared via the oxidative polymerization of phosphonoxyphenols in alkaline water, along with a facile monomer preparation. A poly(phenylene oxide) bearing a sulfamide acid group was prepared by reacting amidosulfate with the corresponding carboxylated poly(phenylene oxide). A sulfonated poly(phenylene sulfone) was prepared by hydrogen peroxide oxidation of the sulfonated poly(phenylene sulfide). All these acid-functionalized polymers showed appropriate thermal stability based on the aromatic backbone. The polymers had a high ion-exchange capacity, were water-soluble, but gave transparent and flexible membranes after compositing with the poly(ethylene oxide). Some of the membranes displayed a high proton conductivity of 10^{-4} S cm^{-1} at 120 °C under dry conditions.

Acid-functionalized polymers have recently become interesting because of their potential usefulness as proton-conducting polymer electrolyte membranes (PEMs) for fuel cells.[1–4] Besides the proton conductivity, thermostability is also crucial for PEMs, and one of the approaches to provide thermostable PEMs is the functionalization of acid groups onto aromatic polymers which have a thermal degradation temperature >250 °C; examples of the backbone aromatic polymers include a polyimide,[5,6] poly(etheretherketone),[7] polysulfone,[8] poly(phenylene),[9] poly(phenylene sulfide),[10] and poly(phenylene oxide).[11]

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), which has a compact repeating unit structure of a rigid aromatic ring and flexible ether linkage, is widely used as a high-performance engineering plastic because it has a high glass-transition temperature ($T_g = 205$–210 °C), good mechanical property, and high hydrolytic and oxidative stabilities.[12] PPO is prepared both industrially and on a laboratory scale by the oxidative polymerization of 2,6-dimethylphenol with a copper–amine catalyst.[13,14] The polymerization proceeds at room temperature, and it is an ideal atom economical reaction that does not require any leaving groups for producing the polymer.[12–16] It has been reported that the sulfonation and phosphonation of PPO produced acid-functionalized PPOs.[17–20] However, the ion-exchange capacity (IEC) of the obtained acid-functionalized PPOs remained up to 1.8 meq g^{-1} based on previous reports. On the other hand, oxidative polymerization of the acid-functionalized phenols has been examined; however, it has been impeded by both their high oxidation potential and also by the formation of a chelate complex with a copper–amine catalyst.[14] From the aspect of a green chemical process, we have developed the oxidative polymerization of 2,6-dimethylphenol to form PPO using alkaline water as the reaction solvent.[15,16] It has been concluded that the reaction in alkaline water reduces the oxidation potential of the acid-functionalized phenols and facilitates the polymerization. The formation of a chelate complex with the catalyst or catalyst inactivation can also be prevented by using a metal oxide, such as a silver oxide, as the oxidizing agent to yield the PPO. We have succeeded in the oxidative polymerization of sulfonatopropoxyphenols in alkaline water using silver oxide to prepare the sulfoalkoxy-pendant PPOs.[21]

Phosphoric acid is known to show a high acid dissociation degree of 13% in the bulk and to display a high proton conductivity of almost 10^{-1} S cm^{-1} at its melting point (42 °C) in a water-free state.[22] Proton-conducting polymers bearing the phosphoric acid group have been studied in hopes of not only a higher proton conductivity in a low humidified and a dry state, but also higher thermal and chemical stabilities than those of the sulfonated polymers.[23–25] In this paper, we first report the preparation of phosphorylated PPOs (**1** and **2**) via the oxidative polymerization of the corresponding phosphonoxyphenols (OPP and MPP) in alkaline water using silver oxide, as well as a facile preparation of the monomer (Schemes 1 and 2).

Recently, we have reported that sulfamide acid (sulfamidocarbonyl: –CONHSO$_3$H) is a novel proton source for PEMs.[26,27] The sulfamide acid has both an electron-withdrawing carbonyl group and a conjugated structure possibly affording a very high proton-dissociation ability in a water-free state upon PEM application in addition to good hydrolytic and thermal stabilities. We have also reported the preparation of a carboxylated PPO via oxidative polymerization and its high thermal stability.[11] We now describe in this paper the preparation of PPO bearing a sulfamide acid group (**4**) and its proton conductivity (Scheme 3).

Poly(1,4-phenylene sulfone) (PPSU) is one of the high-performance engineering plastics with good thermal, chemical, and mechanical stabilities.[28] PPSU has also been prepared from poly(phenylene sulfide) by oxidation using hydrogen peroxide.[29] On the other hand, Miyatake et al. have successfully reported a very high proton conductivity of 10^{-3} S cm^{-1} for

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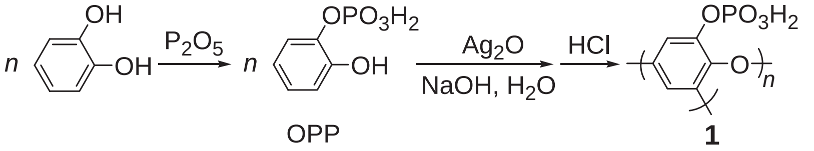
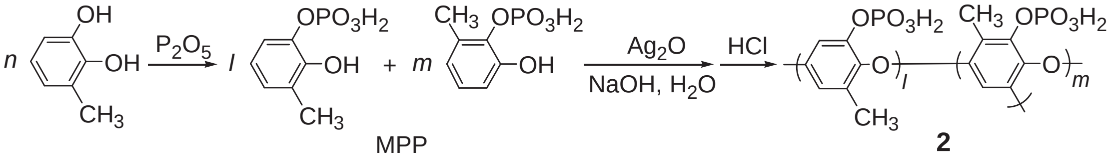
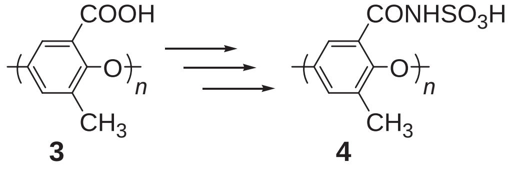


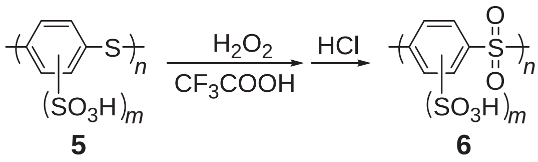
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

the highly sulfonated poly(1,4-phenylene sulfide) (PPS) (**5**) composite membrane with poly(ethylene oxide).[30] In this paper, we also describe the preparation of the sulfonated PPSU (**6**) by the simple hydrogen peroxide oxidation of the sulfonated PPS (Scheme 4): We expect for the sulfonated PPSU an enhanced proton conductivity due to the electron-withdrawing sulfone group. The thermal stability of these acid-functionalized polymers is also described in this paper.

Results and Discussion

Phosphonoxyphenols, *o*-phosphonoxyphenol (OPP), and methylphosphonoxyphenols (MPP), which are the monomers used to produce the phosphorylated PPO polymers, were prepared in high yields by simply mixing the corresponding catechols with diphosphorus pentaoxide at a temperature slightly higher than their melting points.[31] MPP was obtained as 2-methyl-6-phosphonoxyphenol and its structural isomer, 3-methyl-2-phosphonoxyphenol, in a 5/3 molar ratio estimated from the ^{1}H NMR spectra of the reaction product. Irreversible oxidation currents of OPP and MPP in the alkaline water were observed in the cyclic voltammograms with their peak potential at 0.49 and 0.45 V (vs. Ag/AgCl), respectively (Fig. 1). The electron-donating methyl group of MPP is considered to reduce the oxidation potential of phenol when compared to that of OPP. The current value at the oxidation peak potential of OPP was lower than those of 2,6-dimethylphenol and MPP, probably due to the low solubility of OPP in the alkaline water. Anyway, the oxidation potentials of OPP and MPP were not very high and comparable to that (0.33 V) of 2,6-dimethylphenol, which suggests the oxidative polymerizability of OPP and MPP in the alkaline water solvent.

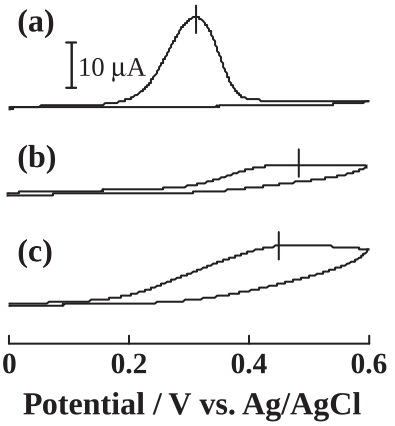


Fig. 1. Cyclic voltammograms of the 10 mM (a) 2,6-dimethylphenol, (b) OPP, and (c) MPP in a 50 mM aqueous sodium hydroxide solution at a scan rate of 25 mV s^{-1}.

Table 1. Oxidative Polymerizations of OPP and MPP[a)]

Entry	Monomer	Temp /°C	Time /day	Yield /%	M_w[b)] ($\times 10^5$)	M_w/M_n
1	OPP	r.t.	1	26	—[c)]	—
2	MPP	r.t.	1	21	1.0	1.5
3	MPP	r.t.	8	14	0.8	1.9
4	MPP	50	1	22	1.0	1.6
5	MPP	80	1	34	1.5	2.0
6	MPP	100	1	87	1.0	1.9

a) The polymerization of the phenol (3 mmol) was carried out in water (30 mL) with sodium hydroxide (15 mmol) and silver oxide (15 mmol) in air. b) The molecular weight was measured using gel permeation chromatography with poly(4-styrenesulfonic acid) standards and a water eluent. c) Poly(phosphonoxyphenylene oxide) was insoluble in water.

The oxidative polymerizations of OPP and MPP were examined in the alkaline water using silver oxide as an oxidizing agent (Table 1). As the polymerization proceeded, a silver mirror formed on the flask glass. Poly(phosphonoxyphenylene oxide) (**1**) was obtained as a solvent-insoluble polymer during the polymerization at room temperature (Table 1, Entry 1). The poor solvent-solubility of OPP in a sodium hydroxide aqueous solution and the cross-linking of the phenylene oxide at the *o*-position of OPP were considered to produce the solvent-insoluble polymer **1**. Poly(methylphosphonoxyphenylene oxide) (**2**) with a high molecular weight of 10^5 was obtained from the polymerization of MPP at room temperature for 1 day (Table 1, Entry 2). The polymerization yield increased with an increase in reaction temperature, but the molecular weight of the polymer **2** remained at almost 10^5 (Table 1, Entries 3–6). Polymers **1** and **2** were obtained as a light-brown powder and characterized by IR, ^{1}H, and ^{31}P NMR spectroscopies. The solid-state ^{31}P NMR spectrum of the polymer **1** showed a peak at 2.5 ppm ascribed to the phosphoric acid group. IR spectrum of the polymer **2** had broad absorption bands at 1233 ($\nu_{P=O}$ of $-PO_3H_2$), 1196 ($\nu_{P=O}$ of $-HPO_3^-$), and 1077 cm^{-1} ($\nu_{P=O}$ of $-PO_3^{2-}$) ascribed to the phosphoric acid group. The peak at 1474 cm^{-1} (δ_{P-O-C}) and the shoulder at 1271 cm^{-1} (ν_{P-O-C}) supported the phosphonoxy structure. The peak at 1201 cm^{-1} (ν_{C-O-C}) attributed to the aromatic ether bond, which overlapped with the broad P=O band, supported the formation of the phenylene oxide polymer. Polymer **2** was insoluble in organic solvents, suggesting a slightly branching and/or cross-linking of the phenylene oxide at the *o*-position of the phenol. Multiplet peaks in the solution ^{1}H NMR spectrum of **2** indicated a *o*- and *p*-substituted branched or cross-linked structure of the phenylene oxide. However, **2** was soluble in water, an aqueous hydrochloric acid solution, and an aqueous sodium hydroxide solution. The *o*-methyl group of MPP is presumed to suppress the cross-linking at the *o*-position in order to maintain the solubility of the formed polymer. The IEC value of the polymer **2** was determined by acid–base titration to be 4.7 meq g^{-1} and almost agreed with the calculated IEC based on the chemical structure of **2** (4.9 meq g^{-1}).

Poly(2-methyl-6-sulfamidocarbonyl-1,4-phenylene oxide) (**4**) was prepared by the following polymer reaction (Scheme 3) of poly(2-carboxy-6-methyl-1,4-phenylene oxide) (**3**), which was prepared according to a previous paper.[11] The carboxylic acid group of the polymer **3** was converted to the corresponding acid chloride, which was reacted with an excess of triethylammonium amidosulfate, then treated with a cation-exchange resin to yield the polymer **4** with the conversion to the sulfamide acid group of 76 and 9% for the water-soluble and insoluble part of **4**, respectively. The IEC values of the water-soluble and -insoluble **4** estimated from sulfur elemental analysis were 3.6 and 0.41 meq g^{-1}, respectively, and almost consistent with the IEC value determined from the ^{1}H NMR spectra (the calculated IEC based on the chemical structure of **4** = 4.4 meq g^{-1}). The polymer **4** with IEC = 3.6 meq g^{-1} was obtained as a light-brown powder and characterized by ^{1}H NMR and IR spectroscopy. In the ^{1}H NMR spectrum of **4**, the phenylene proton peaks at 7.11 and 6.94 ppm ascribed to those of **3** significantly decreased, and new phenylene proton peaks at 7.85 and 7.45 ppm clearly appeared, which supported the high conversion (determined by the elemental analysis) from the carboxylic acid derivative to the sulfamide acid one. From the IR spectrum of **4** the introduction of the sulfamide acid group and the structure of the phenylene oxide backbone were evident: The new absorptions ($\nu_{C=O}$ = 1644 cm^{-1} and $\nu_{S=O}$ = 1171, 1037 cm^{-1}) for the sulfamide acid group clearly appeared and the strong absorption (ν_{C-O-C} = 1219 cm^{-1}) by the phenylene oxide remained. After drying in vacuo at 100 °C for 3 days, the polymer **4** with IEC = 3.6 meq g^{-1} was partially soluble in water, methanol, DMF, and dimethyl sulfoxide, while **3** and **4** with IEC = 0.41 meq g^{-1} was soluble in the same organic solvents, but insoluble in water. The poor solvent solubility of **4** after heating suggested intra- and/or inter-polymer hydrogen-bond formation through the sulfamide acid groups in the solid-state polymer.

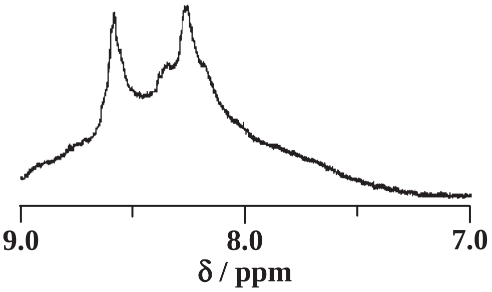


Fig. 2. ^{1}H NMR spectrum of the polymer **6**.

The sulfonated poly(1,4-phenylene sulfone) (PPSU) **6** was prepared by the following hydrogen peroxide oxidation (Scheme 4) of the sulfonated poly(1,4-phenylene sulfide) **5** with IEC = 4.4 meq g^{-1}, which was prepared according to a previous report:[10,30] The backbone sulfide of the polymer **5** was oxidized to the sulfone with an excess of a hydrogen peroxide aqueous solution and trifluoromethanesulfonic acid, based on a previous paper for the oxidation of poly(phenylene sulfide).[29] The polymer **6** was obtained as an off-white powder and characterized by ^{1}H NMR and IR spectroscopies. In the ^{1}H NMR spectrum of **6**, peaks at 6.70–7.25 ppm ascribed to the phenylene protons between the sulfide groups completely disappeared, while new peaks at 8.35–8.64 ppm ascribed to the phenylene protons between the sulfone and sulfonic acid groups clearly appeared (Fig. 2). This supported the almost quantitative conversion of the sulfide backbone to the sulfone one. The IR spectrum of **6** also supported both the introduction of the sulfone and the structure of the sulfonic acid group. The characteristic S=O absorptions at 1334 and 1168 cm^{-1} and 1218 and 1114 cm^{-1} were ascribed to the sulfone and the sulfonic acid, respectively. The polymer **6** was soluble in water, DMF, and dimethyl sulfoxide, but insoluble in methanol, ethanol, acetonitrile, and chloroform. The IEC of the polymer **6** was determined by acid–base titration to be 3.7 meq g^{-1} (the calculated IEC based on the chemical structure of **6** = 6.7 meq g^{-1}).

The thermal property of the obtained acid-functionalized polymers **2**–**6** was measured by thermogravimetry (TG) and differential scanning calorimetry (DSC). TG curves for the polymers **2**–**6** are shown in Fig. 3, and the 10%-degradation temperatures ($T_{d10\%}$) are listed in Table 2. The T_g of the polymers was estimated by DSC and given also in Table 2. Because of their hygroscopicity, the polymers were dried in vacuo at 100 °C for 3 days before the measurement. The $T_{d10\%}$ and T_g of the phosphorylated PPO **2** were more than 70 °C higher than those of the sulfoalkoxy-pendant PPO ($T_{d10\%}$ = 288 and T_g = 115 °C[21]). The thermal stability of **2** was as high as those of the previously reported poly(arylene ether)s bearing the phosphoric acid group and probably derived from the intra- and/or inter-polymer hydrogen-bonding or cross-linking through the phosphoric acids, as has been described for the previous phosphoric acid-bearing poly(arylene ether)s.[23] The $T_{d10\%}$ of a PPO bearing the sulfamide acid group **4** with IEC $= 3.6\,\mathrm{meq\,g^{-1}}$ was ca. 40 °C higher than that of the starting carboxylated PPO **3**, but the T_g of the polymer **4** was ca. 40 °C lower than that of **3**. It was considered that the higher $T_{d10\%}$ of **4** was derived from the stability of the sulfamide acid group conjugated with the backbone, and the lower T_g of **4** was from the relatively weak interaction between the phenylene oxide backbone with the large sulfamide acid group. The $T_{d10\%}$ of the sulfonated PPSU **6** was 130 °C lower than that of the sulfonated PPS **5**, but the T_g of the polymer **6** was 50 °C higher than that of the polymer **5**, which could be due to the strong electron-withdrawing sulfone group on the backbone. All these obtained acid-functionalized polymers showed a sufficient T_g and $T_{d10\%}$ of more than 160 and 350 °C, respectively, based on the aromatic backbone.

Membranes of the acid-functionalized polymers **2** and **4**–**6** were prepared by casting from their aqueous solutions, and that of **3** was from the methanol solution. All of the homopolymer membranes were transparent, but not self-independent enough for the proton conductivity measurement. Compositing of the polymers **2**–**6** with poly(ethylene oxide) of $M_w = 600$ in a 1/1 weight ratio produced transparent and flexible membranes (The composite membrane for the carboxylated PPO **3** with poly(ethylene oxide) in a 1/1 weight ratio was too flexible to measure the conductivity, therefore, the membrane was prepared in a 2/1 weight ratio). The membranes were dried in vacuo at 100 °C for 3 days before the conductivity measurement.

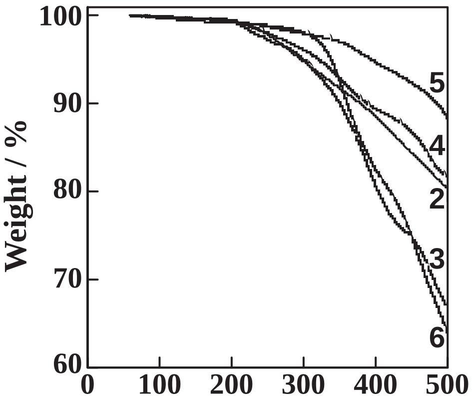


Fig. 3. TG curves of the polymers **2**–**6**.

The proton conductivity of the dry membranes using the acid-functionalized polymers **2**–**6** composited with poly(ethylene oxide) was plotted as a function of the temperature from 30 to 170 °C along with the control data of the Nafion®117 (Fig. 4). The proton conductivity of the composite membrane of the phosphorylated PPO **2** was on the order of 10^{-4}–$10^{-6}\,\mathrm{S\,cm^{-1}}$ which was higher than that of the Nafion®117 membrane (10^{-5}–$10^{-8}\,\mathrm{S\,cm^{-1}}$) with IEC $= 0.9\,\mathrm{meq\,g^{-1}}$ under the same measurement conditions. The proton conductivity of the composite membranes of the PPO bearing the sulfamide acid group **4** with IEC $= 3.6\,\mathrm{meq\,g^{-1}}$ and sulfonated PPSU **6** was on the order of 10^{-5}–10^{-6} and 10^{-4}–$10^{-7}\,\mathrm{S\,cm^{-1}}$, respectively, which was remarkably higher than those (10^{-7}–10^{-12} and 10^{-5}–$10^{-9}\,\mathrm{S\,cm^{-1}}$) for the pre-polymer **3** and **5**, respectively. The highest conductivity reached $10^{-4}\,\mathrm{S\,cm^{-1}}$ at >120 °C for the composite membrane composed of polymers **2** and **6** among all the obtained polymers. The conductivity increase with temperature from 30 to 170 °C obeyed an Arrhenius type plot to give the activation energies of 29, 18, and

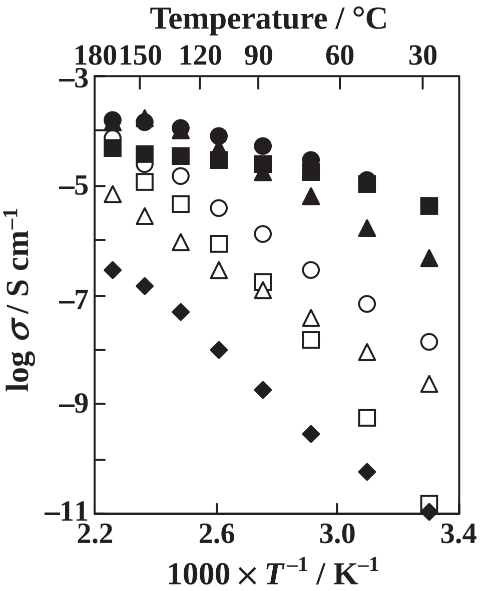


Fig. 4. Proton conductivity of the dry membranes composited with poly(ethylene oxide) for **2** (●), **3** (◆), **4** with IEC $= 3.6\,\mathrm{meq\,g^{-1}}$ (■), **4** with IEC $= 0.41\,\mathrm{meq\,g^{-1}}$ (□), **5** (△), and **6** (▲), and a control of dry Nafion®117 membrane (○).

Table 2. Properties of Acid-Functinalized Polymers **2**–**6**

Polymer	IEC[a)] /meq g^{-1}	M_w[b)] ($\times 10^4$)	M_w/M_n	T_g /°C	$T_{d10\%}$ /°C	Solubility[c)]			
						CHCl$_3$	CH$_3$OH	DMF	H$_2$O
2	4.7	10	1.9	180	383	−	−	−	+
3	6.7	2.0	1.7	193	350	−	+	+	−
4	3.6	N. A.	N. A.	154	390	−	±	±	±
5	4.4	1.3	2.3	202	486	−	−	+	+
6	3.7	1.5	2.3	255	360	−	−	+	+

a) IEC (ion-exchange capacity) for the most acidic proton. b) The molecular weight was measured using gel permeation chromatography with poly(4-styrenesulfonic acid) standards and a water eluent for **2**, and with polystyrene standards and a DMF eluent for **3**–**6**. c) + = Soluble, ± = partially soluble, − = insoluble.

49 kJ mol^{-1} for the composite membrane of polymers **2**, **4**, and **6**, respectively. These activation energies for the proton conductivity of the composite membranes were significantly lower than those (69, 86, and 121 kJ mol^{-1}) of the Nafion® 117 membrane and the composite membrane of polymers **3** and **4** with IEC $= 0.41$ meq g^{-1}. A high conductivity and low activation energy for the composite membranes of the polymers **2**, **4**, and **6** could be considered to be caused by the high proton concentration in the membrane which was derived from the high IEC and the high proton-dissociation ability of the phosphoric acid group, the sulfamide acid group, and the sulfonic acid group conjugated with the electron-withdrawing sulfone group for **2**, **4**, and **6**, respectively.

In conclusion, the poly(phenylene oxide)s bearing a phosphoric acid group and a sulfamide acid group and sulfonated poly(phenylene sulfone) with high IEC were prepared as thermostable proton-conducting PEMs. These highly acid-functionalized polymers gave transparent and flexible membranes after compositing with poly(ethylene oxide). The composite membranes for the phosphorylated poly(phenylene oxide) and the sulfonated poly(phenylene sulfone) displayed the high proton conductivity of 10^{-4} S cm^{-1} at >120 °C under dry conditions.

Experimental

Preparation of *o*-Phosphonoxyphenol (OPP). Catechol (4.95 g, 45 mmol) was warmed at a temperature slightly higher than its melting point (110 °C), and diphosphorus pentaoxide (4.26 g, 30 mmol) was slowly added with vigorous stirring for 2 h. As the reaction proceeded, the mixture became a brownish viscous liquid. After cooling to room temperature, the mixture was dissolved in water (50 mL) and extracted with diethyl ether. The extract was dried over anhydrous sodium sulfate and evaporated. The residue was dissolved in dichloromethane (300 mL) containing a few drop of methanol, and the solution was concentrated. After cooling to room temperature, the precipitate was collected by filtration and dried in vacuo to give OPP as a white powder (5.57 g, yield 65%). ^{1}H NMR (500 MHz, acetone-d_6, TMS) δ 7.19 (1H, d, aromatic C–H), 7.03 (1H, t, aromatic C–H), 6.93 (1H, d, aromatic C–H), 6.80 (1H, t, aromatic C–H); ^{13}C NMR (125 MHz, acetone-d_6, TMS) δ 148.7, 140.0, 127.4, 122.3, 121.1, 118.2; ^{31}P NMR (202 MHz, D$_2$O, H$_3$PO$_4$): δ -1.87; IR (KBr, cm^{-1}) 1461 ($\delta_{\text{P–O–C}}$), 1264 ($\nu_{\text{P–O–C}}$), 1241 ($\nu_{\text{P=O}}$ of –PO$_3$H$_2$), 1182 ($\nu_{\text{P=O}}$ of –HPO$_3{}^-$), 1102 ($\nu_{\text{P=O}}$ of –PO$_3{}^{2-}$), 1035 ($\nu_{\text{P=O}}$ of –HPO$_3{}^-$), 976 ($\nu_{\text{P–O–H}}$);. ESI-MS (m/z) 189.1 (M$^-$), 189.0 (calcd); Anal. Calcd for $C_6H_7O_5P$: C, 37.9; H, 3.7%. Found: C, 37.9; H, 3.7%.

Preparation of Methylphosphonoxyphenol (MPP). 3-Methylcatechol (5.59 g, 45 mmol) was warmed at 100 °C or a temperature slightly higher than its melting point (95 °C). Diphosphorus pentaoxide (4.26 g, 30 mmol) was slowly added with vigorous stirring for 2 h. The reaction mixture was dissolved in water (50 mL) and extracted with diethyl ether. The extract was dried over anhydrous sodium sulfate, and the solvent was evaporated. Recrystallization from dichloromethane gave MPP as white plate crystals (6.80 g, yield 74%). mp 92 °C. ^{1}H NMR (500 MHz, acetone-d_6, TMS) δ 7.06 (1H, d, aromatic C–H), 6.92 (1H, d, aromatic C–H), 6.91 (1H, t, aromatic C–H), 6.76 (1H, d, aromatic C–H), 6.71 (1H, d, aromatic C–H), 6.70 (1H, t, aromatic C–H), 2.27 (3H, s, CH$_3$), 2.20 (3H, s, CH$_3$); ^{13}C NMR (125 MHz, acetone-d_6, TMS) δ 149.5, 147.1, 139.6, 138.7, 132.2, 127.9, 127.8, 126.2, 122.7, 119.9, 119.3, 117.0, 16.6, 16.1; ^{31}P NMR (202 MHz, D$_2$O, H$_3$PO$_4$) δ -2.17, -3.19; IR (KBr, cm^{-1}) 1477 ($\delta_{\text{P–O–C}}$), 1276 ($\nu_{\text{P–O–C}}$), 1209 ($\nu_{\text{P=O}}$ of –PO$_3$H$_2$), 1182 ($\nu_{\text{P=O}}$ of –HPO$_3{}^-$), 1083 ($\nu_{\text{P=O}}$ of –PO$_3{}^{2-}$), 1031 ($\nu_{\text{P=O}}$ of –HPO$_3{}^-$), 977 ($\nu_{\text{P–O–H}}$); ESI-MS (m/z) 203.5 (M$^-$), 203.0 (calcd); Anal. Calcd for $C_7H_9O_5P$: C, 41.1; H, 4.4%. Found: C, 39.7; H, 4.6%.

Oxidative Polymerization of Phosphonoxyphenols. A typical procedure is described as follows. Methylphosphonoxyphenol (0.61 g, 3 mmol) was dissolved in water (30 mL) containing sodium hydroxide (0.60 g, 15 mmol). Silver oxide (3.48 g, 15 mmol) was added to the solution, and the mixture was stirred at room temperature for 24 h. After centrifugation, the residue solution was stirred in 10% aqueous hydrochloric acid (20 mL) for 6 h and dialyzed (M_w cut off $= 1000$) in water for 2 days. After evaporation and drying in vacuo at 100 °C for 3 days, poly(methylphosphonoxyphenylene oxide) (**2**) was obtained as a light-brown powder (0.13 g, yield 21%). ^{1}H NMR (500 MHz, D$_2$O) δ 7.35–6.00 (m, aromatic C–H), 2.27–1.58 (m, CH$_3$); ^{31}P NMR (202 MHz, D$_2$O, H$_3$PO$_4$) δ -4.74; IR (KBr, cm^{-1}) 1474 ($\delta_{\text{P–O–C}}$), 1271 ($\nu_{\text{P–O–C}}$), 1233 ($\nu_{\text{P=O}}$ of –PO$_3$H$_2$), 1201 ($\nu_{\text{C–O–C}}$), 1196 ($\nu_{\text{P=O}}$ of –HPO$_3{}^-$), 1077 ($\nu_{\text{P=O}}$ of –PO$_3{}^{2-}$), 985 ($\nu_{\text{P–O–H}}$);. GPC (poly(4-styrenesulfonic acid) standards and water eluent) $M_w = 1.0 \times 10^5$.

Preparation of Poly(2-methyl-6-sulfamidocarbonyl-1,4-phenylene oxide) (4). Poly(2-carboxy-6-methyl-1,4-phenylene oxide) (**3**) was prepared according to the previous paper.[11] The polymer **3** (0.15 g, 1 unit mmol) was dissolved in anhydrous DMF (20 mL). Thionyl chloride (0.30 g, 2.5 mmol) was added to the solution, and the mixture was stirred under nitrogen at room temperature for 6 h. Amidosulfuric acid (0.49 g, 5 mmol) and triethylamine (0.51 g, 5 mmol) were mixed in dichloromethane (5 mL) to form a clear solution of triethylammonium amidosulfate. The triethylammonium amidosulfate solution was added to the polymer solution, and the mixture was stirred under nitrogen at room temperature for 16 h. The reaction mixture was concentrated, dialyzed (M_w cut off $= 1000$) in water for 2 days, and evaporated. Water-soluble and -insoluble parts were separated by filtration. The residue was dissolved in methanol (400 mL), stirred with a cation-exchange resin, Amberlyst® 15JWET (Organo Co.), at room temperature for 12 h, and the solvent was evaporated. After drying in vacuo at 100 °C for 3 days, poly(2-methyl-6-sulfamidocarbonyl-1,4-phenylene oxide) (**4**) with IEC $= 3.6$ and 0.41 meq g^{-1} for water-soluble and -insoluble parts, respectively, was obtained as a light-brown powder (**4** with IEC $= 3.6$ meq g^{-1}: 0.028 g, yield 13%; **4** with IEC $= 0.41$ meq g^{-1}: 0.13 g, yield 85%). **4** with IEC $= 3.6$ meq g^{-1}: ^{1}H NMR (500 MHz, CD$_3$OD, TMS) δ 7.85 (1H, m, aromatic C–H), 7.45 (1H, m, aromatic C–H), 1.98 (3H, m, CH$_3$); IR (KBr, cm^{-1}) 1714, 1644 ($\nu_{\text{C=O}}$), 1219 ($\nu_{\text{C–O–C}}$), 1171, 1037 ($\nu_{\text{S=O}}$); Anal. Calcd for $C_8H_7NO_5S$: C, 41.9; H, 3.1; N, 6.1; S, 13.9%. Found: C, 42.2; H, 5.6; N, 3.2; S, 10.7%.

Preparation of Sulfonated Poly(1,4-phenylene sulfone) 6. Sulfonated poly(1,4-phenylene sulfide) **5** was prepared according to the previous paper.[10,30] The polymer **5** with IEC $= 4.4$ meq g^{-1} (0.42 g, 2.5 unit mmol) was dissolved in 30% hydrogen peroxide solution (12 mL) and trifluoromethanesulfonic acid (60 mL). The mixture was stirred at 70 °C for 10 h and dialyzed (M_w cut off $= 1000$) in water for 2 days. 10% Aqueous hydrochloric acid (20 mL) was added to the polymer solution. The mixture was stirred at room temperature for 6 h, dialyzed (M_w cut off $= 1000$) in water for 2 days, and the solvent was evaporated. After drying in vacuo at 100 °C for 3 days, the sulfonated poly(1,4-phenylene sulfone) **6** with IEC $= 3.7$ meq g^{-1} was obtained as a off-white powder (0.48 g, yield 97%). ^{1}H NMR (500 MHz, D_2O) δ 8.64–8.35 (br, aromatic C–H), 8.32–8.00 (br, aromatic C–H); IR (KBr, cm^{-1}) 1334, 1168 (ν_{SO2}), 1218, 1114 (ν_{SO3H}).

Membrane Preparation. A typical procedure is as follows. The polymer (30 mg) and poly(ethylene oxide) (30 mg) with $M_w = 600$ were dissolved in water (0.3 mL), mixed, and cast onto a gold plate ($\phi = 1.5$ cm), followed by drying at 70 °C for 2 h and in vacuo at 100 °C for 3 days.

Materials. Catechol and 3-methylcatechol were purchased from the Kanto Chemical Co. and purified by recrystallization from chloroform and hexane, respectively. The Nafion® 117 membrane was purchased from the Aldrich Chemical Co. All other reagents and solvents were purchased from the Kanto Chemical Co. and used without further purification.

Proton Conductivity Measurement. The membrane pressed between a pair of gold plate electrodes was mounted in the two-probe cell. The cell was placed in the temperature-controlled chamber. The proton conductivity was measured using an Autolab PGSTAT30 AC impedance spectrometer over the frequency range from 1 Hz to 1 MHz and the temperature range from 170 to 30 °C at intervals of 20 °C after keeping the cell in the chamber at 170 °C for 3 h.

Thermal Analysis. The thermal analyses were performed via TG/DTA-MS using a Rigaku TG8120 equipped with a Shimadzu GC-17A gas chromatograph mass spectrometer over the temperature range from 60 to 500 °C at a heating rate of 10 °C min^{-1} after keeping it at 150 °C for 1 h and cooling to 60 °C at a cooling rate of 5 °C min^{-1} under helium and via DSC by a Rigaku DSC8230 over the temperature range from 30 to 300 °C at a heating rate of 5 °C min^{-1} under nitrogen.

Other Measurements. ^{1}H, ^{13}C, and ^{31}P NMR, mass, and infrared spectra were recorded on JEOL Lambda 500, Thermo Quest Finnigan LCQ DECA, and JASCO FT/IR-410 spectrometers, respectively. The cyclic voltammetry was carried out for the 10 mM phenol in a 50 mM sodium hydroxide solution using a BAS 100B electrochemical analyzer at a scan rate of 25 mV s^{-1}. Platinum working and Ag/AgCl reference electrodes were used. The formal potential of the ferrocyane/ferricyane couple in water was 0.39 V versus this reference electrode. The molecular weights were determined by gel permeation chromatography (GPC) at 40 °C using a Tosoh TSK GEL α-4000 × 2, α-3000 × 1, and α-2500 × 1 with a water eluent, and a Tosoh TSK GELα-3000 × 1 and α-2500 × 1 with a DMF eluent. The elemental analysis was performed on a Perkin-Elmer PE-2400. The IEC was measured by acid–base titration. The membranes were soaked in a saturated aqueous sodium chloride solution. The released proton was titrated using a 1 mM aqueous sodium hydroxide solution.

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