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Oxidative Polymerization in Water to Form Sulfoalkoxy Poly(phenylene oxide)s

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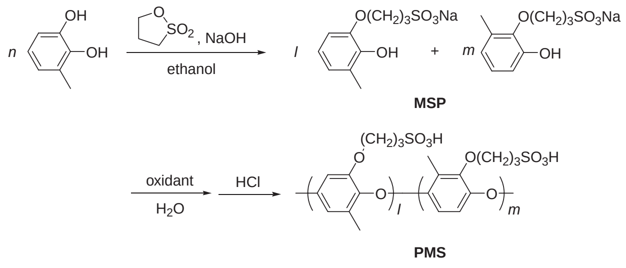
The oxidative polymerization of sulfonatopropoxyphenols in alkaline water, along with the easy monomer preparation, provided a simple and atom economical way to prepare sulfoalkoxy-pendant poly(phenylene oxide)s. The polymerization in alkaline water reduced the oxidation potential of the sulfonated phenols, and produced water-soluble polymers. The polymers produced a transparent, tough, and flexible membrane, which showed high thermal stability and proton conductivity.

A thermostable acid-functionalized aromatic polymer has been especially interesting as a proton-conductive polymer membrane of polymer electrolyte fuel cells.[1–3] Although various sulfonated or phosphonated aromatic polymers have been studied in detail, their synthetic methods are mostly complex condensation polymerizations. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is prepared by the oxidative polymerization of 2,6-dimethylphenol, and is widely used as a high-performance engineering plastic in industrial fields.[4,5] This polymerization proceeds at room temperature, and it is an ideal atom economical reaction that does not require any leaving groups for producing the polymer. The polymer reaction of PPO gives sulfonated PPO, which has been reported. However, the ion-exchange capacity of the obtained sulfonated PPO is not high, and hydrolytic and oxidative degradation proceeds under fuel-cell operating conditions.[6–9] The oxidative polymerization of the phenol with a pendant acid group is expected to yield a hydrolysis- and oxidation-resistant sulfonated PPO. On the other hand, the oxidative polymerization of phenols having acid groups is known to be impeded not only by their high oxidation potentials, but also by their formation of a chelate complex with a copper-amine catalyst. Recently, we succeeded, from the aspect of a green chemical process, to oxidatively polymerize 2,6-dimethylphenol to form PPO using alkaline water as the reaction solvent.[10,11] It is expected that the reaction in alkaline water reduces the oxidation potential of the sulfonated phenols and facilitates poly(phenylene oxide) formation. The formation of a chelate complex with the catalyst or catalyst inactivation would be prevented by using a metal oxide, such as silver oxide, as the oxidizing agent. Methylsulfonatopropoxyphenol (MSP) and 2-(3-sulfonatopropoxy)phenol (SPP) were easily prepared as the monomer. We report on a simple and atom economical preparation of sulfoalkoxy-pendant poly(phenylene oxide)s via the oxidative polymerization of sulfonatopropoxyphenols in alkaline water (Schemes 1 and 2).



Scheme 1.

MSP and SPP were prepared by simple stirring of the corresponding catechols with 1,3-propanesultone at room temperature. MSP was obtained as the 2-methyl-6-(3-sulfonatopropoxy)phenolate sodium salt and 3-methyl-2-(3-sulfonatopropoxy)phenolate sodium salt in an almost 1/1 ratio. The oxidation potential of phenol is known to decrease with the pH of the aqueous media, and the oxidation potential of phenols is expected to be reduced in alkaline water. The oxidation peak potential (vs SCE) was observed at 0.26 and 0.39 V for MSP and SPP, respectively (Fig. 1). The oxidative potential for the MSP and SPP were identical to that of 2,6-dimethylphenol in alkaline water.[11] This result suggests that MSP and SPP could be polymerized to form poly(phenylene oxide)s in alkaline water.

The oxidative polymerization of MSP was examined in alkaline water containing silver oxide under nitrogen. Silver oxide was used as an oxidizing agent to prevent the formation of a chelate complex. The polymerization results are summarized

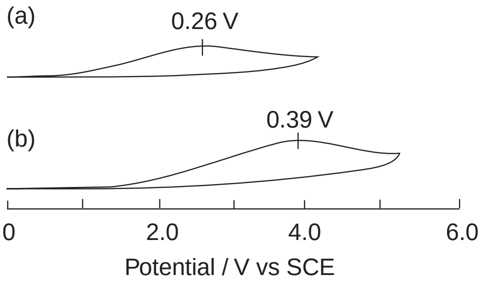
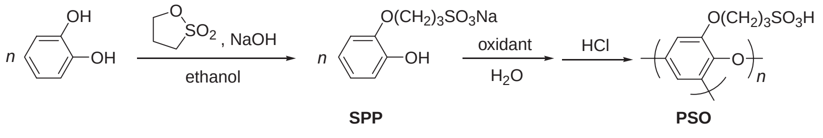


Fig. 1. Cyclic voltammograms in 0.5 M sodium hydroxide (a) MSP, (b) SPP. Phenol conc.: 0.01 M; scan rate: 25 $mV\,s^{-1}$.



Scheme 2.

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Table 1. Oxidative Polymerization of Sulfonatopropoxyphenol[a)]

Entry	Phenol	Temp /°C	Yield /%	Solubility to DMF/wt%	M_n (M_w/M_n)[b)] /10^{-3}(—)
1	MSP	rt	77	85	8.8 (1.4)
2	MSP	50	85	77	6.9 (1.5)
3	SPP	rt	62	81	4.3 (1.3)
4	SPP	50	78	76	3.6 (1.5)

a) Polymerizations of phenols (2 mmol) was carried out in water (100 mL) with sodium hydroxide (2 mmol) and silver oxide (4 mmol) for 72 h under nitrogen. b) The molecular weight of the *N*,*N*-dimethylformamide soluble part was determined using gel permeation chromatography with polystyrene standards in DMF.

in Table 1, Entries 1 and 2. The polymer was obtained as a light-brown powder by precipitation in methanol. The structure was identified by ^{1}H NMR, ^{13}C NMR, and IR spectroscopies ($\nu_{\text{C–O–C}} = 1273$, $\nu_{\text{SO}_2} = 1196, 1060\ \text{cm}^{-1}$) as the *o*- and *p*-position-substituted branched poly(methylsulfonatopropoxy phenylene oxide) (PMS). PMS is soluble in water, methanol, and partly (85 wt%) in *N*,*N*-dimethylformamide, but insoluble in ethanol, chloroform, and toluene. The molecular weight of the *N*,*N*-dimethylformamide soluble part of PMS was determined to be $M_n = 8.8 \times 10^3$ ($M_w/M_n = 1.4$) (Entry 1).

The oxidative polymerization of SPP was examined under the same conditions as MSP (Table 1, Entries 3 and 4). The polymer was obtained as a light-brown powder by precipitation in methanol, and the structure was identified by ^{1}H NMR, ^{13}C NMR, and IR spectroscopies ($\nu_{\text{C–O–C}} = 1273$, $\nu_{\text{SO}_2} = 1202, 1060\ \text{cm}^{-1}$) as the *o*- and *p*-position-substituted branched poly(sulfonatopropoxy phenylene oxide) (PSO). The solubility of PSO was same as PMS, and the molecular weight of the *N*,*N*-dimethylformamide soluble part (81 wt%) of PSO was determined to be $M_n = 4.3 \times 10^3$ ($M_w/M_n = 1.3$) (Entry 3). The yield of the polymers increased with the reaction temperature (Entries 2 and 4).

A prominent thermal property is to be expected for the sulfoalkoxy-pendant polymers based on its polyphenylene ether structure. The thermal property of PMS and PSO were determined using thermogravimetry (TG) and differential scanning calorimetry (DSC). Because of their hygroscopicity, the polymers were dried before determination by heating in a vacuum system at 100 °C. The 10%-thermal degradation temperature ($T_{\text{d10\%}}$) and the glass-transition temperature (T_g) of PMS and PSO were determined to be $T_{\text{d10\%}} = 288$ °C, $T_g = 115$ °C and $T_{\text{d10\%}} = 253$ °C, $T_g = 118$ °C, respectively (Fig. 2). The $T_{\text{d10\%}}$ and T_g of the sulfoalkoxy-pendant polymers decreased compared with PPO due to its large side chain, but showed a high thermal stability.

PMS and PSO were dissolved in water, and independent membranes were prepared by casting. The membranes were transparent, tough, and flexible. The water content and membrane thickness of the obtained membranes of PMS and PSO after vacuum drying for 12 h were determined using TG and a thickness meter to be 6.7%, 240 µm and 7.3%, 100 µm, respectively.

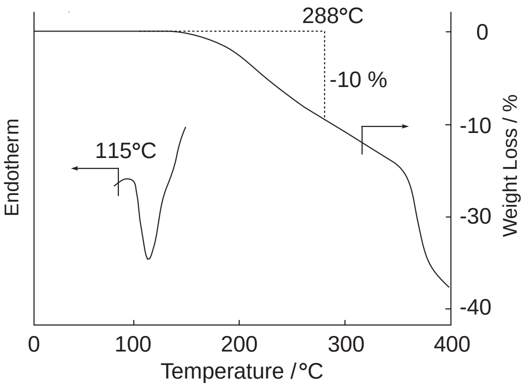

Fig. 2. TG and DSC thermograms of PMS.

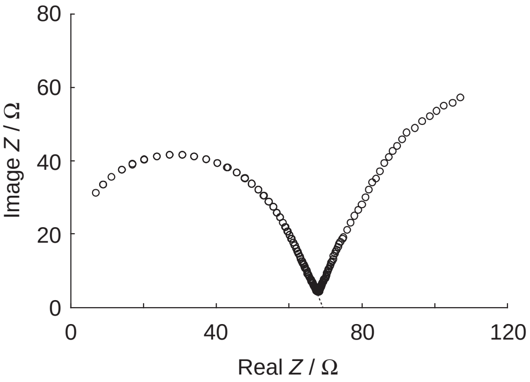

Fig. 3. Cole–Cole plot of PMS (90 °C).

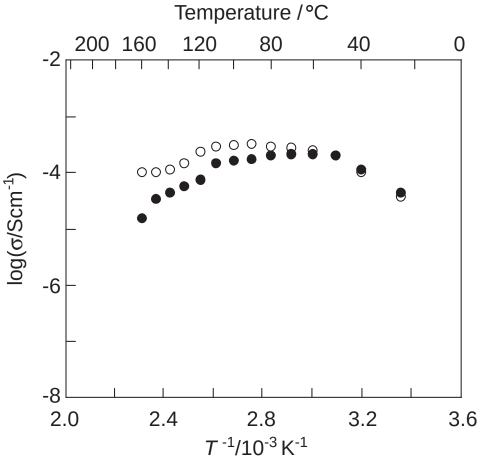

Fig. 4. Proton conductivity of the PMS and PSO membranes. ○ = PMS: membrane thickness 240 µm, ● = PSO: membrane thickness 100 µm.

The proton conductivity was measured by the AC impedance method from 20 °C to 160 °C, and was calculated from a semicircle in a Cole–Cole plot (Fig. 3).[12] The proton conductivities of PMS and PSO increased with the temperature, and reached the maximum values at 90 °C, and were calculated to be 3.1×10^{-4} S cm^{-1} and 2.0×10^{-4} S cm^{-1}, respectively (Fig. 4).

In conclusion, sulfonatopropoxyphenols were easily prepared and their oxidative polymerization in alkaline water produced sulfoalkoxy-pendant poly(phenylene oxide)s. The sulfoalkoxy-pendant poly(phenylene oxide)s produced a transparent, tough, and flexible membrane, which showed a high thermal stability and proton conductivity. The oxidative polymerization of sulfonatopropoxyphenol in water has the potential to provide a thermostable proton conducting polymer for fuel cells in a simple and atom economical way.

Experimental

Preparation of Methyl-Sulfonatopropoxyphenol. 3-Methylcatechol (1.24 g, 10 mmol) was dissolved in ethanol (50 mL). The solution was cooled by dry ice/methanol; then, sodium hydroxide (0.32 g, 8 mmol) in ethanol (50 mL) was slowly added under nitrogen. 1,3-Propanesultone (0.98 g, 8 mmol) in ethanol (25 mL) was dropwise added to the mixture. The reaction temperature slowly rose to room temperature with stirring for 12 h under nitrogen. A white solid was obtained by filtration. It was a mixture of the 2-methyl-6-(3-sulfonatopropoxy)phenolate sodium salt and 3-methyl-2-(3-sulfonatopropoxy)phenolate sodium salt with an almost 1/1 ratio by ^{1}H NMR, ^{13}C NMR, and IR spectroscopies.

Preparation of 2-(3-Sulfonatopropoxy)phenol. Catechol (1.10 g, 10 mmol) was reacted with 1,3-propanesultone (0.98 g, 8 mmol) under the same conditions as the methyl-sulfonatopropoxyphenol preparation. After filtration, the 2-(3-sulfonatopropoxy)phenolate sodium salt was obtained as a white solid in 30% yield. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 6.83 (1H, d, aromatic C–H), 6.75 (1H, t, aromatic C–H), 6.63 (1H, d, aromatic C–H), 6.53 (1H, t, aromatic C–H), 3.99 (2H, t, $-CH_2-$), 2.99 (2H, s, $-CH_2-$), 2.07 (2H, m, $-CH_2-$); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 147.4, 146.4, 123.6, 119.0, 117.0, 115.9, 68.5, 48.9, 25.2; IR (KBr) $\nu_{\text{C–O–C}} = 1284$, $\nu_{SO_2} = 1201$, 1060 cm^{-1}; Mass 231.4 ($M - 2Na^+$).

Oxidative Polymerization of Sulfonatopropoxyphenols. The following is a typical procedure for polymerization. The methyl-sulfonatopropoxyphenolate sodium salt (0.58 g, 2 mmol) was dissolved in water (20 mL) containing sodium hydroxide (0.08 g, 2 mmol). Silver oxide (0.93 g, 4 mmol) was added to the solution, and the mixture was stirred at room temperature for 72 h under nitrogen. The polymer was obtained by precipitation from water to ethanol. The obtained polymer was dissolved in 10% hydrochloric acid (5 mL) and stirred for 10 min. After evaporation, poly(methyl-sulfonatopropoxy phenylene oxide) (PMS) was obtained as a light-brown powder (yield: 77%). IR (KBr): $\nu_{\text{C–O–C}} = 1273$, $\nu_{SO_2} = 1196$, 1060 cm^{-1}. $M_n = 8.8 \times 10^3$, $M_w/M_n = 1.4$.

Materials. 3-Methylcatechol, catechol, 1,3-propanesultone, silver oxide, sodium hydroxide, methanol, and ethanol were purchased from the Kanto Chemical Co.

Electrochemical Measurements. Cyclic voltammetry was carried out in a conventional two-compartment cell using a Nikko Keisoku DPGS-1 dual potentiogalvanostat and a Nikko Keisoku NFG-3 universal programmer. The formal potential of the ferrocyane/ferricyane couple in water was 0.24 V versus the SCE reference electrode. A voltammetric investigation was carried out in water in the presence of 0.01 M phenol and 0.5 M sodium hydroxide, and all potentials were quoted with respect to the SCE reference electrode at a scan rate of 25 mV/s.

Molecular Weight Measurements. Gel permeation chromatography using Tosho TSK GEL α-4000 × 1 and α-2500 × 1 as the columns with *N*,*N*-dimethylformamide as the solvent was used to determine the molecular weights of the sulfoalkoxy-pendant poly(phenylene oxide)s, in which the calibration curves were obtained using polystyrene standards.

Other Measurements. Thermal analyses of the polymers were performed over a temperature range from 0 to 400 °C for the TG and from −100 to 200 °C for the DSC using a Seiko DSC 5200 thermal analyzer at a heating rate of 10 °C/min under nitrogen. The proton conductivity of polymer membrane was measured by a Solartoron AC impedance instrument and calculated from the complex impedance plot using a curve-fitting technique.

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