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Synthesis of Poly(phenylene sulfide sulfonic acid) via Poly(sulfonium cation) as a Thermostable Proton-Conducting Polymer

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Thermostable proton-conducting polymers deserve attention for use in high-energy-density electronic devices such as a polymer battery or a polymer fuel cell. A proton-conducting polymer with a conductivity of 10^{-2} S cm^{-1} above 100 °C is desirable for a polymer electrolyte fuel cell. One representative and important proton-conducting polymer is poly(perfulorosulfonic acid) (Nafion),[1−4] whose conductivity reaches 10^2 S cm^{-1} in the most favorable cases (fully hydrated Nafion).[5] However, the conductivity drastically decreases above 100 °C, due to the loss of water.

Chemically and thermally stable polyaromatics, e.g., poly(ether ether ketone) (PEEK),[6−8] poly(*p*-phenylene) (PPP),[9] and poly(phenylene sulfide) (PPS),[10] have been employed as the base polymer for the proton-conducting electrolytes. These polymers can be sulfonated with a sulfonation degree of 1.0 per repeat unit by heating at 75 °C in concentrated H_2SO_4.[6,8] However, a greater degree of sulfonation is difficult to achieve because of insolubility and side reactions such as interpolymer cross-linking at higher temperature. A soluble precursor for thermostable polymers might be employed in order to overcome the low reactivity due to the insolubility. In this communication, we describe a novel synthetic method of PPS bearing 2.0 sulfonic acid groups per repeat unit via sulfonation of the polysulfonium salt.[11,12] The strong electron-withdrawing property of the sulfonium group in the main chain suppresses the cross-linking reaction and promotes the sulfonation at 120 °C. The resulting sulfonated PPS as a solid polymer electrolyte exhibits proton conductivity as high as 10^{-2} S cm^{-1} in the temperature range 30−180 °C.

Polysulfonium salt **I**, prepared by the polymerization of 4-(methylsulfinyl)diphenyl sulfide,[13] was sulfonated in 10% $SO_3-H_2SO_4$ (Scheme 1).[14] The reaction proceeded homogeneously at 80 °C, and sulfonated polysulfonium salt **II** was quantitatively obtained. Compound **II** is soluble in basic water and can be converted to poly(phenylene sulfide sulfonic acid sodium salt) (**III**) through demethylation by the reaction with aqueous NaCl solution. The introduction of SO_3Na groups was confirmed by the IR spectrum of **III** (Figure 1b), where strong characteristic peaks at 1201 and 1121 cm^{-1} assigned to the S=O stretching vibration were observed. These peaks were not observed in the IR spectrum of the nonsubstituted PPS (Figure 1a). No peak attributed to the sulfone bond was observed, as shown in Figure 1b. These results suggest that the polymer is sulfonated without detectable sulfone cross-linking. The degree of sulfonation per repeat unit (*m*) was determined to be 1.4 by elemental analysis based on the sodium to carbon ratio. The degree of sulfonation increases with an increase in reaction temperature, and *m* = 2.0 was achieved by sulfonation at 120 °C. However, the higher temperature (140 °C) resulted in a decrease in the degree of sulfonation (*m* = 1.7) because the cross-linking reaction took place through dehydration of the sulfonic acid group by a phenyl proton, which was confirmed by the appearance of a peak at 1131 cm^{-1} assigned to the S=O symmetric stretching vibration of the sulfone group in the IR spectrum (Figure 1c).

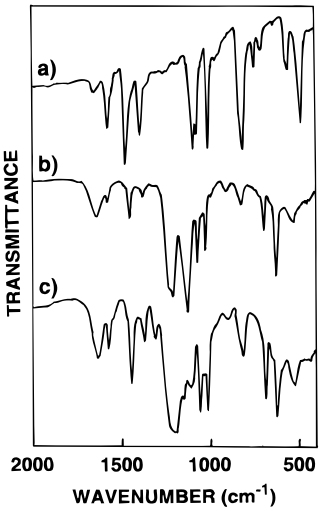


Figure 1. IR spectra of (a) poly(phenylene sulfide) (PPS), (b) poly(phenylene sulfide sulfonic acid sodium salt) (**III**) (reaction temperature = 80 °C), and (c) **III** (reaction temperature = 140 °C).

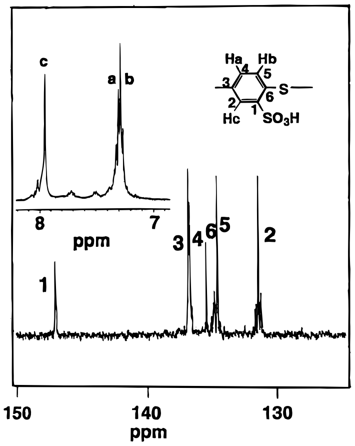
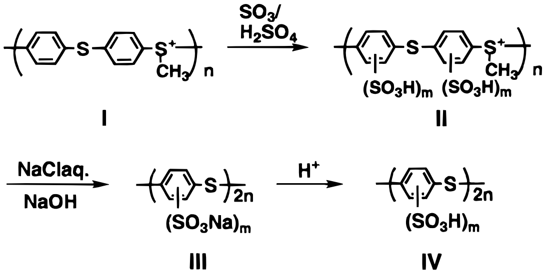


Figure 2. ^{1}H and ^{13}C NMR spectra of poly(phenylene sulfide sulfonic acid) (**IV**) (*m* = 1.0).

Scheme 1



Compound **III** was acidified to poly(phenylene sulfide sulfonic acid) (**IV**) using a cationic exchange resin.[15] Compound **IV** is a pale brown powder and soluble in

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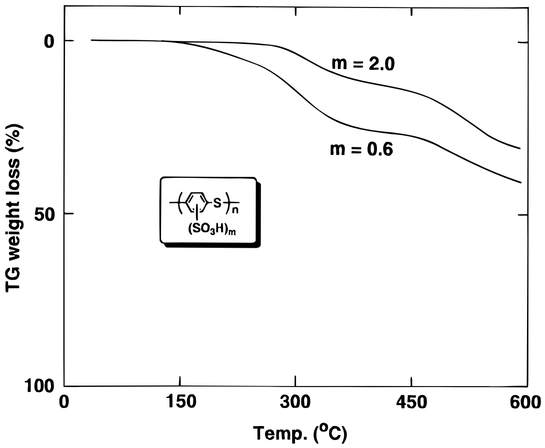

Figure 3. TG curves of poly(phenylene sulfide sulfonic acid) (**IV**) (heating rate: 20 °C/min).

water ($m > 0.3$) and methanol ($m < 1.1$). The structure of **IV** ($m = 1.0$) was confirmed by its ^{1}H and ^{13}C NMR spectra as shown in Figure 2. In the ^{1}H NMR spectrum (CD_3OD), the AB quartet peaks and a single peak assigned to the phenylene protons are observed at 7.26–7.30 and 7.95 ppm, respectively. Six peaks in the region of the aromatic carbon in the ^{13}C NMR spectrum (131.4, 134.5, 135.4, 136.6, 136.7, 146.8 ppm) are also well assigned. In the IR spectrum of **IV**, two large peaks at 1207 and 1121 cm^{-1} attributed to the SO_3H group are also observed.

In the thermogravimetric analysis (Figure 3), **IV** ($m = 0.6$) shows an initial weight loss of ca. 31% of the original weight between 140 and 380 °C, which corresponds to the loss of the sulfonic acid group. The second thermal degradation above 445 °C is attributed to polymer degradation. For more sulfonated **IV** ($m = 2.0$), improved thermal stability is observed. The decomposition temperature of **IV** ($m = 2.0$) is 265 °C and 125 °C higher than that of **IV** ($m = 0.6$), because the C–S bond of the former is stronger due to the two electron-withdrawing sulfonic acid substituents on one phenyl ring.[16] The initial weight loss of **IV** ($m = 2.0$) between 265 and 380 °C is only 13%, which corresponds to the loss of two H_2O molecules per repeat unit. This result suggests that the decomposition of **IV** ($m = 2.0$) begins with the dehydration from a sulfonic acid group and a phenyl proton to form a sulfone bond. The decomposition above 445 °C is via chain degradation of the sulfone cross-linked PPS.

The proton conductivity of poly(phenylene sulfide sulfonic acid) was evaluated by complex impedance analysis[17] using platinum electrodes for a wet pellet sample[18] of **IV** ($m = 2.0$). As shown in Figure 4, the polymer exhibits a high proton conductivity (σ), 2×10^{-2} S cm^{-1} at 20 °C, due to a high carrier concentration. Below 80 °C, the bulk conductivity shows an approximate Arrhenius-type temperature dependence with $E_a = 17$ kJ/mol, which is comparable to that of Nafion (14.3% H_2O; $E_a = 19$ kJ/mol).[2] The conductivity decreases slightly at higher temperature due to a small loss of water; however, it remains on the order of 10^{-2} S cm^{-1} even at 180 °C.

In conclusion, highly sulfonated PPS prepared from the polysulfonium cation exhibits excellent thermal stability ($T_d = 265$ °C) and high conductivity ($>10^{-2}$ S cm^{-1}). These properties arise from the two sulfonic acid groups substituted on one phenyl ring.

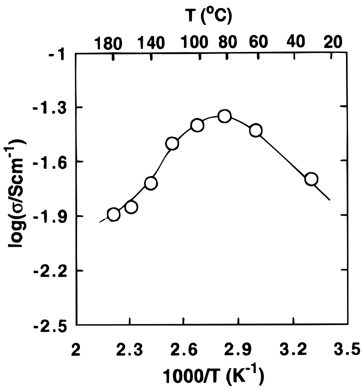

Figure 4. Temperature dependence of the conductivity (σ) of poly(phenylene sulfide sulfonic acid) (**IV**) ($m = 2.0$).

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(13) The polymerization procedure has already been reported (see refs 11 and 12). The degree of polymerization of **I**, poly(methylsulfonio-1,4-phenylenethio-1,4-phenylenetrifluoromethanesulfonate), was determined to be ca. 620 by high-temperature GPC as PPS after demethylation. IR (KBr, cm^{-1}) 3086, 3023, 2932 (ν_{C-H}), 1570, 1478, 1422 ($\nu_{C=C}$), 1258, 639 (ν_{C-F}), 1161, 1067 ($\nu_{S=O}$), 816 (δ_{C-H}); ^{1}H NMR (acetone-d_6, 400 MHz) δ 7.60, 7.70, 7.89, 7.99 (ABq, phenyl, 8H), 3.72 (s, methyl, 3H); ^{13}C NMR (acetone-d_6, 100 MHz) δ 125.4, 131.7, 133.8, 143.2 (phenyl), 28.9 (methyl). Anal. Calcd for ($C_{14}H_{11}F_3O_3S_3$): C, 44.20; H, 2.91; F, 14.98; S, 25.28. Found: C, 44.10; H, 2.73; F, 15.14; S, 25.11.
(14) The typical sulfonation procedure is as follows. Poly(methylsulfonio-1,4-phenylenethio-1,4-phenylenetrifluoromethanesulfonate) (1.00 g) was dissolved in 10 mL of 10% $SO_3-H_2SO_4$. The solution was heated to 80 °C and stirred for 8 h under a dry nitrogen atmosphere. After the reaction, the mixture was poured into 300 mL of ethanol to precipitate a hygroscopic powder. The resulting polymer was dissolved in 150 mL of aqueous 0.5 M NaCl/0.1 M NaOH solution. The solution was refluxed for 10 h to complete demethylation of the polymer. Dialysis of the solution for 2 days followed by evaporation of water under reduced pressure gave a pale brown powder of poly(phenylene sulfide sulfonic acid sodium salt) (0.63 g). IR (KBr, cm^{-1}) 2930, 2895 (ν_{C-H}), 1634, 1570, 1473, 1445 ($\nu_{C=C}$), 1201, 1121 ($\nu_{S=O}$), 890, 816 (δ_{C-H}).
(15) A commercial cation exchange resin, Amberlite 200C, which is based on cross-linked polystyrene substituted by sulfonic acid groups was used.

(16) It has been reported that the desulfonation of benzenesulfonic acid is suppressed by electron-withdrawing substituents, such as the sulfonic acid group or chloride. See: Gilbert, E. E. *Sulfonation and Related Reactions*; Interscience: New York, 1965; pp 425−438.

(17) The complex impedance plot for **IV** shows a normal pattern usually observed for polymer electrolyte. Bulk resistance was estimated from the corresponding component of an equivalent circuit required to account for the impedance spectrum.

(18) The pellet was prepared by compression of the powder sample and equilibrated in a chamber where relative humidity (RH) was controlled at 94%.

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