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Synthesis and Proton Conductivity of Highly Sulfonated Poly(thiophenylene)

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ABSTRACT: The synthesis and characterization of poly(thiophenylenesulfonic acid), a novel class of polyaromatic electrolyte possessing up to 2.0 sulfonic acid groups per phenylene unit ($m = 2.0$), are described. 4-(Methylsulfinyl)diphenyl sulfide (**1**) was polymerized in sulfuric acid upon heating (<140 °C) or in the presence of SO_3 to yield a sulfonated poly(sulfonium cation) (**4**), which can be converted to the corresponding sulfonated poly(thiophenylene). The precursor method using the soluble poly(sulfonium cation) makes it easy to control the sulfonation reaction in a homogeneous system. The resulting poly(thiophenylenesulfonic acid), unlike the nonsubstituted polymer, is soluble in water and methanol and can form a transparent film. The sulfonated polymer exhibits a good water affinity and an excellent proton conductivity due to the high carrier concentration. The highest conductivity ($\sigma = 4.5 \times 10^{-2}$ S cm^{-1}) was achieved for the polymer with $m = 2.0$ at 80 °C.

Introduction

Proton conduction in solid polymers has attracted the attention of many researchers because of applications in electrical engineering; that is apparent from several extensive reviews on the subject.[1] The recent interest has been mainly stimulated by the potential use of such materials as separators in batteries, fuel cells, electronic displays, and chemical sensors and for hydrogen storage. Perfluorosulfonate ionomer (Nafion) membranes have been used for this purpose due to their efficient proton conduction, permselectivity, and long term thermal and chemical stability.[2] The conductivity of Nafion reaches up to 10^2 S cm^{-1} in the fully hydrated protonic form but decreases with temperature above the boiling temperature of water because of the loss of water in the structure[1d] and chemical decomposition.[3] Thermostable polymers with good water affinity at higher temperature have been strongly desired for a solid polymer electrolyte fuel cell with good reliability.

One approach for an alternate material is the introduction of ionic groups onto the aromatic polymers that are well-known as thermally stable organic materials. Much effort has been expended to functionalize poly(1,4-phenylene) (PPP),[4] poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEEK),[5] poly(oxy-1,4-phenylene) (PPO),[6] and other engineering plastics.[7] Poly(thio-1,4-phenylene) [poly(phenylene sulfide) or PPS], a semicrystalline aromatic polymer with a melting temperature (T_m) at 285 °C and a decomposition temperature (T_d) above 400 °C, exhibits remarkable stability toward heat and chemical reagents.[8] Although these properties appear desirable for the application of the polymer in high-temperature ion exchange or electrolysis, the rigidity of the structure makes it difficult to prepare, modify, or shape it in the form of a separator. Several attempts to sulfonate PPS by SO_3 have been reported;[9] however, all suffered from the low degree of sulfonation (usually no more than 0.5 sulfonic acid groups per phenylene) and the formation of ladder or cross-linked structures due to the stringent reaction conditions. In addition, there has not been any description of the proton conductions of sulfonated PPS until now.

Recently we have found a new preparative method for poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene triflate), which acts as a precursor of high molecular weight PPS.[10] The poly(sulfonium cation) is chemically stable and soluble in common solvents, such as acetone, acetonitrile, or protonic acid. These properties are applicable to the modification of the polymer in a homogeneous solution under moderate conditions. In the previous communication, we reported preliminarily a novel preparation of poly(thiophenylenesulfonic acid) via sulfonation of the poly(sulfonium cation).[11] The polymer exhibits a high proton conductivity and good thermal stability due to the higher sulfonic acid density. This paper reports the sulfonation behavior of the poly(sulfonium cation) as well as the structure and proton conducting properties of the resulting poly(thiophenylenesulfonic acid).

Experimental Section

Measurement. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GSX-400 or EX-270 spectrometer. IR spectra were obtained as KBr pellets on a JASCO FT/IR-5300 spectrometer. The band resolution was maintained at 2 cm^{-1} for all measurements. Elemental analysis was performed on a Yanaco MT3 CHN corder and a Metrohm 645Multi-DOSIMAT. Two parallel analyses were performed for each sample. Differential scanning calorimetry (DSC) was carried out with a SEIKO DSC 120 thermal analyzer at a heating rate of 20 °C/min with a sample weight of 5−7 mg under nitrogen atmosphere at a flow rate of 100 mL/min. To investigate the crystallization behavior of the various samples prepared, melt-quenched samples were obtained by heating the samples in the calorimeter to 290 °C followed by quenching them with liquid nitrogen at a cooling rate of 150 °C/min. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out simultaneously with a SEIKO TG/DTA 220 thermal analyzer at a heating rate of 20 °C/min with a sample weight of 10 mg under nitrogen atmosphere at a flow rate of 200 mL/min. The molecular weight of the polymer was determined by high-temperature gel-permeation chromatography (GPC) using a Senshu Kagaku Model VHT-GPC SSC-7000. The GPC system consists of a Spectraphysics SP8810 lamp, a Rheodyne 7125 sample injector, and a modified Soma Optics S-3750 UV/vis absorption detector. A Shodex UT-805L column and a Shodex AT-800P precolumn were used for the analysis with 1-chlo-

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ronaphthalene as the carrier solvent. To obtain a homogeneous polymer slurry, 6 mg of polymer sample was dissolved in 3 mL of 1-chloronaphthalene under stirring at 250 °C for 3 min and quenched to room temperature. On each run, 0.5 mL of polymer slurry was injected at room temperature and redissolved at 250 °C through the capillary (0.5 mm i.d. × 1 m) in the preheater. The temperatures of the column oven, the transfer line, and the flow cell were regulated at 210 °C. A flow rate of 1.0 mL/min was adopted. The molecular weight data were obtained by calibration with linear polystyrene standards substituted with a pyrene group as a fluorescence probe (purchased from Polymer Standards Service). Surface conductivity measurements were conducted on hydrated H^+ form pellets using a Solartron AC impedance instrument with a 1286 electrochemical interface and a 1255 HF frequency response analyzer over the frequency range from 1 Hz to 1 MHz. The cell assembly was comprised of 10 mm diameter disks of the polymer pressed between platinum electrodes. Light pressure was applied to the electrodes by means of a clamp, which was tightened until a constant meter reading was obtained to assure the best interfacial constant. The ac protonic conductivity was calculated from the complex impedance plot with a computer curve-fitting technique.

Materials. Commercial guaranteed products of sulfuric acid (98.0%), diphosphorus pentoxide, potassium chloride, and potassium hydroxide were purchased from Kanto Chemical Co., Inc. and used without further purification. 4-(Methylsulfinyl)diphenyl sulfide (**1**) was prepared according to the method previously described.[10a,b]

Polymerization of 1. The typical procedure is as follows. **1** (0.04 mol) was placed in a 100 mL three-necked round-bottomed flask equipped with a mechanical stirrer to which 50 mL of sulfuric acid was added dropwise under a nitrogen atmosphere over a period of 10 min. The solution changed from colorless to light blue with time. After the reaction for 1 h at 20 °C, the viscous mixture was poured dropwise into 500 mL of ethanol to precipitate a powder, which was washed with ethanol and dried under vacuum for 12 h. A hygroscopic white polymer of poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene hydrogen sulfate) (**2**) was obtained in 100% yield.

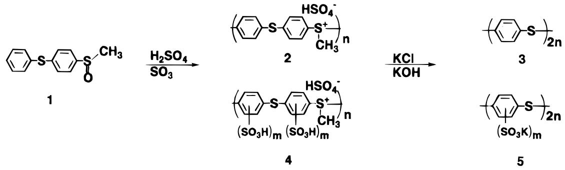
The resulting **2** (1.0 g) was dissolved in 20 mL of acetonitrile in a 100 mL round-bottomed flask equipped with a reflux condenser. To the solution, 30 mL of 10% aqueous potassium chloride was added dropwise over a period of 15 min. After 8 h of stirring, potassium hydroxide (1.0 g) was added in order to exchange protons to potassium ions on the sulfonic group. The white suspension was heated to reflux and stirred for another 4 h to complete demethylation of the polymer. The precipitate was washed with water several times and dried under vacuum for 12 h to obtain a white powder of poly(thio-1,4-phenylene) (PPS) (**3**). In the case that the polymerization was carried out in the presence of P_2O_5, the water soluble part of the polymer was recovered by dialysis using a Spectra/Por membrane (Spectrum Medical Industries, Inc.).

Poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene hydrogen sulfate) (2). IR (KBr, cm^{-1}) 3086, 2985, 2926, 1570, 1473, 1392, 1285, 1170, 814, 740, 695; ^1H NMR (CF_3COOD, ppm) 7.72, 7.75, 7.83, 7.85 (ABq, 8H), 3.69 (s, 3H); ^{13}C NMR (CF_3COOD, ppm) 29.3, 125.1, 131.6, 134.5, 145.1. Anal. Calcd for ($C_{13}H_{12}O_4S_3$): C, 47.54; H, 3.68; S, 29.29. Found: C, 47.44; H, 3.89; S, 29.11.

Poly(thio-1,4-phenylene) (PPS) (3). IR (KBr, cm^{-1}) 3065, 1572, 1471, 1387, 819. Anal. Calcd for (C_6H_4S): C, 66.63; H, 3.73; S, 29.64. Found: C, 66.81; H, 3.59; S, 29.55. $T_m = 268$ °C.

Synthesis of Poly(thio-1,4-phenylenesulfonic Acid Potassium Salt) by the Sulfonation of 2 (Postsulfonation). **2** (1.0 g) was placed in a 100 mL three-necked round-bottomed flask equipped with a mechanical stirrer and a reflux condenser. 10 milliliters of 10% SO_3-sulfuric acid was added dropwise into the flask under a dry nitrogen atmosphere. The mixture was heated to 120 °C and stirred for 8 h. After the reaction, the dark brown viscous solution was poured into 300 mL of cold ethanol to precipitate a pale brown product, which was washed with ethanol and ether several times and dried in vacuum for 12 h. The resulting sulfonated polymer (**4**) was treated with aqueous potassium chloride and potassium hydroxide in a manner similar to that described above to obtain a poly(thio-1,4-phenylenesulfonic acid potassium salt) (**5**) (1.18 g) with the degree of sulfonation (*m*) of 2.0. IR (KBr, cm^{-1}) 2929, 2895, 1634, 1568, 1473, 1442, 1201, 1121, 888, 816. Anal. Calcd for ($C_6H_2O_6S_3K_2$): C, 20.92; H, 0.59; S, 27.92; K, 22.70. Found: C, 21.25; H, 0.89; S, 27.49; K, 23.05.

Scheme 1



Computational Calculation. The equilibrium geometries of benzenesulfonic acid and 1,3-benzenedisulfonic acid were optimized using the PM3/RHF semiempirical method[12] as implemented in the MOPAC-6.00 system of programs[13] on a Fujitsu VP2200 supercomputer. The two center energies in the optimized structures were obtained with keyword ENPART.

Results and Discussion

Polymerization of 4-(Methylsulfinyl)diphenyl Sulfide in Sulfuric Acid. The sulfonium-containing polymer with structure **2** was synthesized by the polymerization of 4-(methylsulfinyl)diphenyl sulfide (**1**) in sulfuric acid as shown in Scheme 1. The chain propagation reaction is based on the successive electrophilic substitution of the aryl hydroxy methyl sulfonium cation as an active species, whose mechanism has already been reported.[10b] The polymerization proceeded efficiently for 1 h under ambient atmosphere at room temperature, which was confirmed by an increase of the viscosity of the reaction mixture. After the polymerization, the mixture was poured into ethanol to obtain the poly(sulfonium cation), having alternate thiophenylene and methylsulfoniophenylene structure in 100% yield. The resulting polymer isolated as a white powder is soluble in acetonitrile, acetone, and formic acid and slightly soluble in methanol and water.

The chemical structure of the polymer was confirmed by elemental analysis, ^1H and ^{13}C NMR, and IR spectra. Elemental analysis reveals that the polymer has the empirical formula $C_{13}H_{12}O_4S_3$, that is, (methylsulfonio)phenylene−thiophenylene hydrogen sulfate structure. In the ^1H NMR spectrum (CF_3COOD) of the polymer obtained by the polymerization for 1 h at 20 °C , a singlet methyl proton peak at 3.69 ppm and AB quartet phenyl proton peaks at 7.72−7.85 ppm are observed (Figure 1a). The AB quartet peaks actually indicate a 1,4-phenylene ring binding different groups. In the ^{13}C NMR spectrum, the existence of four kinds of aromatic carbon (125.1, 131.6, 134.5, 145.1 ppm) and one methyl carbon (29.3 ppm) was confirmed. These NMR data support a linear structure of poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene salt) without detectable defects.

The polymer **2** can be easily converted to poly(thio-1,4-phenylene) (PPS, **3**) by treating with a nucleophile (amine, pyridine, or aqueous potassium chloride). The IR spectrum of the resulting white polymer **3** (Figure 2a) agrees with that of the commercially available linear PPS prepared by the polycondensation of *p*-dichlorobenzene and sodium sulfide. In the region 800−900 cm^{-1}, only one absorption peak at 819 cm^{-1} is observed, which is attributed to the C−H out-of-plane vibration of a 1,4-

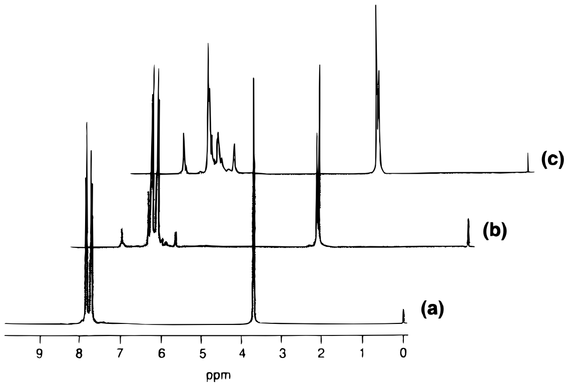


Figure 1. ^{1}H NMR spectra of poly(sulfonium cation) by the polymerization of 4-(methylsulfinyl)diphenyl sulfide. (a) at 20 °C for 1 h; (b) at 25 °C for 1 h in the presence of P_2O_5; and (c) at 100 °C for 10 h in the presence of P_2O_5.

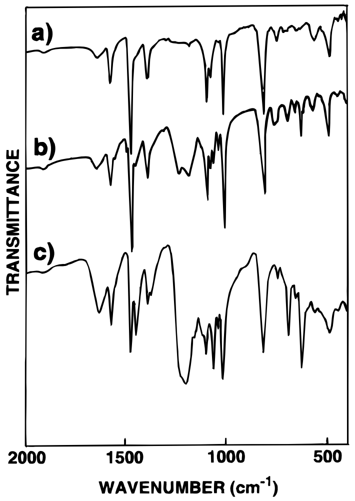


Figure 2. IR spectra of demethylated polymer: (a) at 20 °C for 1 h; (b) at 100 °C for 10 h; and (c) at 100 °C for 10 h in the presence of P_2O_5.

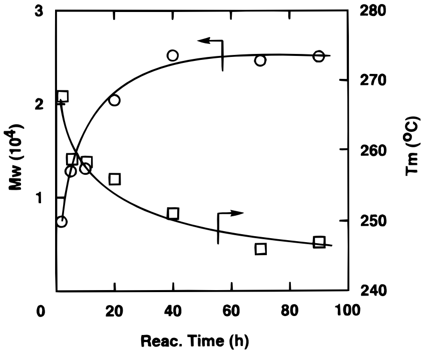


Figure 3. Molecular weight and melting temperature of PPS obtained by the polymerization of 4-(methylsulfinyl)diphenyl sulfide at 20 °C.

disubstituted benzene. The absence of peaks around 1120−1310 cm^{-1} does not support the idea that the polymer contains sulfonate or sulfone groups as a main structure.

The molecular weight of the resulting PPS was measured by very high temperature gel-permeation chromatography (VHT-GPC, 210 °C) calibrated with linear polystyrene standards and was plotted against polymerization time (Figure 3). A polymer with a weight-average molecular weight (M_w) of 7500 and a number-average molecular weight (M_n) of 3400 was obtained by the polymerization for 1 h. The molecular weight of the polymer increases by extending the polymerization time ($M_w = 25\ 200$, $M_n = 10\ 700$ for 40 h). The melting temperature (T_m) of the polymer, however, decreases gradually with the polymerization time from 268 °C for 1 h to 247 °C for 70 h. The decrease of T_m probably results from the sulfonation of the polymer, because the crystallinity of the sulfonated PPS is lower than that of nonsubstituted PPS. In the IR spectrum of the polymer obtained by the polymerization for longer time, a small broad absorption peak attributed to the aromatic sulfonate SO_2 stretching vibration appears at 1120−1200 cm^{-1}, which is not observed in the spectrum of the polymer obtained by 1 h of polymerization. These results suggest that extending the polymerization time results in slight sulfonation on the phenylene ring in the polymer chain; the chain propagation is followed by the rather slow sulfonation reaction. Molecular weight distribution (M_w/M_n) of the polymers is almost constant at about 2.3 for all the polymers obtained, which indicates no occurrence of a decomposition reaction.

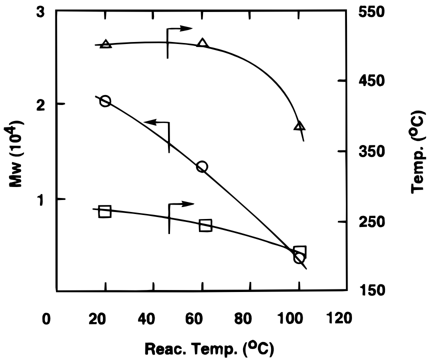


Figure 4. Temperature dependence of the polymerization of 4-(methylsulfinyl)diphenyl sulfide (reaction time = 10 h). Molecular weight (○), melting temperature (□), and $T_{d10\%}$ (△).

As is well-known, the aromatic sulfonation with sulfuric acid is greatly promoted by increasing the reaction temperature. To achieve a higher degree of sulfonation, the polymerization of **1** was carried out at elevated temperatures. Figure 2b shows the IR spectrum of the PPS obtained by the polymerization at 100 °C for 10 h, where two large peaks are observed at 1121 and 1201 cm^{-1}. No peaks assigned to aromatic sulfone SO_2 (1131 and 1310 cm^{-1}) are confirmed. In this case, the degree of sulfonation per phenylene unit (m) was determined to be 0.05 by the IR spectrum and the elemental analysis.[14] The higher temperature polymerization, however, resulted in a decrease in the molecular weight from $M_w = 20\ 400$ at 20 °C to $M_w = 3600$ at 100 °C (Figure 4). The sulfonation reaction should be accelerated at higher temperature, and the sulfonation at the end of the polymer chain suppresses the electrophilic substitution reaction (chain propagation) to give a lower molecular weight product. The decomposition temperature of the polymer is also lowered by the sulfonation; e.g., $T_{d10\%}$ (temperature for 10% weight loss) = 387 °C for the sulfonated PPS with $m = 0.05$ and 510 °C for the nonsubstituted PPS.

It may be reasonably assumed that, in the sulfonated PPS, the sulfonated phenylene unit could not be accommodated in the PPS crystalline lattice and exists in the amorphous region due to the large size of the substituent group. These slightly sulfonated polymers are considered as random copolymers with a crystallizable component of thiophenylene units and noncrystallizable sulfonated thiophenylene units. The noncrystallizable

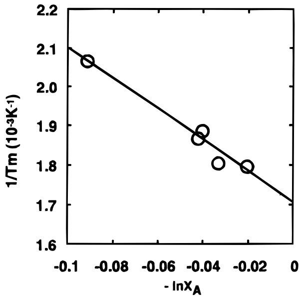


Figure 5. Plot of reciprocal melting temperature against ln X_A for poly(thiophenylenesulfonic acid).

amorphous sulfonated units interrupt crystal growth along the molecular chain direction, resulting in a systematic depression of the T_m. The depression of T_m for random copolymers in which one component (A) crystallizes is given by the Flory equation:[15]

$$\frac{1}{T_m} = \frac{1}{T_m{}^\circ} - \frac{R}{\Delta H_f}\ln(X_A)$$

where $T_m{}^\circ$ and ΔH_f refer to perfectly crystalline homopolymer A and are, respectively, the melting temperature and heat of fusion per mole of repeating units, X_A is the mole fraction of A in the copolymer, and R is the gas constant. T_m data can only be considered to be reliable when A is the major component.[16] While the melting temperatures obtained are by no means ultimate or equilibrium values, they serve as a valid yardstick for comparing a series of samples with the same thermal history. Figure 5 is a plot according to the Flory equation for the slightly sulfonated PPS random copolymers (m < 0.09), which approximate to the above requirements. From this graph, $T_m{}^\circ$ for PPS may be evaluated as 313 °C, which is in good agreement with the previously reported value (315 °C).[17] The slope of this straight line gives a ΔH_f of 21 J/g for perfectly crystalline PPS. While the value of ΔH_f is smaller compared to the reported one (80 J/g),[18] the Flory equation yields estimates of ΔH_f which are sometimes low by a factor of two to three, since it is predicted on the premise that the samples are perfectly crystalline except for the noncrystallizable units.[16] Nevertheless, the success of this approximation implies that the polymers are randomly sulfonated without cross-linking through sulfone bonds and that the sulfonated units are not crystallizable and reside in the amorphous region in the copolymer.

Highly Sulfonated Poly(thiophenylene). In order to obtain a more highly sulfonated PPS, the polymerization of **1** should be carried out in the presence of SO_3, which is a strong sulfonating agent for aromatics. The sulfuric acid−diphosphorus pentoxide (P_2O_5) system was adopted, since P_2O_5 is well-known to dehydrate thrice the moles of sulfuric acid, resulting in the formation of an equivalent amount of SO_3. Besides, the byproduct, H_3PO_4, is also a strong enough acid for the polymerization of **1**. The polymerization of **1** was carried out in sulfuric acid in the presence of P_2O_5 (P_2O_5/**1** = 2). The polymerization proceeds under ambient atmosphere accompanying the formation of SO_3, which makes the color of the reaction mixture somewhat darker than the case in the absence of P_2O_5. After the mixture was worked up according to the above mentioned procedure, a white powder of the sulfonated polysulfonium salt was obtained in >113 wt % yield based on **1**. In the ^{1}H NMR spectrum of the resulting polymer in CF_3COOD (Figure 1b), some minor phenylene proton peaks attributable to the thio-2-sulfo-1,4-phenylenesulfonio structure are observed at 7.18, 7.83 and 8.52 ppm around the AB quartet peaks. The existence of two methyl groups at 3.69 and 3.75 ppm was also confirmed, where the peak at lower magnetic field (3.75 ppm) could be assigned to the methylsulfonium protons attached to a sulfonated phenylene group. The evidence for a decomposition reaction is lacking in the spectrum; the multiplet peaks attributed to the end phenylene group (7.79−8.15 ppm) could not be observed. The polymerization at higher temperature (100 °C) gives rise to a more highly sulfonated polysulfonium salt **4**, whose ^{1}H NMR spectrum is shown in Figure 1c. The integration ratio of the methyl protons at 3.75 ppm to those at 3.69 ppm is 1.36:1, which means m = 0.57 in **4** in Scheme 1. This value is in good agreement with the one obtained by the integration ratio of aromatic protons to methyl protons (m = 0.53).

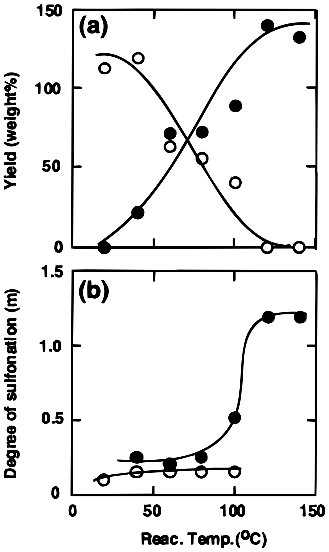


Figure 6. Temperature dependence of the polymerization of 4-(methylsulfinyl)diphenyl sulfide in the presence of P_2O_5 (reaction time = 10 h). (a) Polymer yield (wt %) and (b) degree of sulfonation per phenylene unit (m) of water insoluble part (○) and soluble part (●).

Compound **4** was treated with aqueous potassium chloride and potassium hydroxide at 100 °C to yield a poly(thiophenylenesulfonic acid potassium salt) (**5**). The IR spectrum of **5** is shown in Figure 2c, where a strong characteristic band assigned to the aromatic sulfonate stretching vibration is observed at 1120−1200 cm^{-1}. **5** is a pale brown powder and partly soluble in water. Figure 6a is a plot of the polymer yields (wt %) of water soluble and insoluble parts against the reaction temperature. The polymer obtained by the polymerization at 20 °C is insoluble in water, whereas at higher temperature a water soluble polymer with higher degree of sulfonation is obtained. The yield of the water soluble part increases with the temperature, and above 120 °C the resulting polymer is completely soluble in water. The degree of sulfonation of the water soluble polymer also increases with the temperature and reaches m = 1.2 over 120 °C (Figure 6b). The degree of sulfonation of the water insoluble polymer remains almost constant at 0.1 over the reaction temperature range from 20 to 100 °C. The addition of more P_2O_5 in the polymerization reaction was not effective for improving the degree of sulfonation, because the increased viscosity of the mixture hinders the sulfonation reaction.

A commercial oleum (10% SO_3−H_2SO_4) was also applied as a solvent; however, the polymerization of **1**

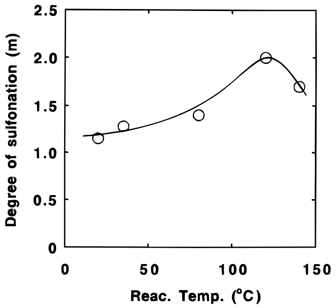


Figure 7. Temperature dependence of the postsulfonation of **2** (reaction time = 10 h).

was unsuccessful because in that case the sulfonation is much more preferential than the chain propagation. Therefore, postsulfonation of the polysulfonium salt **2** was performed in the oleum to achieve a higher sulfonation level than $m = 1.2$. The postsulfonation reaction proceeds efficiently in a homogeneous solution even at room temperature, and a sulfonated PPS **5** with $m = 1.2$ was obtained (Figure 7). The resulting polymer is also a pale brown powder and is soluble in water, DMF, and DMSO. The degree of sulfonation increases with the reaction temperature; e.g., $m = 1.4$ at 80 °C and $m = 2.0$ at 120 °C were achieved, respectively. Higher temperature (140 °C) was not effective; the degree of sulfonation dropped to $m = 1.7$ when the reaction was carried out at 170 °C. A characteristic peak for the sulfone bond (1131 cm^{-1}) is observed in the IR spectrum of the polymer, which suggests cross-linking through dehydration of the sulfonic acid group by a phenyl proton.[19]

The poly(thiophenylenesulfonic acid) ($m = 2.0$) is amorphous and can form a transparent film by casting a water solution. From DSC analysis, no endothermic melting peak could be observed. TG measurement reveals that the polymer in the H^+ form has a decomposition temperature at 265 °C, which is 125 °C higher than that of the one with $m = 0.6$ and 75 °C higher than that of perfluorosulfonate ionomer (Nafion). The higher thermal stability of the disulfobenzene structure agrees with the previously reported results that an electron-withdrawing substituent improves the decomposition temperature of benzenesulfonic acid.[20] From the PM3/RHF calculation, the $C-SO_3H$ bond energy was evaluated for benzene mono- and disulfonic acid as model compounds. The two center energies corresponding to the bond energy are −20.14 eV for benzenesulfonic acid and −20.49 eV for 1,3-benzenedisulfonic acid, which means the $C-SO_3H$ bond of the latter is stronger than that of the former.

Proton Conductivity. Compound **5** was protonated using a cationic exchange resin (cross-linked polystyrenesulfonic acid) to the H^+ form, poly(thiophenylenesulfonic acid), whose proton conductivity was measured by the complex impedance method. The typical complex plane plot (Cole−Cole plot) for the polymer is shown in Figure 8. The observed frequency dependence approximating to a depressed semi-circle is indicative of an equivalent circuit corresponding to ion-blocking Pt electrodes. This is the anticipated behavior for proton conduction as the dominant contribution to the impedance of the polymer. To investigate the effect of water absorption on the proton conduction of the polymer, the conductivity measurement was carried out at controlled relative humidity (RH). As shown in Figure 9, the conductivity (σ) of the poly(thiophenylenesulfonic acid) ($m = 2.0$) is about 10^{-5} S cm^{-1} at RH = 30% and increases exponentially with RH. This probably arises because the absorbed water increases the conductivity by creating hydrogen bridges between sulfonic acid groups, as previously proposed in the case of Nafion.[21] The conductivity at RH = 94% reaches up to 2×10^{-2} S cm^{-1}, where the water content of the polymer is 10.3 H_2O per sulfonic acid group.[22] The number of absorbed water molecules is higher than that of Nafion (ca. 5 H_2O per sulfonic acid group for a Nafion 1200EW with the vapor equilibrium technique).[2a] The high proton conduction and good water affinity of the sulfonated PPS are the properties based on its low equivalent weight (134EW).

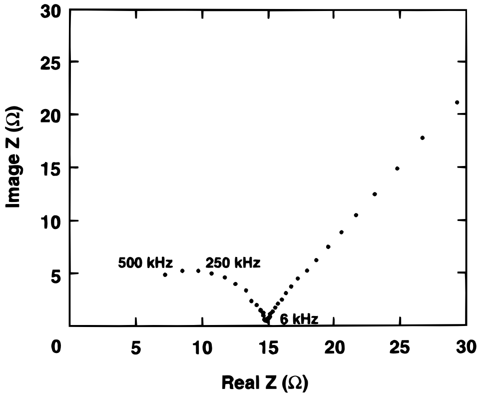


Figure 8. Complex impedance plot for the poly(thiophenylenesulfonic acid) ($m = 2.0$) at 25 °C with Pt electrodes.

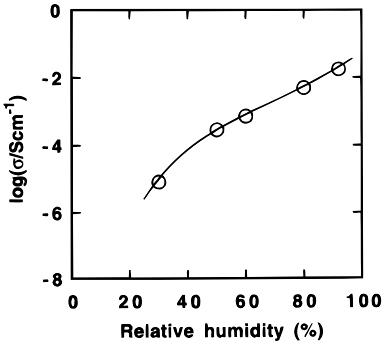


Figure 9. RH dependence of the conductivity of poly(thiophenylenesulfonic acid) ($m = 2.0$) at 25 °C.

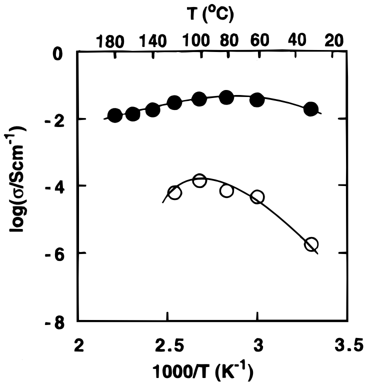


Figure 10. Temperature dependence of the conductivity of poly(thiophenylenesulfonic acid). $m = 1.2$ (○) and $m = 2.0$ (●).

The temperature dependence of conductivity for the polymers with $m = 1.2$ and 2.0 shows that the conductivity increases with the degree of sulfonation (m) of the poly(thiophenylenesulfonic acid) due to the increase in the carrier concentration. (Figure 10). The data show approximately Arrhenius-type dependence for the conductivities in the temperature range below 80 °C, with the activation energy $E_a = 17$ kJ/mol for $m = 2.0$ and 117 kJ/mol for $m = 1.2$. The conductivity of the polymer ($m = 1.2$) is about 10^{-6} S cm^{-1} at 30 °C and has a maximum of 10^{-4} S cm^{-1} at 100 °C with a decrease at higher temperature due to the loss of water from the material. It is noteworthy that the polymer with $m = 2.0$ has very high thermal stability up to 180 °C with the proton conductivity on the order of 10^{-2} S cm^{-1}. The highest conductivity is 4.5×10^{-2} S cm^{-1} at 80 °C. The higher degree of sulfonation and a higher carrier concentration might also effectively retain the absorbed water above 100 °C due to the higher polarity.

Conclusions

A new synthetic strategy has been developed to functionalize PPS. Highly sulfonated PPS was successfully prepared by the polymerization of 4-(methylsulfinyl)diphenyl sulfide in sulfuric acid via polysulfonium salt as a soluble precursor. The sulfonation can be controlled by the reaction time, the temperature, and/or the addition of SO_3 and carried out to a higher level (up to 2.0 sulfonic acid groups per phenylene unit) than previously reported by the postsulfonation of the polysulfonium salt in 10% $SO_3-H_2SO_4$.

The crystallinity and the melting temperature of the resulting PPS are significantly lowered by the presence of the sulfonic acid groups. From the DSC analysis using the Flory equation, melting temperature and heat of fusion for perfectly crystalline PPS are evaluated to be 313 °C and 21 J/g, respectively. The poly(thiophenylenesulfonic acid) shows high thermal stability with a decomposition temperature as high as 265 °C. From the complex impedance analysis, the proton conductivity of the polymer was evaluated to be 4.5×10^{-2} S cm^{-1} in the hydrated H^+ form ($E_a = 17$ kJ/mol). The conductivity remains the same order of magnitude in the temperature range from 30 °C to 180 °C, which is superior to those of conventional proton−conducting polymers. Two sulfonic acid substituents per phenylene unit of PPS contribute good thermal stability, water affinity, and high proton conducting property.

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