Macromolecules **2009**, *42*, 3129−3137

Highly Sulfonated Poly(phenylene sulfone): Preparation and Stability Issues

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Received February 13, 2009; Revised Manuscript Received March 10, 2009

ABSTRACT: This paper presents a preparation route which allows the formation of a poly(phenylene) ionomer containing merely sulfone units ($-SO_2-$) connecting the phenyl rings and in which each phenyl ring is monosulfonated (100% degree of sulfonation). This corresponds to an ion exchange capacity (IEC) of 4.5 mequiv g^{-1} (equivalent weight of EW = 220 g $equiv^{-1}$). The preparation succeeded in a two-step process comprising a polycondensation reaction of sulfonated difluorodiphenyl sulfone with sodium sulfide, yielding sulfonated poly(phenylene sulfide sulfone), and the subsequent oxidation to the corresponding sulfonated poly(phenylene sulfone). The polymer was characterized by elemental analysis, NMR, IR, GPC, viscosity measurement, TGA in air and in pure water vapor atmosphere, DSC at low and high temperatures, and ac impedance spectroscopy. Room temperature water absorption isotherms have been determined by equilibrating samples at different relative humidities. Under the chosen reaction conditions, polymers with molecular weights up to $M_w \approx 61\,000$ g mol^{-1} were obtained, corresponding to intrinsic viscosities up to 0.73 dL g^{-1}. The water-soluble ionomer exhibits a very high density ($\rho = 1.75$ g cm^{-3} in the dry form), no glass transition or melting temperature, and a very high thermooxidative and hydrothermal stability. The latter is attributed to the specific molecular structure consisting of extremely electron-deficient aromatic rings. At high temperature ($T = 110-160$ °C) and low relative humidities (rh = 50−15%) the proton conductivity exceeds that of Nafion by a factor of 5−7.

1. Introduction

Highly sulfonated polymers which are thermooxidatively and hydrolytically stable are of growing interest for many industrial applications. They may be used as conductive polymers, solid acid catalysts, or material for making fuel cell membranes. Highly sulfonated, water-soluble polymers being transparent and exhibiting high stability are of interest for the solubilization and conductivity enhancement of conductive polymers[1−5] such as poly(thiophene)s used as antistatic or conductive coatings, as electrode materials in solid electrolyte capacitors, and in many other applications. Many organic reactions are accelerated by the presence of strong-acid catalysts.[6] Industrial processes such as petroleum cracking, hydrolysis, and esterification requiring acid catalysis favor the use of heterogeneous acids because of the ease of separating the catalyst from the product stream. However, stable highly acidic catalysts are not yet available for all process conditions, in particular high water concentrations and high temperatures.

One of the most prominent application of sulfonated polymers is as constituent of proton conducting membranes serving as separator in PEM fuel cells. For state-of-the-art membranes, e.g., the perfluorosulfonic acid (PFSA) polymer Nafion, the required high proton conductivity is only achieved at high degrees of hydration, which is a severe limitation for the use of such membranes. At low water content, the proton conductivity is significantly reduced because of the poor connectivity (percolation) of the water structures in these ionomers and the strong local retardation of the water diffusion,[7] which is mainly the result of the interaction with the immobile sulfonate groups. Recently, we demonstrated that in sulfonated systems high proton conductivity may be achieved even at low water content (low humidification),[8] provided the separation of the sulfonic acid groups is small, implying that the density of sulfonic acid groups is locally very high according to a locally high ion exchange capacity (IEC).

But for an application of highly sulfonated polymers in fuel cells operating at high temperatures ($T = 100-130$ °C) in a humid environment there are at least two more important requirements the material has to meet: (i) acceptable viscoelastic properties in the dry and wet state and (ii) sufficient hydrolytic stability to avoid any desulfonation reaction under operating conditions.

The current attempts to operate PEM fuel cells at high temperature and low humidification[9,10] have already led to the development of some highly sulfonated polymers with hydrolytic stability. So far only small IEC increases were possible for PFSA-based ionomers (e.g., the short side-chain PFSA materials DOW and Hyflon Ion[11,12]), while much higher ion exchange capacities (IEC > 4.0 mequiv g^{-1}) have already been obtained for hydrocarbon ionomers such as sulfonated poly(*p*-phenylene)s[13,14] and sulfonated poly(phenylene sulfide)s.[15]

As a first step toward highly sulfonated polymers with high hydrolytic stability, we recently developed a new class of sulfonated polymers with extremely electron-poor poly(phenylene) backbones.[16,17] These ionomers contain merely electron-accepting units ($-SO_2-$) connecting the phenyl rings, which are partially sulfonic acid functionalized. The absence of any electron-donating groups such as ether linkages leads to an increased acidity and a higher hydrolytic stability of the sulfonic acid group. Also, high thermooxidative stability and low solubility even at high ion exchange capacities are observed. Membranes with ion exchange capacities ranging from 2.32 to 2.78 mequiv g^{-1} are still insoluble in water and have proton conductivities higher than that of Nafion. These membranes show even distinct methanol rejection properties.[18] However, because of the chosen preparation route, the degree of sulfonation is limited to <50%.

This paper presents a new preparation route which allows the formation of a poly(phenylene) ionomer containing merely

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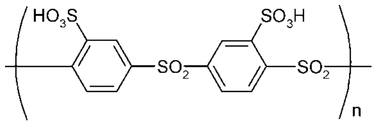
10.1021/ma900333n CCC: $40.75

sulfone units ($-SO_2-$) connecting the phenyl rings in 1,4-position and in which each phenyl ring is monosulfonated (100% degree of sulfonation). This leads to an ion exchange capacity of IEC = 4.5 mequiv g^{-1}, corresponding to an equivalent weight of EW = 220 g mol^{-1}. In the following, we will therefore use the acronym sPSO$_2$-220 for this ionomer [$-(1,4\text{-}C_6H_3(SO_3H)-SO_2-)_n-$]. Since the position of the sulfonic acid groups is alternating between position 2 and 3, the repeating unit is as follows:



sPSO$_2$-220

We also present a comprehensive analysis of the obtained sPSO$_2$-220 polymer. This includes elemental analysis, IR, NMR, material properties such as IEC, solubility, density, viscosities, and molecular weights, information about water uptake and the state of the water, and thermal properties investigated by TGA and DSC. Finally, the high hydrolytic stability of this ionomer is highlighted, and conductivity data are reported. A comprehensive investigation of the microstructure and water transport (water diffusion and electroosmotic drag) is published in a separate paper.[19]

2. Experimental Section

2.1. Characterization. ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker Avance spectrometer operating at a proton frequency of 300 MHz and a carbon frequency of 75.4 MHz. Deuterated dimethyl sulfoxide (DMSO-d_6) was the NMR solvent, and the DMSO signal at 2.50 ppm (^{1}H NMR) and 39.52 ppm (^{13}C NMR) was used as chemical shift references. Differential scanning calorimetry (DSC) was performed with a Setaram DSC121 calorimeter under nitrogen at a heating rate of 2 °C min^{-1}. Samples were dried at $T = 110$ °C under N$_2$ for 30 h prior to measurement. Low-temperature thermograms were obtained with a Perkin-Elmer Pyris 1; the samples were cooled to $T = -50$ °C and then heated at rate of 10 °C min^{-1} under an argon atmosphere. Densities of the dry polymers (H-form) were determined by helium gas pycnometry with an AccuPyc 1330 V2.01. Inherent viscosity was measured at $T = 25$ °C in water at a polymer concentration 0.38 g/dL, using a Cannon-Ubbelohde viscometer, and the resulting values were obtained by calculating specific viscosity $\eta_{sp} = \eta/\eta_0 - 1$, relative viscosity $\eta_{rel} = \eta/\eta_0$ and inherent viscosity $\eta_{inh} = (\ln \eta_{rel})/c$. The corresponding intrinsic viscosity was obtained by one-point method (Solomon−Ciuta equation[20]) as follows:

$$\eta_{int} = \frac{\sqrt{2(\eta_{sp} - \ln \eta_{rel})}}{c}$$

IR spectra of the polymers (H-form) were recorded using a Bruker IFS 66 IR-spectrometer. The ATR (attenuated total reflectance) method with a diamond tip was used. At least 256 scans were performed for each measurement. Gel permeation chromatography (GPC) was performed on coupled SDV columns from Polymer Standard Service (GRAM 3000, 1000, and 100) with UV detector (Soma S-3702) and RI detector (ERC 7512; ERMA), calibrated with polystyrene (Polymer Standard Service). The measurements of the polymers (in H-form) were performed in DMF at $T = 60$ °C with an addition of LiBr (1 g L^{-1}). Thermogravimetric analysis (TGA) was carried out on a Netzsch STA 449 thermobalance with a heating rate of 2 °C min^{-1} in a purge gas mixture of nitrogen and oxygen (80:20, 20 mL min^{-1}). The outlet with the released products was continuously analyzed by a Balzer Prisma quadrupole spectrometer. Only signals between $m/z = 1$ and 100 were detected. Water hydration isotherms at room temperature ($T = 25$ °C) were determined by equilibrating polymer samples in a desiccator purged with nitrogen gas of predefined relative humidity. Relative humidities were changed from high to low and from low to high values, which resulted in somewhat different degrees of hydration (hysteresis). The hydration kinetics of the sPSO$_2$-220 polymer was significantly slower compared to that of Nafion; samples of sPSO$_2$-220 powder required equilibration times of about 2 weeks. The water uptake was determined by quickly weighing the samples after equilibration on an external balance and comparing the weight to that of the dried polymer sample (overnight at $T = 140$ °C in vacuum). With w_{wet} and w_{dry} being the weights of the wet and the dry samples, the water uptake is calculated by wt % = $100 \times (w_{wet} - w_{dry})/w_{dry}$. The number of water molecules per sulfonic acid λ is given by

$$\lambda = \frac{(w_{wet} - w_{dry})\mathrm{EW}}{w_{dry} M_{H_2O}}$$

and the water volume fraction $\Phi(H_2O)$ is given by

$$\Phi(H_2O) = \frac{(M_{H_2O}/\rho_{H_2O})}{(M_{H_2O}/\rho_{H_2O}) + (\mathrm{EW}/\lambda\rho_{ionomer})}$$

where EW and $\rho_{ionomer}$ are the equivalent weight and density of the polymer and M_{H_2O} and ρ_{H_2O} are the molecular weight and density of water. Since the drying procedure is not well-defined (possibility of residual water or condensation of sulfonic acid groups), the water content of equilibrated samples was also analyzed by ^{1}H NMR dissolving samples in DMSO-d_6 and correlating water to polymer peak intensities. In order to correct for the water content of the used DMSO-d_6, its NMR spectrum was measured for reference. Water hydration isobars (absorption/desorption behavior and hydrolytic stability) above $T = 100$ °C were determined by thermogravimetric analysis (TGA) at a water partial pressure of $p(H_2O) = 10^5$ Pa with a Mettler AT20 balance magnetically coupled (Rubotherm) to the sample, which allows measurements in high-humidity environments without condensation of water in the balance. The heating and cooling rate was 0.2 °C min^{-1}. The dc conductivities were derived from impedance spectra of a two-electrode arrangement measured by a HP ac impedance analyzer (4192A LF) in the frequency range from 10 Hz to 10 MHz with oscillating voltage of 0.1 V. Conductivity measurements in pure water vapor ($p(H_2O) = 10^5$ Pa) were carried out in a double-wall temperature-controlled glass chamber with an open outlet at temperatures between $T = 110$ and 160 °C. Liquid water was continuously evaporated by a heater and injected into the chamber with a constant flow rate using a digital peristaltic pump (Ismatec). Inside the chamber pressed pellets of sPSO$_2$-220 polymer powder (diameter 8 mm and total thickness of 2−4 mm) were placed in a porous cylindrical tube with a gold electrode at the bottom. The second gold electrode was pressed from the top onto the pellet by a screw in order to ensure optimum contact. The specific conductivity $\sigma = l/(A \times R)$, where l is the distance between the electrodes, A the area of the pellet, and R the resistance derived from the high-frequency intercept of the complex impedance with the real axis. Ion exchange capacity (IEC, mequiv g^{-1} dry polymer) of the synthesized polymers was analyzed by titration. The polymers were dissolved in water or 1 M NaCl solutions and then titrated with 0.1 N NaOH (Mettler Titrator DL21). The samples (in Na-form) were dried after titration at 140 °C in a vacuum oven. The remaining water was determined by NMR.

2.2. Materials. Disodium 3,3′-disulfonate-4,4′-difluorodiphenyl sulfone was prepared according to refs 21 and 22. Before polymerization, disodium 3,3′-disulfonate-4,4′-difluorodiphenyl sulfone was dried at $T = 145$ °C in a vacuum oven, while anhydrous sodium acetate (99%, J.T. Baker) was dried at $T = 80$ °C in a vacuum oven. Sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$, 98%, Sigma-Aldrich) was used as received without further drying or purification; however, it was immediately used after opening the package. Dialysis was carried out using dialysis tubing cellulose membrane

(12 000 MWCO, Sigma-Aldrich), and ion exchange was carried out with Dowex Marathon C (H-form, Sigma-Aldrich). Anhydrous *N*-methyl-2-pyrrolidone (NMP, 98%, Fluka) and anhydrous sodium sulfide (98%, Sigma-Aldrich) were used as received. Other chemicals were of commercially available grade and used as received unless otherwise mentioned.

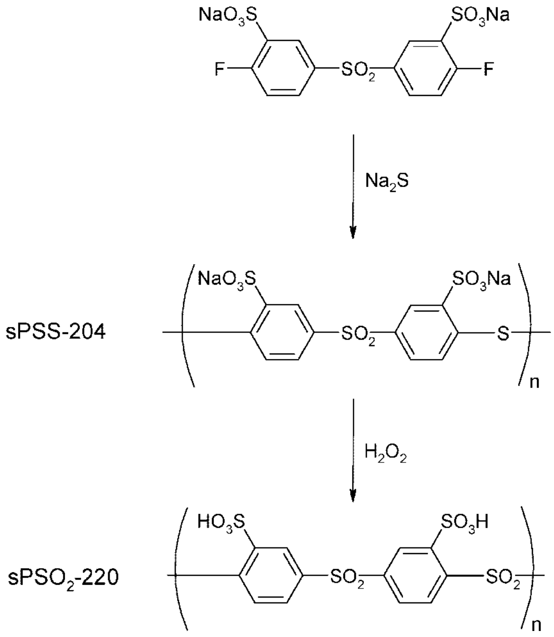
2.3. Preparation of sPSO$_2$-220. *Typical Preparation of the Sulfonated Poly(phenylene sulfide sulfone) Homopolymer sPSS-204 by Polycondensation.* The polymerization was conducted in a dried and argon-filled 750 mL round-bottom flask equipped with an argon gas inlet, mechanical stirrer, and Dean−Stark trap fitted with a condenser. The flask was charged with disodium 3,3′-disulfonate-4,4′-difluorodiphenyl sulfone (38.867 g, 0.1618 mol), sodium sulfide nonahydrate (74.169 g, 0.1618 mol), and sodium acetate (14.60 g, 0.1780 mol). Then NMP (75 g) was added under argon, and the reaction mixture was heated in an oil bath to $T = 150$ °C. During heating, toluene (150 mL) was added, and the temperature was kept at $T = 150$ °C for 4 h to form toluene−water azeotropic mixture. The mixture was removed by emptying the Dean−Stark trap, and the reaction was allowed to proceed for 15−20 h at $T = 185$ °C, while the reaction mixture became highly viscous. After cooling to $T = 110$ °C, NMP was added to dilute the mixture. Finally, the dark reaction mixture was slowly poured into isopropanol (1.5 L) to precipitate the polymer. The precipitate was separated by filtration and washed with isopropanol. The product was redissolved in hot water (200 mL), again precipitated in isopropanol (1.5 L), separated, washed with isopropanol, and dried at $T = 60$ °C. In order to remove all byproduct the aqueous polymer solution was dialyzed for 10 days. The water was removed with a rotary evaporator, and the product was dried at $T = 80$ °C in vacuum (2×10^{-3} mbar), yielding 51.9 g ($M = 452.4$ g mol^{-1} Na-form, 70.9%) of a dark-brown polymer granulate. Conversion of the Na-form into H-form succeeded by ion exchange, yielding a brownish polymer after drying at $T = 60$ °C in a vacuum oven. The reaction was also carried out with anhydrous sodium sulfide instead of its nonahydrate, which eliminates the need of azeotropic distillation. The other reaction conditions and results were practically the same.

sPSS-204. Density: 1.660 g cm^{-3} (H-form, dry). Viscosity in water ($T = 25$ °C, $c = 0.38$ g dL^{-1}): inherent viscosity 0.98 dL g^{-1}, intrinsic viscosity: 1.04 dL g^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 8.29$ (d, 2H, CH, $J_{HH} = 1.7$ Hz), 7.73 (dd, 2H, CH, $J_{HH} = 1.9$, 8.0 Hz), 7.26 (d, 2H, CH, $J_{HH} = 8.3$ Hz), 9.78 (s, 20H, H$_2$O). ^{13}C NMR (75.5 MHz, DMSO-d_6): $\delta = 147.9$ (s), 140.8 (s), 138.2 (s), 134.2 (s), 129.3 (s), 126.3 (s). IR (polymer powder, cm^{-1}): 1573, 1444, 1374, 1313, 1236, 1162, 1110, 1085, 1049, 1008, 912, 890, 824, 808, 748, 713, 691, 645, 613, 490. Anal. Calcd for sPSS-204 (Na-form) with $\lambda = [H_2O]/[-SO_3Na] = 2.0$ after dialysis and equilibration at ambient conditions: C, 27.48; H, 2.69; S, 24.45. Found: C, 27.46; H, 2.39; S, 24.34. Solubility of sPSS-204 (H-form): soluble in water, concentrated sulfuric acid, DMSO, DMF, NMP, and DMAc; insoluble in methanol, ethanol, isopropanol, toluene, THF, chloroform, acetone, ethyl acetate, trifluoroacetic acid.

Typical Preparation of the Homopolymer sPSO$_2$-220 by Oxidation of sPSS-204. Fine-powdered sPSS-204 (40.5 g, 89.5 mmol, Na-form) was suspended in glacial acetic acid (300 mL) at $T = 70$−80 °C. Hydrogen peroxide (80.0 mL of a 30% H$_2$O$_2$ in water, 0.80 mol H$_2$O$_2$) was slowly added within 1 h, resulting in a red-brown solution. Then the reaction mixture was stirred at $T = 70$−80 °C for 6 h and afterward for 1 day at room temperature. The mixture was heated to $T = 100$ °C to evaporate acetic acid. By concentrating a white precipitate was formed. After almost complete evaporation of the acetic acid the white product was dialyzed for 3 days in aqueous solution. The water was removed using a rotary evaporator, and the product was dried at $T = 50$ °C in vacuum (2×10^{-3} mbar) to obtain yellowish-white polymer powder sPSO$_2$-220. Yield 36.4 g ($M = 440.4$ g mol^{-1} H-form, 92.3%). In order to fully convert the polymer into H-form ion exchange was carried out.

sPSO$_2$-220. Density: 1.745 g cm^{-3} (H-form, dry). Viscosity in water ($T = 25$ °C, $c = 0.38$ g dL^{-1}): inherent viscosity 0.70 dL g^{-1}, intrinsic viscosity 0.73 dL g^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 8.45$ (d, 2H, CH, $J_{HH} = 8.2$ Hz), 8.39 (s, 2H, CH), 8.04 (d, 2H, CH, $J_{HH} = 8.4$ Hz), between 11 and 4 ppm (br s, SO$_3$H·nH$_2$O, position depending on water content). ^{13}C NMR (75.5 MHz, DMSO-d_6): $\delta = 147.3$ (s), 143.4 (s), 142.4 (s), 132.9 (s), 127.9 (s), 126.8 (s). IR (polymer powder, cm^{-1}): 1374, 1336, 1282, 1260, 1236, 1162, 1146, 1110, 1085, 1049, 1008, 912, 890, 865, 840, 824, 808, 748, 730, 720, 691, 645, 617, 594, 549, 429. Anal. Calcd for sPSO$_2$-220 (H-form) with $\lambda = [H_2O]/[-SO_3H] = 0.0$ after dialysis, ion-exchange and drying under vacuum at $T = 115$ °C: C, 32.74; H, 1.833; O, 37.92; S, 27.64. Found: C, 32.74; H, 1.81; O, 36.36; S, 29.09. Solubility of sPSO$_2$-220 (H-form): soluble in water, concentrated sulfuric acid, DMSO, DMF, NMP, and DMAc; insoluble in methanol, ethanol, isopropanol, toluene, THF, chloroform, acetone, ethyl acetate, trifluoroacetic acid.

Scheme 1. Synthetic Route to Sulfonated Poly(phenylene sulfone) sPSO$_2$-220 via Sulfonated Poly(phenylene sulfide sulfone) sPSS-204



3. Results and Discussion

Preparation and Characterization. The formation of the highly sulfonated poly(phenylene sulfone) sPSO$_2$-220 requires a preparation route different from the one reported for sulfonated poly(phenylene sulfone)s[16] with ion exchange capacity up to 2.78 mequiv g^{-1}. The preparation of sPSO$_2$-220 succeeded in a two-step process comprising first a polycondensation reaction of sulfonated difluorodiphenyl sulfone with sodium sulfide yielding sulfonated poly(phenylene sulfide sulfone) sPSS-204 and second its subsequent oxidation to sulfonated poly(phenylene sulfone) sPSO$_2$-220 using hydrogen peroxide in acetic acid solution (see Scheme 1).

For the first step, the preparation of the sulfonated poly(phenylene sulfide sulfone) sPSS-204, we adapted reaction conditions known from the preparation of unsulfonated, high molecular weight poly(phenylene sulfide sulfone). This polymer, known from early patent literature[23,24] and recently reinvestigated by Liu et al.,[25] can be prepared by nucleophilic aromatic substitution step polymerization, using sodium sulfide as nucleophile and 4,4′-dichlorodiphenyl sulfone as the activated aromatic dihalide. Several additives, such as alkali metal carboxylate, have been suggested to be useful for accelerating the reaction and for obtaining high molecular weight polymers. Usually these reactions were performed at high temperatures and high pressures. Recently, Yang et al.[26] demonstrated a synthesis between $T = 180$ and 200 °C at normal pressure. In all cases, NMP as

Table 1. Ion Exchange Capacity (IEC), Molecular Weight M_w (Weight Average) and Polydispersity D, Intrinsic Viscosity, and Density of a sPSS-204 Sample and the Corresponding Oxidized Sample $sPSO_2$-220

polymer	IEC/mequiv g^{-1} (theor value)	M_w/kg mol^{-1}, D	intrinsic viscosity/ dL g^{-1}	density/g cm^{-3} dry/ H-form
sPSS-204	4.89 (4.90)	66, 1.36	1.04	1.66
$sPSO_2$-220	4.3−4.5 (4.54)	61, 1.35	0.73	1.75

solvent proved to be an appropriate choice for obtaining high molecular weight polymers.

According to these reports, the preparation of sulfonated poly(phenylene sulfide sulfone) sPSS-204 was carried out by reacting disodium 3,3′-disulfonate-4,4′-difluorodiphenyl sulfone as activated aromatic dihalide and sodium sulfide nonahydrate as nucleophile, both at equimolar ratio, in NMP as solvent under inert atmosphere (water- and O_2-free). Prior to reaction, water was removed by azeotropic distillation with toluene. The reaction was conducted at atmospheric pressure at $T = 185$ °C with a reaction time typically between 15 and 20 h. As suggested in the literature, the reaction was carried out in the presence of an equimolar amount of anhydrous sodium acetate, which may prevent hydrolysis of Na_2S and keep the polymerization free from any unwanted side reactions. The obtained sulfonated poly(phenylene sulfide sulfone) sPSS-204 polymer was isolated by precipitation in isopropanol, then dissolved in water, again precipitated in isopropanol, and finally purified by dialysis. After dialysis the yields were typically in the range 50−80% depending on the achieved molecular weight (due to a certain loss of low molecular weight polymer fraction during dialysis). The sPSS-204 polymer is soluble in water and in common polar aprotic solvents such as DMF, NMP, DMSO, and DMAc. Polymer characterization data of a sample obtained under these reaction conditions are compiled in Table 1. All characterization measurements throughout this paper were done on this polymer sample with a molecular weight $M_w \approx 66\,000$ g mol^{-1}. The use of anhydrous sodium sulfide instead of sodium sulfide nonahydrate led to similar molecular weights; however, regarding cost anhydrous sodium sulfide is less preferred. Any deviation from equimolar ratio of educts in the polycondensation reaction reduced the molecular weight and intrinsic viscosity of the resulting polymer. Other variations such as the usage of dichloro monomer instead of difluoro monomer, the type of sulfide (different sodium sulfide sources and other metal sulfides are possible), solvent, concentration, temperature, duration, additives, and side reactions are currently investigated in order to understand reaction kinetics and to maximize molecular weights.

The second reaction step, the oxidation of the sulfonated poly(phenylene sulfide sulfone) sPSS-204 to the corresponding sulfonated poly(phenylene sulfone) $sPSO_2$-220, succeeded by an excess of hydrogen peroxide (stoichiometry $[H_2O_2]/[-S-] \sim 9$) in acetic acid. The reaction proceeds quantitatively within 12−24 h at $T = 70-80$ °C. These reaction conditions are well-known to fully oxidize sulfide (−S−) via sulfoxide (−SO−) to sulfone ($-SO_2-$) units (see ref 16 and literature cited therein). After removal of the solvent by evaporation, the polymer was purified in water by dialysis yielding off-white to pale yellowish polymer. The oxidation process was indicated by the change of the color of the polymer from dark brown for sPSS-204 to almost colorless for $sPSO_2$-220. In addition, the disappearance of IR bands, which are characteristic for sulfide units (−S−), e.g., at wavenumbers 490, 1444, and 1573 cm^{-1} being also present in poly(1,4-phenylene sulfide),[27] was taken as indicator for complete oxidation of sulfide units (see Figure 1). No characteristic IR band for sulfoxide units (−SO−) at 1030−1040 cm^{-1} is observable, excluding the presence of a significant amount of sulfoxide. The chemical composition of the $sPSO_2$-220 polymer was confirmed by elemental analysis (see Experimental Section).

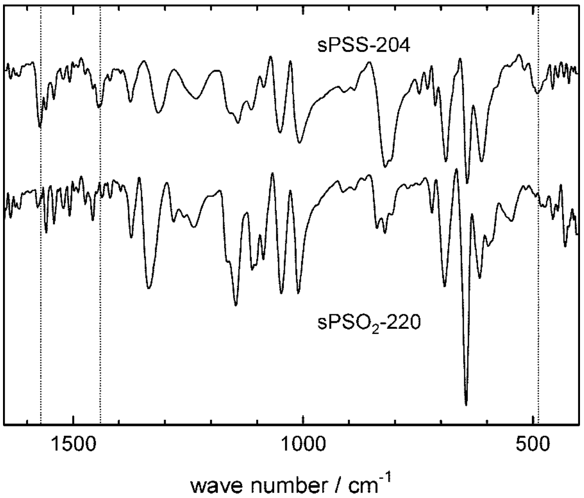


Figure 1. IR spectra of nonoxidized polymer sPSS-204 with sulfide bridges and oxidized polymer $sPSO_2$-220 containing only sulfone bridges, both in H-form.

The ^{1}H NMR spectrum of sPSS-204 exhibits three signals which are assigned to three chemically distinguishable aromatic protons: $\delta(a) = 8.29$, $\delta(b) = 7.73$, and $\delta(c) = 7.26$ ppm, as indicated in Figure 2 (upper part). The complete oxidation of sulfide (−S−) to sulfone ($-SO_2-$) results in a significant downfield shift of the aromatic proton signals due to the strong electron-withdrawing properties of the sulfone groups. Figure 2 (bottom) shows the ^{1}H NMR spectrum of the oxidized polymer $sPSO_2$-220, which exhibits three signals assigned to aromatic protons: $\delta(a) = 8.45$, $\delta(b) = 8.39$, and $\delta(c) = 8.04$ ppm. Their positions at low field are in agreement with ^{1}H NMR resonances reported for the corresponding sulfonated poly(phenylene sulfone)[16] and cyclic oligomers of unsulfonated poly(*p*-phenylene sulfone)[28] and exclude the presence of sulfoxide units which would appear at a higher field. The distinct differences of the ^{13}C NMR spectra of sPSS-204 and $sPSO_2$-220 polymers (Figure 3) once again confirm the complete oxidation of the sPSS-204 polymer to $sPSO_2$-220. In both cases the expected six signals are observed.

The ion exchange capacity determined by titration (see Table 1) is in good agreement with the theoretical value of 4.54 mequiv g^{-1}. In contrast to the water-insoluble sulfonated poly(phenylene sulfone)[16] with ion exchange capacities of up to 2.78 mequiv g^{-1}, the polymer $sPSO_2$-220 is perfectly soluble in water; however, dissolving in NMP DMAc, DMF, and DMSO requires heating. Because of the high IEC and the polar character of the polymeric backbone, $sPSO_2$-220 is insoluble in alcohols (e.g., methanol, ethanol, isopropanol), in agreement with the pronounced alcohol rejection property (selectivity), which has already been shown for sulfonated poly(phenylene sulfone).[18] The polymer $sPSO_2$-220 can be converted into almost colorless, transparent films by casting from water solution; however, the films are brittle in the dry form. The remarkably high density of 1.75 g cm^{-3} for the dry $sPSO_2$-220 polymer is most likely the highest density known for all aromatic nonfluorinated polymers and almost as high as the density of pure sulfuric acid (H_2SO_4, 1.83 g cm^{-3}).

Under the chosen reaction conditions, high molecular weight polymers were obtained as proven by GPC measurements (see Figure 4and Table 1). In the case of the nonoxidized polymer sPSS-204 the measurement showed an almost perfect GPC profile (monomodal distribution with $M_w \approx 66\,000$ g mol^{-1} and

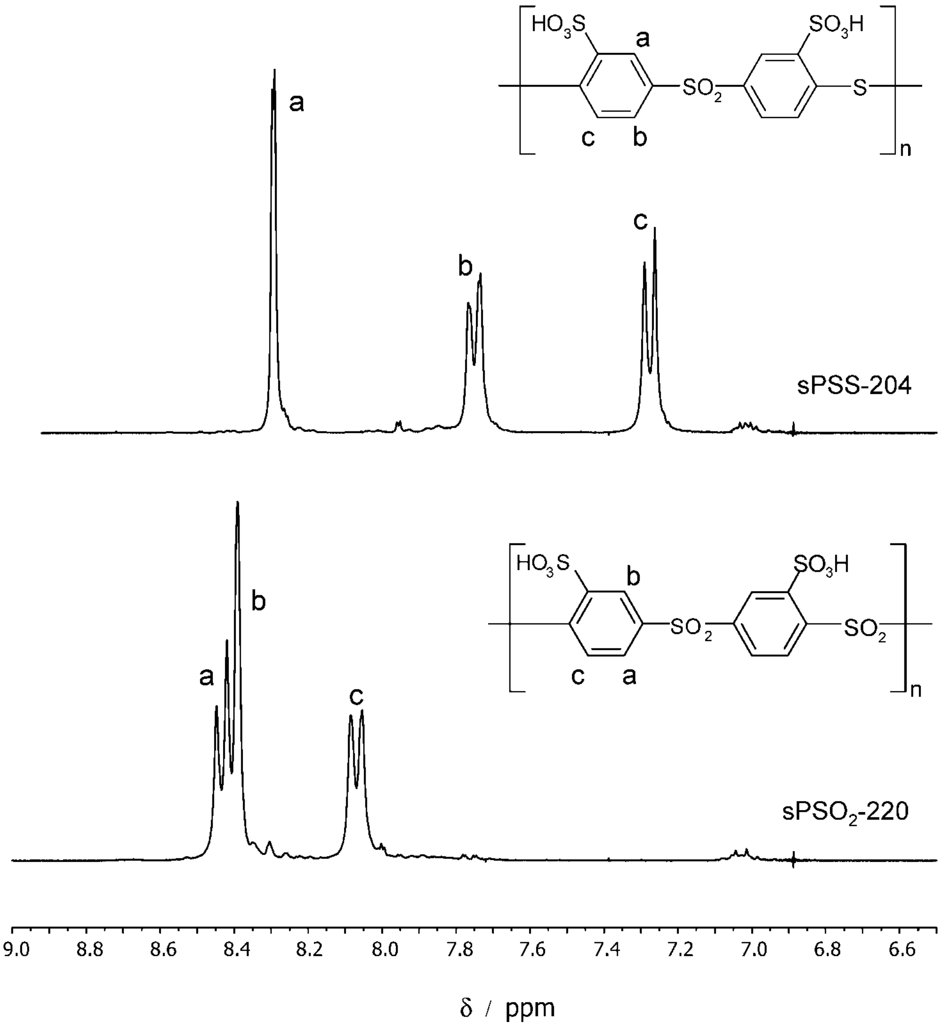


Figure 2. ^{1}H NMR spectra of sPSS-204 and sPSO$_2$-220 in DMSO-d_6.

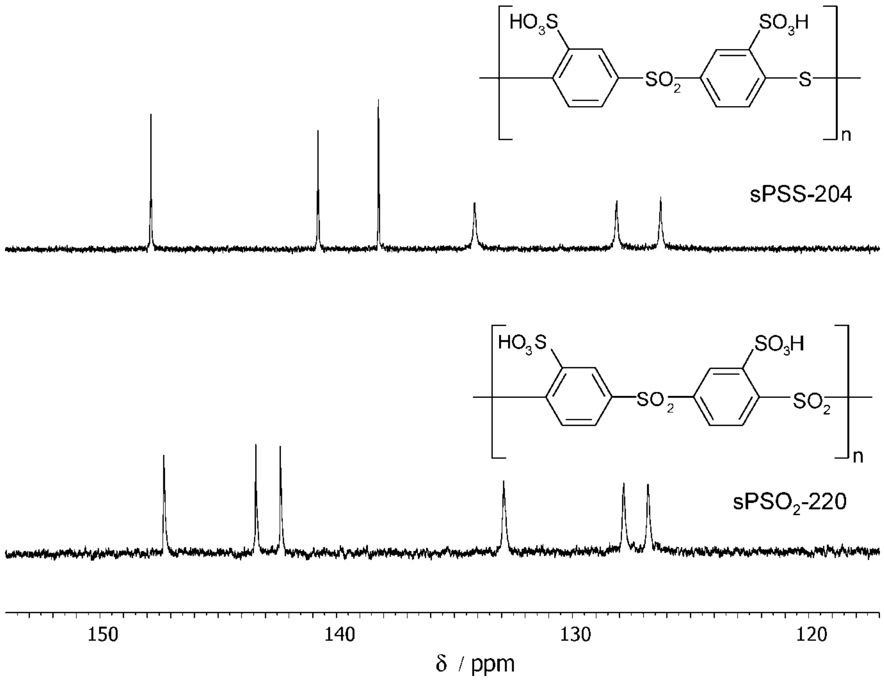


Figure 3. ^{13}C NMR spectra of sPSS-204 and sPSO$_2$-220 in DMSO-d_6.

$D = 1.36$). After oxidation to sPSO$_2$-220, the GPC profile did not change significantly (monomodal distribution with $M_w \approx$ 61 000 g mol^{-1} and $D = 1.35$). Most importantly, no significant decrease of the molecular weight was detected, indicating no

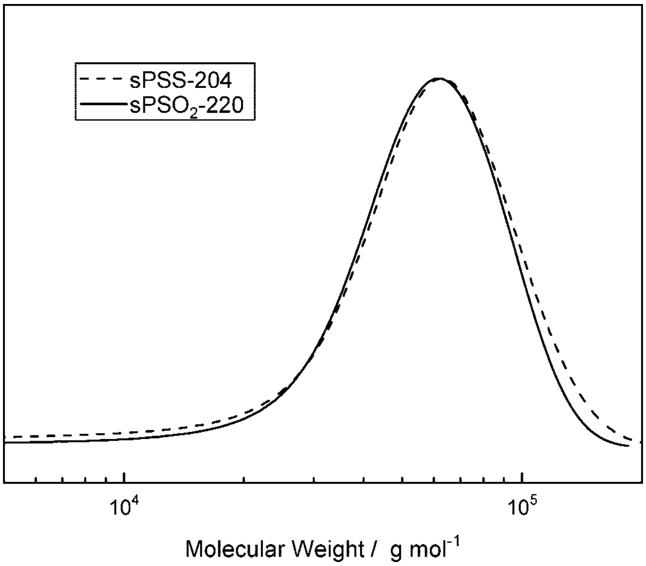


Figure 4. GPC profiles of sPSS-204 and $sPSO_2$-220, both after dialysis and ion exchange into H-form, in DMF at $T = 60$ °C with LiBr addition (1 g L^{-1}), relative to polystyrene standard.

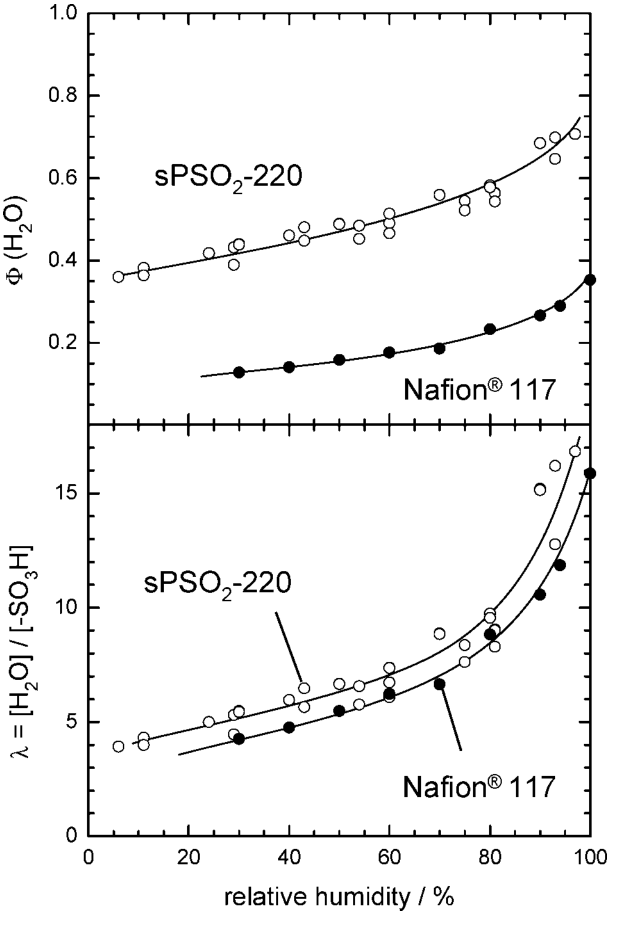


Figure 5. Hydration isotherm for $sPSO_2$-220 at $T = 25$ °C. Top graph shows the water volume fraction $\Phi(H_2O)$ (calculated assuming constant molar volume increments) and bottom graph the water molecules per sulfonic acid group λ as a function of relative humidity. The data for Nafion are given for comparison.

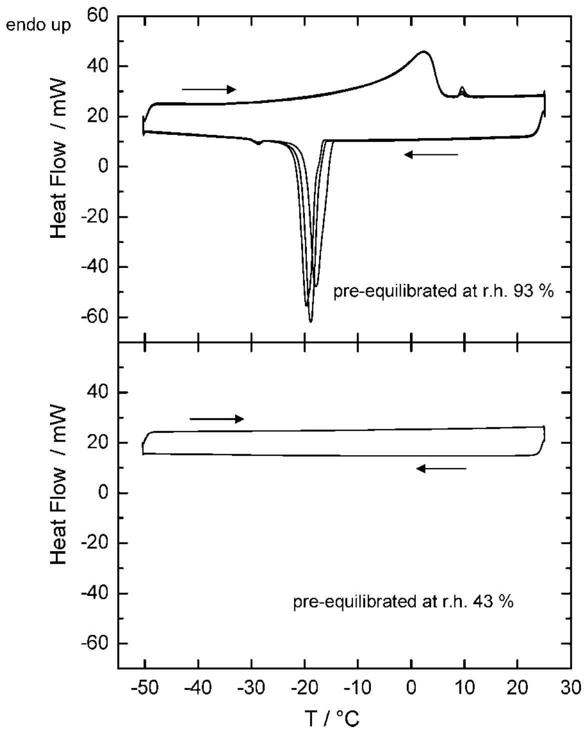


Figure 6. Low-temperature DSC thermograms of sulfonated poly(phenylene sulfone) $sPSO_2$-220 (heating rate 10 °C min^{-1}). Samples were equilibrated at 93% rh (top graph) and 43% rh (bottom graph) prior to measurements.

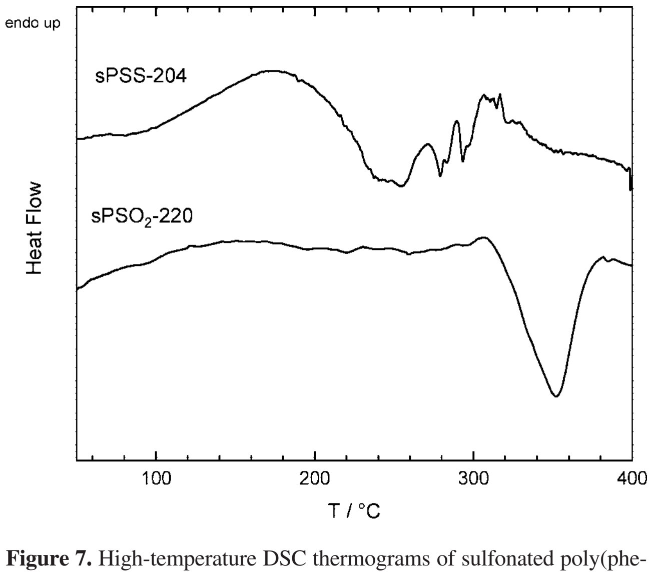


Figure 7. High-temperature DSC thermograms of sulfonated poly(phenylene sulfide sulfone) sPSS-204 and sulfonated poly(phenylene sulfone) $sPSO_2$-220, both in H-form (heating rate 2 °C min^{-1}). Before measurement the samples were dried at $T = 110$ °C for 30 h.

remarkable decomposition (e.g., main-chain cleavage) by oxidation. The apparent small decrease of the molecular weight (instead of a slight increase anticipated after oxidation) may be the consequence of the difference in nature of the oxidized and the nonoxidized polymers affecting the GPC. Indeed, the conversion of sulfide to sulfone bridges is expected to increase rigidity of the polymer backbone. This together with the increased density from 1.66 g cm^{-3} for sPSS-204 to 1.75 g cm^{-3} for $sPSO_2$-220 and the decreased intrinsic viscosity from 1.04 dL g^{-1} for sPSS-204 to 0.73 dL g^{-1} for $sPSO_2$-220 (see Table 1) may point to a decrease of the hydrodynamic radius of $sPSO_2$-220 compared to sPSS-204.

Hydration and State of Water. Water uptake measurements of $sPSO_2$-220 polymer at $T = 25$ °C under different relative humidities (hydration isotherm) were complicated by the uncertainty of the determination of the absolute water content and the very low hydration kinetics of $sPSO_2$-220. Especially at low relative humidities reaching equilibrium took several

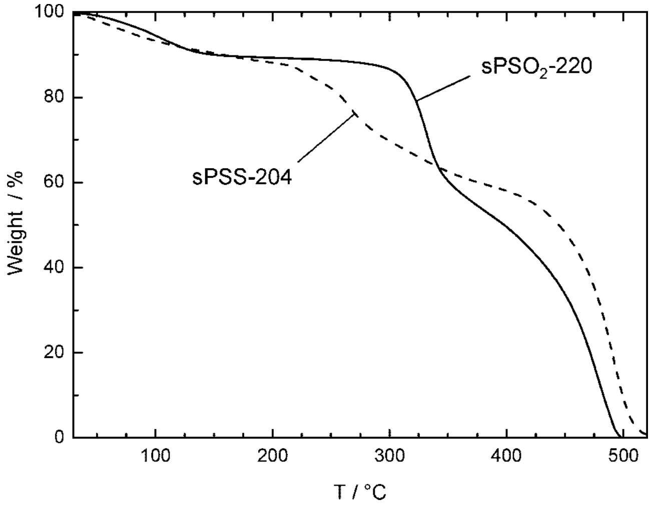


Figure 8. TGA in air of sulfonated poly(phenylene sulfide sulfone) sPSS-204 and sulfonated poly(phenylene sulfone) sPSO$_2$-220, both in H-form (heating rate 2 °C min^{-1}).

weeks. Despite these complications the general trend is evident: The hydration number (λ = [H_2O]/[$-SO_3H$]) for sPSO$_2$-220 appears to be slightly higher than that of Nafion (see Figure 5, bottom graph), which is somewhat unexpected for low relative humidity where the hydration is usually determined by the thermodynamics of the hydration of the sulfonic acid group. For sPSO$_2$-220, however, there may be some extra exothermic hydration of the polymer backbone as a consequence of its distinct polar character. For high relative humidities (rh > 80%), where the driving force for hydration is mainly entropic in nature (osmosis), the water uptake for sPSO$_2$-220 is progressively higher than for Nafion. Obviously, the very high osmotic pressure (as a result of the high IEC) is not balanced by elastic counter forces as is the case for Nafion. This and the possible hydration of the backbone (see above) may eventually cause the dissolution of sPSO$_2$-220 in water.

Because of the much higher ion exchange capacity of sPSO$_2$-220 compared to that of Nafion, the similar water hydration curves imply significantly higher water volume fractions $\Phi(H_2O)$ for sPSO$_2$-220. For example, at 50% rh both polymers take up about 5−6 water molecules per sulfonic acid groups. While this corresponds to only 15 vol % water in Nafion, in the case of sPSO$_2$-220 almost 50% of the volume is water. With so much water dispersed in the polymer it is interesting to investigate the state of this water. Therefore, low-temperature DSC thermograms were measured on samples pre-equilibrated at different relative humidities (see Figure 6). The sample with a very high water content (pre-equilibrated at rh = 93% corresponding to water volume fraction around 60−70%) shows endothermic melting and exothermic freezing peaks within the scanned temperature range, indicating the presence of water taken up by osmosis (freezable water). The extended hysteresis ranging from $T \sim 0$ °C (heating) to $T \sim -20$ °C (cooling) points toward a low nucleation probability, which is expected for the very low extension of the water domains.[19] It should be noted that the peak positions did not change significantly with different scan rates (not shown).

For a sample with 40 vol % water (pre-equilibrated at rh = 43%, Figure 6, bottom) these peaks totally disappeared within the scanned temperature range, suggesting that the interaction of the water with the ions and its extreme confinement in the particular microstructure[19] results in a complete depression of water melting and freezing (nonfreezing water). This situation also leads to very low water diffusion coefficients,[19] which may also explain the sluggish hydration kinetics.

Thermal Properties. In Figure 7 the DSC thermograms of samples of sPSO$_2$-220 (oxidized form) and sPSS-204 (nonoxidized form) are shown (heating rate 2 °C min^{-1}). The nonoxidized polymer sPSS-204 exhibits several exothermal peaks between T = 230−300 °C, indicating decomposition reactions that may cover a possible glass transition temperature. However, the oxidized polymer sPSO$_2$-220 does not show any glass transition temperature or melting up to T = 300 °C, where decomposition reaction starts occurring (exothermal peak). This also demonstrates the very high thermal stability of sPSO$_2$-220. The absence of any glass transition temperature is one of the most unique features of this class of polymers. This may be ascribed to the very rigid structure of the sulfone units and its very high polar character inducing significant interchain interaction especially in the dry state, where this ionomer is very brittle.

The thermal and thermooxidative stability of sPSO$_2$-220, as examined by TGA/MS (2 °C min^{-1}) in air atmosphere, is significantly higher than the stability of the corresponding nonoxidized polymer sPSS-204 (Figure 8). After an initial weight loss due to evaporation of absorbed water, a two-step decomposition process is observed for both polymers. For the nonoxidized polymer sPSS-204 the decomposition reaction starts

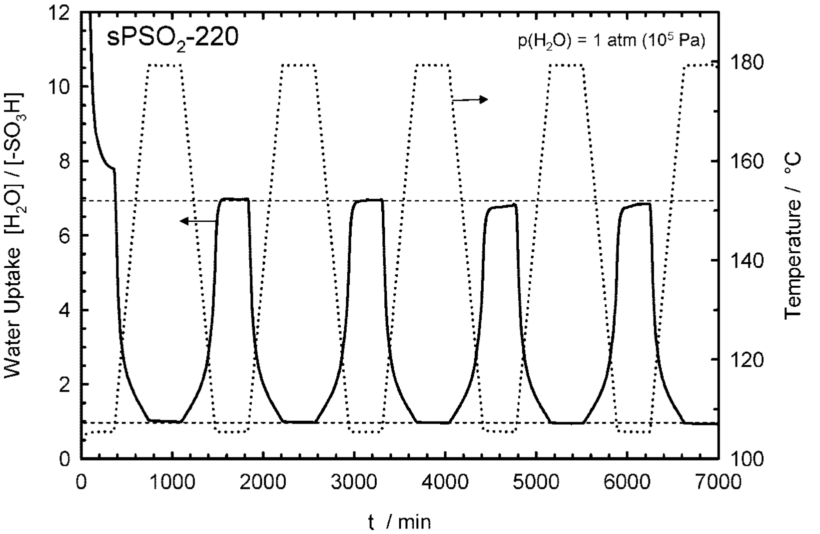


Figure 9. Reversible water desorption/absorption for oxidized polymer sPSO$_2$-220 in the temperature range T = 105−180 °C at a water pressure of $p(H_2O)$ = 1 atm (10^5 Pa) as obtained by TGA (heating and cooling rate 0.2 °C min^{-1}).

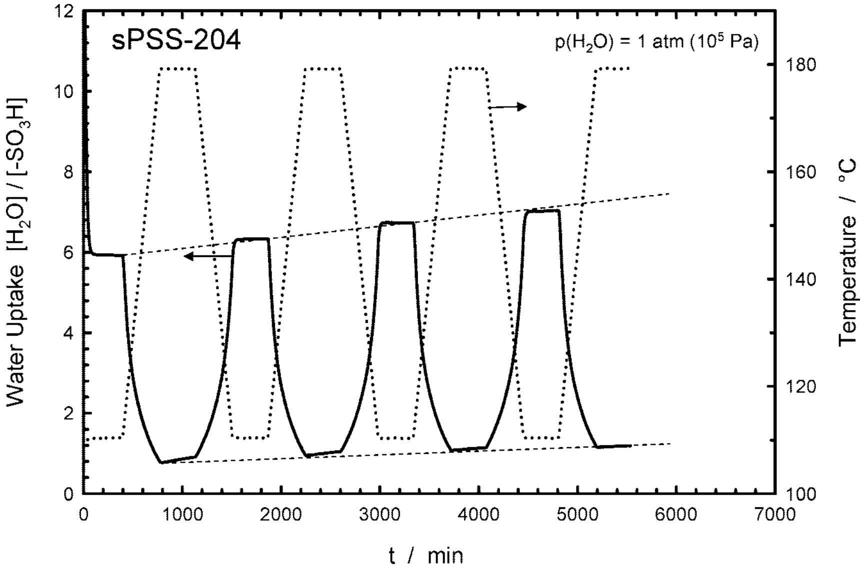


Figure 10. Irreversible water desorption/absorption for nonoxidized polymer sPSS-204 in the temperature range $T = 110-180$ °C at a water pressure of $p(H_2O) = 1$ atm (10^5 Pa) as obtained by TGA.

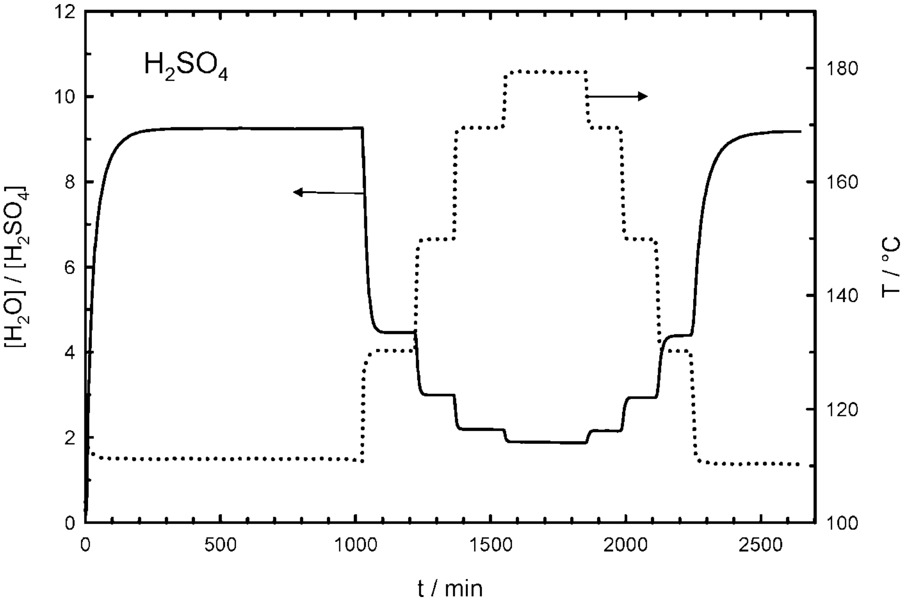


Figure 11. Reversible water desorption/absorption for sulfuric acid (H_2SO_4) in the temperature range $T = 110-180$ °C at a water pressure of $p(H_2O) = 1$ atm (10^5 Pa) as obtained by TGA.

at around $T = 230-250$ °C, while for $sPSO_2$-220 this reaction commences only above $T = 300$ °C. For both polymers, the TGA features are in good agreement with the exothermal peaks in the DSC thermograms (see Figure 7). The decomposition reaction was analyzed in detail by detecting the volatile reaction products by mass spectrometry. In the first decomposition step between $T = 300$ and 350 °C essentially SO ($m/z = 48$) and SO_2 ($m/z = 64$) are observed, indicating the cleavage of the $-SO_3H$ group from the polymer backbone. In the second step additionally CO_2 was observed as reaction product, indicating the oxidation of the polymeric backbone.

Hydrolytic Stability. It is well-know that sulfonated aromates undergo desulfonation when subject to high temperatures and high water activities:[16,29,30] $Ar-SO_3H + H_2O \rightarrow Ar-H + H_2SO_4$ with Ar = aromatic ring. The hydrolytic stability of aromatic sulfonic acid groups depends on the electronic structure of the aromatic ring: while electron-donor groups generally facilitate desulfonation, electron-withdrawing groups impede desulfonation. The hydrolytic stability of the polymers have been determined by cycling TGA measurements between $T = 105$ (110) and 180 °C in an all water vapor atmosphere ($p(H_2O) = 1$ atm $= 10^5$ Pa). Reversible weight changes due to water desorption and absorption during the heating and cooling runs indicate high hydrolytic stability in the scanned temperature range. Any desulfonation reaction is expected to show up as some irreversibility of the weight changes. As shown in Figure 9, the sulfonated poly(phenylene sulfone) $sPSO_2$-220 is absolutely stable under these high temperature and high water activity conditions, while the TGA traces of nonoxidized polymer sPSS-204 shows an increasing baseline (Figure 10). This increased water uptake can be explained by the desulfonation reaction, consuming one water molecule to form free sulfuric acid (H_2SO_4). In addition, free sulfuric acid is expected to absorb slightly more water than the corresponding sulfonic acid based polymer. Therefore, we also measured the water absorption and desorption of pure sulfuric acid (H_2SO_4) under the same conditions (Figure 11). Indeed, it turned out that the water uptake of sulfuric acid (H_2SO_4) is slightly higher (9−10 H_2O/H_2SO_4

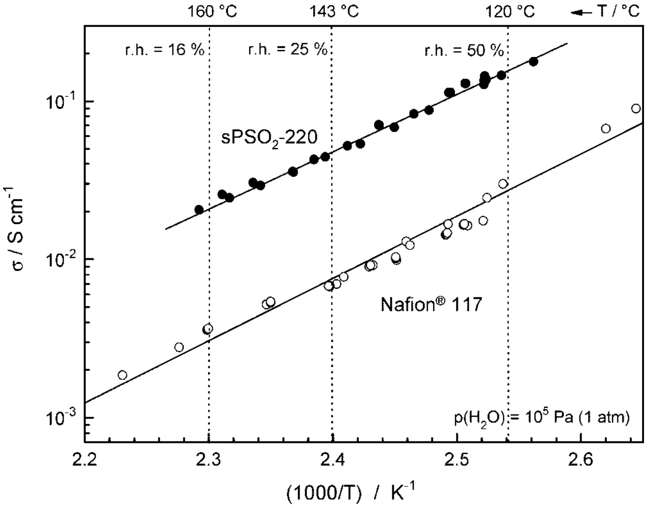


Figure 12. Proton conductivity of sPSO$_2$-220 in the temperature range $T = 110-160$ °C at a water pressure of $p(H_2O) = 1$ atm (10^5 Pa). Data for Nafion 117 are shown for comparison.

at $T = 110$ °C) than the typical uptake of sulfonic acid groups ($6-8$ $H_2O/-SO_3H$ at $T = 110$ °C). This experiment also clearly demonstrates the general reversibility of the sulfonation reaction and the fact that desulfonation takes place easily at high temperatures and high water activities when the aromatic sulfonic acid group is not stabilized by an electron-poor aromatic ring. It also shows the exceptionally high hydrolytic stability of this class of polymers in acidic aqueous environment up to at least $T = 180$ °C. This comprises the stability of both the sulfonic acid functional group and the polymer backbone.

Proton Conductivity. Although sPSO$_2$-220 is water-soluble and film-forming properties are rather poor (brittle in dry state), the conductivity at high temperatures and under complete water atmosphere ($p(H_2O) = 1$ atm) has been determined using pressed pellets of sPSO$_2$-220 polymer powder. As a consequence of the high ion exchange capacity and the high water content in terms of mass or volume fraction, the proton conductivity is significantly higher than that of Nafion (factor 5−7).

4. Summary and Outlook

The preparation of a poly(phenylene) containing merely sulfone units ($-SO_2-$) connecting the phenyl rings and in which each phenyl ring is monosulfonated (100% degree of sulfonation corresponding to an ion exchange capacity of 4.5 mequiv g^{-1}) succeeded in a two-step process: the polycondensation reaction of sulfonated difluorodiphenyl sulfone with sodium sulfide yielding sulfonated poly(phenylene sulfide sulfone) sPSS-204 and its subsequent oxidation to sulfonated poly(phenylene sulfone) sPSO$_2$-220 using hydrogen peroxide in acetic acid. Molecular weights up to $M_w \approx 61\,000$ g mol^{-1} were obtained. The water-soluble sPSO$_2$-220 polymer exhibits a very high density, no glass transition or melting temperature, and high thermooxidative and hydrothermal stability. The latter is attributed to the specific molecular structure consisting of very electron-poor aromatic rings. The proton conductivity exceeds that of Nafion by a factor of 5−7 at high temperature ($T = 110-160$ °C). A comprehensive investigation of the transport properties including water diffusion and electroosmotic drag is published in a separate paper.[19]

Since sPSO$_2$-220 is water-soluble and brittle in the dry state, we currently focus on optimizing the reaction conditions in order to control and maximize molecular weight. We are also attempting to form insoluble and dimensionally stable membranes, e.g., by using sPSO$_2$-220 as part of blends, graft copolymers, and block copolymers. This also comprises cross-linking within sPSO$_2$-220 or the different constituents of the membrane. In any case, maintaining locally the high density of sulfonic acid groups is important for optimum percolation.

Acknowledgment. The authors thank Rotraut Merkle for reading the proofs, Annette Fuchs and Udo Klock for technical assistance, and the Max-Planck-Institute for Polymer Research in Mainz for carrying out GPC measurements. Furthermore, the authors acknowledge the financial support by the Stiftung Energieforschung Baden-Württemberg (FKZ A 23305) and the BMBF (03SF0323C).

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MA900333N