# Sulfonated Poly(phenylene sulfone) Polymers as Hydrolytically and Thermooxidatively Stable Proton Conducting Ionomers

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ABSTRACT: Sulfonated poly(arylene) ionomers containing merely electron-accepting sulfone units (−$SO_2$−) connecting the phenyl rings have been synthesized and characterized in detail, in particular with respect to properties relevant for their application as membrane materials in polymer-electrolyte-membrane (PEM) fuel cells. The copolymers were prepared by a two-step process comprising (1) a nucleophilic aromatic polycondensation reaction of 4,4′-difluorodiphenylsulfone and disodium 3,3′-disulfonate-4,4′-difluorodiphenylsulfone with 4,4′-thiobisbenzenethiol at various molar ratios yielding sulfonated poly(phenylene sulfide sulfone)s and (2) their subsequent oxidation to sulfonated poly(phenylene sulfone)s using peroxide in acidic solution. This new class of polymers with extremely electron-deficient aromatic rings shows very high thermal, thermooxidative and hydrolytic stabilities, low solubilities, and reduced swelling in water at enhanced temperature compared to other sulfonated poly(arylene)s. The latter property allows for the preparation of membranes with very high ion exchange capacity and high proton conductivity especially at high temperature and low humidification, which makes them interesting materials for chemical and electrochemical applications such as PEM fuel cells. The flexible preparation route provides a path for obtaining various molecular structures and ion exchange capacities.

## 1. Introduction

The electrolyte material used in current PEM fuel cells is commonly a hydrated sulfonic acid functionalized polymer. Because of the harsh conditions in operating fuel cells (high temperatures, high water activities, and the appearance of highly reactive oxidizing radicals), hydrolytic, thermooxidative, and (electro-)chemical stabilities are key issues in the choice of the ionomer. Today's membranes are perfluorosulfonic acid (PFSA) polymers such as Nafion (DuPont), featuring superior stability compared to most hydrocarbon-based membranes. But their high water and methanol "crossover" and their low proton conductivity as well as their poor mechanical stability at elevated temperatures ($T$ > 80 °C) and low degrees of humidification are still severe disadvantages of these state-of-the-art membrane materials.[1,2] According to recent reports, the transport properties of sulfonated poly(arylene) membranes seem to be advantageous over these perfluorosulfonic acid ionomers,[3−5] which renders them promising alternatives, provided that their stability problems are solved.

Recent research activities based on poly(arylene) materials have focused on sulfonated poly(ether ketone), poly(ether sulfone), poly(imide), poly(benzimidazole), poly(phthalazinone ether ketone), poly(phenylene oxide), poly(phenylene sulfide), and other ionomers (for reviews see refs 6−11). It is a general observation for these poly(arylene) ionomers that water and methanol "crossover" is lower and mechanical integrity higher (higher glass transition temperature and higher tensile strength) than for perfluorosulfonic acid polymers. Stability and performance of these membranes in operating hydrogen PEM fuel cells are, however, far from being acceptable and do not even meet the performance of PFSA membranes.

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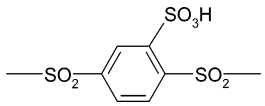
In this paper we present a new class of sulfonic acid functionalized poly(arylene) ionomers combining high stability and high proton conductivity. The materials are the first outcome of our attempts to form an extremely electron-deficient poly(arylene) with high ion exchange capacity (IEC). The first is anticipated to increase stability and acidity, while the latter is essential for obtaining high proton conductivity. The high acidity is anticipated to favor charge carrier formation especially at low degrees of hydration which is also beneficial for obtaining a high conductivity at low humidification. In these ionomers,[12] the aromatic ring bearing the sulfonic acid group is connected to two sulfone linkages (−$SO_2$−) which are strongly electron-withdrawing (electron acceptor); i.e., the structural environment of the sulfonated aromatic ring is




While the unsulfonated analogue poly(*p*-phenylene sulfone) (PSO2)[13−18] is only poorly characterized because of its complete insolubility, there are no reports on sulfonated poly(*p*-phenylene sulfone) (sPSO2) polymers.

Because of the reduced aromaticity, the hydrolytic stability of the sulfonic acid group on the ring is expected to be significantly enhanced. This may be rationalized by considering the mechanism of electrophilic aromatic sulfonation and its reverse reaction, the hydrolysis reaction (desulfonation) of sulfonated arylenes. Although this mechanism is complex[19] and details are still under debate, a generalized and simplified reaction scheme with $SO_3$ being the sulfonating agent may be considered (see Scheme 1). At elevated temperatures and high water activities this reaction can easily be reversed (hydrolysis, desulfonation), as frequently exploited to direct *meta*-substitution of aromates.

In general, the sulfonation reaction is an exothermic process (≈−170 kJ $mol^{-1}$ for gaseous $SO_3$ and ≈−140 kJ $mol^{-1}$ for

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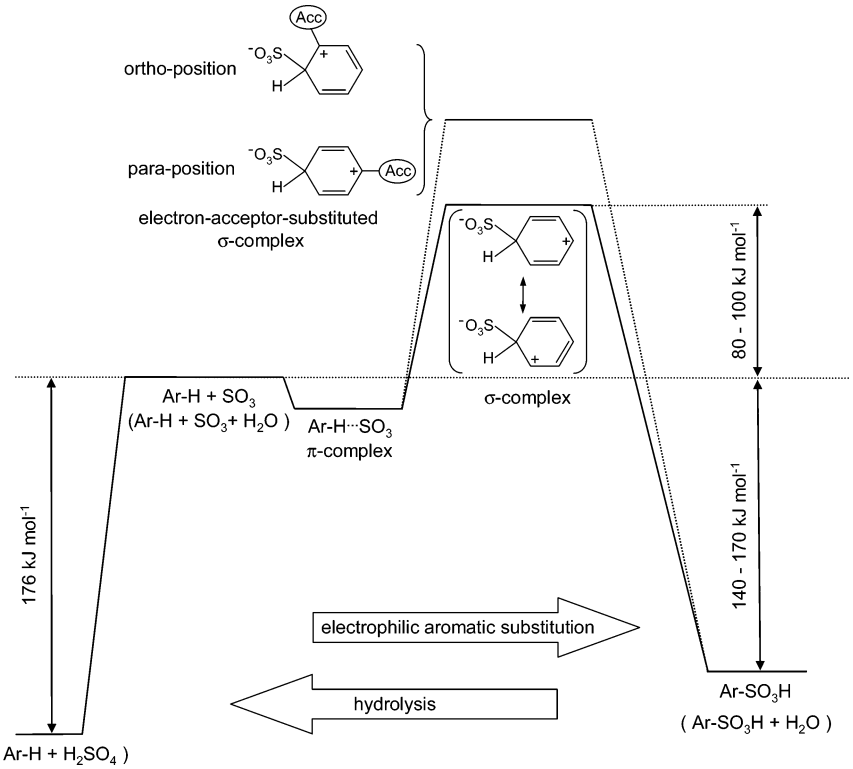
**Scheme 1. Enthalpy Profile of the Electrophilic Aromatic Sulfonation (Ar = Aromatic Ring, Acc = Electron Acceptor Group)**[a]




[a] Relative molecular energies of different species involved in the sulfonation reaction are taken from an ab-initio calculation on the sulfonation of toluene[20] neglecting entropy changes.

solvated $SO_3$), but also a highly activated reaction with a barrier of 80−100 kJ mol$^{-1}$. (Relative energies are taken from an ab initio calculation at the 4-31 G/S* level on the sulfonation of toluene,[20] and no account has been taken of the entropy changes.) A simplified sulfonation scheme (see Scheme 1) comprises (i) the attack of the electrophile ($SO_3$) by formation of the so-called $\pi$-complex, (ii) followed by the formation of the intermediate $\sigma$-complex (Wheland intermediate), and (iii) finally the abstraction of the proton (deprotonation and rearomatization) by formation of the aromatic sulfonic acid. The rate-determining step of the sulfonation is the formation of the intermediate $\sigma$-complex, which is energetically strongly unfavored because of its drastically reduced aromaticity. The back-reaction, i.e., the hydrolysis, preferentially takes place at enhanced temperature and high water activity, where the reaction is exothermic mainly because of the high hydration enthalpy of $SO_3$ (−176 kJ mol$^{-1}$, 81 kJ mol$^{-1}$ for the formation of $H_2SO_4$ and 95 kJ mol$^{-1}$ for the hydration of the latter). As in the case of the sulfonation reaction, the rate-determining step of the hydrolysis reaction is the formation of the intermediate $\sigma$-complex. Hence, both the ease of sulfonation and the hydrolytic "stability" of an aromatic sulfonic acid essentially depend on the energetics of the intermediate $\sigma$-complex (easy on, easy off). In general, less stable intermediates enhance the activation enthalpy of the hydrolysis reaction and therefore increase the kinetic stability of the sulfonic acid group on the aromatic ring.

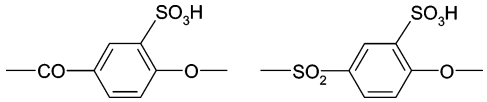
The stability of the intermediate $\sigma$-complex is affected by the kind of substitution of the aromatic ring. From simple electrostatic considerations it is evident, that electron-withdrawing (electron-acceptor) groups like sulfone (−$SO_2$−), ketone (−CO−), or phosphine oxide (−PO−) in the *ortho*- and *para*-position to the sulfonic acid group destabilize the $\sigma$-complex and therefore increase the hydrolytic "stability". Electron-donor substituents like ether (−O−) or sulfide (−S−) groups in *ortho*- and *para*-position to the sulfonic acid group stabilize the $\sigma$-complex, resulting in hydrolytically less stable aromatic sulfonic acid groups.

Many sulfonic acid functionalized poly(arylene)s reported in the literature contain electron-donor linkages in *ortho*- or *para*-position to the sulfonic acid group, which may be critical for their application at $T > 100$ °C in high-humidity environments.

As explained above, the electrophilic sulfonation of poly(arylene)s bearing exclusively electron-withdrawing groups is extremely difficult or virtually impossible because of the very high activation enthalpy of the corresponding electrophilic aromatic sulfonation reaction. Commonly, postsulfonation of poly(arylene) polymers is making use of electrophilic reagents such as sulfuric acid, oleum, chlorosulfonic acid, etc., sulfonating the aromatic ring at activated positions. There are various approaches to avoid or block these activated sites, which eventually lead to the sulfonation of nonactivated positions. Among others, poly(arylene)s have been synthesized containing sulfonated phenyl,[21,22] fluorenylbiphenyl,[23,24] tetraphenylphenylene,[25,26] hexaphenylbiphenylene,[25] and tri- and tetraphenylmethane[27,28] moieties, and in some cases an improved hydrolytic stability has indeed been reported.

Recently, there have been several attempts to obtain sulfonated poly(arylene)s with enhanced hydrolytic stability by circumventing the conventional electrophilic aromatic postsulfonation reaction. One route reported by Kerres[29−32] is utilizing the nucleophilic aromatic substitution reaction, based on a metalation (lithiation) of conventional poly(ether sulfone) PSU, followed by the reaction with either $SO_2$ forming the corresponding sulfinic acid PSU−$SO_2$H, which is then oxidized to the sulfonic acid PSU−$SO_3$H, or with $SO_2Cl_2$ forming the corresponding sulfochloride PSU−$SO_2$Cl, which can easily be hydrolyzed to the sulfonic acid PSU−$SO_3$H. Another approach first reported by Ueda[33] and later elaborated by McGrath[34−38] and others[39,40] comprises well-established polycondensation

reactions, but with the use of the already sulfonated monomers 3,3′-disulfonate-4,4′-dichlorodiphenylsulfone[41] or 3,3′-disulfonate-4,4′-difluorodiphenylsulfone to form sulfonated poly(phenylene ether sulfone) polymers, where the sulfonic acid group is placed on the deactivated (electron-acceptor-substituted) aromatic ring (see below). The corresponding sulfonated poly(phenylene ether ketone)s have been prepared by using a sulfonated difluorodiphenylketone monomer, as first reported by Wang.[42,43] But in these cases only mixed electron-donor−acceptor-substituted sulfonated poly(arylene)s are obtained. In addition, the stabilization effect is expected to be less pronounced because of the sulfonic acid group being in the *meta*-position to the electron-acceptor group and in the *ortho*-position to the electron-donor group (ether linkage).



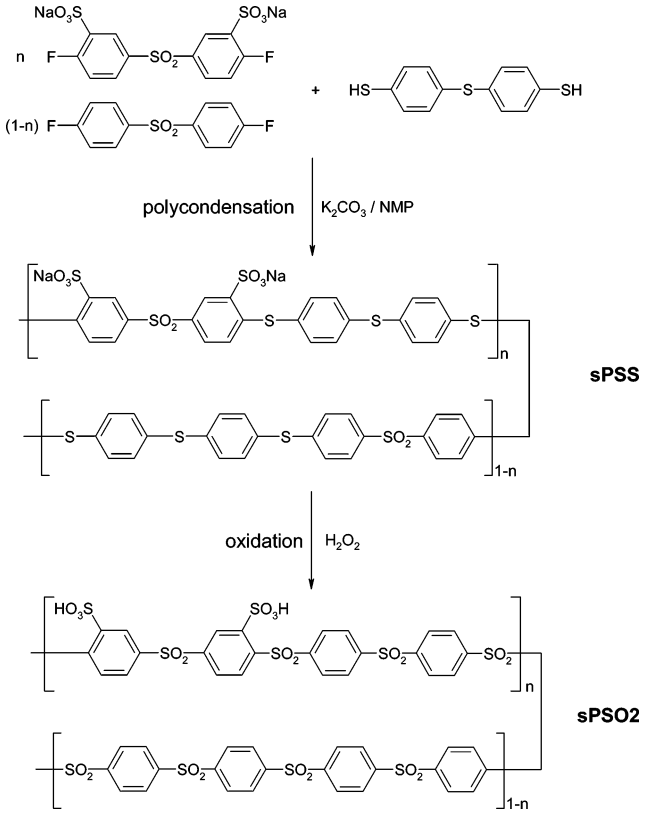

Alternatively, sulfonated poly(phthalazinone ether sulfone)s,[44] poly(phthalazinone ether ketone)s,[45] and polymers containing sulfonated naphthalene structures[46−48] have been synthesized via direct copolymerisation, which do not have the undesired ether linkage in the *ortho*-position to the sulfonic acid group.

A number of modified poly(arylene)s have been prepared by attaching pendent sulfonated phenyl groups via ketone, sulfone, and phosphine oxide links to the aromatic main chain: (i) by postsulfonation,[49] (ii) by lithiation and anionic reaction with 2-sulfobenzoic acid cyclic anhydride[50] or with pentafluorobenzene sulfochloride,[32] and (iii) by the use of already sulfonated monomers.[51−53] In these cases the sulfonic acid group is hydrolytically stabilized by one electron-withdrawing group. Apparently, the presence of one ketone function attached to the phenyl ring still allows electrophilic aromatic sulfonation, whereas two ketone groups seem to prevent easy sulfonation.[54,55]

In order to overcome the apparent synthetic difficulties for exclusively electron-acceptor-substituted sulfonated arylenes, we adopted a reaction that consists of a simple synthesis of sulfonated poly(arylene)s bearing both an electron-donor and electron-acceptor group at each sulfonated aromatic ring and which then allows the conversion of the donor group into an acceptor group. This conversion is an oxidation of a sulfide to a sulfone functional group, corresponding to a conversion of a poly(phenylene sulfide sulfone) to a poly(phenylene sulfone). The detailed procedure (see Scheme 2) comprises the following steps: (1) polycondensation of sulfonated 4,4′-difluorodiphenylsulfone with 4,4′-thiobisbenzenethiol to the corresponding sulfonated poly(phenylene sulfide sulfone) and (2) oxidation of the sulfonated poly(phenylene sulfide sulfone) to the corresponding sulfonated poly(phenylene sulfone) by using peroxide in acidic solution.

The polycondensation reaction of 4,4′-dichlorodiphenylsulfone with 4,4′-thiobisbenzenethiol has already been reported in 1967 by Gabler,[56] and the corresponding polycondensation reaction with sulfonated monomers has been employed for the first time by McGrath[57−61] in 2000 and later by Dang.[62−64] While the oxidation of unsulfonated poly(phenylene sulfide)s and poly(phenylene sulfide sulfone)s to poly(phenylene sulfone)s is well-known since the work of Gabler and Studinka[14,15] and has been described and discussed in a number of publications[18,65−70] and patents,[71−75] the combination of both the polycondensation of sulfonated monomers with bis-thiol functionalized monomers and the subsequent oxidation of the corresponding sulfonated poly(phenylene sulfide sulfone)s has not yet been reported so

**Scheme 2. Synthesis of Sulfonated Poly(phenylene sulfone) Polymers sPSO2**




far. Although there had been some doubts on the feasibility of the oxidation of poly(phenylene sulfide)s by peroxide,[13] recent studies[16,17] clearly confirm the controlled oxidative conversion of poly(phenylene sulfide)s to poly(phenylene sulfone)s.

A major advantage of this approach is its high flexibility. It allows a wide variation of the ion exchange capacity by copolymerization of sulfonated and non-sulfonated monomers and even the formation of block copolymers. Apart from an increased hydrolytic stability, polymers with the structural building unit $-SO_2-Ar(SO_3H)-SO_2-$ (Ar = aromatic ring) are also expected to show increased thermooxidative stability and even increased acidity (lower p$K_a$ value). The latter may enhance the affinity toward water especially at low relative humidity and guarantees quasi-full dissociation even at low degrees of hydration. Other interesting features are the exceptionally rigid structure of the diarylsulfone unit $Ar-SO_2-Ar$ with its preferred "open-book" conformation and the significant intermolecular contacts between hydrogen of phenyl rings and oxygen of sulfone units ($C-H^{\delta+}\cdots O^{\delta-}$) interpreted as weak hydrogen bonds.[16,17] This gives rise to some ordered stacking or even crystallinity as observed in plain (unsulfonated) poly(*p*-phenylene sulfone)s, which is the main reason for its low solubility. This allows achieving high ion exchange capacities without dissolving or vast swelling in water. In other words, this type of ionomers is anticipated to combine high stability and high proton conductivity in a unique way.

## 2. Experimental Section

**2.1. Materials.** *N*-Methyl-2-pyrrolidone (NMP) was dried over $P_4O_{10}$, distilled at reduced pressure, and stored under argon and over molecular sieve (4 Å). Toluene was dried over calcium hydride, distilled, and stored under argon and over molecular sieve (4 Å). Dimethyl sulfoxide (DMSO) and 2-propanol were used without further purification.

**2.2. Disodium 3,3′-Disulfonate-4,4′-difluorodiphenylsulfone Has Been Prepared in Analogy to Ref 37.** In a flask equipped with a condenser 4,4′-difluorodiphenylsulfone (100 g, 0.393 mol, Aldrich) and oleum (200 mL, 65% $SO_3$ in $H_2SO_4$, Merck) were heated in an oil bath to 110 °C and stirred for 12 h. After cooling to room temperature, the reaction mixture was poured into 1500 mL of ice−water. Sodium chloride (≈350 g, Merck) was added to precipitate the product. The white precipitate was collected by filtration and redissolved in 1000 mL of water. After neutralization of the solution with NaOH (Merck), the product was again precipitated with sodium chloride (≈350 g), separated by filtration, and purified several times by recrystallization from a water/2-propanol (1:4) mixture until the product was chloride-free. Finally, the white product was dried at 140 °C for 24 h in vacuo ($1 \times 10^{-3}$ mbar). The yield was 122 g (68%) of disodium 3,3′-disulfonate-4,4′-difluorodiphenylsulfone. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta = 8.16$ (dd, 2H, $J_{HH} = 2.5$ Hz, $J_{HF} = 6.4$ Hz), 7.97 (ddd, 2H, $J_{HH} = 2.6$, 8.7 Hz, $J_{HF} = 4.3$ Hz), 7.43 (dd, 2H, $J_{HH} = 8.8$ Hz, $J_{HF} = 9.2$ Hz). $^{13}$C NMR (75.5 MHz, DMSO-$d_6$): $\delta = 161.6$ (d, $J_{CF} = 259.2$ Hz), 136.9 (d, $J_{CF} = 18.9$ Hz), 136.2 (d, $J_{CF} = 2.0$ Hz), 131.0 (d, $J_{CF} = 10.0$ Hz), 128.4 (d, $J_{CF} = 4.6$ Hz), 118.5 (d, $J_{CF} = 24.6$ Hz).

**2.3. Typical Polymerization and Oxidation Procedure.** *Polymerization: Preparation of the Homopolymer sPSS-312.* Before polymerization, disodium 3,3′-disulfonate-4,4′-difluorodiphenylsulfone and potassium carbonate (Roth) were dried overnight at $T = 145$ °C in a vacuum oven ($2 \times 10^{-3}$ mbar). 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 30.170 g (0.0658 mol) of disodium 3,3′-disulfonate-4,4′-difluorodiphenylsulfone, 16.482 g (0.0658 mol) of 4,4′-thiobisbenzenethiol (Aldrich) and 19.1 g (0.138 mol) of anhydrous potassium carbonate. This mixture was dried for 2 h at $T = 90$ °C in vacuo ($2 \times 10^{-3}$ mbar). Then anhydrous 1-methyl-2-pyrrolidone NMP (200 mL, Fluka) and dry toluene (80 mL, Merck) were added under argon, and the reaction mixture was heated in an oil bath to $T = 150$ °C for 4 h to remove any water. The toluene was then removed by emptying the Dean−Stark trap, and the reaction was allowed to continue for 36 h at $T = 175$ °C. After cooling to room temperature, the dark purple reaction mixture was slowly poured into 2-propanol (1200 mL) to precipitate the polymer. The purple precipitate was separated by filtration and washed with 2-propanol. The product was redissolved in water (600 mL), again precipitated in 2-propanol (1200 mL), separated, washed with 2-propanol, and dried at $T = 60$ °C. In order to remove all byproducts, the polymer was purified by dialysis for 48 h (dialysis tubing cellulose membrane, 12 000 MWCO, Aldrich D9777). The water was removed using a rotary evaporator, and the product dried at $T = 50$ °C in vacuo ($2 \times 10^{-3}$ mbar), yielding 42.89 g ($M = 700.9$ g/mol K-form, 93%) of a dark-purple polymer. Conversion of the K-form into H-form succeeded by ion exchange with Dowex Marathon C (H-form, Aldrich), yielding a brownish polymer after drying at $T = 60$ °C in a vacuum oven. sPSS-312: $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta = 8.20$ (s, 2H, $H_A$), 7.68 (d, 2H, $H_C$, $J = 8.3$ Hz), 7.56 (d, 4H, $H_D$, $J = 7.9$ Hz), 7.48 (d, 4H, $H_E$, $J = 7.9$ Hz), 6.91 (d, 2H, $H_G$, $J = 8.3$ Hz). $^{13}$C NMR (75.5 MHz, DMSO-$d_6$): $\delta = 144.7$ (s), 144.1 (s), 136.5 (s), 136.2 (s), 135.9 (s), 132.0 (s), 130.8 (s), 127.6 (s), 126.0 (s).

*Oxidation: Preparation of the Homopolymer sPSO2-360.* 20.0 g (28.5 mmol, $M = 700.9$ g/mol K-form) of fine-powdered sPSS-312 were suspended in 400 mL of glacial acetic acid (Merck) and 30 mL of concentrated sulfuric acid (97%, Merck), resulting in a brown suspension. Hydrogen peroxide (26.0 mL of a 31% $H_2O_2$ in water, 0.26 mol of $H_2O_2$, Merck) was slowly added. Then the reaction mixture was stirred for 2 days at $T = 30$ °C, while the color changed from brown to virtually colorless. The reaction mixture was heated to $T = 100$ °C for 10 min to remove excess peroxide. After diluting the mixture with 200 mL of glacial acetic acid, the product was separated by filtration and washed with glacial acetic acid. In order to remove all byproducts, the polymer was purified by dialysis for 48 h (dialysis tubing cellulose membrane, 12 000 MWCO, Aldrich D9777). The water was removed using a rotary evaporator, and the product was dried at $T = 50$ °C in vacuo ($2 \times 10^{-3}$ mbar) to obtain the colorless polymer sPSO2-360 in 95% yield (19.5 g, $M = 720.7$ g/mol H-form). $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta = 8.59$ ($H_A$), 8.54 ($H_B$), 8.28 ($H_C$), 8.06 ($H_E$), 7.99 ($H_F$) with intensity ratio A+B:C:E+F = 2.0:0.9:3.9. $^{13}$C NMR (75.5 MHz, DMSO-$d_6$): $\delta = 149.5$ (s), 146.4 (s), 144.1 (s), 143.6 (s), 140.7 (s), 133.6 (s), 129.3 (s), 128.1 (s). IR (film, cm$^{-1}$): 1684, 1577, 1396, 1371, 1332, 1293, 1257, 1166, 1106, 1090, 1070, 1052, 1012, 843, 716, 688, 645, 621, 591, 562, 426. Anal. Calcd for sPSO2-360 (K-form) with $\lambda = [H_2O]/[\text{-}SO_3K] = 1.25$: C, 34.59; H, 2.57; S, 22.71. Found: C, 34.23; H, 2.27; S, 22.84.

The copolymers sPSS-370, sPSS-661, sPSO2-430, and sPSO2-781 have been prepared following the same route by adding adequate amounts of unsulfonated monomer 4,4′-difluorodiphenylsulfone to the polymerization and varying the fractions of the starting components. Polymer sPSS-661 was purified by thoroughly washing with distilled water instead using dialysis. Membranes of sPSO2-781 were obtained by direct oxidation of membranes of sPSS-661 in a bath of acetic acid (see below).

sPSS-370. Purple (K-form) or brown (H-form) polymer, 90% yield. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta = 8.19$ (s, $H_A$), 7.83 (s, $H_B$), 7.67 (d, $H_C$), 7.55 (d, $H_D$), 7.47 (d, $H_E$), 7.36 (s, $H_F$), 6.90 (s, $H_G$). $^{13}$C NMR (75.5 MHz, DMSO-$d_6$): $\delta = 144.7$ (s), 144.4 (weak s), 144.2 (s), 138.5 (weak s), 136.6 (s), 136.3 (s), 136.0 (s), 135.6 (weak s), 134.8 (s), 132.1 (s), 130.8 (s), 130.2 (weak s), 128.4 (s), 128.3 (s), 127.7 (s), 126.1 (s).

sPSS-661. Brown polymer (H-form), 89% yield. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta = 8.19$ (s, $H_A$), 7.82 (s, $H_B$), 7.63 ($H_C$), 7.5 − 7.4 ($H_D$ and $H_E$), 7.31 (s, $H_F$), 6.87 (s, $H_G$). $^{13}$C NMR (75.5 MHz, DMSO-$d_6$): $\delta = 144.9$ (s), 144.3 (s), 144.0 (s), 139.4 (weak s), 138.3 (s), 136.5 (s), 136.1 (s), 135.8 (weak s), 135.7 (s), 134.7 (s), 132.0 (s), 131.0 (weak s), 130.0 (s), 128.3 (s), 128.1 (s), 127.5 (s), 126.0 (weak s).

sPSO2-430. Colorless polymer, 96% yield. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta = 8.59$ (d, $H_A$), 8.54 (s, $H_B$), 8.26 (d, $H_C$), 8.20 (s, $H_D$), 8.06 (d, $H_E$), 7.98 (d, $H_F$) with intensity ratio: A+B:C+D:E+F = 1.0:1.4:2:1. $^{13}$C NMR (75.5 MHz, DMSO-$d_6$): $\delta = 149.5$ (s), 146.3 (s), 144.5 (weak s), 144.0 (s), 143.4 (s), 142.9 (weak s), 140.5 (s), 133.4 (s), 129.5 (s), 129.2 (s), 127.9 (s). IR (film, cm$^{-1}$): 1684, 1577, 1394, 1371, 1334, 1290, 1252, 1164, 1106, 1086, 1072, 1049, 1012, 842, 715, 687, 645, 618, 591, 565, 425. Anal. Calcd for sPSO2-430 (K-form) with $\lambda = [H_2O]/[\text{-}SO_3K] = 2.0$: C, 35.70; H, 2.60; S, 23.06. Found: C, 34.18; H, 2.55; S, 22.97.

sPSO2-781. Colorless polymer, 100% yield. NMR was not possible because of the insolubility of sPSO2-781. IR (film, cm$^{-1}$): 1685, 1578, 1473, 1393, 1334, 1291, 1260, 1161, 1107, 1070, 1052, 1012, 841, 763, 749, 712, 687, 645, 621, 587, 527, 406. Anal. Calcd for sPSO2-781 (K-form) with $\lambda = [H_2O]/[\text{-}SO_3K] = 2.5$: C, 41.70; H, 2.80; S, 22.26. Found: C, 42.10; H, 2.81; S, 21.23.

**2.4. Membrane Preparation and Conditioning.** DMSO or NMP solutions of sPSO2-360 and sPSO2-430 (20 wt %) were cast onto glass plates after filtration (5 $\mu$m filter) and degassing to form membranes which were dried at $T = 50$ °C for 2 h and at $T = 70$ °C for 2 h. The membranes were delaminated from the glass plate in water and conditioned (transformation in acid form) by soaking in 10 wt % sulfuric acid for 12 h at room temperature. Afterward, the membranes were immersed for 24 h in distilled water which was changed several times. In the case of sPSS-661 prior to oxidation the films were casted from DMSO solutions (20 wt %, after filtration with 5 $\mu$m filter and degassing) onto glass plates and dried at 60 °C for 1 h, then 80 °C for 1 h, and finally 100 °C for 12 h. These membranes (10 × 10 cm) were oxidized in a bath of acetic acid with a small amount of concentrated sulfuric acid and 31% hydrogen peroxide (volume ratio: 400:20:10 mL) for 1−2 days at room temperature, while an accelerated oxidation succeeded at elevated temperature ($T = 60$ °C). After oxidation, the membranes were conditioned as described above. The thickness of the membranes was in the range 50−150 $\mu$m.

**Table 1. Ion Exchange Capacity (IEC) Determined by Titration, Molecular Weight $M_n$ and $M_w$, Polydispersity $D$, Maxima of Molecular Weight Distribution $M_{max}$, Density, and Solubility of Sulfonated Poly(phenylene sulfide sulfone)s sPSS and Sulfonated Poly(phenylene sulfone)s sPSO2**

| | IEC, mequiv g$^{-1}$ (theor) | $M_n$, g mol$^{-1}$<br>$M_w$, g mol$^{-1}$<br>$D$ | $M_{max}$, g mol$^{-1}$ | density, g cm$^{-3}$ dry polymer | solubility (H-form) |
|---|---|---|---|---|---|
| sPSS-312 ($n = 1.0$) | 3.12 (3.20) | 40780<br>165337<br>4.05 | 172707<br>7308 | 1.53 | water, methanol, NMP, DMAc, DMSO, DMF |
| sPSS-370 ($n = 0.8$) | 2.54 (2.70) | 15282929<br>8837<br>1.96 | 233415 | 1.48 | water, methanol, NMP, DMAc, DMSO, DMF |
| sPSS-661 ($n = 0.4$) | 1.47 (1.51) | 26231<br>72124<br>2.75 | 80469<br>4751 | 1.43 | NMP, DMAc, DMSO, DMF |
| sPSO2-360 ($n = 1.0$) | 2.64 (2.78) | 62448<br>141682<br>2.27 | 141638 | 1.69 | NMP, DMSO, slightly in DMF and DMAc |
| sPSO2-430 ($n = 0.8$) | 2.30 (2.32) | 44151<br>679752<br>15.4 | 162904<br>691255<br>1589890 | 1.66 | NMP, DMSO, slightly in DMF and DMAc |
| sPSO2-781 ($n = 0.4$) | 1.29 (1.28) | | | 1.55 | insoluble (swelling) |

**2.5. Characterization**. $^1$H and $^{13}$C NMR spectra were recorded at room temperature on a Bruker 300 MHz 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 20 °C/min. Prior to measurement, the samples were dried for 12 h at $T = 120$ °C. The densities of the dry polymers (H-form) were measured with an AccuPyc 1330 V2.01. IR spectra of thin films (H-form) were recorded using a Bruker IFS 66 IR-spectrometer. 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 K-form, except sPSO2-430 in H-form) were performed in DMF at $T = 60$ °C with an addition of LiBr (1 g/L). The injection volume was 50 $\mu$L. Thermogravimetric analysis (TGA) was carried out on a Netzsch STA 449 thermobalance with a heating rate of 2 K/min in a purge gas mixture of nitrogen and oxygen (80:20, 20 mL/min). The outlet with the released products was continuously analyzed by a Balzer Prisma quadrupol spectrometer. Only signals between $m/z = 1$ and 100 were detected. The oxidative stability was determined by soaking a membrane sample ($20 \times 10 \times 0.05 - 0.10$ mm) in 100 mL of Fenton's reagent (30 ppm $Fe^{2+}$ ions corresponding to 150 mg of $FeSO_4 \cdot 7H_2O$ in 1 L of 30% $H_2O_2$ solution) at $T = 25$ °C. The stability was tested by recording the time at which the film started to break into pieces and eventually dissolved completely. The water absorption behavior (hydrolytic stability) above $T = 100$ °C was 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 K/min. 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. The measurements were performed in a closed cell with preequilibrated samples (10−30 stacked slices of membranes with preadjusted water content, diameter ~ 6 mm, thickness 2−5 mm) with gold electrodes. 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 the membranes (10−20 stacked slices of membranes with 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 stack of membranes by a screw in order to ensure optimum contact. The specific conductivity was calculated using $\sigma = l/(AR)$, where $l$ is the distance between the electrodes, $A$ the area of the membrane slices, and $R$ the resistance derived from the high-frequency intercept of the complex impedance with the real axis. The proton diffusion coefficients $D_\sigma$ are obtained from conductivity data $\sigma$ using the Nernst−Einstein relation

$$D_\sigma = \frac{RT}{F^2}\frac{\sigma}{c(H^+)}$$

with $c(H^+)$ being the concentration of protonic charge carriers and $T$ the temperature, with $R$ and $F$ having their usual meaning. The ion exchange capacity (IEC, mequiv/g dry polymer) of the synthesized polymers was analyzed by NMR and titration. Water-soluble acidic polymers were dissolved in water or 1 M NaCl solutions and then titrated with 0.1 N NaOH; water-insoluble acidic polymers were immersed for 1 day in 1 M NaCl solution 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. Dynamic mechanical analysis (DMA) was performed on a Triton DMA analyzer (Tritec 2000) in liquid water at $T = 30$ °C with a maximum elongation of 0.02 mm at a frequency of 1 Hz (sample dimensions typically in the range of $3 \times 2 \times 0.05 - 0.15$ mm). The water uptake was obtained by measuring the weight difference of dry and hydrated membranes ($w_{dry} - w_{wet}$). Membranes (≈200 mg) were immersed in bidistilled water at different temperatures for 2 h. The liquid water on the surface of the wet membranes was quickly removed using tissue paper before weighing. Finally, the weight of the dry membrane was obtained by drying the membrane for 12 h at $T = 140$ °C in a vacuum oven.

## 3. Results and Discussion

Sulfonated poly(phenylene sulfide sulfone) polymers (sPSS) were synthesized as described in the literature[56−58,61−64] (see Scheme 2) by standard polycondensation reaction (nucleophilic aromatic substitution) of disodium 3,3′-disulfonate-4,4′-difluorodiphenylsulfone and 4,4′-difluorodiphenylsulfone with 4,4′-thiobisbenzenethiol (ratio 1:0:1 for polymer sPSS-312, ratio 8:2:10 for polymer sPSS-370, and ratio 4:6:10 for polymer sPSS-661; the numbers 312, 370, and 661 refer to the intended equivalent weight in g/mol). The polycondensation proceeds with $K_2CO_3$ in anhydrous NMP at $T = 175$ °C under inert atmosphere (water- and $O_2$-free) within ≈36 h. After precipitation in 2-propanol the obtained polymers were purified by

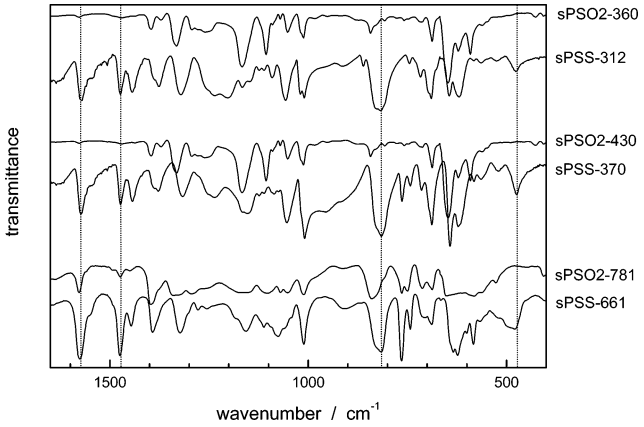



**Figure 1.** IR spectra of sulfonated poly(phenylene sulfide sulfone)s sPSS and sulfonated poly(phenylene sulfone)s sPSO2.

dialysis or in the case of the water-insoluble polymer sPSS-661 by thoroughly washing with distilled water. The yield was typically in the range of 90%. The brown (H-form) or purple (K-form) polymers are soluble in common polar aprotic solvents such as DMF, NMP, DMSO, and DMAc (see Table 1), but the solubility decreases with decreasing IEC. While polymers sPSS-312 and sPSS-370 in their protonic form are still soluble in water (after heating) and methanol, sPSS-661 is insoluble in water.

Oxidation of sulfonated poly(phenylene sulfide sulfone)s sPSS to sulfonated poly(phenylene sulfone)s sPSO2 succeeds by a heterogeneous reaction with hydrogen peroxide (stoichiometry $[H_2O_2]/[-S-] = 3$) in acetic acid with a small amount of sulfuric acid (stoichiometry $[H_2SO_4]/[H_2O_2] \approx 2$). The reaction proceeds quantitatively within 1−2 days at moderate temperatures (25−60 °C), yielding colorless polymers. The polymers were separated by filtration and purified in water by dialysis. The solubility of sPSO2 polymers decreases with decreasing ion exchange capacity and is generally significantly lower than the solubility of corresponding sPSS polymers. The polymers sPSO2-360 and sPSO2-430 in their protonic form are insoluble in water and methanol, only slightly soluble in DMF and DMAc, and soluble in DMSO and NMP (after heating at $T > 100$ °C for several hours). Although the solubility in DMSO and NMP is rather low, casting of membranes from solution is still possible. Membranes are transparent and colorless, tough, and flexible in the water-swollen form, while becoming somewhat brittle in the dry state. The polymer sPSO2-781 is virtually insoluble in all common solvents. However, membranes of sPSO2-781 were obtained by direct oxidation of sPSS-661 membranes in a bath of acetic acid with hydrogen peroxide and a small amount of sulfuric acid. Complete oxidation was indicated by the change of the color of the films from brown to colorless and by the disappearance of some IR bands, which are characteristic for structural building units being present in poly(*p*-phenylene sulfide),[76] e.g., at 478, 816, 1472, and to some extent at 1572 $cm^{-1}$ (see Figure 1). Attempts to oxidize sPSS polymers to polysulfone in aqueous acidic hydrogen peroxide solution failed and resulted most likely in the formation of sulfoxide (−SO−).

The structures of sPSS and sPSO2 polymers have been elucidated by $^1H$ and $^{13}C$ NMR spectroscopy. The $^1H$ NMR spectrum of sPSS-312 exhibits five signals (Figure 2), which can easily be assigned to the five chemically distinguishable aromatic protons: $\delta(H_A) = 8.20$, $\delta(H_C) = 7.68$, $\delta(H_D) = 7.56$, $\delta(H_E) = 7.48$, and $\delta(H_G) = 6.91$ ppm in the expected intensity ratio of 1:1:2:2:1. In the case of sPSS-370 ($n = 0.8$) and sPSS-661 ($n = 0.4$) two further signals appear at $\delta(H_B) = 7.8$ and $\delta(H_F) = 7.3$ ppm. The intensities $I_A$ and $I_B$ of the proton signals of $H_A$ and $H_B$ allow the determination of $n = 2I_A/(2I_A + I_B)$ and accordingly the determination of the IEC. For polymer sPSS-370 the intensities imply a stoichiometry of $n = 0.81$ close to the intended stoichiometry of $n = 0.8$. For sPSS-661 ($n = 0.4$) the derived stoichiometry is $n = 0.39$. $^1H$ NMR spectra of the oxidized polymers sPSO2-360 and sPSO2-430 confirm the quantitative conversion of the sulfide (−S−) to sulfone groups ($-SO_2-$). As a consequence of the strongly electron-withdrawing properties of the sulfone groups, the NMR signals of the aromatic protons are shifted to lower fields (deshielding effect). The position of the signals at low field between $\delta = 8.6$ and 8.0 ppm are in agreement with $^1H$ NMR resonances reported for cyclic oligomers of poly(*p*-phenylene sulfone)[65] ($\delta = 8.2-8.0$ ppm). The intensities of the signals match well with the targeted sPSO2 structures. As shown in Figure 3, totally different $^{13}C$ NMR spectra of sPSO2-360 and sPSS-312 once again confirm the complete conversion of the sulfide groups to sulfone groups. The $^{13}C$ NMR spectrum of sPSS-312 ($n = 1.0$) is expected to exhibit 10 singlets; however, only 9 NMR signals are distinguishable, indicating two overlapping signals. The number of $^{13}C$ NMR signals of sPSO2-360 ($n = 1$) is even reduced to 8, which is most likely due to the increased chemical similarity and the higher molecular symmetry.

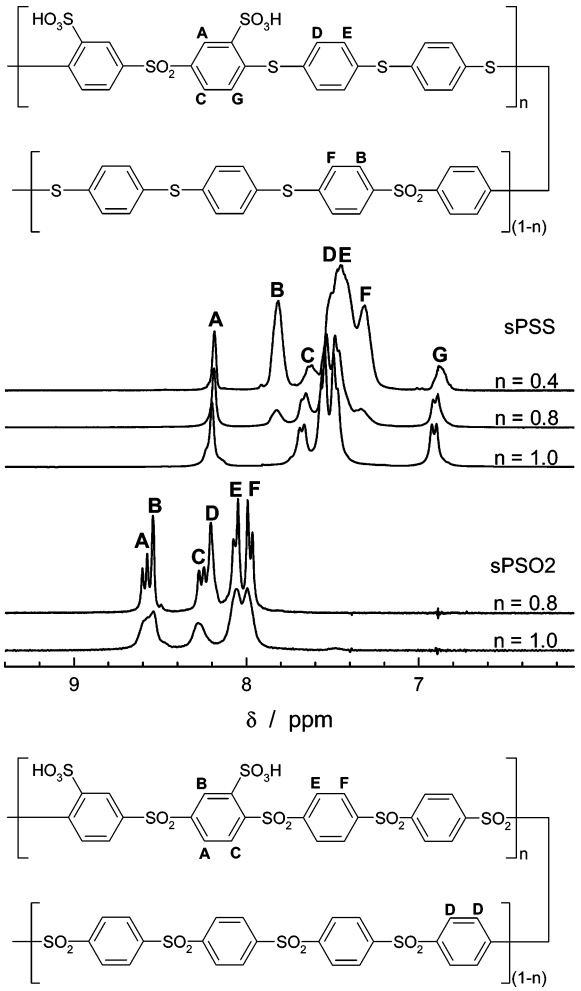



**Figure 2.** $^1H$ NMR spectra of sulfonated poly(phenylene sulfide sulfone)s sPSS (top) and sulfonated poly(phenylene sulfone)s sPSO2 (bottom) in DMSO. Polymer sPSO2-781 ($n = 0.4$) is inaccessible for NMR because of its insolubility.

In order to obtain information about the molecular weight, GPC measurements of the sodium/potassium salts of the

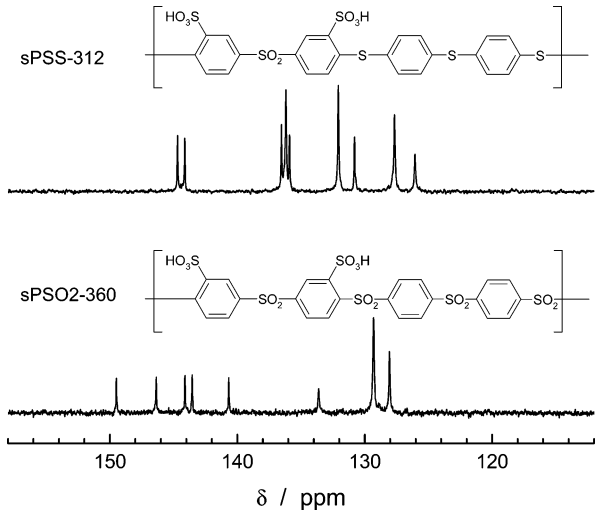



**Figure 3.** $^{13}C$ NMR spectra of sulfonated poly(phenylene sulfide sulfone) sPSS-312 (top) and sulfonated poly(phenylene sulfone) sPSO2-360 (bottom) in DMSO.

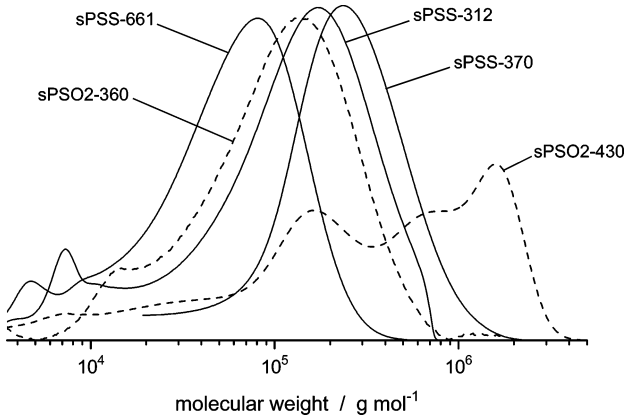



**Figure 4.** GPC profiles of sulfonated poly(phenylene sulfide sulfone)s sPSS and sulfonated poly(phenylene sulfone)s sPSO2 in DMF at $T = 60$ °C with LiBr addition (1 g/L), relative to polystyrene standard. Polymer sPSO2-781 ($n = 0.4$) is inaccessible for GPC because of its insolubility.

polymers in DMF at 60 °C have been performed. LiBr was added (1 g/L) to suppress the polyelectrolyte effect. Although these highly charged polyelectrolytes still adsorb on the GPC column, which complicates precise measurements, at least a rough estimate about the molecular weight was possible (see Figure 4 and Table 1). While in the case of polymer sPSS-370 a high molecular weight polymer with an almost perfect GPC profile was obtained (monomodal distribution with $M_{max} \approx 233\,400$ g/mol), for sPSS-312 and sPSS-661 the molecular weight maxima ($M_{max} \approx 172\,700$ and 80 500 g/mol, respectively) are lower, and even small amounts of low molecular components ($M \approx 5000-10\,000$ g/mol) have been detected, indicating slight deviations from ideal progress of the polycondensation reaction. As mentioned above, the oxidation of sPSS to sPSO2 polymers drastically reduces the solubility in DMF, which even impairs accurate GPC measurements. GPC data could not be recorded for sPSO2-781 because of its complete insolubility in DMF, polymers sPSO2-360 and sPSO2-430 are slightly soluble in DMF, and after filtration GPC data of the filtrate could be acquired. But the fact that for sPSO2-360 and sPSO2-430 no significant decrease of molecular weight is detected indicates no severe main-chain cleavages occurring during oxidation. The apparent increasing molecular weight in the case of sPSO2-430 could be the result of a slight chemical

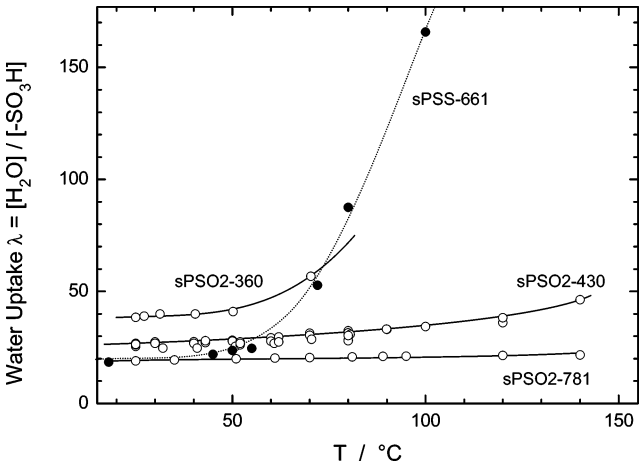



**Figure 5.** Water uptake $\lambda$ (expressed in number of water molecules per sulfonic acid group) in liquid water as a function of temperature. The corresponding polymers sPSS-312 and sPSS-370 are water-soluble at room temperature.

cross-linking of the polymer by oxidation (which is in fact not substantiated by NMR), but it also could simply reflect the lower solubility of the polymer in DMF and/or the presence of aggregated structures[77] (sPSO2-430 was measured in H-form, and the K-form was virtually insoluble in DMF); i.e., chemical cross-linking cannot be excluded completely.

The ion exchange capacities of sPSS and sPSO2 polymers determined by titration are close to the theoretical values (see Table 1, IEC were corrected by the remaining water which has been determined by NMR) and are in good agreement with the results from the analysis of the $^1H$ NMR intensities.

The molecular weight and the ion exchange capacity also show up in the film forming and swelling properties of the polymers; in other words, high ion exchange capacities lead to high swelling or even solubility, while high molecular weights reduce swelling and support good film forming properties. Although polymers sPSO2-360 and sPSO2-430 possess very high ion exchange capacities, both polymers in their protonic forms do not dissolve in water, while their nonoxidized pendants are soluble in water. Unlike the detrimental swelling behavior of sPSS-661 (see Figure 5) or sulfonated poly(ether ketone)s sPEEK[3] in water at elevated temperatures ($T > 70$ °C), the water uptake of the corresponding sPSO2 membranes remains almost constant up to $T = 140$ °C (Figure 5 and Table 2), even though more water per sulfonic acid group is absorbed at room temperature ($\lambda \approx 19-27$ $H_2O/SO_3H$ compared to $\lambda \approx 18$ $H_2O/SO_3H$ for sPSS-661). The low solubility of sPSO2 polymers may be the consequence of crystallinity (physical cross-linking) as discussed above. Because of the presence of low molecular weight components in polymer sPSO2-360, the mechanical strength of the film was not sufficiently high to prevent excessive swelling in water at room temperature ($\lambda \approx 37$) and even destruction of the film at temperatures higher than $T = 80$ °C (see Figure 5). The lower mechanical strength of sPSO2-360 membrane also shows up in the low storage modulus of $E' = 16$ MPa, determined by dynamic-mechanical analysis (DMA) in water at $T = 30$ °C, in contrast to higher storage moduli of sPSO2-430 (65 MPa) and sPSO2-781 (416 MPa) membranes (see Table 2).

The oxidative stability of sPSO2 polymers as examined by Fenton's test (30 ppm $Fe^{2+}$ ions in 30% $H_2O_2$ solution at $T = 25$ °C) appears to fall into a narrow range; i.e., it is almost independent of the IEC. The sPSO2-781 membrane (thickness 70 $\mu$m) lost its integrity after 60 h and was completely dissolved

**Table 2. Proton Conductivity, Water Uptake (wt % and $\lambda = [H_2O]/[-SO_3H]$), Water Volume Fraction $\Phi$, Concentration of Protonic Charge Carriers $c(H^+)$, Proton Diffusion Coefficient $D_\sigma$, Storage Modulus $E'$ [MPa], and Loss Tangent Tan $\delta$ of Sulfonated Poly(phenylene sulfone)s sPSO2 in Liquid Water at $T = 30$ °C**

| | $\sigma$, mS cm$^{-1}$ | wt %[a] | $\lambda$[b] | $\Phi$[c] | $c(H^+)$, mol L$^{-1}$ | $D_\sigma$, cm$^2$ s$^{-1}$ | $E'$, MPa | tan $\delta$ |
|---|---|---|---|---|---|---|---|---|
| sPSO2-360 ($n = 1.0$) | 169 | 185 | 37.0 | 0.76 | 1.14 | $3.98 \times 10^{-5}$ | 16 | 0.13 |
| sPSO2-430 ($n = 0.8$) | 129 | 115 | 27.5 | 0.66 | 1.33 | $2.61 \times 10^{-5}$ | 65 | 0.15 |
| sPSO2-781 ($n = 0.4$) | 62 | 44 | 19.1 | 0.41 | 1.18 | $1.41 \times 10^{-5}$ | 416 | 0.16 |

[a] The water uptake is calculated by wt % $= 100 \times (w_{wet} - w_{dry})/w_{dry}$. [b] The number of water molecules per sulfonic acid is given by $\lambda = [(w_{wet} - w_{dry})EW]/w_{dry}M_{H_2O}$. [c] The water volume fraction is given by $\Phi = (M_{H_2O}/\rho_{H_2O})/[(M_{H_2O}/\rho_{H_2O}) + (EW/\lambda\ \rho_{ionomer})]$, where $EW$ and $\rho_{ionomer}$ are the equivalent weight and density of the polymer and $M_{H_2O}$ and $\rho_{H_2O}$ are the molecular weight and density of water.

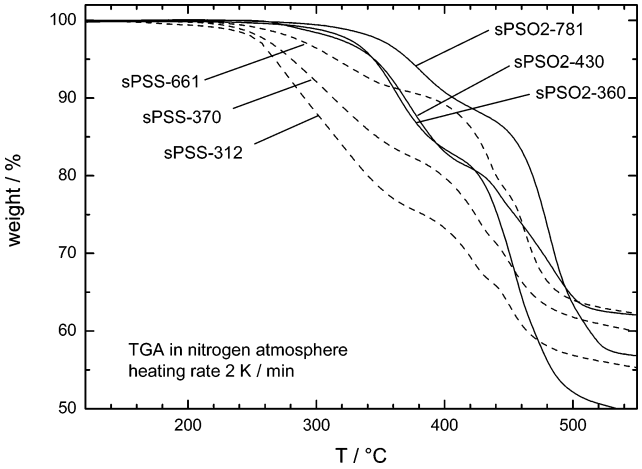



**Figure 6.** TGA in a nitrogen atmosphere of sulfonated poly(phenylene sulfide sulfone)s sPSS and sulfonated poly(phenylene sulfone)s sPSO2; heating rate 2 K/min.

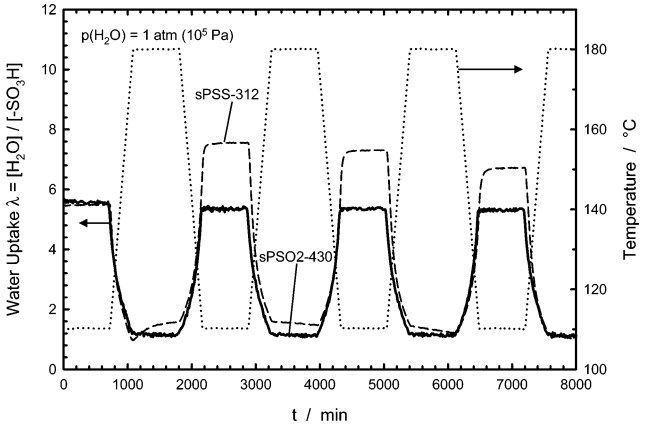



**Figure 7.** TGA in complete water atmosphere ($p(H_2O) = 1 \times 10^5$ Pa) of sulfonated poly(phenylene sulfide sulfone) sPSS-312 and sulfonated poly(phenylene sulfone) sPSO2-430.

after 105 h. The high-IEC polymers sPSO2-430 and sPSO2-360 (thickness 100 $\mu$m) started to disintegrate after 80 h and were completely dissolved after 135 h. These results indicate an excellent oxidative stability considering the fact that the corresponding sulfonated poly(phenylene sulfide sulfone) sPSS-661 membrane (thickness 50 $\mu$m) already commenced to decompose after 35 h, and dissolution was completed after 53 h. This observation also suggests that oxidation and destruction of poly(phenylene sulfide sulfone) membranes by Fenton's reagent does not proceed via poly(phenylene sulfone)s.

The thermal and thermooxidative stability of sulfonated poly(phenylene sulfone)s sPSO2, as examined by TGA/MS (2 K/min) in nitrogen and air atmosphere, is significantly enhanced compared to the stability of corresponding sulfonated poly(phenylene sulfide sulfone)s sPSS (Figure 6 in a nitrogen atmosphere). The decomposition reaction of sPSS commences below $T = 250$ °C, while for sPSO2 this reaction starts around $T = 300$ °C. In both cases a two-step decomposition process is observed, accompanied by the detection of SO ($m/z = 48$) and $SO_2$ ($m/z = 64$) species in the mass spectrometer. Most likely the first step is due to the cleavage of the $-SO_3H$ group from the polymer backbone, while the second step is the decomposition of the polymer backbone itself. Apparently, the stability increases with decreasing IEC. No significant difference has been detected in nitrogen and air (the curves in air are virtually identical up to $T = 450$ °C, hence not shown).

Differential scanning calorimetry (DSC) did not show any glass transition or melting up to about $T = 300$ °C, which is not unexpected considering the very high melting point ($T_m >$ 500 °C) of unsulfonated poly(*p*-phenylene sulfone).[15] Above $T = 300$ °C an exothermic reaction starts occurring, which is most likely a signature of the cleavage of the bond between the sulfonic acid group and the aromatic ring (see also TGA/MS measurements).

The water absorption behavior and the hydrolytic stability of the polymers have been determined by cycled TGA measurements between $T = 110$ and 180 °C in an all water atmosphere ($p(H_2O) = 10^5$ 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. Only sulfonated poly(phenylene sulfone)s are stable under these high temperature and high water activity conditions (Figure 7). Polymers containing sulfide bridges ($-S-$) show an ascending weight baseline during the first cycle, indicating an increased water uptake. The reason may be the formation of sulfuric acid, which is even more hygroscopic than the corresponding sulfonic acid-based polymer.

Although sPSO2 shows the typical conductivity behavior of a sulfonated poly(arylene) ionomer, the low solubility even at high IEC renders possible the formation of membranes with a conductivity higher than that of Nafion 117. This is probably the result of some ordering or even crystallization, which is well-known to occur in poly(*p*-phenylene sulfone)s and which is held responsible for the extremely low solubility of this class of polymers.[13−18] The room temperature proton conductivity as a function of the water content is actually higher than for sulfonated poly(ether ketone)s of similar IEC (compare the conductivity of sPSO2-781 and sPEEKK-685 in Figure 8), and higher IECs lead to a further increase of the conductivity, which finally exceeds that of Nafion 117 in the case of sPSO2-430 and sPSO2-360 (Figure 8 and Table 2). For sPSO2-360 the conductivity as a function of the water content passes through a maximum at a conductivity of 169 mS cm$^{-1}$. The decreasing conductivity for very high degrees of swelling is simply the consequence of the charge carrier dilution.

Note that in Figure 8 the water content is given in units of $\lambda = [H_2O]/[-SO_3H]$; i.e., the total water content (water volume fraction) increases with increasing IEC for a given value of $\lambda$. Indeed, the increasing conductivity with increasing IEC is solely a consequence of the increasing total water content improving

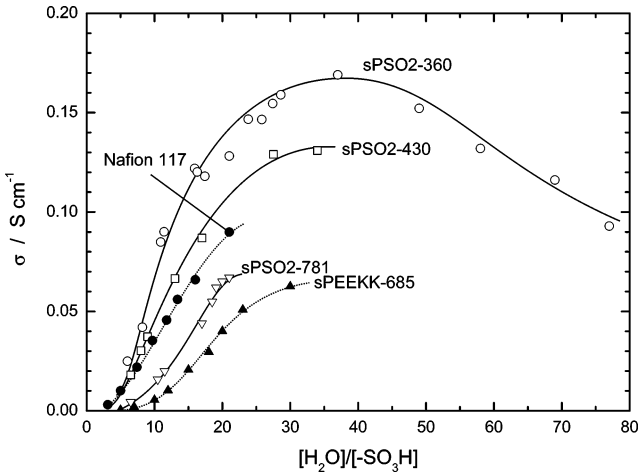



**Figure 8.** Proton conductivity at $T = 30$ °C as a function of water content. The conductivity of Nafion 117 (EW = 1100 g/mol) and sPEEKK (EW = 685 g/mol) is given for comparison.

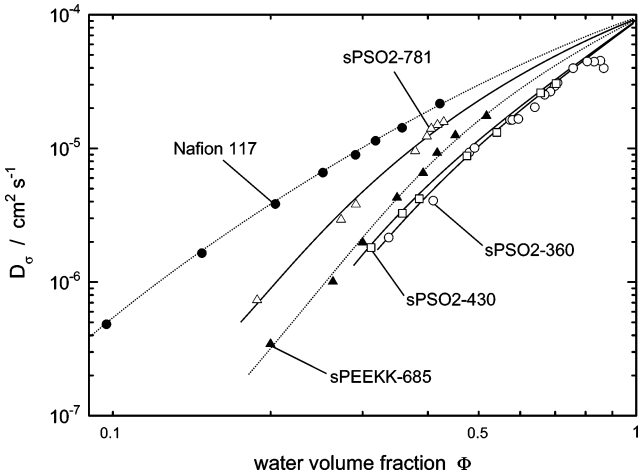



**Figure 9.** Proton diffusion coefficient $D_\sigma$ (proton mobility) as a function of water volume fraction at $T = 30$ °C. The proton diffusion coefficients were calculated from conductivity data by using the Nernst−Einstein relation.

the percolation within the hydrated hydrophilic domain. For a given water volume fraction, i.e., for a similar geometric percolation of the hydrophilic domain, the proton diffusion coefficient $D_\sigma$ (mobility of protonic defects, calculated from conductivity data by using the Nernst−Einstein relation) even decreases with increasing IEC (Figure 9 and Table 2). This is expected because the water is involved in the solvation of an increasing concentration of immobilized sulfonic acid groups, retarding the local diffusion of water and therefore also the mobility of protonic charge carriers.[3,4] It is worth mentioning that the proton diffusion coefficient of sPEEKK-685 (an ionomer with similar volumetric charge carrier concentration as of sPSO2-781 and Nafion 117, see Table 2) is slightly lower than this of sPSO2-781, suggesting some microstructural differences for these two types of sulfonated poly(arylene)s.

For the use of such ionomers as membrane material in fuel cells, the proton conductivity as a function of relative humidity is the most relevant datum. This has been varied by changing the temperature of an all water atmosphere ($p(H_2O) = 10^5$ Pa) within a range of $T = 100-160$ °C, corresponding to relative humidities of 100−16%. Conductivities under these conditions are shown in Figure 10, and again the conductivity of sPSO2-360 is higher, that of sPSO2-781 lower, and the conductivity of sPSO2-430 virtually coincides with the conductivity of Nafion 117. According to above discussion, this

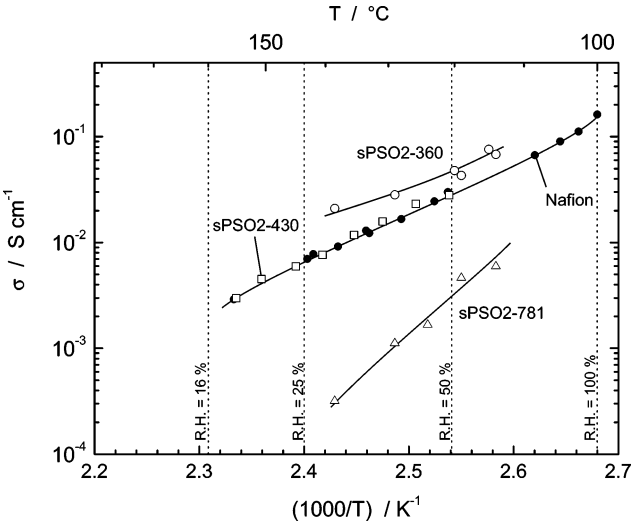



**Figure 10.** Proton conductivity in an all water atmosphere ($p(H_2O) = 1 \times 10^5$ Pa) as a function of temperature. The conductivity of Nafion 117 is given for comparison. The dotted lines indicate the corresponding relative humidities (RH) of 100−16%.

trend is simply the result of the increasing water volume fraction with increasing IEC.

## 4. Conclusion

For the first time, sulfonated poly(arylene) ionomers containing merely sulfone units (−$SO_2$−) have been synthesized. The preparation of the copolymers succeeds by a two-step process comprising (1) a nucleophilic aromatic polycondensation reaction of 4,4′-difluorodiphenylsulfone and disodium 3,3′-disulfonate-4,4′-difluorodiphenylsulfone with 4,4′-thiobisbenzenethiol resulting in sulfonated poly(phenylene sulfide sulfone)s and (2) their subsequent oxidation to sulfonated poly(phenylene sulfone)s using peroxide in acidic solution. This new class of polymers with extremely electron-deficient aromatic rings shows very high thermal, thermooxidative and hydrolytic stability. Their lower solubility and degree of swelling in water compared to other sulfonated poly(arylene)s allow for the preparation of membranes with high ion exchange capacity and high proton conductivity. The flexible preparation route provides a path for obtaining various molecular structures and ion exchange capacities. Microstructural studies (by XRD and SAXS), the characterization of mechanical properties, and testing of membranes under fuel cell operating conditions are underway.

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