Partially Fluorinated Sulfonated Poly(arylene sulfone)s Blended with Polybenzimidazole

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ABSTRACT: A partially fluorinated and sulfonated poly(arylene sulfone) (SPSO) was successfully synthesized via nucleophilic polycondensation of 2,2-bis(4-fluorophenyl)hexafluoro-propane with 4,4'-thiobisbenzenethiol (TBBT). In a second step, the prepared poly(arylene sulfide) was oxidized to SPSO. The polymer was blended with the polybenzimidazole PBIOO[®] to obtain a mechanically stable membrane. This film was compared with other polymer blends, which were synthesized in our group in the last years. We were especially interested in the influence of different bridging groups such as ether, ketone, and sulfone groups. The affect on properties such as water uptake (WU), thermal stability, proton conductivity, and oxidative stability were analyzed in this work. Additionally, the blend membranes were characterized by gel permeation chromatography. The novel SPSO blend shows a high molecular weight, and its blend membrane with PBIOO has an excellent onset of $-SO_3H$ group splitting-off temperature ($T_{SO_3H,onset}$) of 334 °C. The proton conductivity amounts to 0.11 S cm⁻¹, and the water uptake reaches 30%. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 1919–1927, 2011

KEYWORDS: blends, crosslinking; gel permeation chromatography (GPC); ionical crosslinking; PBIOO[®]; sulfonated poly(arylene sulfone)s

INTRODUCTION Sulfonated arylene main chain ionomers show the best chemical stabilities next to the perfluorinated ionomers. A huge amount of different types of sulfonated arylene main chain ionomers has been developed in the last decades as potential substitutes for the perfluorinated ionomers in electrochemical applications, particularly in membrane fuel cells, including poly(phenylene)s,^{1,2} poly (ether sulfone)s,³⁻⁵ poly(ether ketone)s,⁶⁻⁹ poly(phenylene oxide)s,^{10,11} partially fluorinated poly(phenylene ether)s,^{12,13} poly(phenylene sulfide)s,14 poly(phenylene phosphine oxide ether)s,15 poly(thioether sulfone)s,16 poly(arylene thioether ketone sulfone)s,¹⁷ poly(sulfone)s by oxidation of the poly (thioether sulfone)s,¹⁸ and poly(thioether ketone)s.¹⁹ In our group, we have synthesized many different types of these polymers in the last years, among them nonfluorinated and partially fluorinated poly(ether)s, poly(ether sulfone)s, poly (ether ketone)s, and poly(ether phosphine oxide)s.^{13,20-22} When comparing the nonfluorinated sulfonated arylene main chain ionomers with those which are partially fluorinated, we found that the partially fluorinated ionomer types show better chemical stabilities compared to the nonfluorinated ones.²³ This can be attributed to the higher bond energy of C-F bonds, compared to C-H bonds,^{24,25} and to the strong -I effect of the F bond to the polymer, leading to a decrease of the electron density of the aromatic building blocks, which results in a good polymer stability against ipso desulfonation and against attack of electrophilic radicals such as the OH-

radical. Another positive effect of electron-deficient aromatic polymer building blocks-bearing sulfonic acid groups is their higher acidity, which leads to a higher dissociation degree of the pendent SO₃H group, which is associated with high proton conductivity. From the investigations of the different polymer types prepared in our group, we found that their mechanical and radical stabilities were not as good as desired. Particularly, when having a high content in proton conducting SO₃H groups, the polymers were very brittle and even dissolved in water at ion-exchange capacities (IECs) of higher than 2- to 2.5-meq SO₃H g⁻¹ polymer. Moreover, the radical stability, namely, of the nonfluorinated arylene main chain ionomers was not satisfying.

We achieved further improvement of the chemical and the mechanical stabilities of arylene main chain ionomer membranes by ionical crosslinking of the sulfonated ionomers via blending with a stable basic polymer such as polybenzimidazole (PBIOO)[®], in which the imidazole groups of PBIOO are protonated by acid-base reaction with $-SO_3H$ groups, forming [ImidazoleH⁺] [SO₃⁻] crosslinking sites.^{26–35} As a matter of fact, a part of the $-SO_3H$ groups of the arylene ionomers is sacrificed by the ionical crosslinking, leading to a reduction of the proton conductivity of the formed blend membrane, compared to the pure polymer. Therefore, the sulfonated ionomer must have a sufficient SO_3H content to be suitable for use in ionical crosslinking reactions. By using an ionical crosslinker such as PBI, the oxidative and thermal

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stability of the respective acid-base blend membrane is increased.¹³ This enhancement of stability of an ionically crosslinked blend membrane can be explained as follows: when individual polymer chains within the blend membrane are suffering from degradation, they cannot leave the membrane matrix because of the ionical crosslinks, which retains them in the membrane matrix. Therefore, membranes comprising a stable crosslinking network show a better oxidative and thermal stability than membranes without a network. Consequently, it requires more time until a membrane, which contains a crosslinking network, is deteriorated.

Apart from ionical crosslinking with basic polymers, the chemical stability of arylene main chain ionomers can be improved by avoidance of -0-, alkyl, and =C=0 bridges in the arylene main chain, which are preferred sites for radical,^{23,36,37} and/or nucleophile attack.^{23,38} Schuster et al.¹⁸ have shown that sulfonated polysulfone, which does not contain any of the aforementioned radical attack-sensitive groups but solely consists of repeating units $-(-S(0)_2)^{-3}$ sulfo-1,4-phenylene-, comprises excellent hydrolysis (e.g., high stability against splitting-off of the sulfonic acid group via ipso reaction) and radical stability.³⁹⁻⁴¹ They have explained these findings with the electron-attracting capability of the sulfone bridge by their -I and the -M effect, which strongly lowers the electron density in the aromatic building blocks of the polymer. Moreover, this polymer shows excellent proton conductivities (factor 5–7 higher than Nafion[®], even at low relative humidities).⁴¹ However, a disadvantage of this polymer is its brittleness (if every second aromatic ring of the polymer is sulfonated) or even water solubility (if every aromatic ring of the polymer is sulfonated), which makes the application of this polymer to membrane fuel cells questionable or, in the case of the water-soluble polymer, impossible. There are different possibilities to overcome the mentioned disadvantages of the reported sulfonated poly (sulfone)s: one is to blend the highly sulfonated/water-soluble polymer with a basic polymer such as polybenzimidazole (PBI) to generate water insoluble ionically crosslinked membranes as mentioned above. The membrane properties are tunable in a wide range by variation of the amount of the basic PBI component in the blend membrane. Another possibility to improve, particularly, the mechanical properties of the membranes is to introduce flexible groups into the poly(sulfone) backbone, which lower the membrane brittleness and the water affinity of the polymer. One possible bridging group to fulfill this objective is the extremely hydrophobic hexafluoroisopropylidene group $-C(CF_3)_2$, which is more flexible than the sulfone group and decreases the polymer's water affinity due to its higher hydrophobicity.

On the basis of this concept, we decided to develop a sulfonated poly(sulfone) in which some of the sulfone bridges are substituted by hexafluoroisopropylidene bridges to increase the mechanical flexibility of the ionomer.

We have synthesized a novel sulfonated poly(phenylene sulfone) in which every fourth sulfone bridge was substituted by a hexafluoroisopropylidene group by the polycondensation of a novel monomer, 2,2-bis(4-fluoro-3-sulfonatophenyl)hexafluoropropane with TBBT, followed by oxidation using a H_2O_2/CH_3COOH mixture. The procedure for the polycondensation is presented in Figure 1. The obtained high molecular partially fluorinated poly(sulfone) was blended in a second step with PBIO0 to fine tailor the membrane properties. The synthesis and characterization of the novel polymer and blend membrane are reported in this contribution for the first time. Furthermore, the polymer was compared to three different polymers that have been synthesized in the past by our group. We reported about a partially fluorinated sulfonated poly(arylene ether) (SFS), a sulfonated poly(arylene ether sulfone) (SPSU) and a sulfonated poly(arylene ether ketone) in several publications.^{13,20,21,26,42} All polymers, which are discussed in this contribution are shown in Figure 2.

EXPERIMENTAL

Materials

2,2-Bis(4-aminophenyl)hexafluoropropane from ABCR and N,N-dimethylacetamid (DMAc) from Aldrich were used as received. Thiobisbenzenethiol (TBBT) and anhydrous potassium carbonate were also purchased at Aldrich and dried at 80 °C in a vacuum oven (100 mbar) for 20 h before use. The sulfonated monomer, which was prepared in our laboratory, was dried at 50 °C in a vacuum oven (100 mbar) for 20 h before use. Fumion[®] PBIOO was purchased from Fuma-Tech.

2,2-Bis(4-fluorophenyl)hexafluoropropane (M1)

The preparation of 2,2-bis(4-fluorophenyl)hexafluoropropane has already been described earlier by Lau and Dougherty.⁴³ Our group changed some of the reaction conditions, which resulted in better yields.

2,2-Bis(4-aminophenyl)hexafluoropropane (20 g, 59.83 mmol) was mixed with a 48 wt % tetrafluoroboric acid solution (70 mL). After cooling down to 0 °C, sodium nitrite (16.51 g, 239.33 mmol) in water (60 mL) was added dropwise during 30 min. After stirring for 30 min at 0 °C, the light yellow solid was filtered and washed with cold water. The bisdiazonium salt was dried in a desiccator at room temperature for 24 h. The dry component was dissolved in 300-mL anhydrous toluene, stirred 1 h at 90 °C, and, subsequently, 2 h at 120 °C. After cooling down to room temperature, the solution was washed with water, saturated sodium hydrogen carbonate, and finally sodium chloride. To isolate the product fractional vacuum distillation was used.

M1 (3.3 × 10⁻² mbar, 65–75 °C). Yield: 15.22 g (74.76%).



 $\delta_{\rm H}$ (200 MHz; CDCl₃) 7.06 (m, H-2), 7.35 (m, H-3); $\delta_{\rm C}$ (100 MHz; CDCl3) 64.15 (quintet, *J* = 25.62 Hz, C-5), 115.81 (d, *J* =



FIGURE 1 Polycondensation of 2, 2-bis(4-fluoro-3-sulfonatophenyl)-hexafluoropropane with TBBT, followed by oxidation with H_2O_2/CH_3COOH .

21.80 Hz, C-2), 124.42 (q, J = 286.82 Hz, C-6), 129.51 (s, C-4), 132.48 (m, C-3), 163.25 (d, J = 250.49 Hz, C-1); $\delta_{\rm F}$ (200 MHz; CDCl3) –112.10 (m, F-1), –64.38 (s, F-6).

M2

The monomer **M1** was sulfonated using fuming sulfuric acid (30% SO₃) as described in the following. To **M1** (10 g, 29.39 mmol), fuming sulfuric acid (24 mL) were added. The solution was stirred 4.5 h at 110 °C and 2.5 h at 120 °C. After cooling down to room temperature, the brown solution was slowly poured into 500 mL of ice water. Some sodium chloride was added until all product precipitated. After filtering, the product was redissolved in water and the pH of the solution adjusted with sodium hydroxide to pH 7. The product was filtered off. After drying at 50 °C in a vacuum oven (100 mbar) there was no more purification needed. Yield: 12.66 g (86.09%).



 $δ_{\rm H}$ (400 MHz; CDCl₃) 7.31 (m, H-2 + H-3), 7.83 (d, J = 4.96 Hz, H-7); $δ_{\rm C}$ (100 MHz; CDCl₃) 63.59 (quintet, J = 26.00 Hz, C-5), 117.31 (d, J = 23.52 Hz, C-2), 124.17 (q, J = 287.11 Hz, C-6), 127.44 (s, C-8), 130.42 (s, C-4), 132.95 (s, C-7), 135.75 (d, J17.59 Hz, C-3), 159.22 (d, J = 254.31 Hz, C-1); $δ_{\rm F}$ (200 MHz; CDCl₃) -109.67 (m, F-1), -63.76 (s, F-6).

SPT

M2 (5.99 mmol) and 4,4'-TBBT (5.99 mmol) were loaded into a 100-mL three-neck flask equipped with an argon inlet, a reflux

condenser and a mechanical stirrer. N-methylpyrrolidone (NMP) (40 mL) was added and after dissolving, potassium carbonate (47.97 mmol) was added to the solution. After stirring at 180 °C for 24 h, the solution was cooled down to room temperature and poured into 1 L of isopropanol to precipitate the polymer. After filtration and washing with several portions of isopropanol, the polymer was redissolved in water, dialyzed for 3 days, and dried at 80 °C for three more days. Yield: 4.04 g (94.96%).



 $δ_{\rm H}$ (400 MHz; DMSO) 7.86 (s, H-9), 7.52 (d, J = 8.16 Hz, H-3), 7.47 (d, J = 7.93 Hz, H-2), 7.1 (d, J = 7.63 Hz, H-7), 6.82 (d, J = 8.55 Hz, H-6); $δ_{\rm C}$ (100 MHz; DMSO) 145.56 (C-10), 139.19 (C-5), 136.81 (C-8), 136.32 (C-3), 132,92 (C-2), 131.1 (C-6), 129.7 (C-9), 128.92 (1 + 4), 128.28 (C-7); $δ_{\rm F}$ (200 MHz; DMSO) -58.66 (F-12). C-11 and C-12 could not be detected because of their splitting and low intensity.

SPSO

SPT (4.22 mmol) was dissolved in acetic acid (60 mL) and water (30 mL). Hydrogen peroxide (12 mL) and sulfuric acid (2 mL) were added, and the brown mixture was stirred for 16 h at 80 $^{\circ}$ C. After cooling down to room temperature, the



FIGURE 2 Polymers investigated in this report.

yellow solution was dialyzed 3 days and dried at 60 $^{\circ}$ C for three more days. Yield: 1.88 g (55.22%).



 $δ_{\rm H}$ (400 MHz; DMSO) 8.49 (d, J = 8.39 Hz, H-6), 8.33 (s, H-9), 8.18 (d, J = 8.01 Hz, H-2), 8.10 (d, J = 8.09 Hz, H-3), 7.61 (d, J = 7.71 Hz, H-7); $δ_{\rm C}$ (100 MHz; DMSO) 148.46 (C-10), 147.03 (C-4), 143.73 (C-1), 137.49 (C-5), 137.08 (C-8), 132.35 (C-6), 131.87 (C-7), 131,47 (C-9), 129.60 (C-3), 128.27 (C-2); $δ_{\rm F}$ (200 MHz; DMSO): -58.32 (F-12).

Blend Membrane Preparation

The composition of the membrane solution is usually calculated from the IEC value of the acidic and the basic components.²² The acidic polymer was dissolved in DMAc (10 wt %) and neutralized with *n*-propylamine. The calculated amount of PBIOO in DMAc was added and, after stirring, the solution was casted on a glass plate and dried at 50 °C. To obtain their SO₃H form, all membranes were soaked in 0.5 N H_2SO_4 for 2 h at 100 °C and washed with water for further 2 h at 100 °C.

Polymer and Membrane Characterization Molecular Weight Determination via GPC (SEC)

The molecular weight distributions (MWDs) of the polymers and of the blend membranes were determined by GPC, which was performed at 50 °C on a polymer standards service (PSS) system equipped with Agilent 1200 series refractive index detector, PSS SLD 7000 multiangle-lightscattering detector and a ETA2010 viscometer detector, PSS 30 and 3000 Å columns, and Agilent 1200 series pump using polystyrene standards for calibration. Eluent DMAc containing 5 wt % LiBr was used to increase the solubility of the ionic polymer and to reduce the interaction between solutes and packing materials. The blend membrane and polymer solutions were injected with a concentration of 2 g L⁻¹. The obtained curves were integrated to ascertain the MWD of the polymers and blend membranes.

Structure Analysis

To characterize the structure of the novel monomers and polymers, NMR spectra were measured on a Bruker Avance 400 spectrometer, and IR spectra were detected on a Nicolet 6700 FTIR instrument.

Ion-Exchange Capacity

The IEC describes the amount of ion-exchange groups per weight unit of dry ion-exchange resin in meq g^{-1} or mmol g^{-1} . Membranes in protonated form were dried at 90 °C for 24 h and weighed. After this, the membranes were immersed in saturated sodium chloride solution (NaCl) for 24 h to replace the protons of the sulfonic acid groups with sodium ions. The exchanged and delivered protons were then determined by titration with 0.1 M NaOH to the equivalent point

(IEC_{direct}). After that, an excess of NaOH was added, and this solution was then back titrated with 0.1 M HCl to obtain the $\rm IEC_{total}.$

Specific Resistance

The specific resistance of the membranes was determined via impedance spectroscopy using a Zahner elektrik IM6 impedance spectrometer. The samples were measured in through plane mode in a frequency range of 200 KHz to 2 MHz and with amplitude of 5 mV. We used 0.5 N H_2SO_4 for the measurements to achieve better reproducibility in the measured values, compared to measurements in water.

Thermal Stability

The thermal stabilities of the blend membranes were determined by thermogravimetry (TGA, Netzsch, model STA 449C) with a heating rate of 20 °C min⁻¹ under a 65–70% O_2 atmosphere. The sulfonated polymers and blend membranes have been investigated by TGA-FTIR coupling (Nicolet Nexus FTIR spectrometer) to ascertain the onset of the SO₃H group splitting-off temperature (T_{SO₂H,onset}).

Water Uptake

The water uptake (WU) of the samples was determined after equilibration in water of defined temperatures. The weight of the wet and the dry membrane (drying at 90 $^{\circ}$ C) was measured, and the WU was calculated using the following formula:

WU [%] =
$$\frac{m_{\rm wet} - m_{\rm dry}}{m_{\rm dry}}$$

Oxidative Stability

The oxidative stability of the membranes was determined with H_2O_2 oxidation tests. The membrane samples were dried and weighed, followed by equilibration in 5 wt % H_2O_2 solution. After specified times of 6, 24, and 48 h at 60 °C, the samples were removed from the oxidizing solution, washed with water, dried, and weighed a second time to calculate the weight loss caused by the H_2O_2 treatment. Moreover, the degradation of all samples was measured via gel permeation chromatography (GPC).

RESULTS AND DISCUSSION

Polycondensation and Oxidation Reactions

The successful synthesis of SPT was performed via polycondensation using 4,4'-TBBT and the self produced monomer **M2**. In the presence of K_2CO_3 and NMP, the reaction required 24 h at 180 °C. The monomer concentration was around 10 wt %. An excess of K_2CO_3 was necessary to react with water traces, which are present in the reaction mixture. The reaction of SPT to SPSO succeeded by applying an oxidation route using hydrogen peroxide, acetic acid and, as a catalytic component, sulfuric acid. After 16 h, the whole SPT was converted into SPSO. The advancement of the oxidation was indicated by a color change of the reaction mixture from brown to yellow. The completeness of the oxidation was proved via NMR and IR measurements. Moreover, GPC measurements shows only a slight reduction of the MWD



during the oxidation from $M_{\rm w}=30.000$ Da (SPT) to $M_{\rm w}=29.000$ Da (SPSO).

NMR Characterization

Typical ¹H NMR spectra of SPT and SPSO are shown in Figure 3. The ¹H NMR spectra of SPT clearly show the expected five peaks. Based on the electron withdrawing effect caused by the $-SO_3H$ group, the signal of proton **E** in *ortho* position to the $-SO_3H$ group, can be found downfield at 7.86 ppm with an intensity of 1. The two doublets at 7.52 and 7.47 ppm with an intensity of 2 for each can be identified as the protons A and **B**. In which order the signals appear is again dependent on the electron withdrawing character of the $-SO_3H$ group. There is still an influence, which is demonstrated by the downfield shift of **B** relative to **A**. The signal of **C** appeared at 6.82 ppm and **D** at 7.1 ppm. That C is located in the upfield has two reasons. First, the $-SO_3H$ group has a stronger influence onto the ortho and para positions because of mesomeric effects and, therefore, D is located downfield. Second, the thioether linkages, which are electron-donating groups next to C, shift the C protons to the upfield. These findings were backed up using 2D-NMR measurements.

For the identification of the signals to the arylene H's of SPSO, it was necessary to carry out a 2D-NMR experiment. The analysis shows that the whole arylene H's shifted to downfield. This large shift reflects the very strong electron-withdrawing character of the SO₂ group and proves in turn that the oxidation of SPT to SPSO was complete. One indication of the electron-withdrawing character is shown by the position of the ¹H NMR signal of C at 8.49 ppm. This is the strongest downfield shift, compared to the other protons. A further effect is the change of the positions of **A** and **B**. **A** moves to the downfield at 8.18 ppm and **B** appears at 8.10 ppm. It seems that the influence of the $-SO_3H$ group together with the SO₂ linkage has an interesting effect for the position of **B**. A satisfying explanation of this ¹H NMR signal interchange cannot be given now.



FIGURE 4 IR spectra of SPT and SPSO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

FTIR Characterization

Additional to NMR, FTIR spectra of the SPT, and SPSO polymers, respectively, were recorded. In Figure 4, three bands of the SPT-FTIR spectrum at 480, 816, and 1472 cm⁻¹ could be assigned, which are the characteristic vibrations of a poly(*p*-phenylene sulfide) structure.⁴⁴ When the complete oxidation of SPT to SPSO was reached, these three bands should have disappeared. The bands marked in Figure 4 cannot be found in the spectra of SPSO. However, a new absorption band at 1350 cm⁻¹ can be found in the FTIR spectrum of SPSO, which is characteristic for SO₂ group-containing polymers.

The IR spectra, together with the NMR spectra results, led to the conclusion that the oxidation of SPT to SPSO was complete.

Ion-Exchange Capacity and Specific Resistance

The IEC, sulfonation degree per repeating unit, and specific resistance values of the polymer blends are listed in Table 1. All used polymers were water soluble. SPSU has an IEC_{total} of 3.2 meq g^{-1} , and the other investigated polymers have an IEC_{total} of 2.4 meq g^{-1} . The polymer blends SPSU-PBIOO contained 27 wt % PBIOO, and the other polymer blends contained 19 wt % PBIOO. Experimentally determined IECs of the PBIOO blends ranged between 1.1 and 1.6 meq g^{-1} . It is important to recognize that the IEC_{direct} values were nearly the same for all polymer blends. The IEC_{direct} values represent the directly available and exchangeable protons. All the

TABLE 1 Properties of the Polymer Blends

lonomer Blends	IEC _{direct} (meq g ⁻¹)	IEC _{total} (meq g ⁻¹)	$R_{ m sp}$ ($\Omega~ m cm^{-1}$)	σ (S cm ⁻¹)
SFS-PBIOO	0.8	1.6	24.1	0.042
SPSU-PBIOO	0.7	1.1	41.7	0.024
SPEEK-PBIOO	0.7	1.1	36.8	0.027
SPSO-PBIOO	0.7	1.4	9.1	0.11

 $R_{\rm sp}$ Specific resistance; measured at RT and 100% RH.

 σ Proton conductivity.

TABLE 2 Thermal Stabilities of the Polymer Blend Membranes

<i>T</i> _{5 wt %loss} (°C)	T _{SO₃Honset} (°C)
353	260
382	290
362	297
409	334
	75 wt %loss (°C) 353 382 362 409

polymer blends showed low specific resistance values. It is remarkable that the novel polymer SPSO comprises the highest proton conductivity among all blend samples. The low electron density of the aromatic building block of SPSO causes a higher degree of dissociation of the $-SO_3^-H^+$ group. This leads to a higher mobility of the protons, ending up in a higher conductivity, compared to the other blend membranes.

Thermal Stability

The thermal stability of the polymer blends was determined using TGA-FTIR coupling technique. The analysis of the TGA traces was started at 200 °C at which all water had evaporated from the sample. As it is summarized in Table 2, the $T_{\rm 5wt\%loss}$ ranged between 350 and 410 °C. The poly(arylene ether) and poly(arylene ether ketone) sample, respectively, started to degrade thermally at lower temperatures than the other investigated membranes. The samples with sulfone bridges in their repeating units showed the highest thermal stabilities and the highest onset of splitting-off temperatures of the sulfonic acid group. One reason for this finding might be the electron-attracting capability of the sulfone bridge by its -I and -M effect,^{18,39-41} leading to higher thermal stability of the poly(sulfone), compared to the other arylene main chain ionomers, which comprise electrondonating groups in the polymer backbone (-0-, -S-). Furthermore, it is assumed that our SPSO polymer shows a high-morphological stability comparable with that of the poly(arylene sulfone)s (SPSOs) Kreuer and coworkers¹⁸ presented.⁴¹ This high morphological stability leads to a high thermal stability of SPSO. In Figure 5, it is clearly shown by the TGA traces that the novel SPSO blend polymer has the highest thermal stability among all membranes under comparison in this study.

Water Uptake

The water uptake values of the PBIOO blend membranes as a function of temperature are presented in Figure 6. At room temperature, the polymer blends absorbed between 19 and 30% water of their own weight. In contrast to the initial expectations, there was no significant increase of water uptake when the samples were equilibrated in water at higher temperatures. The SPSO-PBIOO membrane showed the highest water uptake values at all investigated temperatures but never more than 35%. The high water uptake of the SPSO-PBIOO blend membrane is thought to be caused by its higher hydrophilicity, compared to the other investigated membranes. Based on the low electron density of the aromatic building blocks of the SPSO, its pendent —SO₃H groups have a better charge separation and, therefore, a higher



FIGURE 5 TGA curves of the blend membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

degree of dissociation, compared to the other investigated arylene main chain ionomers investigated in this study. Therefore, it can be speculated that the stronger separated a $SO_3^-H^+$ ion pair is, the more water molecules can be taken up into the hydration spheres of both ions.

Oxidative Stability

An accelerated degradation test of the SPSO-PBIOO blend membranes, in which the membranes were exposed to an oxidative environment (H_2O_2) , has been performed. Two molecular weight reduction mechanisms are possible as a matter of principle. The first one is the splitting-off of the sulfonic acid group and the second mechanism comprises the reduction of the molecular weight of the polymer chains by radical attack, followed by radical chain scission, at the bridging groups. The attack at the main chain is the most critical one, since it strongly reduces the molecular weight of the polymer. Therefore, we tried to elucidate the degradation mechanism of the SPSO-PBIOO blend membrane by GPC measurements. A clarification of the degradation mechanisms of fuel cell membranes is crucial for fuel cell membrane



FIGURE 6 Water uptake of the blend membranes at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]





FIGURE 7 Weight loss of SPSO-PBIOO in function of immersion time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

development. The knowledge of the molecular weight reduction mechanism gives valuable information for the development of more stable membranes. A molecular weight reduction of the macromolecular chains building up the blend membrane leads to a significant loss in mechanical membrane stability. If mechanical weakening of a membrane takes place during fuel cell test by attack of radicals formed during the fuel cell reaction onto the membrane polymer(s), pinhole formation in the membrane might be the result, leading to mixing of the fuel cell reaction components O_2 and H_2 , which can ignite, ending up in combustion of the membrane and fuel cell failure.

In Figure 7, the weight loss values of SPSO-PBIOO blend membrane are presented as a function of H_2O_2 immersion time. After 6-h treatment, no weight loss can be observed for the blend membrane. The significant weight loss starts at 24 h and further increases up to 48 h. An explanation for the weight loss of this membrane can be given on comparison of these results with the GPC measurement results.

The GPC measurement results of the blend membrane are shown in Figure 8. The molecular weight of the untreated

sample is presented at 0 h. It is of interest, that the degradation process starts at an immersion time of 6 h. Up to this time, no significant weight loss could be observed. This means that the reduction of the molecular weight starts, but the reduction is not strong enough to be reflected in weight loss, since the slightly degraded macromolecular chains are retained by the ionical crosslinking network inside the blend membrane, as stated earlier in this study.

It is interesting to see that the molecular weight reduction has reached nearly 50%. However, this value is not as high as it seems to be, because the blend membrane had an initial M_n of 39.000 Da. After 48 h of oxidative treatment, the degradation process has led to a M_n of 21.000 Da. As the polycondensation procedure for SPSO will be optimized in ongoing research, ending up in higher molecular weight SPSO, it is expected that the percentage of molecular weight reduction by oxidative molecular weight reduction will be lower and the membrane stability can be retained for a longer time interval.

In Figure 9, the reduction of the MWD of the SPSO-PBIOO blend membrane as a function of W (log M) is depicted. W(log *M*) is defined as the intensity of the mass fraction of the logarithmic molecular mass. From 0 to 6 h and from 6 to 24 h, no significant shift in the MWD profile to lower molecular weight can be observed. As expected, the polydispersity index value expanded with increasing immersion time, which can be explained with dissimilar molecular weight reduction of the polymer chains of the blend membrane. To interpret this result, it is important to understand the ionical crosslinking mechanism of sulfonated polymers with PBIOOs. The proton of the sulfonic acid group interacts with the basic nitrogen atom of the imidazole group from the PBI. These ionical interactions are quite strong and lead to a better oxidative stability of the blend membrane, compared to the pure sulfonated ionomer. The macromolecular chains of the blend membrane sustain molecular weight reduction/degradation by the radical attack and subsequent breakage of the macromolecular chains. The reason for this stabilization is



FIGURE 8 Molecular weight reduction of SPSO-PBIOO as function of immersion time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]





FIGURE 9 GPC curves of SPSO-PBIOO samples after different immersion times shown as the intensity of mass fraction of the logarithmic molecular mass against $M_{\rm n}$.

that they are retained in the macromolecular ionically crosslinked network of the membrane by the ionic interactions as long as they are not degraded to low molecular compounds. Another reason for the deceleration of the degradation of PBI-containing blend membranes might be in the OH radical scavenging properties of the imidazole group, which has been proven for biochemical imidazole-containing substances such as histidine.⁴⁵

By suitable combinations of sulfonated ionomer/PBIOO, further optimization of the blend membranes can be brought about. The strength of the ionical interactions in acid-base blend membranes depends (1) on the acidity of the sulfonated ionomer, (2) on the basicity of the imidazole-N of the used PBI, and (3) on the chemical nature of both the acidic and the basic polymer. Recently, it was found by Kerres et al.46 that blend membranes formed by use of the same sulfonated polymer (SFS, see Fig. 2), but different types of PBI show different thermal and oxidative stabilities. Each type of PBI, as for example, PBI Celazol[®], PBIOO, SO₂-PBI, and F₆-PBI, has a different electron density of the aromatic polymer chain. PBI Celazol and PBIOO can be regarded as electron-rich PBIOOs, while SO₂-PBI and F₆-PBI are PBIOOs comprising electron-deficient aromatic building blocks due to their strongly electron-attracting SO₂ and hexafluoroisopropylidene groups, respectively. It was found that the combination of the electron-deficient SFS with each of the electron-deficient PBIs SO₂-PBI and F₆-PBI yielded blend membranes, which were very stable in Fenton's test. While the blending of SFS with the two-mentioned electron-rich PBIs led to membranes, which lost much more weight when immersed in Fenton's reagent for the same retention time.⁴⁶

Compared to the other blend membranes presented in this study, the advantage of SPSO, compared to the other sulfonated ionomers, is based upon the bridging groups. The novel polymer has no ether linkages, which can easily break off, because ether linkages are susceptible to ipso attack of HO, which is an accepted degradation mechanism.⁴⁴ Instead of ether linkages, SO₂ and hexafluoroisopropylidene bridging groups are present in the polymer chain. Both groups have an electron-withdrawing character, which lowers the electron density of the polymer chain. This is important in terms of the radical attack, which is hindered with decreasing electron density of the radical target polymer. Moreover, the hexafluoroisopropylidene-bridging group has a steric hindrance effect which leads to a hindrance of radical addition. We conclude from the obtained results that if these two bridging groups are present in the polymer backbone, it is possible to reduce the extent of radical attack and to increase the oxidative stability.

CONCLUSIONS

A novel sulfonated SPSO was successfully synthesized by an aromatic nucleophilic polycondensation. The polymer was blended with PBIOO to form a stable membrane. Different blend membrane types comprising several sulfonated arylene main chain ionomers and PBIOO were compared in terms of specific resistance, thermal stability, and water uptake. The novel SPSO has a proton conductivity of 0.11 S cm⁻¹ and a $T_{SO_3H \text{ onset}}$ of 334 °C, which is 40 °C higher than those of the other polymer blends taken into account in this study. The reason for the advantageous properties of the SPSO blend membrane, compared to the other blend membranes, is the strong electron-withdrawing character of the sulfone linkages, which markedly improves the properties of the polymer, compared to polymers comprising ether and ketone linkages. In terms of water uptake, SPSO showed a higher uptake behavior than the other investigated membranes. Compared with polymers, which have only sulfone bridges in their backbone, the water uptake always remained below 50%.

The optimization of the polycondensation reaction to reach further increase in molecular weight will be carried out in ongoing research. The motivation for continuative work is to obtain polymer blend membranes, which show better mechanical and chemical stabilities. Furthermore, it is planned to prepare novel electron deficient partially fluorinated SPSO s by polycondensation of other fluorinated arylene monomers with TBBT or related bis(thiophenol)s, followed by oxidation of the polymeric thioethers to poly(sulfone)s. The sulfonated poly(sulfone)s will be blended with electron-deficient PBIOOs such as F_6 -PBI and SO₂-PBI, for use in H₂-PEFC, DMFC, and PEM-H₂-electrolysis.

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