Copoly(arylene ether nitrile) and Copoly(arylene ether sulfone) Ionomers with Pendant Sulfobenzoyl Groups for Proton Conducting Fuel Cell Membranes

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ABSTRACT: Three series of fully aromatic ionomers with naphthalene moieties and pendant sulfobenzoyl side chains were prepared via K_2CO_3 mediated nucleophilic aromatic substitution reactions. The first series consisted of poly(arylene ether)s prepared by polycondensations of 2,6-difluoro-2'-sulfobenzophenone (DFSBP) and 2,6-dihydroxynaphthalene or 2,7-dihydroxynaphthalene (2,7-DHN). In the second series, copoly-(arylene ether nitrile)s with different ion-exchange capacities (IECs) were prepared by polycondensations of DFSBP, 2,6difluorobenzonitrile (DFBN), and 2,7-DHN. In the third series, bis(4-fluorophenyl)sulfone was used instead of DFBN to prepare copoly(arylene ether sulfone)s. Thus, all the ionomers had sulfonic acid units placed in stable positions close to the electron withdrawing ketone link of the side chains. Mechanically strong proton-exchange membranes with IECs between 1.1

INTRODUCTION The development of polymer electrolyte membrane fuel cells (PEMFCs) as efficient and environmentally benign power sources is currently given great attention globally because of increasing environmental concerns and a wish to move away from the dependence of fossil fuels.¹⁻³ Today, considerable efforts are directed to bring PEMFCs to various markets. In this context, the development work is primarily focused on increasing the durability and performance, reducing the cost, and to expand the operating window of the PEMFC, for example, to higher operating temperatures. State-of-the-art perfluorosulfonic acid (PFSA) membranes such as Nafion[®] exhibit good mechanical properties, high oxidative stability and high proton conductivity below 90 °C.⁴ However, at higher temperatures, where considerable advantages can be reached on the PEMFC system level, the PFSA membranes typically suffer from dehydration and loss of proton conductivity.⁵ Because of these shortcomings, an extensive worldwide research is ongoing to develop new alternative ionomers with improved properties.^{6–10} Aromatic hydrocarbon polymers, such as poly(arylene ether)s (PAEs), poly(arylene ether sulfone)s, poly(arylene ether ketone)s, and poly(phenylene)s are well-known for their excellent

and 2.3 meq g⁻¹ were cast from dimethylsulfoxide solutions. High thermal stability was indicted by high degradation temperatures between 266 and 287 °C (1 °C min⁻¹ under air) and high glass transition temperatures between 245 and 306 °C, depending on the IEC. The copolymer membranes reached proton conductivities of 0.3 S cm⁻¹ under fully humidified conditions. At IECs above ~1.6 meq g⁻¹, the copolymer membranes reached higher proton conductivities than Nafion[®] in the range between -20 and 120 °C. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 734–745, 2011

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thermal, mechanical, and chemical stability. Consequently over the last few years, a large number of aromatic polymers have been functionalized with sulfonic acid groups and evaluated as PEMFC membranes.⁷⁻¹¹

Sulfonated aromatic polymers designed for PEMFC membranes usually have a balanced composition of hydrophilic and hydrophobic segments. When these ionomer membranes take up water, they normally phase separate into a hydrophobic polymer-rich phase domain and a percolating network of nanopores containing water. In these nanopores, the water dissociates the acid units and functions as the proton solvent to facilitate the conduction. Although it is obvious that the hydrophilic phase domain is important for the proton transport, the properties of the membrane are also highly dependent on the nature of the hydrophobic phase domain. The hydrophobic component plays the important role of maintaining the mechanical strength and dimensional stability of the membrane during PEMFC operation. One of the main challenges is to optimize the molecular structure, and, hence, balance the combination of hydrophobic and hydrophilic segments, to obtain the overall best membrane properties.¹²⁻¹⁴

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DFSBP

SO₃Li

Aromatic ionomers with sulfonic acid units placed along the polymer backbone have shown to develop quite inefficient networks of nanopores for proton transport. Consequently, these membranes characteristically reach lower proton conductivity compared with Nafion^{® 15-17} A number of different ionomer architectures have been developed to enhance the properties of sulfonated aromatic membranes, including concentrating the sulfonic acid groups to specific chain segments in the chain.¹² By using this approach, a more distinct phase separated membrane morphology is promoted, where the hydrophobic phase domain may efficiently restrict the water uptake of the sulfonated hydrophilic phase domain. Thus, enhanced properties have been reported for ionomers with sulfonic acid groups located on side chains grafted onto the polymer backbone, including ionomers with sulfonated aromatic, $^{18-22}$ alifatic, $^{23-25}$ and aromatic-alifatic 26 side chains. Another successful approach is to locate the sulfonic acid groups on specific blocks in the polymer backbone, separated by nonsulfonated blocks.²⁷⁻²⁹ These multiblock copolymers have shown higher proton conductivity under reduced relative humidity (RH) in comparison with homopolymers and statistical copolymers. However, the ease of preparation and the larger number of available synthetic routes of the latter polymer classes explains why these are the membrane polymers primarily selected for today's PEMFCs, especially by the industry.

We have recently reported on the synthesis and polymerization of 2,6-difluoro-2'-sulfobenzophenone (DFSBP).³⁰ The lithium salt of this new monomer is conveniently synthesized in one pot by reacting 2,6-difluorophenyllithium with 2-sulfobenzoic acid cyclic anhydride in tetrahydrofuran (THF) at -70 °C, whereafter the product crystallizes out of solution. More recently, we have reported on the polymerization of DFSBP with various diols and a dithiol to yield ionomers consisting of aromatic polymer backbones bearing pendant sulfobenzoyl side chains.³¹ Among these homopolymers, a PAE derived from DFSBP and 2,7-dihydroxynaphthalene (2,7-DHN) showed an attractive combination of properties, including a high thermal stability and glass transition temperature (T_g) . However, because of its high ion-exchange capacity (IEC) value, the level of water uptake of membranes based on this ionomer was too high for practical use as a proton-exchange membrane.

In this work, various statistical copolymers bearing sulfobenzoyl side chains were prepared to control the IEC and vary the polymer backbone structure. Thus, DFSBP was copolymerized with 2,6-difluorobenzonitrile (DFBN) and 2,7-DHN to prepare a series of copoly(arylene ether nitrile)s (PAENs). The introduction of highly polar nitrile groups into sulfonated aromatic ionomers has previously been reported to increase the interchain molecular interactions and decrease the water uptake of the membranes.^{32–35} In a second series of copolymers, bis(4-fluorophenyl)sulfone was used instead of DFBN to prepare copoly(arylene ether sulfone)s (PAESs). In addition, two PAEs were prepared by polycondensations of DFSBP with 2,6-dihydroxynaphthalene (2,6-DHN) and 2,7-DHN, respectively. Important membrane properties, such



*n-*BuLi

as water uptake, proton conductivity, and thermal characteristics were investigated and correlated to the IEC as well as to differences in the copolymer configuration and functionality.

EXPERIMENTAL

Materials

DFSBP was prepared by reacting 2,6-difluorophenyllithium with 2-sulfobenzoic acid cyclic anhydride in THF at -70 °C, according to Scheme 1. The product precipitated out in the reactor and was recrystallized in methanol. Further details have been described previously.³⁰ Potassium carbonate (Acrôs, 99+%) was dried at 120 °C overnight before use. 2,7-DHN (TCI Europe, >99%) and 2,6-DHN (Alfa Aesar, 98%) were recrystallized from water, and bis(4-fluorophenyl) sulfone (DFDPS, Alfa Aesar, 98+%) was recrystallized from toluene before being dried *in vacuo* at 80 °C overnight. DFBN (Acrôs, 97%), *N*,*N*-dimethylacetamide (DMAc, Acrôs, 99%), toluene (Fisher Scientific, HPLC grade), 2-propanol (IPA, Fisher Scientific, HPLC grade), and dimethylsulfoxide (DMSO, Acrôs, 99.9+%) were all used as received.

Homopolymer Synthesis

Two different PAE homopolymers were synthesized by nucleophilic aromatic substitution reactions of DFSBP with 2,7-DHN and 2,6-DHN, respectively, as outlined in Scheme 2. The resulting polymers were designated PAE2,7 and PAE2,6, respectively. Using the preparation of PAE2,6 as an example, DFSBP (0.8063 g, 2.650 mmol), 2,6-DHN (0.4245 g, 2.650 mmol), and K₂CO₃ (0.457 g, 3.31 mmol) were added to a mixture of DMAc (6 mL) and toluene (6 mL) in a two-necked flask equipped with a magnetic stirrer, a nitrogen inlet, and a Dean-Stark trap with both a condenser and an outlet fitted with a calcium chloride filter. The reaction mixture was first heated to 160 °C for 4 h. After dehydration and removal of the toluene, the reaction temperature was increased to 175 °C, and kept at this temperature for 1.5 h (PAE2,6) or until the polymer precipitated, which occurred after 1 h for PAE2,7. Temperature was then lowered until the polymer regained solubility, which occurred at 110 °C and 70 °C for the PAE2,7 and PAE2,6, respectively. This reaction temperature was kept for 15 h before precipitation of the polymer in an excess of IPA at room temperature. The precipitates of the polymers were filtered and washed repeatedly with fresh IPA and water. After drying, the products were redissolved in DMAc and the same purification procedure was repeated from a more dilute solution. Finally, the polymers were dried in vacuo at 80 °C for 24 h.



SCHEME 2 Synthetic pathway to the PAE homopolymers via potassium carbonate mediated nucleophilic aromatic substitution reactions.

Copolymer Synthesis

Eight different PAEN and PAES copolymers were synthesized by nucleophilic aromatic substitution reactions involving DFSBP, as outlined in Scheme 3. The copolymers were designated PAEN*a* and PAES*a*, where *a* denoted the molar percentage of the sulfonated DFSBP monomer in total feed of the difluoro monomers. In a typical procedure, using the preparation of PAEN80 as an example, DFSBP (0.8556 g, 2.812 mmol), DFBN (0.0978 g, 0.703 mmol), 2,7-DHN (0.5631 g, 3.515 mmol), and K_2CO_3 (0.607 g, 4.39 mmol) were added to a mixture of DMAc (8 mL) and toluene (8 mL) in a two-necked flask equipped with a magnetic stirrer, a nitrogen inlet, and a Dean–Stark trap with both a condenser and an outlet fitted with a calcium chloride filter. The reaction mixture was first heated to 160 °C for 4 h. After dehydration and removal of the toluene, the reaction



SCHEME 3 Synthetic pathway to the various PAEN and PAES copolymers via potassium carbonate mediated nucleophilic aromatic substitution reactions. The parameter *a* designates the value of [DFSBP]/([DFSBP] + [DFBN]) \times 100% or [DFSBP]/([DFSBP] + [DFDPS]) \times 100%, respectively, used in the polycondensations.

temperature was increased to 175 °C and kept at this temperature for 20 h (PAEN60, PAEN40, PAEN20, PAES49, and PAES27) or until the copolymer precipitated, which occurred after 1.5, 3, and 2 h for PAEN80, PAES85 and PAES68, respectively. For the latter three ionomers, the reaction temperature was subsequently lowered until the polymer regained solubility, which occurred at 120, 140, and 155 °C, respectively. This reaction temperature was kept for 15 h before precipitation of the copolymers in an excess of IPA at room temperature. The copolymers were then purified using the same procedure as described above for the homopolymers.

Structural Characterization

¹H NMR data were collected using a Bruker DRX400 spectrometer. Spectra were recorded at 400.13 MHz and the chemical shifts are reported relative to DMSO- d_6 (δ 2.50 ppm). Fourier transform infrared (FTIR) analysis was carried out on a Bruker IFS 66 spectrometer. The polymers were ground together with KBr before tablets were pressed. Spectra of the samples were recorded between 400 and 4000 cm⁻¹ at a resolution of 4 cm⁻¹ using 128 cumulative scans. The intrinsic viscosity ([η]) of the polymers was measured by using an Ostwald capillary viscometer in a thermostated water bath at 25 °C. The samples were dissolved in a 0.05-M solution of LiBr in DMSO and analyzed in the concentration range 1.0–12.2 g L⁻¹.

Ionomer Membrane Preparation

Membranes of the ionomers were cast in their potassium salt form from 7 wt % solutions in DMSO. All solutions were passed through 0.45 μ m porous polytetrafluoroethylene filters before membrane casting in Petri dishes under N₂ flow at 90 °C for 24 h, followed by drying *in vacuo* at 80 °C for 24 h. Membranes with a thickness of 70–140 μ m were ion-exchanged to the protonated form by immersion in 1 M aqueous HCl for at least 24 h, followed by leaching with distilled water for 2 days during which the water was exchanged several times.

Thermal Characterizations

A Q1000 calorimeter from TA Instruments was used to carry out the differential scanning calorimetry (DSC) investigations. During the DSC experiment, the polymers were first heated to 10 °C below degradation temperature (T_d). The samples were then cooled to 50 °C, followed by a heating scan to 380 °C. All heating and cooling rates were kept at 10 °C min⁻¹. T_g s were taken as the midpoint of the transition recorded during the second heating scan.

The thermal stability was evaluated by thermogravimetric analysis (TGA) using a Q500 analyzer from TA Instruments. The samples were analyzed, both in the protonated form and the sodium salt form, under N₂ during heating from 50 to 600 °C at 10 °C min⁻¹ and under air during heating from 50 to 600 °C at 1 °C min⁻¹. Before the heating scan, the samples were predried under N₂ at 150 °C for 10 min to remove water. The $T_{\rm d}$ was taken as the temperature at which the polymer had lost 5% of its original weight during the heating.

Water Uptake and IEC Measurements

The water uptake (w_{water}) was measured under immersed conditions after equilibration in distilled water for at least 48 h, and at 98% RH after storage in a sealed vessel with a saturated aqueous solution of CuSO₄·5H₂O. To obtain the wet weight (W_{wet}), the excess water was gently removed with tissue paper before weighing the swollen membranes. The dry weight (W_{dry}) was obtained after drying under vacuum at 80 °C overnight. The water uptake was then calculated as follows:

$$W_{\text{water}} = (W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \times 100\%$$
 (1)

The IEC was measured by titration of acidic membranes. Protonated membranes were soaked in an aqueous 2 M NaCl solution for at least 72 h. The solutions were titrated with a 0.01-M KOH solution, using phenolphthalein as indicator.

The state of the water in the membranes was investigated via DSC by observing the endothermic peaks associated with water melting. The membranes were first allowed to equilibrate at room temperature in distilled water for at least 24 h. Excess water was carefully removed with tissue paper before placing the samples in a sealed aluminum container. In the DSC experiment, the samples were first cooled from 25 °C to -60 °C, kept isothermally for 3 min at this temperature, before heating to 25 °C. The scan rate was 5 °C min⁻¹ in all cases. The amount of freezing water was calculated by integrating the peak of the melt endotherm and comparing this value with the heat of fusion of pure ice, 334 J $g^{-1.36}$ By combining the calculated amount of freezing water and the gravimetrically determined total water absorption, the total number of water molecules per sulfonic acid group (λ) and the freezing number of water molecules per sulfonic acid group ($\lambda_{\text{freezing}}$) were determined.

Conductivity Measurements

Proton conductivity was evaluated by electrochemical impedance spectroscopy (EIS) using a Novocontrol high-resolution dielectric analyzer V 1.01S equipped with a Novocontrol temperature system. Impedance data were collected using a two-electrode cell in the frequency range of 10^{-1} – 10^7 Hz at a voltage amplitude of 50 mV and was then analyzed using the software WinDeta[®] from Novocontrol. The proton conductivity data of all the membranes were recorded under immersed conditions during heating from –20 to 120 °C, cooling to –20 °C, and finally heating to 120 °C. The reported data were collected during the second heating scan. For the PAE2,7 membrane, measurements were also performed at 100% RH with the membrane preequilibrated at 98% RH. The sample was placed together with a small droplet of pure water in the sealed measurement cell.

RESULTS AND DISCUSSION

Homopolymer Preparation and Characterization

We have previously described the synthesis of DFSBP and demonstrated the efficiency of this monomer in polycondensations to prepare sulfonated aromatic homopolymers with various backbone structures.^{30,31} In particular, the

TABLE 1 Homopolymer	[,] and Copo	lymer Synthesis
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	N	iol)			
Polymer	DHN^b	DFSBP	DFBN	DFDPS	$[\eta]^{c} (dL g^{-1})$
PAE2,7	1.826	1.826	-	-	0.84
PAE2,6	2.650	2.650	-	-	0.70
PAEN80	3.515	2.812	0.703	-	0.66
PAEN60	3.641	2.185	1.456	-	0.43
PAEN40	4.100	1.640	2.460	-	0.69
PAES85	3.091	2.628	-	0.464	0.57
PAES68	3.245	2.206	_	1.038	0.46
PAES49	3.227	1.581	_	1.646	0.32

 $^{\rm a}$ Monomers fed together with a 25% excess of potassium carbonate to yield 20 wt % solutions in DMAc.

^b 2,6-DHN used for PAE2,6 and 2,7-DHN for the remaining polymers.

^c Measured in solutions of 0.05 M LiBr in DMSO.

polymerization of DFSBP and 2,7-DHN produced an ionomer with a high intrinsic viscosity, high thermal stability, and high level of proton conductivity.³¹ This ionomer evidently also had a very high T_g as no glass transition was detected in the temperature range up to the onset of degradation at 400 °C. The primary focus of this study was the synthesis and study of copolymers and membranes based on DFSBP. However, initially we were interested to investigate if an ionomer with a stiffer configuration of the naphthalene moieties in the backbone polymer would give significantly improved properties. Thus, an ionomer was prepared by polycondensation of DFSBP and 2,6-DHN.

In the preparation of the homopolymers, DFSBP was charged in equimolar amounts to the respective DHN together with a 25% excess of potassium carbonate (Scheme 2 and Table 1). During the 4-h dehydration step, the di-phenolate salts slowly precipitated. However, in the preparation of PAE2,7, they regained solubility when the toluene was boiled off during heating to 175 °C. At this temperature, the reaction solution increased in viscosity and the polymerization was continued until the polymer lost solubility, which occurred after 1 h. The reaction temperature was then decreased to a temperature at which the polymer regained solubility, and was then maintained at this temperature for 15 h before isolation of the polymer. On the other hand, PAE2,6 remained insoluble as the toluene was boiled off during heating to 175 $^{\circ}$ C. However, during slow cooling to 70 $^\circ$ C, the ionomer regained solubility, and this temperature was kept for 18 h before isolation of the product.

The intrinsic viscosities of PAE2,7 and PAE2,6 were found to be 0.84 and 0.70 dL g^{-1} , respectively (Table 1). Notably, the intrinsic viscosity was found to be high for PAE2,6, despite the precipitation during the reaction. This may indicate that the polymerization proceeded beyond the point of precipitation or that the ionomer had reached a high molecular weight already before the precipitation.

Figure 1 shows the ¹H NMR spectra of the purified homopolymers. As expected, the spectra were very similar, with all aromatic shifts between $\delta = 6.4$ –7.9 ppm. The signal arising from the proton next to the sulfonic acid group (denoted *a*) was in both cases found between $\delta = 7.6$ –7.7 ppm, whereas the protons *ortho*-to-ether on the DFSBP residues (denoted *e*) gave rise to signals between $\delta = 6.4$ –6.5 ppm. The signals originating from the protons of the naphthalene moieties (denoted *g* and *h*) were shifted upward in the case of PAE2,6 as compared to PAE2,7. The integrals of the peaks were in excellent agreement with the respective ionomer structures. Both the homopolymers were found to be soluble in polar aprotic solvents like DMAc, DMSO, *N*-methylpyrrolidone (NMP), and *N*,*N*-dimethylformamide (DMF) (Table 2).

The thermal characterizations as well as the water uptake and proton conductivity measurements were conducted on membranes cast from DMSO solutions. As expected, the use of 2,6-DHN gave a more stiff backbone polymer, and PAE2,6 showed a T_g at 334 °C in comparison with the T_g of PAE2,7 at 300 °C. In addition, the thermal stability was found to be higher for the PAE2,6 membrane as compared to the PAE2,7membrane (Table 3). The water uptake of the PAE2,6 and PAE2,7 membranes were 103 and 89%, respectively, under immersed conditions at 20 °C. However, the proton conductivity of the two membranes was quite similar at 0.15 S cm⁻¹ under immersed conditions at the same temperature. On the whole, there were seemingly no significant advantages of using 2,6-DHN, and thus 2,7-DHN was used in the subsequent preparation of the copolymers.

Copolymer Preparation and Characterization

Four PAEN copolymers and four PAES copolymers with different IECs were prepared on the basis of DFSBP and 2,7-



FIGURE 1 ¹H NMR spectra of the homopolymers (a) PAE2,7, and (b) PAE2,6 recorded using DMSO- d_6 solutions.

	DMSO	DMF	NMP	DMAc
Polymer	($\delta=$ 13.0)	$(\delta = 12.1)$	($\delta =$ 11.2)	$(\delta = 11.1)$
PAE2,6	S	S	S	S
PAE2,7	S	S	S	S
PAEN80	S	S	S	S
PAEN60	S	S	р	S
PAEN40	S	р	р	р
PAEN20	р	р	р	р
PAES85	S	S	S	S
PAES68	S	S	S	s
PAES49	S	S	S	р
PAES27	s	p	p	р

TABLE 2 Solubility of Sulfonated Polymers (δ = Solubility Parameter [cal^{1/2}cm^{-3/2}])

s, completely soluble; p, partially soluble.

DHN as shown in Scheme 3. Copolymers containing polar nitrile groups have previously been reported to reduce the water uptake of proton-exchange membranes.³² Therefore, DFBN was chosen as one of the comonomers in this study. The properties of the resulting copolymers were compared with corresponding copolymers prepared with DFDPS as comonomer. The IEC value was controlled by varying the feed ratio of DFSBP:DFBN and DFSBP:DFDPS for the PAEN an PAES copolymers, respectively. The monomers were charged in equimolar amounts, according to Table 1, together with a 25% excess of potassium carbonate. During the 4-h dehydration step, the reactants slowly precipitated, but regained solubility when the toluene was boiled off during heating to 175 °C. At this temperature, the reaction solutions increased in viscosity and the polymerizations were continued until the polymer lost solubility after 1.5 to 3 h. The reaction temperature was then decreased to a temperature at which the polymers regained solubility, possibly because the solubility of the salts decreased, which in turn increased the solubility of the polymers. This temperature

TABLE 3 Sulfonated	lonomer	Membrane	Data
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decreased with increasing IEC values of the copolymer. Notably, the copolymers with an IEC of 1.55 meq g^{-1} , or lower, remained in solution throughout the polymerizations and were kept at 175 °C for 20 h before isolation of the products. The intrinsic viscosities of the copolymers were measured in DMSO solutions and ranged from 0.32 to 0.69 dL g^{-1} (Table 1). The lower intrinsic viscosities of the copolymers, were most likely due to a lower solubility in DMSO of the

former.

Figure 2 shows the ¹H NMR spectra of the purified copolymers. In comparison with the PAE homopolymers, the spectra of the PAEN copolymers expectedly contained a larger number of peaks that were broader and partly overlapped. All shifts were found between $\delta = 6.4$ –8.2 ppm. The protons ortho-to-ether on the DFSBP residues (denoted a) gave rise to signals between $\delta = 6.5$ -6.6 ppm and were found to increase with an increasing feed ratio of DFSBP. In parallel, the shift from the protons placed ortho-to-ether on the DFBN residue at $\delta = 6.7-6.9$ (denoted *b*) decreased in intensity. The ratios of the integrals from these two peaks were 25:75, 41:59, and 60:40, respectively, which was in agreement with the feed ratio of the monomers. For the PAES copolymers, all shifts were found between $\delta = 6.4$ –8.2 ppm. The signal originating from the protons ortho-to-ether on the DFSBP residues (denoted *c*) was found between $\delta = 6.5$ -6.6 ppm, and increased with increasing feed ratio of DFSBP. The shift originating from the protons *ortho*-to-sulfone in the DFDPS residue (denoted d) was found between $\delta = 7.9$ -8.0 ppm and decreased in intensity with increasing feed ratios of DFSBP. Unfortunately, this peak was overlapped by adjacent peaks, which prevented quantification by NMR.

FTIR spectra of the copolymers are depicted in Figure 3 together with the spectrum of the PAE2,7 homopolymer. For the PAEN copolymers, the incorporation of DFBN was confirmed by the appearance of a vibrational band at 2229 cm⁻¹ arising from the nitrile triple bond stretch. As expected, this band increased in intensity with an increase in

		Sodium Salt Form		Acid Form		98% RH		Immersed			
Membrane	IEC ^a (meq g ⁻¹)	<i>Τ</i> _g (°C)	T _d ^b (°C) Under N₂	T _d ^c (°C) Under air	T _d ^b (°C) Under N₂	T _d ^c (°C) Under air	W _{water} (%)	λ	W _{water} (%)	λ	$\lambda_{ extsf{freezing}}$
PAE2,6	2.29 (2.38)	334	412	372	298	270	51	12	103	25	5
PAE2,7	2.28 (2.38)	300	386	339	291	261	44	11	89	22	4
PAEN80	1.97 (2.07)	306	400	361	294	266	36	10	54	15	0
PAEN60	1.55 (1.69)	266	385	342	303	278	24	9	43	15	0
PAEN40	1.16 (1.24)	254	395	356	303	284	19	9	21	10	0
PAES85	1.91 (2.06)	300	393	354	297	269	37	11	61	18	1
PAES68	1.58 (1.68)	276	395	352	298	276	25	9	43	15	0
PAES49	1.13 (1.24)	245	397	364	310	287	19	9	27	13	0

^a Measured by titration; theoretical values within parenthesis.

^b Measured at 10 °C min⁻¹.



FIGURE 2 ¹H NMR spectra of the PAEN and PAES copolymers recorded using DMSO-d₆ solutions.

DFBN contents. In parallel, the vibrational bands at 1680 cm⁻¹ and 1088 cm⁻¹, arising from the carbonyl stretch and the S=0 stretch in the sulfonic acid groups, respectively, were found to decrease in intensity. In the spectra of the PAES copolymers, the incorporation of DFDPS was confirmed by the appearance of a vibrational band at 1105 cm⁻¹, arising from the S=0 stretch of the sulfone link. The intensity of this vibrational band was found to increase with an increase of the DFDPS feed, whereas the intensity of the vibrational bands from the carbonyl stretch and the S=0 stretch in the sulfonic acid groups decreased, just as observed for the PAEN copolymers.

The solubility of the purified copolymers was investigated in DMAc, DMSO, NMP, and DMF, and the results are shown in Table 2. In general, the solubility was found to increase with increasing IEC of the ionomers in these polar aprotic solvents with high dielectric constants, presumably because of increasing polarity of the ionomers. All but one of the ionomers (PAEN20) were soluble in DMSO at room temperature. Consequently DMSO was chosen for the subsequent membrane preparation. At this point, PAEN20 and PAES27 copolymers were not investigated further because the former copolymer lacked solubility in DMSO and the latter copoly-

mer showed a very low water uptake, below 16% under immersed conditions at room temperature.

Thermal Properties

The ionomer structure and the IEC value had large impact on the $T_{\rm g}$, as seen in Table 3. The $T_{\rm g}$ s were only measured for the membranes in the sodium salt form, and no glass transitions were detected for the membranes in the acid form. As already mentioned, the homopolymer membranes cast from DMSO showed high $T_{\rm g}$ s. Previously, we have reported that no $T_{\rm g}$ was detected for PAE2,7 cast from NMP in the temperature range up to the onset of degradation at 400 °C.³¹ These results indicated differences in the membrane properties depending on the solvent used in the casting process. For both PAEN and PAES copolymer series, the $T_{\rm g}$ was found to increase with increasing IECs. This was expected because of the increasing ionic contents, which increased the intermolecular interactions, and hence decreased the segmental mobility leading to higher $T_{\rm o}$ s.

The thermal stability of the ionomer membranes both in the sodium salt and in the acid form was evaluated by TGA measurements. The measurements under air at 1 $^{\circ}$ C min⁻¹ were undertaken to study the stability under oxidative



FIGURE 3 FTIR spectra of the PAEN and PAES copolymers.

conditions, whereas the measurements under nitrogen at 10 °C min⁻¹ were performed to study the degradation under less drastic conditions. Figure 4 shows the TGA traces of the membranes in the acid form when heated under air. Of the two homopolymers, PAE2,6 was found to have the highest $T_{\rm d}$ value. For both the copolymer series, the $T_{\rm d}$ values were

observed to increase from 260 to 290 °C with decreasing IECs. In addition, at temperatures between $T_{\rm d}$ and 400 °C, the TGA traces were shifted toward increasing temperatures with decreasing IEC values. Comparing copolymers with comparable IEC values, the $T_{\rm d}$ s were very similar for the PAEN and PAES copolymers, indicating the same degradation mechanisms. As seen in Table 3, all but one ionomer followed the trends described above, with the sodium salt



FIGURE 4 TGA traces of the ionomer membranes in the acid form recorded under air at $1 \degree C \min^{-1}$.



FIGURE 5 Water uptake (a) and the corresponding λ -values (b) of the ionomer membranes as a function of IEC after equilibration at RH 98% at 25 °C.

form of PAEN60 showing lower T_d values than expected. As anticipated, the stability was in all cases higher under nitrogen than under air, and the ionomers in the acid form showed lower values of T_d than those in the sodium salt form.

Water Uptake Characteristics

The water uptake of proton-exchange membranes is highly dependent on the IEC and has a great influence on the proton conductivity. However, at high water contents the mechanical properties typically deteriorate because of the high degree of swelling. Consequently, the membrane properties should be tuned, so that the water uptake is controlled and kept at a moderate level.

Figure 5(a,b) shows the water uptake data and λ -values (i.e., the number of water molecules per sulfonic acid group), respectively, for the different ionomer membranes as a function of IEC at 98% RH. As expected for the copolymers, decreasing IECs led to a decreasing water uptake. The water uptake of the PAES and PAEN membranes at a given IEC was quite similar with only a slightly higher water uptake of the

PAES membranes. As seen in Figure 5(b), the λ -value seemingly varied less with the IEC than the water uptake, particularly at lower IEC values.

In Figure 6(a), the water uptake is shown for the membranes under immersed conditions. As previously discussed, the water uptake of the PAE2,6 homopolymer membrane was higher (103%) than that of the PAE2,7 homopolymer membrane (89%). Moreover, PAE2,7 membranes cast from NMP have previously shown to take up excessive amounts of water, 627% under immersed conditions.³¹ These results indicated that the choice of solvent for the membrane casting had a very strong influence on the water uptake, which is in agreement with observations previously reported by Guiver and coworkers.³⁷ The water uptake was efficiently restricted at lower IECs and followed similar trends as observed at 98% RH. However, under immersed conditions the water uptake was more distinctly dependent on the IEC. Again, as was already seen at 98% RH, the PAEN and the PAES membranes showed a very similar water uptake as function of IEC, with the PAEN membranes showing slightly higher values. However, the reductions in the water uptake



FIGURE 6 Water uptake (a) and the corresponding λ -values (b) of the ionomer membranes as a function of IEC after immersion in water at 25 °C.



FIGURE 7 Arrhenius proton conductivity plots for (a) the PAE homopolymers, (b) PAE2,7 cast from different solvents, (c) the PAEN copolymers, and (d) the PAES copolymers. The data were measured under fully immersed conditions, if not otherwise stated. The corresponding data of Nafion® 117 has been included for comparison.

was lower than expected, as compared to the reductions of 10–15% previously reported by Sumner et al.³² from a study of sulfonated poly(arylene ether nitrile) copolymers. A possible explanation for this might be the quite low concentrations of dissimilar segments in the copolymers in the present case. In contrast to the data at 98% RH, the λ -values increased with an increase in IEC under immersed conditions, as seen in Figure 6(b).

On the basis of DSC measurements, the amount of freezable water in the membranes was determined after immersion. The local environment of water in the membrane can be identified from the temperature at which water in the membrane freezes.³⁸ Nonfreezable water strongly interacts with sulfonic acid groups, whereas freezable water is "free" and is not intimately bound to the sulfonic acid groups. Under hydrated conditions, the tightly bound nonfreezable water has a critical influence on the depression of the $T_{\rm g}$, which indirectly affects the proton conductivity.^{38,39} The number of

freezable water molecules per sulfonic acid group ($\lambda_{\text{freezing}}$) is presented in Table 3 and shows that all the studied ionomers contained no, or only very little, freezable water. Thus, PAE2,7 and PAE2,6 contained 4 and 5 freezable water molecules per sulfonic acid group, respectively. These numbers were expectedly lower than the value of $\lambda_{\text{freezing}} =$ 87 previously measured for the highly swollen PAE2,7 membrane cast from NMP.³¹ Of the copolymers, only membrane PAES85 contained small amounts of freezable water ($\lambda_{\text{freezing}} = 1$).

Proton Conductivity

The proton conductivity was measured by EIS during heating from -20 °C and 120 °C. Figure 7(a) shows the proton conductivity of PAE2,6 and PAE2,7 membranes measured under immersed conditions. At subzero temperatures, the PAE2,6 membrane had a lower proton conductivity, which may be explained by its higher water uptake and higher amount of freezable water.³⁸ Above 0 °C, the proton conductivity of both membranes reached similar values, despite their differences in water uptake. This may be explained by dilution effects in membrane PAE2,6, which had a negative influence on the conductivity. The proton conductivity data of PAE2,7 membranes cast from NMP and DMSO, respectively, under 100% RH are depicted in Figure 7(b). Measurements under fully immersed conditions were not possible for the PAE2,7 membrane cast from NMP because of its excessive water uptake. As seen, the proton conductivity of the membrane cast from DMSO was nearly an order of magnitude higher than for the membrane cast from NMP, indicating that the solvent used for the membrane casting had a profound influence on the proton conductivity. Similar solvent effects have previously been reported from studies of sulfonated poly (ether ether ketone)s.⁴⁰ These solvent effects have been explained by differences in solvent-ionomer interaction during the membrane casting, which affect the conformation and interactions of the polymer chains in the membrane, and hence the proton conductivity.⁴¹

Overall, the copolymer membranes reached high proton conductivities, up to 0.3 S $\rm cm^{-1}$ under fully humidified conditions at 80 °C [Fig. 7(c,d)]. At IECs above \sim 1.5 meg g⁻¹, the copolymer membranes reached higher proton conductivities than Nafion[®] in the range between -20 and 120 °C. As expected, the proton conductivity increased with increasing IEC. However, within the range between 20 and 80 $^\circ\text{C},$ the proton conductivity of PAES68 exceeded just above that of the PAES85 [Fig. 7(d)]. Despite the rather similar water uptake, the membranes in the PAEN series reached a higher proton conductivity than the membranes of the PAES series when compared at IEC values above 1.5 meq g^{-1} . However, at an IEC of 1.1 meq g^{-1} the proton conductivity was higher for the PAES49 compared with the PAEN40. At subzero temperatures, all membranes had proton conductivities exceeding that of Nafion[®], which showed a sharp increase between -20 to 20 °C, presumably because of the melting of freezable water.

CONCLUSIONS

Fully aromatic PAES and PAEN copolymers, as well as PAE homopolymers, with naphthalene moieties and pendant sulfobenzoyl side chains were successfully prepared via potassium carbonate mediated nucleophilic aromatic substitution reactions using DFSBP. Consequently, all the polymers had the sulfonic acid units placed in hydrolytically stable positions close to the electron withdrawing ketone links of the side chains. The PAE2,6 homopolymer, derived from 2,6-DHN, showed a higher thermal stability and T_g in comparison with the PAE2,7 homopolymer prepared with 2,7-DHN. Measurements on membranes cast from DMSO indicated a considerably higher water uptake for membranes based on the former polymer. Still, the proton conductivity reached by the two membranes was quite similar. Comparison of PAE2,7 membranes cast from DMSO and NMP, respectively, indicated that the nature of the solvent strongly influenced the water uptake and the proton conductivity of the membranes, with the membranes cast from DMSO reaching the highest conductivity. Both copolymer series had a high thermal stability with values of $T_{\rm d}$ s between 266 and 287 °C (1 °C min⁻¹ under air) and T_{gs} between 245 and 306 °C, depending on IEC. At IECs above ~ 1.6 meq g⁻¹, the copolymer membranes reached higher proton conductivities than Nafion[®] between -20 and 120 °C under immersed conditions. Despite different structures and functionalities of the copolymer backbones, the PAES and the PAEN membrane series showed surprisingly similar thermal and water uptake properties, and proton conductivity at a given IEC. One possible explanation for this may be that the concentration of dissimilar segments in the two copolymer series was too low. Thus, the presence of the strongly polar nitrile groups in the PAEN copolymers did not lead to a significantly decreased water uptake in relation to the PAES copolymers. Future work will focus on evaluating the hydrolytical stability, as well as measuring the proton conductivity of the membranes under reduced RH.

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