Carboxylated and Sulfonated Poly(arylene-*co*-arylene sulfone)s: Thermostable Polyelectrolytes for Fuel Cell Applications

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ABSTRACT: The synthesis of novel soluble copolyarylenes, their functionalization with sulfonic and carboxylic acid groups, and the determination of fuel cell relevant parameters (swelling behavior, methanol permeation, and ionic conductivity) are described. The Ni(0)-catalyzed homocoupling reaction of aryl chlorides was employed for the polymerizations. Carboxylic acid groups were incorporated by copolymerization of methyl 2,5-dichlorobenzoate and subsequent hydrolysis. The composition was varied from 53 to 100 mol % carboxylic acid groups. Sulfonic acid groups were introduced by sulfonation with chlorosulfonic acid. Flexible and transparent membranes with sulfonic and/or carboxylic acid groups were prepared that exhibited higher proton conductivities (values in the range of $\sigma = 0.11-0.23$ S/cm) compared to those of Nafion and sulfonated PEEK as a result of higher ion exchange capacity and water content. Incorporation of carboxylic acid groups led to a reduced water uptake but lower conductivities.

Introduction

The development and improvement of advanced fuel cell systems is a major topic of current research, since fuel cells are considerably more efficient than other energy converters and therefore represent a main instrument for reducing CO_2 emission. In PEMFCs (proton-exchange membrane fuel cells)—and particularly in DMFCs (direct methanol fuel cells)—the polymer membrane represents a key component. The membrane material has to fulfill complex requirements: It has to combine electrochemical stability, workability, high ionic conductivity, low permeation of the reactants (hydrogen, methanol, oxygen), and mechanical integrity.[1] The most commonly used materials are Nafion and sulfonated poly(ether ether ketone)s (PEEK). The properties of these materials are described in detail in the literature.[2]

Polyelectrolytes containing hydrolytically and thermally stable polyarylene backbones represent attractive candidates for fuel cell membranes. Synthesis and characterization of polyarylene polyelectrolytes were pioneered by Wegner et al.[3,4] and Rehahn et al.,[5,6] who also reported the two-step synthesis of carboxylated poly(*p*-phenylene)s, starting with a substituted poly(*p*-phenylene) precursor.[7] Also, Wallow and Novak reported carboxylated poly(*p*-phenylene)s (PPPs) prepared by an elegant direct synthesis in aqueous solution.[8,9] However, problems related to molecular weight determination were encountered. As was shown by our group some years ago, poly(*m*-phenylene-*co*-*p*-phenylene)s at certain compositions are soluble without additional alkyl chain substitution.[10] The corresponding polyelectrolytes were stable under conditions typical for fuel cell application. However, all the above-mentioned polymers were synthesized using the Suzuki coupling reaction[11] which possesses severe drawbacks with respect to problematic monomer availability and unfavorable mass balance. For the preparation of materials for fuel cell membranes this synthetic route is not suitable.

To produce nonsubstituted polyarylene copolymers, we employed a polymerization method based on the reductive coupling of aryl chlorides.[12,13] The scope of this synthetic approach has been extended to poly(benzophenone)s[14] and other low dielectric constant materials by Sheares and co-workers.[15] Additionally, they were able to synthesize building blocks for complex polymer architectures by specific functionalization.[16,17] Furthermore, McGrath and Ghassemi produced novel poly(arylene phosphine oxide)s.[18] Percec et al. demonstrated the usefulness of the Ni(0)-catalyzed reaction for the preparation of soluble PPPs containing CF_3 or OCF_3 substituents[19] and, more recently, PPPs with mesogenic side groups.[20] The polymerization of methyl 2,5-dichlorobenzoate (**E**)[21−23] and other dihalides or bistriflates[23] to poly(methoxycarbonyl-*p*-phenylene) is known in the literature. Although there is an increasing interest in using this method for the synthesis of new polyarylene architectures, to date few publications have dealt with copolymerization.[19,24]

Here we report the synthesis of novel functional, soluble copolyarylenes which are thermooxidatively stable and therefore represent materials with promising potential for fuel cell application. Ionic conducting groups have been incorporated via two different routes: (i) postpolymerization sulfonation of copoly(arylene sulfone)s and (ii) copolymerization of methyl 2,5-dichlorobenzoate and subsequent hydrolysis to produce carboxylated poly(arylene)s. Since to our knowledge there are no systematic studies concerning the effect of carboxylic acid groups in fuel cell membranes, copolymers with these two functionalities as well as blends of different polyelectrolytes have been prepared. Characterization of these new polymers also involved the

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Table 1. Copolymerization of 4,4′-Dichlorodiphenyl Sulfone (S) and *m*-Dichlorobenzene (M)

	molar ratio **S**:**M**	solubility	η_{inh}/dL g^{-1}	T_g/°C
1	100:0			
2	75:25			262
3	63:37	≈DMF	0.26	
4	50:50	DMF, $CHCl_3$	0.29	261
5	25:75	DMF, $CHCl_3$	0.29	246
6	11:89			
7	0:100			146

determination of fuel-cell-relevant parameters like swelling behavior, ionic conductivity, and methanol permeation.

Experimental Section

a. Materials. All reagents were purchased from Aldrich or Merck and used as received, unless indicated otherwise. Bipyridyl was dried at 60 °C in vacuo. Sodium bromide and nickel chloride were dried at 180 °C in vacuo. Triphenylphosphine and methyl 2,5-dichlorobenzoate (**E**) were purified by sublimation. *m*-Dichlorobenzene (**M**) was distilled under argon. 4,4′-Dichlorodiphenyl sulfone (**S**) was purified by recrystallization from a 2:1 mixture of *n*-heptane and ethyl acetate. *N*,*N*-Dimethylformamide (DMF) was dried over CaH_2, distilled, and stored under Ar prior to use.

b. Polymers 1−7. In a typical polymerization, 4,4′-dichlorodiphenyl sulfone (**S**), zinc (4.00 g, 61.2 mmol), nickel chloride (60.0 mg, 0.463 mmol), triphenylphosphine (2.5 g, 9.53 mmol), sodium bromide (200.0 mg, 1.94 mmol), and bipyridyl (100 mg, 0.640 mmol) were added to a three-necked 100 mL round-bottomed flask under Ar. *m*-Dichlorobenzene (**M**) and DMF (50 mL) were added via a syringe. **S** and **M** amounted to a total of 34 mmol. The mixture was stirred at 60 °C, and a deep red-brown to blood red color (matured Bordeaux) was observed. When a significant loss of color intensity (light Burgundy) had been observed (3−6 h), the same amount of nickel chloride was added. This procedure was repeated once more. Subsequently, the reaction mixture was cooled to −16 °C, and a colorless precipitate was formed. This solid was filtered, twice dissolved in DMF, and reprecipitated in diluted hydrochloric acid. Finally, it was twice dissolved in chloroform, reprecipitated in methanol, and dried in vacuo.

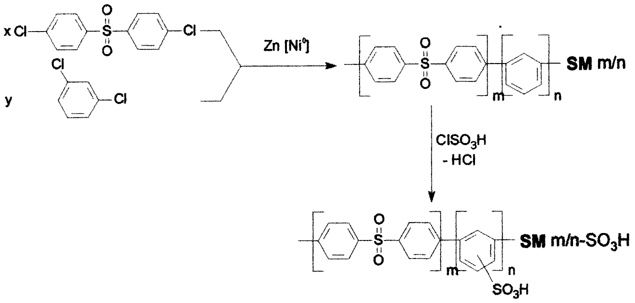
c. Sulfonation of SM25/75 (5). In a typical sulfonation, 200 mg of **5** was dissolved in 60 mL of chloroform. Under argon and cooled by a water/ice mixture, 6 mL of chlorosulfonic acid was added dropwise. After 3 min, quenching of the reaction by addition of methanol afforded precipitation of a light brown solid. It was washed twice each with methanol and diethyl ether and dried in vacuo at 90 °C. We received a product with a degree of sulfonation of 32%. Use of the 2-fold concentration of the polymer in solution led to a material with a higher degree of sulfonation of 38%. In the case of refluxing the mixture overnight before quenching, we obtained a material with a degree of sulfonation of 57%.

d. Polymers 8−17. The synthesis of polymers **8**, **12**, **13**, and **17** (Table 1) has been reported in a preliminary account.[25] **9**−**11** and **16** were prepared following the same procedure. **14** and **15** are a scale-up of **13**, using a 5 times larger monomer batch.

e. Hydrolysis of SE25/75 (13, 14). The hydrolysis has been described elsewhere.[25]

f. Characterization. ^1H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ using a Bruker ARX-300 spectrometer at 300 and 75 MHz, respectively. Molecular weights were determined by size exclusion chromatography (SEC) employing a Knauer microgel set A22 at 35 °C, using chloroform as eluent and polystyrene standards for calibration. SEC was equipped with multiangle laser light scattering (MALLS) and refractive index (RI) detector. Thermogravimetric analyses (TGA) under air and nitrogen were carried out on a Netzsch STA 409 with a heating rate of 10 K/min.

Scheme 1. Synthesis of Sulfonated Co(polyarylene sulfone)s



g. Membrane Preparation. In addition to sulfonic (**SM25/75-SO$_3$H**) and carboxylic (**SE25/75-COOH**) acid-functionalized membranes, we prepared different blend membranes. To this end we mixed **SM25/75-SO$_3$H** and **SE25/75-COOH** in various ratios, dissolved them in DMF and cast membranes. Homogeneous films with good mechanical properties were obtained. Before measurements the membranes were conditioned at 60 °C in nitric acid (5%) and afterward washed with distilled water.

h. Swelling Measurements. The membranes were swollen in water at different temperatures up to constant weight. Masses of swollen (m_s) and dry membranes (m_d) were determined. The degree of swelling (DS) is defined as water uptake ($m_s - m_d$) divided by the mass of the dry membrane (m_d).

j. Permeation Measurements. The membranes were placed between two diffusion layers in a small fuel cell. A stream of aqueous methanol was led through one half cell, and the other was rinsed with nitrogen. The methanol that permeated through the membrane was transported by the nitrogen flow to a flame ionization detector, which determined the methanol concentration.

k. Proton Conductivities. Ionic conductivities were measured by an HP impedance analyzer (4192A LF) using gold electrodes in a gastight sample holder, permitting to vary the temperature for a given water content. The degree of swelling was approximately 100% for **19** and **20** and 50% for **21**.

Results and Discussion

a. Synthesis of Sulfonated Poly(arylene-*co*-arylene sulfone)s. Using the Ni-catalyzed coupling of aryl chlorides, we have been able to synthesize various novel poly(arylene-*co*-arylene sulfone)s (Scheme 1). As shown in Table 1, we have been able to prepare the whole range of compositions. Copolymer compositions were determined by elemental analysis and were found to correspond to the composition of the respective monomer mixture. While both homopolymers (**1**, **7**) are generally insoluble in all common solvents, there is a range of copolymer compositions (**3**−**5**) that lead to soluble materials.

The molecular weight of SM25/75 (**5**) was measured by static light scattering in DMF to M_w = 8400 g/mol (DP$_w$ = 74). Because of poor solubility, molecular weights of other samples have not been determined.

TGA showed no thermal degradation in air up to 450 °C (Figure 1), evidencing the expected high thermal stability of the materials. Ionic conducting groups were introduced after the synthesis of the polymers, using chlorosulfonic acid (Scheme 1). The degree of sulfonation of **SM25/75** (**5**) was varied between 27% and 57%. All materials are soluble in DMF but not in water, methanol, and ethanol. The degree of sulfonation was determined by elemental analysis, because evaluation by NMR spectroscopy was not possible. Whereas membranes cast from DMF solution with a degree of sulfonation of 38 and 43% are brittle and disintegrated in

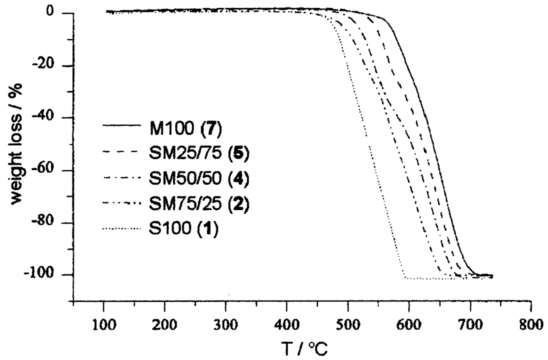
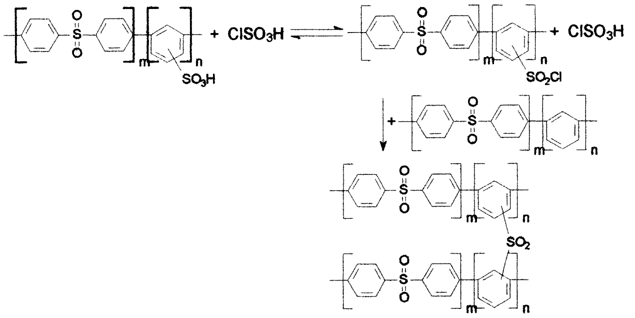
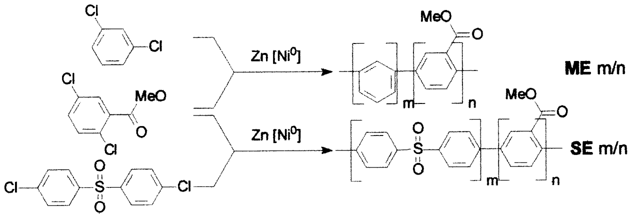


Figure 1. TGA traces of co(polyarylene sulfone)s in air.

Scheme 2. Proposed Side Reaction of the Sulfonation



Scheme 3. Copolymerization of Methyl 2,5-Dichlorobenzoate with *m*-Dichlorobenzene and 4,4′-Dichlorodiphenyl Sulfone



the presence of water, the materials with a lower degree of sulfonation (27−32%) form transparent films that are flexible and mechanically stable. Interestingly, also a highly functionalized membrane (57% sulfonic acid groups) showed the same good mechanical integrity. Most likely, the side reaction depicted in Scheme 2—or the formation of anydrides as additional step—afforded molecular weight buildup and ultimately network formation. Molecular weight buildup is reflected by improved mechanical properties. It should be noted that SEC and other molecular weight determination methods failed to prove this hypothesis due to severe aggregation of the polyelectrolytes in solution. However, the degree of sulfonation of 2.3 mmol/g, as measured by titration of the polyelectrolytes, is considerably lower than that of 3.64 mmol/g determined via the sulfur content, supporting cross-linking by sulfone bridges.

b. Carboxylated Copoly(arylene sulfone)s. To incorporate COOH functionalities, methyl 2,5-dichlorobenzoate (**E**) was copolymerized with *m*-dichlorobenzene (**M**) as well as 4,4′-dichlorodiphenyl sulfone, respectively (**S**) (Scheme 3). We have already reported the syntheses of **8**, **12**, **13**, and **17** in a preliminary communication.[25] All other polymers have not been reported in the literature to date. As shown in Table 2, all homo- and copolymers prepared are soluble in $CHCl_3$. The molecular weight of the homopolymer of methyl 2,5-dichlorobenzoate (**E100**, **8**) was determined by SEC, calibrated to PS standards, to $M_w = 7000$ g/mol. For the same polymerization, Percec et al.[23] reported similar molecular weights, whereas Chaturvedi et al.[21] observed approximately twice this value. Unfortunately, incorporation of *m*-dichlorobenzene (**9**−**11**) caused a decrease of the molar masses, thus producing oligomeric products.

Since these materials are too brittle for membrane preparation, the system had to be modified. Again, the preferred comonomer was dichlorodiphenyl sulfone (**12**−**17**). The copolymer composition was determined by ^{1}H NMR spectroscopy from the comparison of the integral values of the aromatic (δ = 8.5−7.0 ppm) and the methoxy group (δ = 4.0−3.5 ppm) proton signals. Slightly increased incorporation of **E** in comparison to the monomer mixture was observed for polymers **12**−**16**; only sample **17** showed distinctively larger incorporation. The NMR signals of the aromatic protons are shown in Figure 2 for various copolymer compositions. With increasing diphenyl sulfone content the spectra become increasingly complex, and a significant loss of fine structure is observed. This is caused by an increase of chemically similar, but not equal, protons due to the microstructure of the copolymers. New signals at δ = 7.65, 7.75, and 8.1 ppm can be assigned to the protons in the *ortho* (δ = 8.1 ppm) and *meta* position to the sulfone group. The latter protons show two signals dependent on the adjacent monomer units, e.g., for an ester at δ = 7.75 ppm or for a diphenyl sulfone group at δ = 7.65 ppm.

In addition to SEC characterization, for polymer **13** weight-average molecular weight (M_w = 21 100 g/mol; DP_w = 136) and polydispersity (M_w/M_n = 1.49) were determined by MALLS. As expected, molecular weights determined by SEC are overestimated due to the increased chain stiffness of polyarylenes compared to the PS standards employed. The syntheses of **14** and **15** were carried out on a 5 times larger scale than synthesis of **13**. Since we obtained comparable results concerning composition, solubility, and molecular weights, it has been demonstrated that scale-up of the reaction is possible. The variance of molar masses, which is frequently observed for this synthetic method,[19] is due to the step-growth mechanism of the polymerization and related high sensitivity toward impurities. Unfortunately, this variance has a pronounced effect on the mechanical properties: transparent films were cast from $CHCl_3$ for all polymers. However, whereas **13**, **14**, and **15** gave mechanically stable, flexible materials, **12** and **16**, possessing considerably lower molecular weights, formed brittle films. DSC measurements of all copolymers within a temperature range of 100−350 °C did not reveal glass temperatures below thermal decomposition.

Hydrolysis of **SE25/75** (Scheme 4) led to a polyelectrolyte which was soluble in DMF, its deprotonated form also in water and pyridine. The protonated polymer was insoluble in methanol and water, but it was swollen in the latter without losing its mechanical integrity.

A superposition of the signals of the ester group and water (δ = 4.0−3.5 ppm) impeded the evaluation of the extent of ester hydrolysis in ^{1}H NMR spectra. However, by ^{13}C NMR spectroscopy the reaction could be followed. The signal of the ester group at δ = 51 ppm was not observed in the product spectrum after hydrolysis. In addition, the signal of the carbonyl carbon shifted from

Table 2. Synthesis of Poly(arylene sulfone)s with Ester Side Groups

	molar ratio								
	monomers			polymers				SEC ($CHCl_3$)	
	S	M	E	S	M	E	solubility	M_w/g/mol	M_w/M_n
8			1			100	$CHCl_3$	7000	1.92
9		1	1		38	62	DMF, $CHCl_3$	2700	1.71
10		2	1		65	35	DMF, $CHCl_3$	1600	1.53
11		10	1		76	24	DMF, $CHCl_3$	1300	2.33
12	1		3	17		83	DMF, $CHCl_3$	7500	1.83
13	1		2	25		75	DMF, $CHCl_3$	36500[a]	1.70
14	1		2	30		70	DMF, $CHCl_3$	20800	1.54
15	1		1.8	32		68	DMF, $CHCl_3$	32800	2.62
16	1		1	47		53	DMF, $CHCl_3$	3100	1.81
17	2		1	10		90	$CHCl_3$	18500	2.51

[a] M_w = 21100 g/mol and M_w/M_n = 1.49 by MALLS.

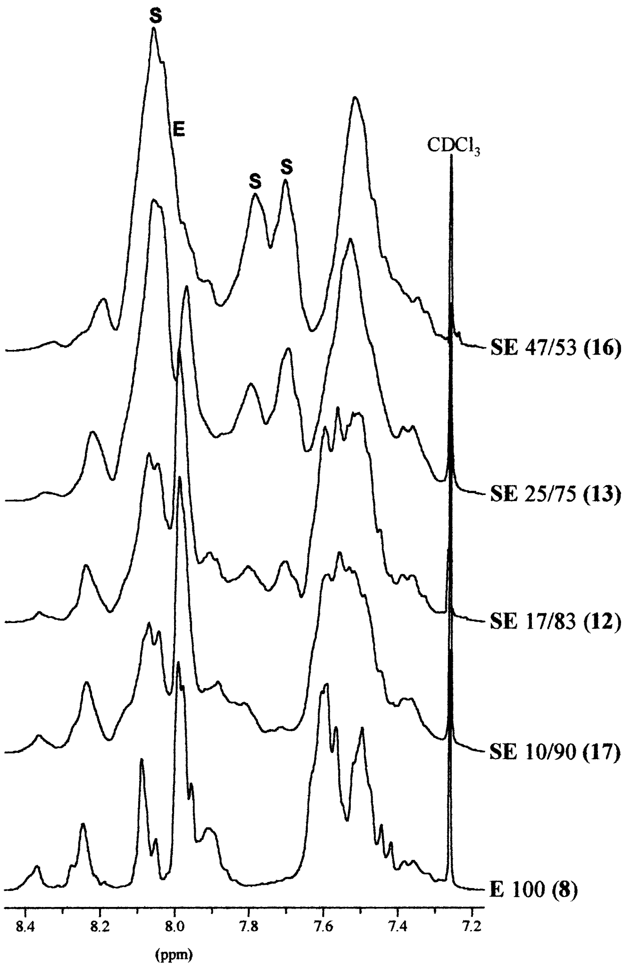
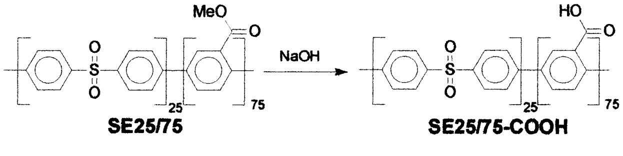


Figure 2. Signals of the aromatic protons in ^1H NMR spectra of various copolymers SE, showing a gradual change with composition.

Scheme 4. Hydrolysis of SE25/75 (13)



δ = 167 ppm to δ = 169 ppm. This supports complete hydrolysis of all methyl ester groups.

TGA showed good thermal stability (Figure 3), even though no plateau was observed, due to the hygroscopic nature of this polymer. No T_g was observed by DSC up to the decomposition temperature. In analogy to **SE25/75**, films were cast from **SE25/75-COOH** in DMF, which still remained flexible, although the presence of hydrogen bonds should lead to a more brittle material.

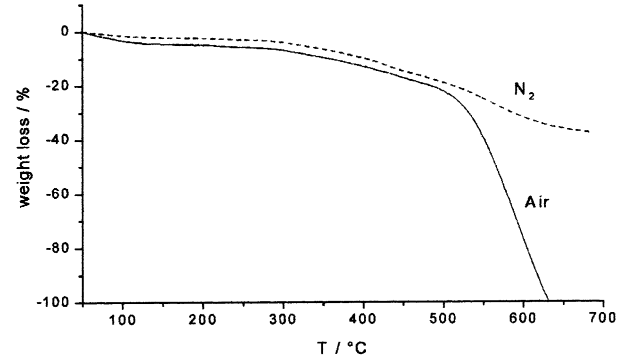


Figure 3. TGA thermograms of **SE25/75-COOH**.

Table 3. Degree of Swelling (DS) of the Copolymers in Water

	sample	25 °C	60 °C	80 °C	90 °C
18	SM25/75-SO_3H (32% SO_3H)	31			44
19	SM25/75-SO_3H (57% SO_3H)	154	161	297	516
20	COOH/SO_3H blend 3:17[a]	96	104	203	349
21	COOH/SO_3H blend 3:7[a]	44	47	76	132
22	COOH/SO_3H blend 1:1[a]	47	46	47	47
23	COOH/SO_3H blend 1:1[b]	14	14	15	15
24	SE25/75-COOH	12	13	13	12

[a] 57% SO_3H. [b] 43% SO_3H.

c. Membrane Properties. To test the synthesized materials with respect to fuel cell application, we determined the dependence of the degree of swelling (DS) in water on the temperature (Table 3). Low swelling is favorable, since this usually corresponds to good mechanical integrity.

The degree of swelling (DS) of the sulfonic acid-substituted poly(arylene sulfone) with 32% SO_3H groups is comparable to established fuel cell membrane materials (**18**). The highly sulfonated and therefore very polar second membrane (**19**) showed increased water uptake, but up to 90 °C did not lose its mechanical integrity. For the carboxylic acid-based material **SE25/75-COOH** (**24**) a low DS is observed that remained constant with increasing temperature. Surprisingly, a 1:1 blend (**23**) exhibited approximately the same reduced swelling. Also, in the other blends (**20**, **21**, **22**) addition of the carboxylic acid component reduced water swelling. Thus, incorporation of COOH functionalities represents a concept to reduce water uptake.

For the use in a DMFC, low methanol permeation is a basic prerequisite. To study this property, a membrane

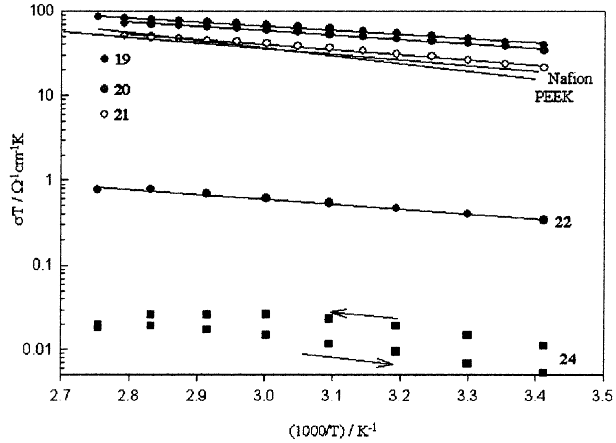


Figure 4. Proton conductivity of sulfonated (**19**, DS ≈ 100%) and blend (**20**, DS ≈ 100%; **21**, DS ≈ 50%; **22**, DS ≈ 50%; **24**, DS ≈ 13%) membranes compared to Nafion and sulfonated PEEK (DS ≈ 30%).

Table 4. Methanol Permeation of the Poly(arylene sulfone) Materials in Comparison to Nafion

		d/μm	permeation/ppm
19	SM25/75-SO_3H (57% SO_3H)	53	9.2
25	COOH/SO_3H blend 1:4	51	17.8
	Nafion 117	200	13.6

was placed in a fuel cell like device described in the Experimental Section. To obtain comparable results, we prepared various test membranes. As is shown in Table 4, in comparison to a 4 times thicker Nafion 117 membrane, the sulfonic acid-functionalized copolyarylene (**19**) showed a permeation reduced by one-third. On the other hand, incorporation of carboxylic acid groups (**25**) unfortunately led to increased methanol permeation. It should be emphasized that these are only preliminary measurements because of the rather low water content of the membranes compared to actual fuel cell conditions. Additionally, we measured only one blend membrane. Further experiments are required to clarify whether carboxylic/sulfonic acid-functionalized membranes generally show higher permeation.

The most important feature of a fuel cell membrane is its proton conductivity. As shown in Figure 4, the SO_3H-functionalized membrane **19** showed very high conductivity compared to those of Nafion and sulfonated poly(ether ketone) (PEEK) which is most likely the result of the higher degree of functionalization (3 times larger than in Nafion) and a significantly higher water content (see Table 3). The first increases the concentration of protonic charge carriers while the latter generally improves the percolation of the hydrophilic domain carrying the proton conductivity.[2] Also for blend membrane **20** an improved conductivity was observed. The material **21** with its high amount of COOH groups showed a similar conductivity as Nafion, even though the degree of swelling was higher. Membrane **22** exhibited a drastic decrease of conductivity compared to the other blend membranes, although the water content was comparable to **21**. The lower degree of dissociation of the COOH groups—compared to that of the SO_3H groups—accounts for lower ionic conductivity, evidently shown by the carboxylic acid-based material **SE25/75-COOH** (**24**).

Conclusion

New functional poly(arylene-*co*-arylene sulfone)s have been prepared by Ni(0)-catalyzed coupling copolycondensation. Incorporation of functionalities was achieved either by postpolymerization sulfonation (SO_3H groups) or by copolymerization of dichlorobenzoate and subsequent ester hydrolysis.

While for the poly(arylene sulfone) copolymers **SM** there is only a certain range of copolymer compositions (from 25% **S** to 63% **S**) that leads to soluble materials (the homopolymers are insoluble), all ester copolymers (**ME**, **SE**) are soluble. For **ME** only oligomers were observed. In contrast, the system **SE** led to higher molecular weights. However, although we were able to adjust copolymer composition, control over molecular weights was limited. Functionalization with both sulfonic and carboxylic acid groups resulted in novel polyelectrolytes with good thermal and mechanical properties.

Further investigation concerning the suitability of these materials for fuel cell application showed that carboxylic acid functionalities in poly(arylene sulfone) blends led to reduced swelling behavior in water, but preliminary data indicate increased methanol permeation. Membranes based on a high content of sulfonic acid-functionalized material showed improved ionic conductivities due to their high degree of functionalization. However, a high degree of functionalization also resulted in high water uptake. Sulfonated polyarylenes are very promising materials due to their stability, low permeation of methanol, and high ionic conductivity. Incorporation of carboxylic acid groups reduced water uptake; however, it also caused lower conductivity. Since these blend membranes showed similar conductivities as Nafion in the swollen state, the carboxylic/sulfonic acid blends appear to be problematic for the actual application in fuel cell membranes.

Currently, we are investigating additional concepts based on the sulfonated materials like hydrophilic/hydrophobic blends and inorganic/organic hybrid systems in order to reduce water uptake without losing the advantageous conductivities of such poly(arylene)-based membranes. The incorporation of inorganic materials should lower water uptake and the already advantageous low methanol permeation.

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