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Partially fluorinated poly(arylene ether)s: Investigation of the dependence of monomeric structures on polymerisability and degradation during sulfonation

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ABSTRACT

A series of partially fluorinated poly(arylene ether)s with systematical structure variations (variations in the (bi)phenylene, bisphenol moiety, and the fluorine content) was synthesized and characterized. Main objective of this contribution was the investigation of structure-property relationships of the different polymer structures, and how the chemical structure of the aromatic monomers influences (1) polymerisability of the monomers; (2) chemical and thermal stability of the poly(arylene ether)s, and (3) properties of the referring sulfonated polymers, particularly their chemical and mechanical stability. Polymers from this series comprising high molecular weight and excellent film-forming properties were targeted to various sulfonation routes, and their degradation behavior during sulfonation was investigated by gel permeation chromatography (GPC). Finally, (polybenzimidazole blend) membrane properties of the most promising candidates for potential application in polymer electrolyte membrane fuel cells were evaluated. The best of the investigated blend membranes was investigated in an air-breathing DMFC and yielded markedly improved performance, compared to Nafion®105. This study gives both insight into structure-property-relationships and directions for future polymer and membrane developments.

1. Introduction

Against the background of limitations of natural resources, import dependencies of fossil fuels and global environmental problems, the fuel cell technology is thought to be one of the future power sources. Polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) which are based on a proton-conductive membrane material as one key component have attracted much attention in automotive and portable electronic applications in recent years [1]. Many different approaches have been made to overcome the main drawbacks of poly(perfluoroalkyl) sulfonic acids (such as Nafion®) which are reviewed in the literature [2–5]. These materials show excellent chemical, mechanical and thermal stability and high proton conductivity, but suffer from high methanol permeability (which is relevant for the DMFC mode) and a significant drop in proton conductivity at temperature above 80 °C because of the increased water evaporation. Different strategies have been used in order to overcome the crucial shortcomings of the poly(perfluoroalkyl)sulfonic acids including for example the reinforcement by a porous PTFE matrix [6,7], the incorporation of hygroscopic oxides [8,9] (like SiO_2, ZrO_2 and TiO_2) or of inorganic solid proton conductors such as layered metal^{IV} phosphates (e.g. α- or γ-zirconium phosphates or phosphonates) [10]. Much more effort has been invested into the development of alternative proton-conducting membrane materials including many different functionalised polymer families, e.g. sulfonated polysiloxanes [11], polyphosphazenes [12,13], styrene-grafted (partially) fluorinated polyolefins [14] and aromatic main-chain polymers. The last polymer class covers different chemical structures and a detailed description would go beyond the scope of this article so that the authors would like to refer to review articles for more information [2–5]. Common structural moieties of aromatic main-chain polymer are phenylene rings connected by chemical bonds and/or linkage groups. Typical examples are sulfonated poly(phenylene ethers)s [15], poly(ether ether ketone)s (sPEEK) [16], poly(ether sulfone)s (sPES) [17], poly(sulfone)s [18] and polyimides (sPI) [19], which are accessible by sulfonation of the corresponding main-chain polymers. Although the sulfonation can be accompanied by polymer backbone degradation as side reaction (depending on the substitution pattern and the nature of chemical bonds and linkage groups in the polymer backbone) [3,20], this route offers the

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advantage of an easy and economically reasonable working-up procedure (sulfonation, precipitation, filtration) [21]. The focus of the present work lies on the preparation of partially fluorinated polymeric structures in the first step and of their sulfonated analogues by postsulfonation in the second step as far as the polymerisation led to polymers with a sufficiently high polymerisation degree ($M_n > 10{,}000$ Da). In principle fluorinated ionomers are expected to have superior stability and acid strength than their nonfluorinated analogues [20,21]. Apart from developing partially fluorinated ionomers for fuel cell application [1,22,23], there is a strong interest in the preparation of the basic poly(aryl)s for example for polymer optical waveguides [24,25] for detection of fluoride ions [26], and gas separation membrane materials [27]. These partially fluorinated poly(aryl)s are synthetically accessible by step-growth polycondensation methods which can be realized by reacting an activated difluoro-, dichloro- or dibromoaryl monomer with a diphenol.

The Pd-catalyzed [28] or CuCl-catalyzed [29] Ullmann biaryl polycondensation shows limited applicability to the targeted partially fluorinated polymers. The first method only offers an advantage for the coupling of sterically hindered monomers. The second method is limited to monomers without any $C_{sp}2$-F bonds due to the applied high temperatures and the risk of side reactions such as branching or eventually cross-linking.

Therefore, the preferred method for the preparation of the targeted partially fluorinated poly(aryl)s is the nucleophilic displacement polycondensation reaction between a difluoro- (or dichloro) aryl monomer and a diphenol in the presence of a deprotonating reagent under mild conditions. This reaction is normally carried out in dipolar-aprotic solvents such as *N,N*-dimethylacetamide (DMAc) or *N*-methylpyrrolidinone (NMP) with potassium carbonate as the base without [30] or with water entrainer [31] or in the presence of molecular sieves to remove water formed during the deprotonation reaction of the diphenol [32]. The use of calcium hydride in combination with caesium fluoride as a catalyst can be advantageous in some cases due to the reduction of water formation during the deprotonation step and the concomitant precipitation of CaF_2 which facilitates the nucleophilic exchange of fluoride by phenolate during the polycondensation [33].

The main part of this contribution deals with the systematic investigation of how the monomers polymerisability depends on their chemical nature.

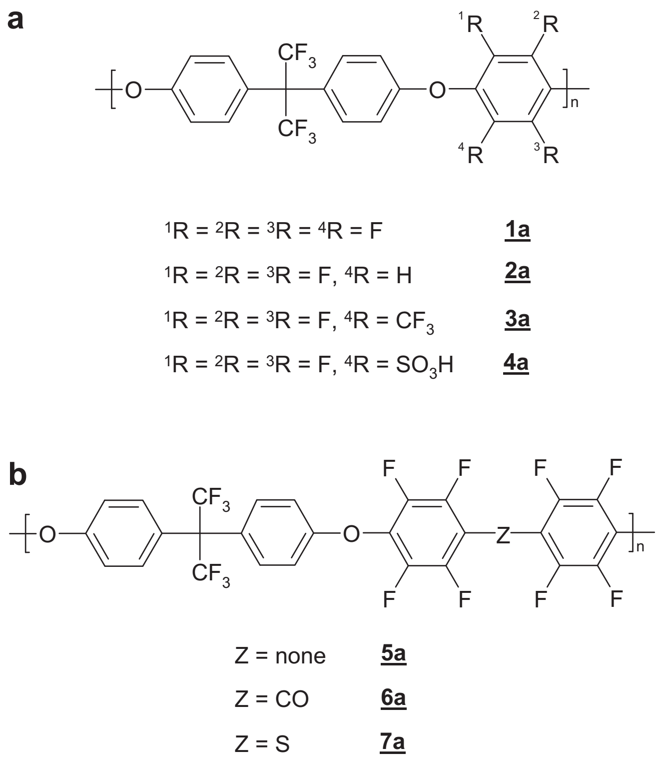
The achievable molecular weight will serve as a measure for the polymerisability of various monomers. With this aim, variations in the (bi)phenylene moiety (Scheme 1), in the bisphenol moiety (Scheme 2) as well as fluorine content variations (Scheme 3) were investigated and analyzed.

Providing that the polymers showed good film-forming properties, they were sulfonated (using common sulfonating reagents like concentrated or fuming sulfuric acid [20,21], chlorosulfonic acid [34] or trimethylsilyl chlorosulfonate) [35], and investigated further in terms of their properties relevant for use as polymer electrolyte membrane in fuel cells.

2. Experimental section

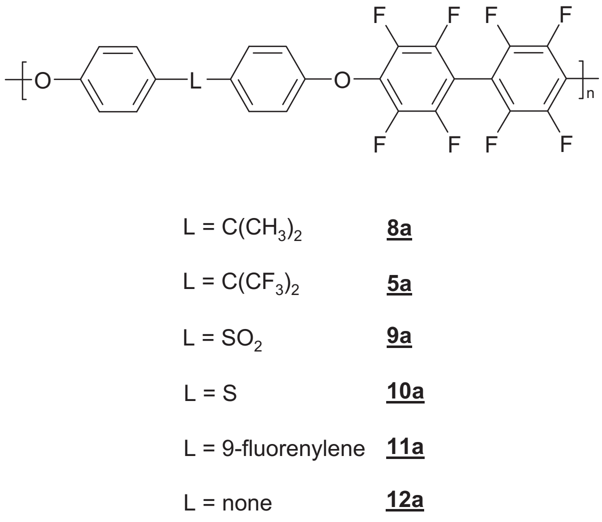
2.1. Instrumentation

NMR spectra were recorded using a Bruker Avance 400 spectrometer at a resonance frequency of 400 MHz or 250 MHz for ^{1}H, 188 MHz for ^{19}F and 250 MHz for ^{1}H-^{13}C HSQC (heteronuclear single quantum coherence).

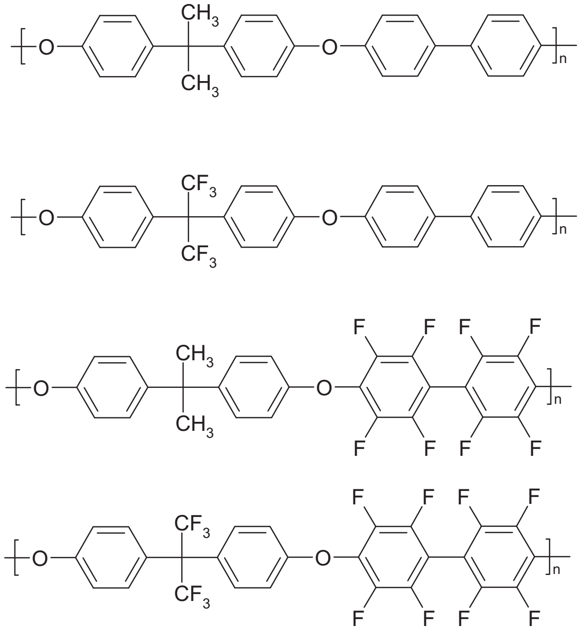


Scheme 1. Arylene polyethers - variations in the (bi)phenylene moiety.

The molecular weight distributions of the polymers (M_n, PDI) were determined by gel permeation chromatography (GPC) using an Agilent Technology GPC system (Series 1200) coupled with a viscosity detector (PSS ETA-2010) and a refractive index detector (Shodex RI71). A set of three PSS GRAM columns (30, 3000, 3000 Å) was used and calibrated with a series of polystyrene standards in *N,N*-dimethylacetamide containing 5 wt.% LiBr. All the samples were filtered by a Whatman syringe filter over a microporous PTFE membrane (1.0 µm, Whatman 6878-2510) before injecting into the column system. As tensile strength testing is not an in-house technique, the mechanical stability of the polymers and membranes have been estimated qualitatively in terms of their relative film-forming properties in the following way:



Scheme 2. Arylene polyethers - variations in the bisphenol moiety.



13a

14a

8a

5a

Scheme 3. Arylene polyethers - variations in the fluorine content.

- Membrane is very brittle (no further membrane characterization possible: Symbol −)
- Membrane easily ruptures when mechanically stressed (no temperature-dependent characterization possible: Symbol −/+)
- Membrane is flexible in the hydrated state (temperature-dependent characterization possible: Symbol +)
- Membrane is highly flexible, even in the dried state (Symbol: ++)

The thermal stability of the polymers and membranes was determined by thermogravimetry (TGA, Netzsch, model STA 449C) with a heating rate of 20 °C/min under an atmosphere enriched with oxygen (65–70% O_2, 35–30% N_2). Nonsulfonated polymers are compared by the temperature at which the sample has lost 5% of its initial weight ($T_{5\ \mathrm{wt.\%\ loss}}$). In the case of the sulfonated polymers the decomposition gases were further examined in a coupled FTIR spectrometer (Nicolet Nexus FTIR spectrometer) in order to identify the splitting-off temperature of the sulfonic acid group ($T^{\mathrm{onset}}_{\mathrm{SO_3H}}$) for which the asymmetric stretching vibration of the S=O group at 1352–1342 $\mathrm{cm^{-1}}$ was used. The glass transition temperatures (T_g) were determined by differential scanning calorimetry (Netzsch DSC 204 F1). Membrane pieces were dried in a vacuum oven at 90 °C for 16 h before determination of their thermal properties by TGA and DSC.

Ion-exchange capacities ($\mathrm{IEC_{direct}}$ and $\mathrm{IEC_{total}}$) were determined by titration. Membranes in the H^+ form were immersed in saturated sodium chloride solution (NaCl) for 24 h to convert them into the Na^+ form. The exchanged H^+ ions were then titrated with 0.1 M NaOH to the equivalent point ($\mathrm{IEC_{direct}}$). After that a defined excess of NaOH was added and this solution was back-titrated with 0.1 M HCl ($\mathrm{IEC_{total}}$).

The specific resistance (R_{spec}) of the membranes was determined at 25 °C to 70 °C in 0.5 M HCl by electrochemical impedance spectroscopy (EIS) using a method described in the literature [36] on an IM6 Model of Zahner Elektrik.

The water uptake (WU) of the samples was determined after equilibrating in water of defined temperatures (25 °C, 40 °C, 60 °C, 90 °C). After 48 h the sample was removed from the water solution, quickly dry wiped and immediately weighed (m_{wet}). Then the sample was dried to weight constancy at 90 °C and weighed once again (M_{dry}). The water uptake was obtained from these two values according to the following equation.

$$WU[\%] = \frac{m_{\mathrm{wet}} - m_{\mathrm{dry}}}{m_{\mathrm{dry}}} \times 100[\%] \tag{1}$$

The number of water molecules per sulfonic acid group λ is defined as the quantity of H_2O molecules ($n(H_2O)$) related to the number of sulfonic acid groups of the polymer [18] ($n(SO_3H)$) and is calculated according to equation (3):

$$\lambda = \frac{WU[\%]}{M(H_2O)\left[g\cdot mol^{-1}\right]\cdot IEC\left[mmol\cdot g^{-1}\right]} \times 10 \tag{2}$$

The procedure for the determination of the swelling degree is similar and is calculated from the length in the dry (l_{dry}) and in the wet (l_{wet}) state as follows.

$$\text{Swelling Degree}[\%] = \frac{l_{\mathrm{wet}} - l_{\mathrm{dry}}}{l_{\mathrm{dry}}} \times 100[\%] \tag{3}$$

2.2. Materials

2.2.1. Polymer preparation

Three different polycondensation methods were used in this study and will be described in the following. For each single polycondensation reaction it was tested which solvent was the most appropriate (i. e. which solvent yielded the polymer with the highest molecular weight). The solvents used in the polycondensation reactions (N-Methylpyrrolidinone NMP, N,N-Dimethylacetamide DMAc) were of “anhydrous” quality (<0.005% H_2O, 99.5% purity, Aldrich).

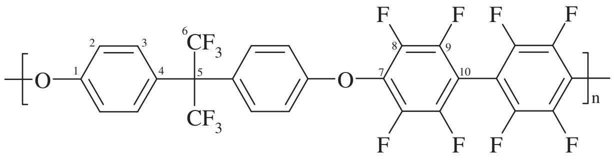
*2.2.1.1. Type 1: polycondensation with K_2CO_3 (for all polymers except for **6a**, **13a**, and **14a**).* This procedure is described for polymer **8a** as an example. The other polymers were prepared analogously. 16.0397 g (70.26 mmol) 2,2-bis-(4-hydroxyphenyl)propane (≥99%, Aldrich), 24.0366 g (71.94 mmol) decafluorobiphenyl (99%, Aldrich), 27.1444 g (0.196 mol) potassium carbonate (≥99%, anhydrous, Aldrich) and 360 ml of DMAc were added to a 500 ml round flask. The mixture was heated with stirring under argon to 80 °C for 23 h. Then the temperature was raised to 90 °C for 2 h and finally to 100 °C for another 2 h. The mixture was hot-filtered to remove the unreacted potassium carbonate and potassium fluoride by-product. After the solution was cooled to room temperature it was poured into 4 L of water to precipitate the polymer. The polymer was filtered, washed six times with water/methanol and dried at 55 °C for 16 h.

Polymers **1a**, **2a**, **3a**, and **4a**: As can be seen from Table 1, these reactions yielded only oligomers with low-molecular weights and therefore extremely bad mechanical stabilities (extreme brittleness). Therefore, they were not analyzed in detail by NMR.

Table 1
Overview of molecular weight distribution, film-forming and thermal properties of the prepared polymers with variations in the (bi)phenylene moiety (see Scheme 1) and 2,2-bis(4-hydroxyphenyl)hexafluoropropane.

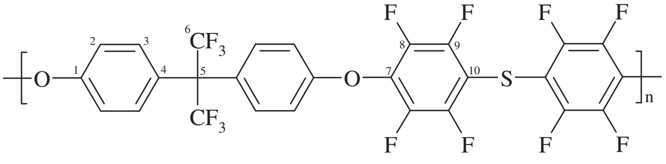
Polymer	R^1–R^3	R^4	Z	M_n [Da]	PDI	Film-forming properties	T_g [°C]	$T_{5\ \mathrm{wt.\%\ loss}}$ [°C]
1a	F	F	–	3700	2.20	–	n.a.	483
2a	F	H	–	7800	2.44	–	n.a.	n.a.
3a	F	CF_3	–	5400	3.90	–	n.a.	n.a.
4a	F	SO_3K	–	1700	1.40	–	n.a.	n.a.
5a	–	–	None	17200	3.44	++	175	507
6a	–	–	CO	16000	4.11	+	163	490
7a	–	–	S	12600	10.41	+	159	487

Polymer **5a**: 15.0295 g (44.70 mmol) 2,2-bis(4-hydroxyphenyl) hexafluoropropane (≥98%, Fluka) and 15.3027 g (45.80 mmol) decafluorobiphenyl (99%, Aldrich), 254 ml DMAc and 17.2763 g (0.125 mol) K_2CO_3 (≥99%, anhydrous, Aldrich) were warmed up in a 500 ml 3-neck reaction flask, which was equipped with Ar-inlet and -outlet, reflux cooler and a mechanical stirrer, for 23 h to 80 °C. After cooling down to room temperature excess K_2CO_3 and formed KF were filtered off, and the filtrate was precipitated in water. The product was separated, washed 2 times with water and methanol, and finally dried for 16 h at 55 °C in vacuum. Yield: 95%.



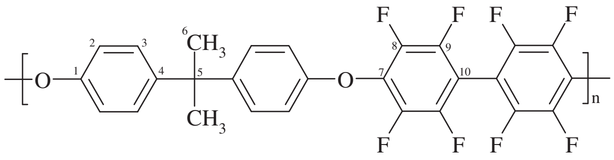
^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.43 (d, $^3J_{H\text{-}H} = 8.71$ Hz, H-3, 1 H), 7.07 (d, $^3J_{H-H} = 8.52$ Hz, H-2, 1 H). ^{13}C NMR ($CDCl_3$, 50 MHz, δ): 157.04 (C-1), 144.88 (d, $^1J_{C\text{-}F} = 253$ Hz, C-8), 141.80 (d, $^1J_{C\text{-}F} = 253$ Hz, C-9), 134.78 (m, C-7), 132.02 (C-3), 128.95 (C-4), 124.07 (q, $^1J_{C-F} = 287$ Hz, C-6), 115.50 (C-2), 103.17 (m, C-10), 63.26 (Septett, $^2J_{C\text{-}F} = 26$ Hz, C-5). ^{19}F NMR ($CDCl_3$, 188 MHz, δ): −152.69 (s, F-8, 4 F), −137.78 (s, F-9, 4 F), −64.33 (s, F-6, 6 F).

Polymer **7a**: Reaction conditions: 80 °C (7 h); stoichiometric ratio of monomers: 0.947, monomer concentration: 11.5 wt.%, solvent: NMP, yield: 70%.



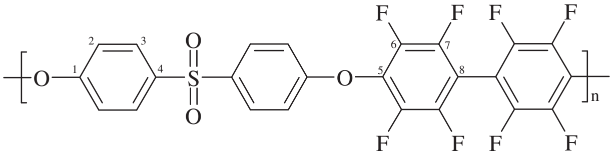
^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.35 (d, $^3J_{H-H} = 8.31$ Hz, H-3, 1 H), 6.96 (d, $^3J_{H-H} = 8.10$ Hz, H-2, 1 H). ^{13}C NMR ($CDCl_3$, 50 MHz, δ): 156.93 (C-1), 147.53 (d, $^1J_{C-F} = 253$ Hz, C-9), 141.66 (d, $^1J_{C\text{-}F} = 253$ Hz, C-8), 134.62 (m, C-7), 131.94 (C-3), 128.87 (C-4), 123.97 (d, $^1J_{C-F} = 286$ Hz, C-6), 115.37 (C-2), 107.35 (m, C-10), 63.69 (septet, $^2J_{C-F} = 25.6$ Hz, C-5).

Polymer **8a**: Reaction conditions: 80 °C (23 h), 90 °C (2 h), 100 °C (2 h), stoichiometric ratio of monomers: 0.977, monomer concentration: 10.6 wt.%, solvent: DMAc, yield: 82%.



^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.22 (d, $^3J_{H-H} = 8.54$ Hz, H-2, 4 H), 6.96 (d, $^3J_{H-H} = 8.54$ Hz, H-3, 4 H), 1.68 (s, H-6, 6 H). ^{13}C NMR ($CDCl_3$, 63 MHz, δ): 154.98 (C-1), 146.31 (C-4), 144.81 (d, $^1J_{C-F} = 253$ Hz, C-8), 141.82 (d, $^1J_{C-F} = 253$ Hz, C-9), 135.58 (t, $^2J_{C-F} = 13$ Hz, C-7)-, 128.22 (C-3), 115.41 (C-2)-, 102.55 (t, $^2J_{C-F} = 13$ Hz, C-10), 42.21 (C-5), 30.94 (C-6). ^{19}F NMR ($CDCl_3$, 188 MHz, δ): −152.73 (s, F-8, 4 F), −138.37 (s, F-9, 4 F).

Polymer **9a**: Reaction conditions: 80 °C (23 h), stoichiometric ratio of monomers: 0.977, monomer concentration: 11.2 wt.%, solvent: DMAc, yield: 82%.

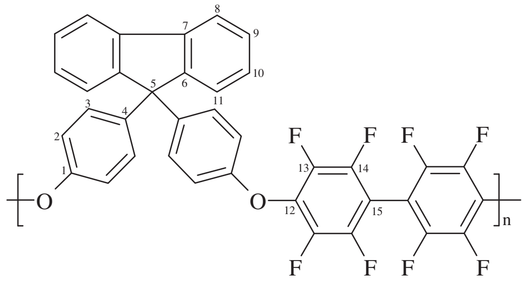


^{1}H NMR ($CDCl_3$, 200 MHz, δ): 7.98 (d, $^3J_{H-H} = 8.31$ Hz, H-3, 1 H), 7.16 (d, $^3J_{H-H} = 8.72$ Hz, H-2, 1 H). ^{13}C NMR ($CDCl_3$, 63 MHz, δ): 160.03 (C-1), 144.58 (d, $^1J_{C-F} = 253$ Hz, C-6), 141.58 (d, $^1J_{C-F} = 253$ Hz, C-7), 137.25 (C-4), 134.17 (t, $^2J_{C-F} = 13$ Hz, C-5), 130.27 (C-3), 116.46 (C-2), 103.61 (t, $^2J_{C-F} = 13$ Hz, C-8). ^{19}F NMR ($CDCl_3$, 188 MHz, δ): −152.28 (s, F-6, 4 F), −137.07 (s, F-7, 4 F).

Polymer **10a**: Reaction conditions: 80 °C (23 h), stoichiometric ratio of monomers: 0.977, monomer concentration: 10.1 wt.%, solvent: DMAc, yield: 92%.

Since this polymer was insoluble in the tested deuterated solvents, no NMR spectra could be recorded of it. Therefore the polymer was characterized only *via* elemental analysis {experimental (theoretical) values in [%]}: C: 55.78 (56.26), H: 1.69 (1.57), S: 6.35 (6.26), F: 26.57 (29.66).

Polymer **11a**: Reaction conditions: 75 °C (16 h); stoichiometric ratio of monomers: 0.997, monomer concentration: 14.9 wt.%, solvent: DMAc, yield: 89%.



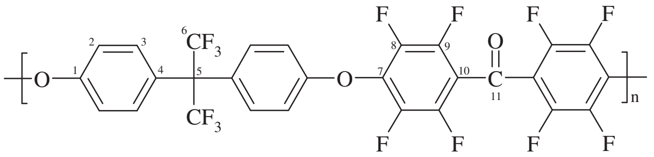
^{1}H,^{13}C HSQC NMR (250 MHz, 63 MHz, $CDCl_3$, δ): 7.78/120.34 (H-8/C-8), 7.39/125.97 (H-11/C-11), 7.37/127.79 (H-9/C-9), 7.26/127.89 (H-10/C-10), 7.19/129.59 (H-3/C-3), 6.90/115.58 (H-2/C-2). ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.78 (d, $^3J_{H-H} = 7.77$ Hz, H-8, 1 H), 7.39–7.30 (H-9, H-11, 2 H), 7.26 (t, $^3J_{H-H} = 7.28$ Hz, H-10, 1 H), 7.19 (d, $^3J_{H-H} = 7.21$ Hz, H-3, 2 H), 6.90 (d, $^3J_{H-H} = 6.91$ Hz, H-2, 2 H). ^{13}C NMR ($CDCl_3$, 50 MHz, δ): 155.76 (C-1), 150.84 (C-6), 144.81 (d, $^1J_{C-F} = 253$ Hz, C-13), 142.00 (d, $^1J_{C-F} = 253$ Hz, C-14), 141.55 (C-7), 140.00 (C-4), 135.76-135.13 (C-12), 129.59 (C-3), 127.89 (C-10), 127.79 (C-9), 125.97 (C-11), 120.34 (C-8), 115.58 (C-2), 103.12-102.25 (C-15), 64.23 (C-5). ^{19}F NMR ($CDCl_3$, 188 MHz, δ): −152.97 (s, F-13, 1 F), −138.22 (s, F-14, 1 F).

Polymer **12a**: A 250 ml 3-neck flask equipped with Ar-inlet and -outlet, mechanical stirrer and reflux condenser was charged with 3.8769 g (20.82 mmol) 4,4′-dihydroxybiphenyl (99%, Aldrich), 7.1234 g (21.32 mmol) decafluorobiphenyl (99%, Aldrich), 120 ml DMAc and 8.0466 g (58.22 mmol) potassium carbonate (≥99%, anhydrous, Aldrich). The mixture was heated to 80 °C for 38 h under inert atmosphere (argon flow). It was then cooled down to room temperature and poured into 1.5 L water with stirring. The precipitate was filtered off, washed three times with water at room temperature and coagulated in hot water (90 °C) for 12 h. Finally, the product was isolated by filtration and dried at 55 °C *in vacuo*.

Due to insufficient solubility of the product in common solvents, like chloroform, dimethylsulfoxide DMSO and NMP, the polymer could only be characterized *via* elemental analysis: {experimental (theoretical) values in [%]}: C: 58.09 (60.02), H: 1.86 (1.68), F: 28.32 (31.64).

*2.2.1.2. Type 2: polycondensation with CaH$_2$/CsF (**6a**).* Polymer **6a** was synthesized using a procedure from the literature [33] which was optimized in terms of the stoichiometric imbalance of monomers, reaction time and reaction temperature.

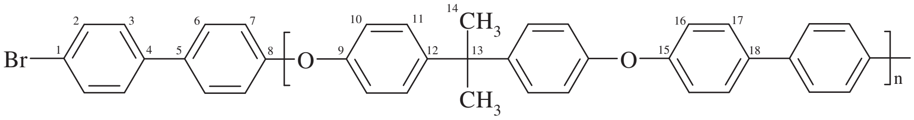
94 mg (0.619 mmol) caesium fluoride (99%, Aldrich) and 562 mg (13.55 mmol) calcium hydride (powder, 99.99%, Aldrich) were added to a solution of 2.2618 g (6.25 mmol) decafluorobenzophenone (98%, Aldrich) and 2.1003 g (6.25 mmol) 2,2-bis (4-hydroxyphenyl)hexafluoropropane (≥98%, Fluka) in 40 ml DMAc and stirred at 75 °C for 19 h under argon atmosphere. The reaction mixture was cooled down to room temperature and poured into 1 L of 1 M HCl. After the precipitate was filtered, it was washed with water and methanol twice and finally dried at 70 °C under vacuum.



^{1}H NMR (CDCl$_3$, 200 MHz, δ): 7.40 (d, $^{3}J_{H-H}$ = 8.31 Hz, H-3, 4 H), 7.02 (d, $^{3}J_{H-H}$ = 8.51 Hz, H-2, 4 H). ^{13}C NMR (CDCl$_3$, 50 MHz, δ): 176.36 (C-11), 156.71 (C-1), 145.36 (d, $^{1}J_{C-F}$ = 258 Hz, C-9), 141,46 (d, $^{1}J_{C-F}$ = 258 Hz, C-8), 136.91 (m, C-7), 132.03 (C-3), 129.21 (C-4), 123.98 (q, $^{1}J_{C-F}$ = 287 Hz, C-6), 115.60 (C-2), 115.08 (m, C-10), 63.50 (Septett, $^{2}J_{C-F}$ = 25.6 Hz, C-5). ^{19}F NMR (CDCl$_3$, 188 MHz, δ): −151.76 (s, F-8, 2 F), −141.49 (s, F-9, 2 F), −64.35 (s, F-6, 3 F).

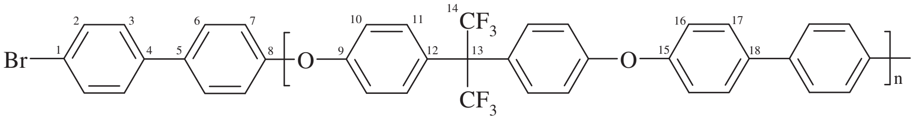
*2.2.1.3. Type 3: CuCl-catalyzed Ullmann biaryl polycondensation (**13a** and **14a**).* A 500 ml 3-neck flask equipped with a mechanical stirrer, argon inlet, dropping funnel, Dean–Stark apparatus, reflux condenser and mercury bubbler was charged with 22.829 g (0.10 mol) 2,2-bis(4-hydroxyphenyl)propane (≥99%, Aldrich) (**13a**) or 33.624 g (0.10 mol) 2,2-bis(4-hydroxyphenyl)-hexafluoropropane (≥98%, Fluka) (**14a**), respectively, and 75 g toluene (anhydrous, 99.8%, Aldrich), 120 g (0.659 mol) benzophenone puriss., (≥99.0%, Fluka). This mixture was heated to 60 °C under continuous stirring until a homogenous solution was obtained. 16.00 g of a 12.5 M NaOH solution were dropwise added and the reaction mixture was then heated to 145 °C for 4 h to remove the formed water/toluene azeotrope. The reaction mixture was allowed to cool down to 80 °C and 31.200 g (0.10 mol) of 4,4′-dibromobiphenyl were added, the temperature was gradually raised to 210 °C and maintained at this temperature to remove the excess toluene. Then it was cooled down again to 80 °C and the catalyst solution (0.1 g CuCl (reagent grade, 97%, Aldrich) in 10 ml quinoline (≥99.0%, Aldrich)) was injected and heated to 200 °C for 9 h. The reaction was stopped by injecting 0.7851 g (5.00 mmol) bromobenzene (ReagentPlus, 99%, Aldrich) and diluted by 200 ml toluene (anhydrous, 99.8%, Aldrich). This solution was poured into 1 L methanol (acidified with 50 ml acetic acid). The fibrous precipitate was filtered, washed in boiling water and methanol and dried at 90 °C under vacuum for 16 h.

NMR results of polymer **13a**



^{1}H,^{13}C HSQC NMR (250 MHz, 63 MHz, CDCl$_3$, δ): 7.54 (d, $^{3}J_{H-H}$ = 8.4 Hz, 0.60 H)/131.79 (H-2/C-2), 7.50 (d, $^{3}J_{H-H}$ = 8.5 Hz, 1.02 H)/128.19 (H-17/C-17, H-6/H-6), 7.42 (d, $^{3}J_{H-H}$ = 8.0 Hz, 0.60 H)/128.35 (H-3/C-3), 7.25 (d, $^{3}J_{H-H}$ = 8.0 Hz, 1.00 H)/128.07 (H-11/C-11), 7.08 (d, $^{3}J_{H-H}$ = 8.7 Hz, 1.01 H)/118.94 (H-16/C-16, H-7/C-7), 6.98 (d, $^{3}J_{H-H}$ = 7.3 Hz, 0.99 H)/118.47 (H-10/C-10). ^{13}C NMR (63 MHz, CDCl$_3$, δ): 157.28 (C-8, C-15), 154.71 (C-9), 145.80 (C-12), 139.43 (C-4, C-5), 134.77 (C-18), 131.79 (C-2), 128.35 (C-3), 128.19 (C-6, C-17), 128.07 (C-11), 121.18 (C-1), 118.94 (C-7, C-16), 118.47 (C-10), 42.15 (C-13), 31.02 (C-14).

NMR results of polymer **14a**



^{1}H,^{13}C HSQC NMR (250 MHz, 63 MHz, CDCl$_3$, δ): 7.57 (d, $^{3}J_{H-H}$ = 6.6 Hz, 1.00 H)/128.35 (H-6/C-6, H-17/C-17), 7.56 (d, $^{3}J_{H-H}$ = 5.90 Hz, 0.11 H)/131.94 (H-2/C-2), 7.43 (d, $^{3}J_{H-H}$ = 6.0 Hz, 0.11 H)/128.51 (H-3/C-3), 7.40 (d, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 1.01 H)/131.69 (H-11/C-11), 7.15 (d, $^{3}J_{H-H}$ = 7.3 Hz, 1.00 H)/120.07 (H-7/C-7, H-16/C-16), 7.04 (d, $^{3}J_{H-H}$ = 7.7 Hz, 1.00 H)/117.48 (H-10/C-10). ^{13}C NMR (63 MHz, CDCl$_3$, δ): 158.05 (C-8, C-15), 155.39 (C-9), 139.24 (C-4, C-5), 136.42 (C-18), 131.94 (C-2), 131.94 (C-11), 128.51 (C-3), 128.35 (C-6, C-17), 127.62 (C-12), 124.28 (q, $^{1}J_{C-F}$ = 287 Hz, C-14), 120.07 (C-7, C-16), 117.48 (C-10), 63.75 (Septett, $^{2}J_{C-F}$ = 22.70 Hz).

Elemental analysis results of polymer **14a**

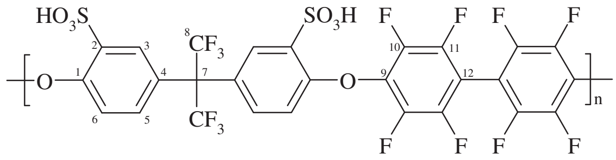
{experimental (theoretical) values in [%]}: C: 65.91 (65.31); H: 3.53 (3.27), Br: 3.50 (3.41). The theoretical results corresponds to $BrC_{12}H_8(C_{27}H_{16}O_2F_6)_9Br$

2.2.2. Sulfonation reactions

Those polymers with molecular weight > 10 kDa and good membrane formation properties were sulfonated under conditions described in the following [20,21,37]. The strength of the sulfonation agents had to be varied since the polymers showed different electron density within their aromatic systems – the more electron-deficient an aromatic ring is, the more difficult is its sulfonation, and consequently the stronger a suitable sulfonation agent has to be. Among the sulfonation agents, sulfuric acid with varying content of free SO$_3$ ("oleum") is a good choice, because the sulfonation strength of this sulfonation agent is the higher the higher its free SO$_3$ content is. Therefore, the strength of the sulfonation agent could be tailored to the respective polymer to be sulfonated to obtain maximum sulfonation degree combined with as small as possible polymer degradation during sulfonation.

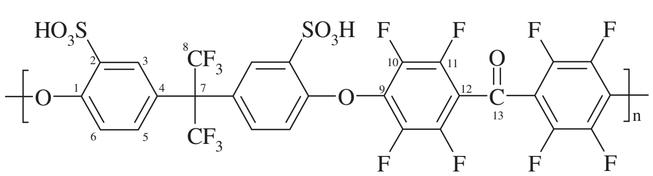
2.2.2.1. Heterogeneous sulfonation with (fuming) sulfuric acid. 12.00 g of the dried poly(arylene) and the amount of fuming sulfuric acid with different SO$_3$ concentrations (Aldrich), given below for the individual polymers, was stirred in a 3-neck flask (equipped with a mechanical stirrer, reflux condenser and drying tube (P$_2$O$_5$)). Subsequently, the reaction mixture was slowly poured onto ice, and the formed suspension/solution was dialyzed for 4 days (Visking dialysis tube, MWCO 12,000–14,000 Da). Ionomers were recovered after filtration and polyelectrolytes after evaporating water. The final products were dried at 110 °C in a vacuum oven for 16 h.

Ionomer **5b**: Sulfonation reagent: 220 ml H_2SO_4 (65% w/w SO_3); reaction time: 2 h; yield: 78%.



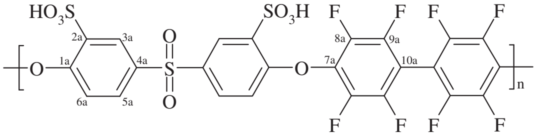
^{1}H,^{13}C HSQC NMR (250 MHz, 63 MHz, DMSO-*d6*, δ): 7.99/130.36 (1 H, H-3/C-3), 7.30/117.25 (1.02 H, H-6/C-6), 7.24/132.25 (0.98 H, H-5/C-5). Coupling pattern could not be resolved. ^{13}C NMR (DMSO-*d6*, 63 MHz, δ): 153.29 (C-1), 144.37 (d, $^{1}J_{C-F} = 255$ Hz, C-10), 140.72 (d, $^{1}J_{C\text{-}F} = 255$ Hz, C-11), 137.23 (C2)-, 135.25 (m, C-9), 132.25 (C-5), 130.36 (C-3), 127.18 (C-4), 124.03 (q, $^{1}J_{C-F} = 293$ Hz, C-8), 117.25 (C-6), 101.28 (C-12), 63.41 (septet, $^{2}J_{C-F} = 25.8$ Hz, C-7). ^{19}F NMR (DMSO-*d6*, 188 MHz, δ): −58.83 (F-8, 3 F), −134.34 (d, $^{3}J_{C-F} = 15.3$ Hz, F-11, 2 F) 149.42 (d, $^{3}J_{C-F} = 17.1$ Hz, F-10, 2 F).

Ionomer **6c**: Sulfonation reagent: 220 ml H_2SO_4 (20% w/w SO_3); reaction time: 16 h; yield: 74%

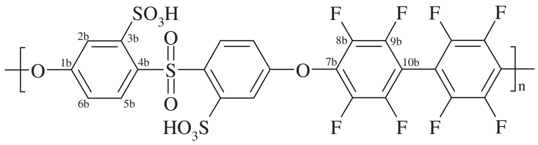


^{1}H,^{13}C HSQC NMR (250 MHz, 63 MHz, $CDCl_3$, δ): 7.95/130.15 (s, H-3/C-3), 7.27/117.79 (d, $^{3}J_{H\text{-}H} = 8.2$ Hz, H-6/C-6), 7.21/132.18 (d, $^{3}J_{H-H} = 8.3$ Hz, H-5/C-5). ^{13}C NMR (DMSO-*d6*, 63 MHz, δ): 176.70 (C-13), 152.93 (C-1), 145.09 (d, $^{1}J_{C-F} = 254$ Hz, C-11), 142.13 (d, $^{1}J_{C-F} = 254$ Hz, C-10), 137.49 (C-2), 137.81 (C-9), 132.18 (C-5), 130.15 (C-3), 127.60 (C-4), 123.93 (q, $^{1}J_{C-F} = 285$ Hz, C-8), 117.79 (C-6), 113.12 (t, $^{2}J_{C-F} = 14.8$ Hz, C-12). C-7 not found. ^{19}F NMR (188 MHz, DMSO-*d6*, δ): −58.86 (s, F-8, 6 F), −138.17 (s, F-11), 149.08 (s, F-10).

Ionomer **9b**: Sulfonation reagent: 220 ml H_2SO_4 (65% w/w SO_3); reaction time: 2 h; yield: 98%



9b (**1**): 95.2%

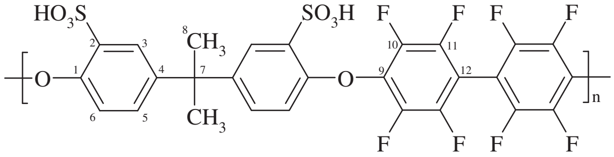


9b (**2**): 4.8%

^{1}H,^{13}C HSQC NMR (250 MHz, 63 MHz, DMSO-*d6*, δ): 8.32 (d, $^{4}J_{H-H} = 2.1$ Hz, 1 H)/128.43 (H-3a/C-3a), 8.12 (d, $^{4}J_{H-H} = 2.1$ Hz, 0.05 H)/126.98 (H-2b/C-2b), 7.91 (dd, $^{3}J_{H-H} = 8.5$ Hz, $^{4}J_{H-H} = 2.0$ Hz, 1 H)/130.44 (H-5a/C-5a), 7.58 (dd, $^{3}J_{H-H} = 8.4$ Hz, $^{4}J_{H-H} = 1.8$ Hz, 0.05 H)/128.05 (H-5b/C-5b), 7.44 (d, $^{3}J_{H-H} = 8.6$ Hz, 1 H)/118.04 (H-6a/C-6a), 7.15 (d, $^{3}J_{H-H} = 8.3$ Hz, 0.05 H)/116.65 (H-6b/C-6b). ^{13}C NMR (100 MHz, DMSO-*d6*, δ): 156.39 (C-1a), 152.83 (C-1b), 144.51 (d, $^{1}J_{C-F} = 254$ Hz, C-8a, C-8b), 143.50 (C-4b), 140.73 (d, $^{1}J_{C-F} = 254$ Hz, C-9a, C-9b), 138.21 (C-4a), 136.42 (C-3b), 135.98 (C-2a), 134.71 (m, C-7a, C-7b), 130.44 (5a), 128.43 (C-3a), 128.05 (C-5b), 126.98 (C-2b), 118.04 (C-6a), 116.65 (C-6b), 101.92 (m, C-10a, C-10b). ^{19}F NMR (188 MHz, DMSO-*d6*, δ): −133.81 (d, $^{3}J_{F-F} = 17.1$ Hz, F-9a), −134.65 (m, F-9b), −148.99 (d, $^{3}J_{F-F} = 16.2$ Hz, F-8a), 149.83 (m, F-8b).

Ionomer **11c**: 12.00 g of the polymer **11a** were dissolved in 200 ml concentrated sulfuric acid (Aldrich, 98%). The solution was stirred for 4 h at 60 °C and then at 80 °C for 14 h. The colour of the reaction mixture changed from brownish to purple, and the largest fraction of the polymer was dissolved. Finally, the reaction mixture was carefully poured onto ≈2000 g ice, and unreacted **11a** was filtered off. Polyelectrolyte **11c** was recovered as a solid after dialysis. It was dried in a vacuum oven at 120 °C for 16 h. In the NMR spectra, it was not possible to assign the ^{1}H and ^{13}C or ^{19}F signals to the respective nuclei due to broad signals, multiple couplings and signal superpositions.

2.2.2.2. Homogeneous sulfonation with chlorosulfonic acid in dichloromethane. Ionomer **8c**: 19.6313 g chlorosulfonic acid $ClSO_3H$ (99%, Aldrich) in 175 ml dichloromethane (anhydrous, 99.8%, Aldrich) were slowly dropped to a solution of 11 g **8a** (21.06 mmol) in 100 ml dichloromethane. The reaction mixture was stirred for 3 h at room temperature until the light-brown product was precipitated. The precipitate was filtered off, washed three times with *n*-pentane, and was subsequently dissolved in 200 ml DMSO (≥99.8%, Aldrich). 830 ml KOH solution (3 wt.%) were added, and the mixture was stirred for 12 h. After that, 200 ml concentrated HCl (36% w/w, Aldrich) were added to the mixture. The reaction solution was dialyzed, the solvent was evaporated, and the product was dried at 110 °C in a vacuum oven.



^{1}H NMR (200 MHz, DMSO-*d6*, δ): 7.72 (s, H-3, 1 H), 7.16–7.12 (H-5, H-6, 2 H), 1.64 (s, H-8, 3 H). ^{13}C NMR (50 MHz, DMSO-*d6*, δ): 150.81 (C-1), 145.62 (C-4), 144.32 (d, $^{1}J_{C-F} = 254$ Hz, C-10), 140.50 (d, $^{1}J_{C-F} = 254$ Hz, C-11), 136.37 (C-2), 136.20 (C-9), 128.97 (C-5), 126.86 (C-3), 116.87 (C-6), 100.43 (t, $^{3}J_{C-F} = 16.3$ Hz, C-12), 42.10 (C-7), 30.76 (C-8).

2.2.2.3. Homogeneous sulfonation with trimethylsilylchlorosulfonic acid in CH_2Cl_2. Ionomer **11d**: 5.00 g (7.758 mmol) of dried polymer **11a** were dissolved in 45 g (*ca.* 34 ml) anhydrous dichloromethane (99.8%, Aldrich) under argon atmosphere. 2.9280 g (*ca.* 2.4 ml) trimethylsilylchlorosulfonic acid (ABCR) in 6.832 g dichloromethane was dropped slowly to the polymer solution. After 17 h stirring at room temperature, the reaction mixture was poured into a large excess of water. The polymer was washed with water two times. Finally, it was dried at 60 °C in a vacuum oven. Yield: 3.207 g.

2.2.3. Preparation of ionically crosslinked blend membranes

The proper amount of sulfonated polymer (in H^+ form) was dissolved in *N*-methylpyrrolidinone (ACS Reagent, ≥99%, Aldrich) to yield a 10 wt.% polymer solution. Then, 1.5 equivalents of *n*-propylamine (≥99%, Aldrich), referring to the SO_3H content of the polymer, were added to the solution in order to neutralize the SO_3H groups of the sulfonated polymer – if a sulfonated polymer in the SO_3H form would be mixed with PBI, a polyelectrolyte complex of the sulfonated polymer with PBI would immediately precipitate. The calculated amount of PBI DMAc solution (m_{PBI}, cf. Equation (1)) which is required to obtain the desired IEC of the blend membrane is added to the solution.

$$m_{PBI} = m_A \cdot \frac{IEC_A - IEC_0}{IEC_{PBI} + IEC_0} \tag{4}$$

herein, m_{PBI} refers to the mass of PBI, m_A to the mass of the sulfonated polymer; IEC_A is the ion-exchange capacity of the acidic component, IEC_{PBI} that of PBI and IEC_0 is the desired IEC of the blend membrane.

The polymer blend solution was cast into an alumina bowl (12 cm × 12 cm), and the solvent mixture was evaporated at 130 °C under atmospheric pressure in a convection oven. Prior to characterization, the membranes were post-treated 48 h in 10%

hydrochloric acid at 90 °C, followed by a post-treatment in deionised water at 60 °C for 48 h to remove excess acid.

2.2.4. MEA preparation and DMFC testing

The MEA preparation and DMFC testing of the membranes was done at Center for Solar Energy and Hydrogen Reasearch (ZSW), GB3, Ulm. The procedures are described in [38].

3. Results and discussion

3.1. Structure variations in the (bi)phenylene moiety

Variations in the phenylene (**1a**–**4a**) and in the biphenylene (**5a**–**7a**) were made by reacting 2,2-bis(4-hydroxyphenyl)hexafluoropropane (BHPHFP) with the corresponding difluoroaryl or difluorobiaryl monomers. Although the nucleophilicity of BHPHFP is less than that of the corresponding nonfluorinated species, it was chosen as model compound in order to avoid any weak points for potential radical attack in the final poly(arylene ether)s. In Table 1, an overview of the molecular weight distribution, the film-forming properties and the thermal properties of those polymers is given. All the polycondensations using BHPHFP and different oligofluorophenylenes (**1a** to **4a**, Scheme 1a) did not yield polymers, but oligomers. Their molecular weights were moderately low, leading to poor film-forming properties. In contrast, the polycondensation of BHPHFP with decafluorobiphenyl (**5a**), decafluorobenzophenone (**6a**) and bis(pentafluorophenyl)sulphide (**7a**) (Scheme 1b) yielded polymeric products as the considerably higher molecular weights and the superior film-forming properties indicate (Table 1). Therefore, the three poly(arylene ether)s **5a**–**7a** will be discussed in greater depth.

The polycondensation of BHPHFP with decafluorobiphenyl (Z = chemical bond) under weakly basic conditions (K_2CO_3) in DMAc leads to high-molecular structures (**5a**) with a slightly asymmetric, monomodal molecular weight distribution with a broad shoulder in the low-molecular range of the molecular weight distribution (MWD) curve corresponding to a percentage of low-molecular compounds of *ca.* 1.3% (estimated, Fig. 1). This shoulder in the MWD curve probably arises from cyclic oligomers formed during the polycondensation reaction [39,40]. However, end group signals of linear oligomeric species (*para*-hydroxyphenyl or pentafluorophenyl) are neither found in the ^{1}H NMR nor in the ^{19}F NMR spectra of **5a** (Figs. 2 and 3). On the other hand, signals caused by cyclic oligomeres would not be distinguishable from the signals that arise from the long-chained poly(aryl) structures. It can be concluded from the absence of such signals that either the concentration of the linear oligomers is below the detection threshold of NMR, or cyclic oligomers dominate in the low-molecular range of the distribution. A doubtless clarification of these structures would, however, necessitate fractioning of the polymer samples and subsequent MALDI-TOF mass spectroscopy [41] which is not an in-house technique at our institute. However, the ^{1}H NMR spectra of **6a** (Z = CO) and **7a** (Z = S) show signals that originate from linear oligomeric structures. *para*-hydroxyphenyl groups are visible for both poly(arylene ether)s (H-1′ in Fig. 2, the signals of H-2′ overlap with the much more intensive signal of the analogous protons from cyclic oligomers and long-chained poly (arylene ether)s). The signal at $\delta = 6.91$ ppm in the ^{1}H NMR spectrum of **6a** is caused by the proton of 2,3,5,6-tetrafluorophenoxy end groups (H-3′). This end group can be formed under the basic conditions of the polycondensation (if traces of water are present) *via* nucleophilic addition of OH^- to the activated carbonyl bridge and subsequent decarboxylation (Fig. 4). The absence of the corresponding signals in the ^{19}F NMR spectrum can be explained with the lower detection sensitivity of ^{19}F nuclei, compared to ^{1}H nuclei [42].

Furthermore, the molecular weight distribution curves (Fig. 1) of **5a**–**7a** reveal significant differences in their composition. While the MWD curve of **5a** is monomodal, that of **6a** shows a distinct shoulder, and that of **7a** even a bimodal characteristic. The distributions of **6a**

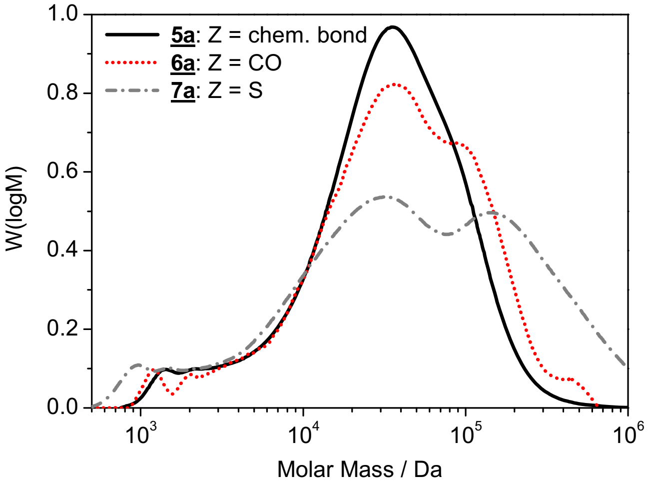


Fig. 1. Comparison of the molecular weight distribution of the three poly(arylene ether)s **5a**–**7a** with the different bridges **Z** in the electron-deficient, perfluorinated moiety.

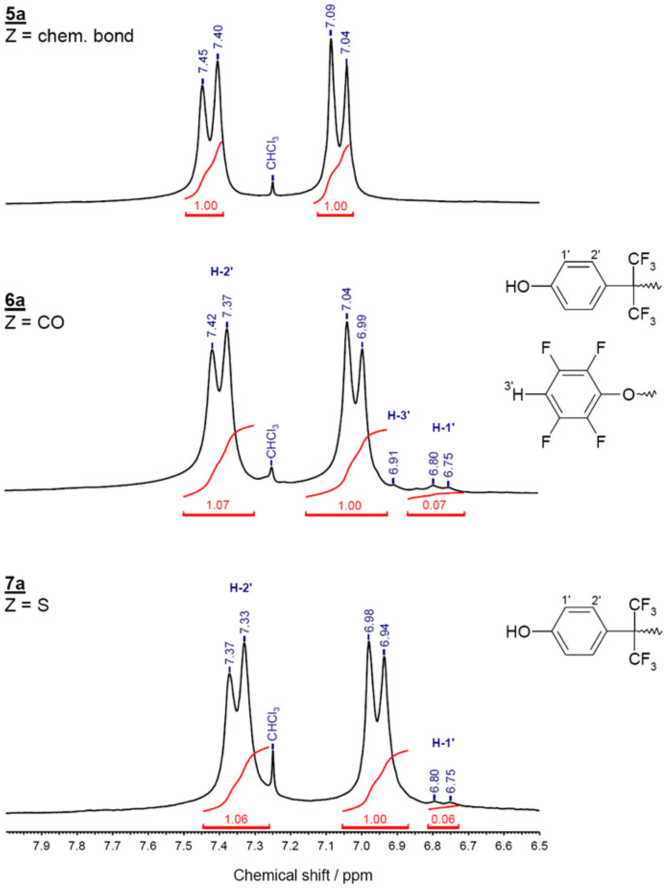


Fig. 2. ^{1}H NMR spectra of the poly(arylene ether)s **5a**–**7a** with different bridges in the electron-deficient, perfluorinated part (assignment of main signals see experimental part).

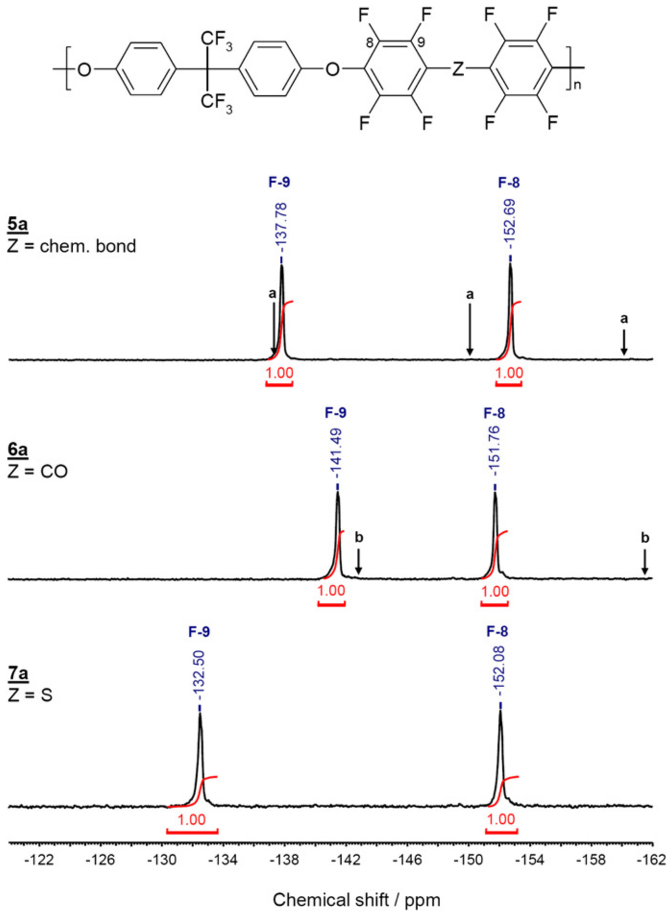


Fig. 3. ^{19}F NMR spectra of the poly(arylene ether)s **5a**–**7a** with different bridges **Z** in the electron-deficient, perfluorinated part. The chemical shifts expected for pentafluorophenyl end groups are assigned with "a", those with the 2,3,5,6-tetrafluorophenoxy end group in the case of **7a** with "b" (see text).

Table 2
Overview of molecular weight distribution, film-forming and thermal properties of the polymers with various bisphenol moieties.

Polymer	L	M_n [Da]	PDI	Film-forming properties	T_g [°C]	$T_{5\ \mathrm{wt.\%\ loss}}$ [°C]
8a	$C(CH_3)_3$	19400	3.04	++	165	441
5a	$C(CF_3)_3$	17200	3.44	++	175	507
9a	SO_2	19000	5.14	++	212	476
10a	S	insoluble	insoluble	[a]	145	538
11a	9-fluorenylene	13400	2.74	+	255	529
12a	none	insoluble	insoluble	[a]	n.a.	514

[a] not completely soluble in DMAc, DMF, NMP and DMSO.

(PDI = 4.11) and even more of **7a** (PDI = 10.41) are very broad which affect the mechanical properties adversely. Therefore, it can be concluded that poly(arylene ether) **5a** (with the direct bond in the perfluorinated moiety) has the most advantageous properties in terms of polymerisability, width of MWD, degradation reactions, and thermal stability (Table 1) among the polymeric structures **5a**–**7a**. For this reason, structural variations in the bisphenol part were focussed on polymers with octafluorobiphenylene in the biphenylene moiety (Z = chemical bond).

3.2. Structure variations in the bisphenol moiety

In order to identify suitable groups L (Scheme 2), 6 different bisphenols were reacted with decafluorobiphenyl. Table 2 surveys the molecular weight distribution (M_n, PDI) as well as the film-forming and thermal properties. The molecular weight distribution curves of the poly(arylene ether)s **5a**, **8a**, **9a**, and **11a** are shown in Fig. 5. Products soluble in common organic solvents could not be obtained in the course of the polymerisation processes for **10a** and **12a**. Obviously, cross-linking reactions took place in the course of the polycondensation process, such as reaction of phenolate groups with the 2/2′ or 3/3′ fluorine atoms of the octafluorobiphenylene of a growing chain. This hypothesis is supported by the fact that the fluorine content of the polymers **10a** and **12a**, experimentally found, is markedly lower than calculated for exclusive 4,4′-substitution. These results suggest a higher reactivity of the bisphenolates of 4,4′-thiodiphenol (TDP) and 4,4′-dihydroxybiphenyl (DHBP), compared to the other bisphenolates of this series. The reactivity during the nucleophilic aromatic polycondensation is mainly governed by the deprotonation equilibrium between bisphenol and potassium carbonate as well as by the solubility and the nucleophilicity of the bisphenolate in the dipolar-aprotic solvent [43].

The nucleophilicity of the dissolved bisphenolate and of the oligomeric bisphenolates, formed during the polycondensation, particularily determine the reaction progress. Table 3 gathers the pK_a values of the bisphenol monomers for the polymers **5a** and **8a**–**12a** from which the basicities of the corresponding bisphenolates can easily be calculated. The basicities are commonly used to

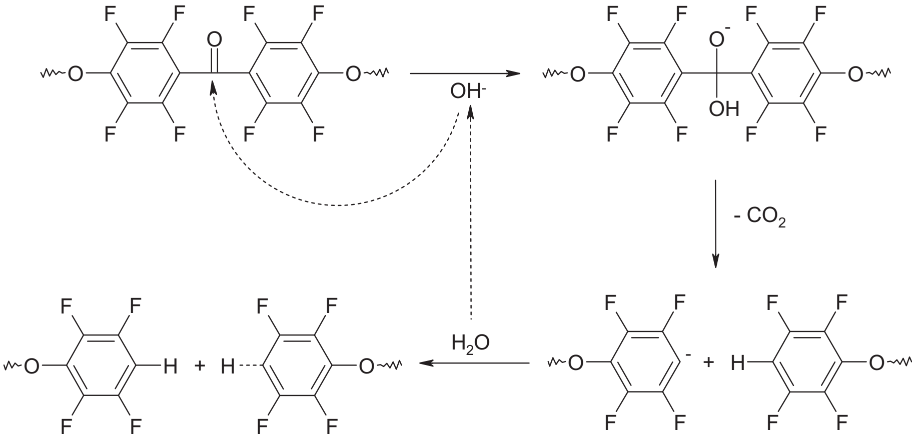


Fig. 4. Proposed mechanism for the formation of 2,3,5,6 tetrafluorophenoxy end groups during the polycondensation of **6a**.

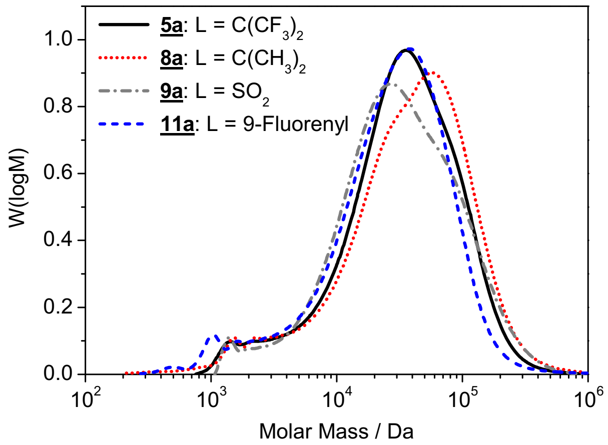


Fig. 5. Comparison of the molecular weight distributions of the poly(arylene ether)s **5a**, **8a**, **9a**, and **11a** with different bridges **L** in the bisphenol moiety (while **Z** being constant, **Z** = chemical bond).

Table 4
Overview of molecular weight distribution, film-forming and thermal properties of the polymers with variations in the fluorine content (for chemical structures see Scheme 3).

Polymer	M_n [Da]	PDI	Film-forming properties	T_g [°C]	$T_{5\ \mathrm{wt.\%\ loss}}$ [°C]
13a	2650	1.02	–	–	408
14a	5000	1.38	–	137	499
8a	19400	3.04	++	165	441
5a	17200	3.44	++	175	507

estimate their relative nucleophilicities [44–47]. As can be seen from the pK_a values of the various bisphenols, the bisphenolates of TDP and DHBP show the highest basicity and thus nucleophilicity, which is in accordance with their higher polycondensation reactivities.

The thermal properties of the various poly(arylene ether)s differ significantly. For example, when $T_{5\ \mathrm{wt.\%\ loss}}$ (which represents the temperature at which the polymer has lost 5 wt.% of its initial weight and which is used as a measure of thermal stability) of **5a** is compared with that of **8a**, the significant stabilization effect of the $C(CF_3)_2$ bridge can be seen (Table 2), which is due to the higher binding energy of the C–F bonds, compared to C–H bonds [4,48]. The different groups L have also strong impact onto the glass transition temperature (T_g).

The bulky and stiff fluorenylene bridge in **11a** causes high T_g. In the series of increasing polarity of L bridges ($C(CH_3)_2 < C(CF_3)_2 < SO_2$), T_g also increases in the same order according to the expectations [49].

3.3. Variations in the fluorine content

In order to investigate the influence of fluorine substituents onto the polymerisability and the polymer properties, a set of poly(arylene ether)s with different fluorine content and types of C–F bonds (C_{sp2}–F, C_{sp3}–F) were synthesized and analyzed in terms of relevant properties (cf. Table 4). The structures **5a** and **8a** are obtained *via* polycondensation of the respective bisphenolate with decafluorobiphenyl in relatively high and similar molecular masses. The higher F content of **5a**, compared to **8a**, obviously leads to a better thermal stability of the **5a** polymer which is reflected by the ≈60 °C higher 5% weight loss temperature ($T_{5\%\ \mathrm{weight\ loss}}$). Much more pronounced is the effect of F content onto the properties of these two polymers after they had been sulfonated (see Section 3.4). The structures **13a** and **14a** could not be obtained using this procedure because of the markedly lower activation of the C_{sp2}–F bonds of the 4,4′-difluorobiphenyl for S_NAr reactions. The preparation of these polymers can be accomplished by Ullmann's biaryl ether condensation at high temperatures from 4,4′-dibromobiphenyl. Despite these drastic reaction conditions, **13a** and **14a** can only be obtained as oligomers (see Fig. 6). T_g could not be found for **13a**, and T_g of **14a** is typically low for poly(arylene ether)s with moderate molecular weight (Table 4). Due to low molecular weight of **13a** and **14a**, the impact of different fluorine content onto their properties cannot be determined (the higher TGA 5% weight loss temperature of **14a** could also be caused by its higher molecular weight, compared to **13a**).

Because of low molecular masses and insufficient film-forming properties, the structures **13a** and **14a** have not been considered for further investigation (sulfonation, blending).

3.4. Sulfonation reactions

Only polymers with sufficient molecular weight (>10 kDa), good film-forming properties and without significant cross-linking were selected for the preparation of proton-conducting ionomers *via* sulfonation. Table 5 lists the conditions and results for sulfonation experiments of these polymers.

Preferred structures will be identified in the following, i.e. polymers that can be sulfonated without significant molecular weight degradation and without loss of their membrane formation properties. However, the direct comparison between the molecular

Table 3
Overview of the acid constants (pK_a values) of the various bisphenol monomers (in ethanol/water 50/50 w/w at 25 °C) and the mass concentrations of the monomers (c_m), reaction temperatures (ϑ) and reaction times (t).

Monomer (abbrev.)	L (Poly (arylene ether))	pK_{a1}	pK_{a2}	c_m [wt.%]	ϑ [°C] (t [h])
2,2-bis(4-hydroxyphenyl) hexafluoropropane (BHPHFP)	$C(CF_3)_2$ (**5a**)	8.31[41]	–	10.1	80 (23)
2,2-bis(4-hydroxy-phenyl) propane (BHPP)	$C(CH_3)_3$ (**8a**)	9.4[41]	–	10.6	80 (23) 90 (2) 100 (2)
2,2-bis(4-hydroxyphenyl) sulfone (BHPS)	SO_2 (**9a**)	8.52	9.42[42]	11.2	80 (23)
4,4'-thiodiphenole (TDP)	S (**10a**)	10.28	11.10[42]	10.1	80 (23)
9,9-bis(4-hydroxyphenyl) fluorene (BHPF)	9-Fluorenyl (**11a**)	9.58[43]	10.19[43]	14.9	75 (16)
4,4'-dihydroxybiphenyl (DHBP)	– (**12a**)	10.40[a] [44]	11.10[a] [44]	10.1	80 (23)

[a] in methanol/water(50/50, w/w) at 25 °C.

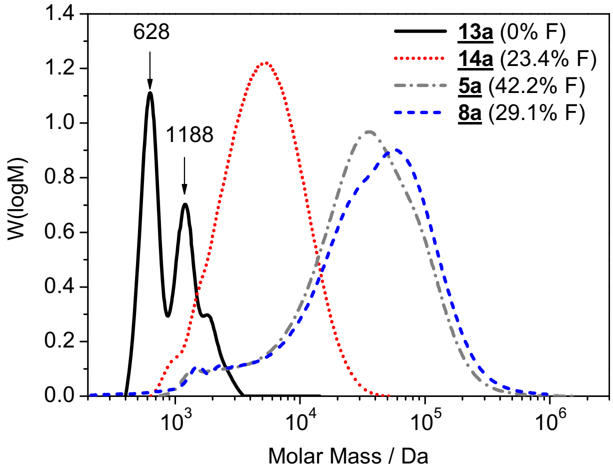


Fig. 6. Molecular weight distributions of poly(arylene ether)s **5a**, **8a**, **13a**, and **14a** with different fluorine and different types of C–F bonds.

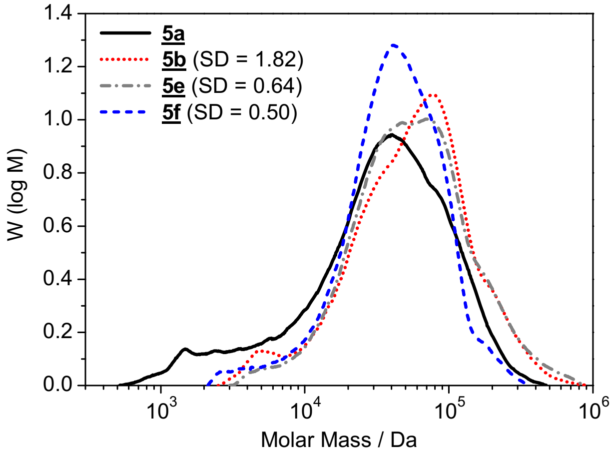


Fig. 7. Molecular mass distributions of 5a and the ionomers **5b**, **5e** and **5f**.

weights of the sulfonated, strongly polar ionomers and their non-sulfonated precursors, obtained by GPC, is difficult. The elution volume of an ionomer in the GPC experiment and thus the molecular weight computed against polystyrene standards could be influenced by a number of various phenomena, such as intra- and intermolecular association of ionomers [50–52] and inter- and intramolecular electrostatic interactions such as ion-exchange, ion exclusion, ion inclusion, hydrogen bridges, and hydrophobic interactions [53], and interactions between the ionomer macromolecules and the pore walls of the GPC columns. Due to a lack of commercially available sulfonated polystyrene standards for the non-aqueous GPC [54], the reported molecular weights are relative to polystyrene for both the non-sulfonated and the sulfonated polymers. Even in literature, molecular weight distributions of sulfonated polymers are usually determined against polystyrene [18,55] or polyvinylpyrrolidinone [56] as the standards. However, this certainly dictates another variable in the direct comparability between sulfonated and non-sulfonated polymer samples. But having these limitations in mind, GPC is thought to be an appropriate tool to estimate degradation reactions during the sulfonation processes. In order to investigate the influence of degree of sulfonation (DS) onto the molecular weight, the non-sulfonated ionomer **5a** is compared to the sulfonated ionomers **5b**, **5e** and **5f** with different degrees of sulfonation.

The following conclusions can be drawn from the results presented in Fig. 7 and Table 5:

- Obviously no (or only minor) molecular weight degradation of polymer **5a** takes places during sulfonation with different SO_3 concentrations.

Table 5
Overview and results of sulfonation experiments.

Poly (aryl)	Sulfonation agent (Poly(aryl) ionomer)	IEC_{total} [mmol/g]	SD[a]	RMP[c]	M_n[b] [g/mol]	PDI[b]
5a	H_2SO_4 (65% SO_3) (**5b**)	2.35	1.82	+	30,900	3.28
	H_2SO_4 (50% SO_3) (**5c**)	2.42	1.89	+	29,900	2.02
	H_2SO_4 (40% SO_3) (**5d**)	2.35	1.82	+	32,700	2.66
	H_2SO_4 (30% SO_3) (**5e**)	0.94	0.64	+	35,900	2.30
	H_2SO_4 (20% SO_3) (**5f**)	0.75	0.50	+	27,800	1.93
6a	H_2SO_4 (60% SO_3) (**6b**)	2.66	2.22	–	23,300	5.66
	H_2SO_4 (20% SO_3) (**6c**)	2.22	1.78	–	20,400	6.69
	H_2SO_4 (5% SO_3) (**6d**)	1.02	0.73	–	30,000	7.44
	HSO_3Cl (**6f**)	Gel form.				
7a	HSO_3Cl (**7c**)	Gel form.				
8a	H_2SO_4 (20% SO_3) (**8b**)	5.02	4.38	–	6500	1.71
	HSO_3Cl (**8c**)	3.21	2.26	–/+	14100	1.67
9a	H_2SO_4 (65% SO_3) (**9b**)	2.78	1.94	+	12600	1.74
	H_2SO_4 (20% SO_3) (**9c**)	2.83	1.99	+	13300	1.74
	H_2SO_4 (10% SO_3) (**9d**)	2.59	1.78	+	12800	1.50
11a	H_2SO_4 (20% SO_3) (**11b**)	4.40	4.38	–	n. a.	n. a.
	H_2SO_4 (98%) (**11c**)	3.43	3.05	–/+	11300	2.83
	$(CH_3)_3SiSO_3Cl$ (**11d**)	0.89	0.62	–/+	12900	4.00

[a] SD = Sulfonation degree.
[b] RMP = Relative membrane-forming properties.
[c] determined *via* gel permeation chromatography *via* universal calibration against polystyrene standards.

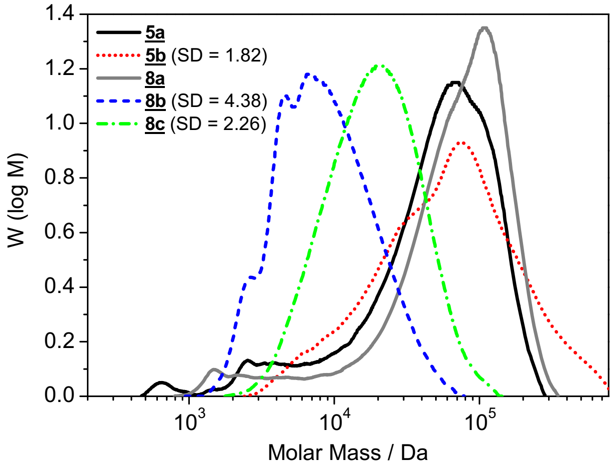


Fig. 8. MWDs of the sulfonated poly(arylene ether)s **5b**, **8b**, and **8c** and their basic polymers **5a** and **8a** (against polystyrene).

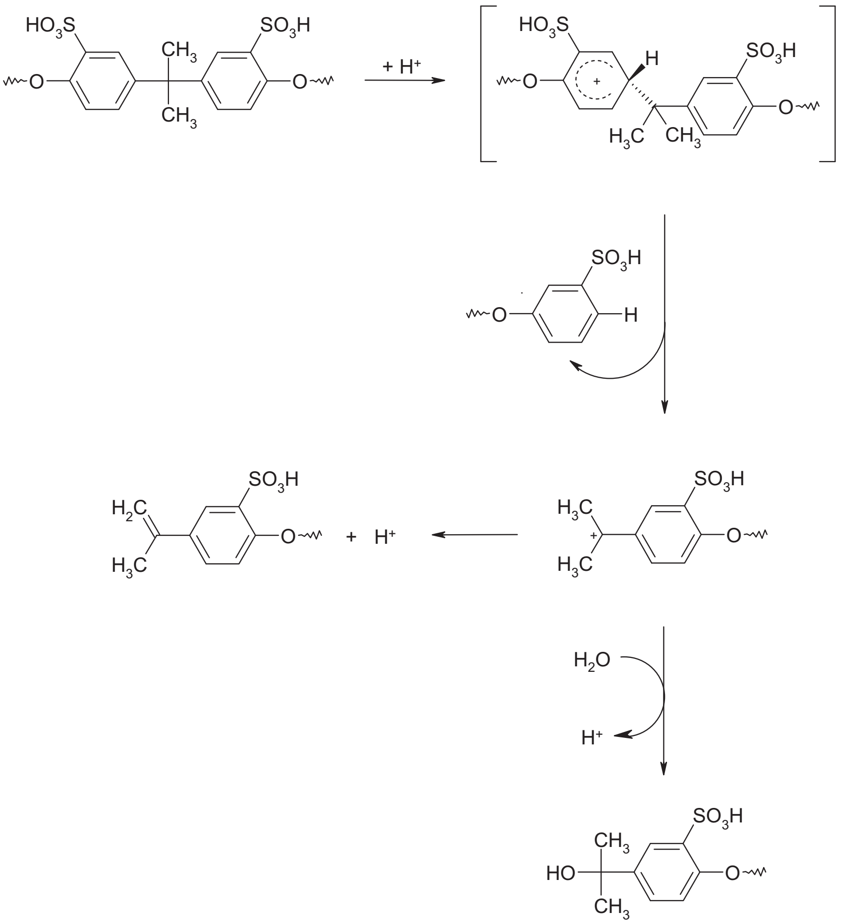


Fig. 9. Possible degradation mechanisms of the sulfonated poly(arylene ether)s **8b** and **8c** under the acidic conditions during the sulfonation reaction.

- The fraction of oligomeric species is significantly smaller for the sulfonated polymer **5b** in comparison to the referring non-sulfonated polymer **5a** (plateau on low-molecular side of the MWD curve of **5a**). The oligomeric sulfonated species are removed during the working-up procedure of the sulfonated polymer (dialysis, MWCO = 12000–14000 Da). Therefore, and due to the higher molecular weight per repeating unit in the sulfonated polymer **5b** compared to **5a**, the MWD curve and thus M_n are shifted to higher values (cf. Tables 2 and 5, Fig. 7). This MWD shift is more pronounced for the ionomers with higher sulfonation degrees (Fig. 7), as expected (higher concentration of SO_3 used in their synthesis).

Fig. 8 shows the MWD of sulfonated polymers **5b** (L = $C(CF_3)_2$, SD = 1.82), **8b** (L = $C(CH_3)_2$, SD = 4.38), and **8c** (L = $C(CH_3)_2$, SD = 2.26) in comparison with their non-sulfonated analogues. These MWD curves suggest that polymer **8a** degrades significantly more during the sulfonation reaction than polymer **5a**. This is even more pronounced when the stronger sulfonation reagent SO_3 in sulfuric acid (**8b**) was used instead of HSO_3Cl (**8c**). This finding can be explained by the higher sensitivity of the isopropylidene bridge in **8a** toward acid-induced cleavage, compared to polymer **5a** with the hexafluoroisopropylidene bridge in the backbone. The easier formation of carbocations [57] in **8a** might open a broad spectrum of acid-catalyzed degradation reactions. A couple of possible mechanisms for acid-catalyzed degradation reactions for polymer **8a** during sulfonation are proposed in Fig. 9.

The molecular weight distributions of the sulfonated poly(arylene ether)s **6b**, **6c** and **6d** (Fig. 10) with the carbonyl bridge (Z = CO) in the perfluorinated moiety are characteristically different from those of the polymers **5a** and **8a**. The sulfonated species show a marked broadening (PDI ≈ 5–7), compared to the non-sulfonated polymer **6a** and the ionomer **5b** comprising a direct bond in the perfluorinated moiety.

However, it must be noted that the non-sulfonated polymer **6a** has already a broader MWD (PDI = 4.11), compared to **5a** (PDI = 3.44). Therefore, the broadening of the sulfonated polymers

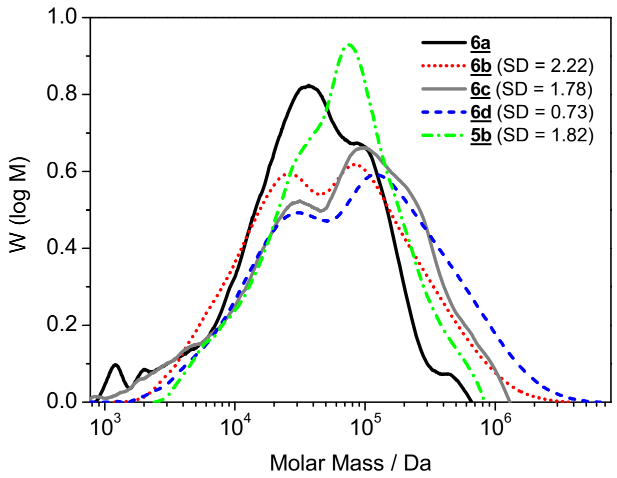


Fig. 10. MWDs of the poly(arylene ether)s **6a**–**6d** (comparison: **5b**).

6b – **6d** can be traced back to be caused during both the polycondensation and the sulfonation reaction. Moreover, the sulfonated species **6b**, **6c**, and **6d** show more or less pronounced maxima in their MWDs whose intensities behave inversely to those suggested by the shoulder in the MWD of **6a**. The reason for this finding might be the preferred removal of shorter-chained oligomeric polyelectrolyte fraction during the dialysis of **6b**–**6d**. The width of the MWD of the sulfonated polymers **6b**–**6d** is most probably responsible for their observed brittleness. However, it must be stated that brittleness in sulfonated versus non-sulfonated polymers can be caused by other factors as well, such as steric hindrance, ionic interactions, water content, etc.

These reasons suggest that a chemical bond in the perfluorinated part of the polymer (**5a**) is preferred over a carbonyl group (**6a**), or a thioether bridge (**7a)** in terms of chemical stability during the sulfonation process (cf. Table 5). The weak point of a polymer architecture containing chemical bridge atoms or groups Z in the perfluorinated part is thought to be their potential reactivity. Therefore, such structures have to be avoided if they cannot be utilized for directed modification reactions such as cross-linking. One possible reaction site at Z = CO is the electrophilic carbonyl carbon atom which, for instance, can react with suitable carbanions (e.g. phenyllithium) [58]. The monomer bis(pentafluorophenyl) sulphide, for example, can also react with metalorganic compounds under splitting of the C–S bond [59] and can be oxidized under specific conditions to sulfone ($Z = SO_2$) [60]. Since this oxidation reaction proceeds *via* the sulfoxide intermediate (Z = SO), even further side reactions are possible. For example, bis(pentafluorophenyl)sulfoxide can be applied *in situ* as reactive intermediate for the preparation of pentafluorophenyl amino acid esters from the corresponding (N-protected) amino acid [61]. Similar reactions might be the reason for the observed broadening of the MWD of **6a** to **6d** (Fig. 10).

Summarizing the results of the investigated ionomers it can be stated that only the structures comprising the bridge groups $L = C(CF_3)_2$ (**5b**–**5f**) and $L = SO_2$ (**9b**–**9d**) in the bisphenol part can be sulfonated without severe polymer degradation. A specific advantage of structure **5a** is the fact that it is not water-soluble even at high sulfonation degree (SD = 1.82) and at elevated temperatures. The specific resistances and the thermal behaviour ($T_{SO3H,\ onset}$ and T_g) of three membranes of type **5** with different sulfonation degrees are summarized in Table 6. In Fig. 11, the corresponding water uptake values are shown in dependence of temperature.

It can clearly be seen that the low-sulfonated membranes show both high resistances (Table 6) connected with water uptake values in the range of Nafion®, which makes them inappropriate for the application in fuel cells, while Nafion® comprises concomitant low resistance values. The comparatively high water uptake of the type **5** membranes is thought to be caused by the higher number of dead end ion-conducting channels in low-sulfonated poly(arylene)s [62,63]. With increasing sulfonation degree the specific resistance of the membranes decreases significantly and is even lower than that of Nafion117®. However, their water uptake increases excessively, particularly at elevated temperatures. In order to reduce their high water uptake, the ionomer membranes can be cross-linked covalently or ionically [2], as shown in earlier publications and discussed below (Section 3.5). In this study, ionically cross-linked membranes consisting of sulfonated poly(arylene) ionomers and polybenzimidazole (PBI Celazol®), were prepared. Their properties will be discussed in the next paragraph.

Table 6
Overview of properties of the poly(arylene ether) ionomer membranes 5 with different sulfonation degrees.

	SD	R_{sp} [Ω cm]	$T_{SO3H,\ onset}$ [°C]	T_g [°C]
Nafion® 117		6.59	229	110 [58,70,71]
mem5b	1.82	3.16	241	252
mem5e	0.64	188.36	248	188
mem5f	0.50	720.03	261	183

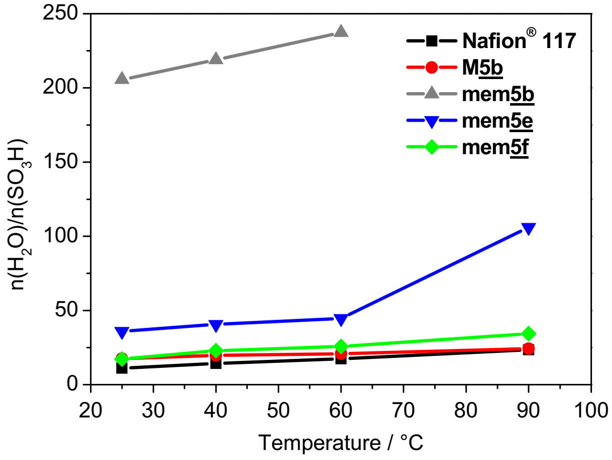


Fig. 11. Water uptake of the membranes mem**5b**, mem**5e** and mem**5f** with different sulfonation degrees in comparison to Nafion 117®.

3.5. *Ionically crosslinked blend membranes*

Among all poly(arylene ether) ionomers presented above, only ionomers **5b**–**5f** and **9b**–**9d** show adequate membrane formation properties (see Table 5) for the preparation of pure membranes. However, the strong interaction of these ionomers with water (which in the case of the ionomers **9b**–**9d** leads even to water-solubility) does not allow their application to fuel cells. Therefore, for a reduction of these interactions and an improvement of the mechanical membrane properties, the concept of ionical cross-linking using (basic) polybenzimidazole (Celazol® PBI) was used [2,64,65]. In previous work we could show that acid-base blend membranes of sulfonated arylene ionomers with polybenzimidazole or other basic polymers do comprise not only increased thermal and oxidation stability, but also markedly reduced swelling and water uptake, compared to the pure sulfonated ionomers, and they show excellent performance particularly in DMFC [2,21,65]. PBI-excess PBI-sulfonated ionomer-H_3PO_4 blend membranes, where the sulfonated ionomer **5b** acted as the acidic macromolecular cross-linker for the PBI component, exhibited chemical stabilities in Fentons Reagent which were

Table 7
IEC, specific resistance and splitting-off temperature of the sulfonic acid group of the ionically crosslinked membranes with a calculated IEC of 1.35 meq SO_3H/g membrane.

Blend membrane (bridge L)[a]	content PBI [wt.%]	IEC_{direct} [mmol/g]	IEC_{total} [mmol/g]	R_{sp} [Ω cm]	$T^{onset}_{SO_3H}$ [°C]	RMP[b]
M5b ($C(CF_3)_2$)	11.3	1.34	2.07	10.53	263	++
M8c ($C(CH_3)_2$)	19.2	1.29	2.63	13.66	256	−/+
M9b (SO_2)	15.5	1.36	2.22	3.82	271	++
M11c (9-Fluorenyl)	21.0	1.48	2.21	5.03	263	−/+

[a] in bisphenol part.
[b] RMP = relative membrane formation properties.

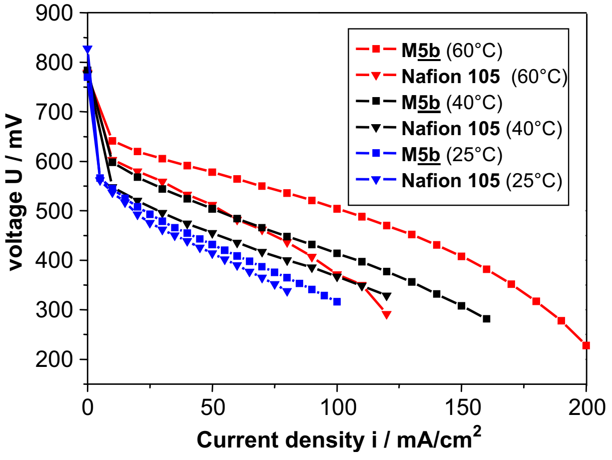


Fig. 12. U-i polarization curve of M5b in DMFC in comparison to Nafion® 105 (Membrane area: $25\,cm^2$, membrane thickness: 150 µm; loading anode: $6\,mg/cm^2$ PtRu (JM), Toray paper nonteflonated; loading cathode: $6\,mg/cm^2$ Pt (JM), Toray paper teflonated (26% PTFE); c(MeOH) = 1 M, flux (methanol) = 4 ml/min, flux (dry air) = 0.625–0.688 l/min, self-breathing at cathode side).

comparable to Nafion® membranes [66]. Moreover, the **5b**/PBI blend membranes were not soluble in hot H_3PO_4, in contrast to pure PBI [67]. Membranes with a calculated ion-exchange capacity (IEC) of 1.35 mmol SO_3H/g membrane were prepared and comparatively characterized (Table 7).

Blend membranes of high flexibility and stability were made from the ionomers **5b** and **9b**, while **8c** and **11c** were much less stable and can only be characterized at room temperature – the determination of the temperature-dependent water uptake behaviour was not possible. This could be due to the lower restoring forces of the blend membranes **M8c** and **M11c** resulting from the chemical nature of the bridges (L = $C(CH_3)_2$) and (*L* = 9-fluorenyl). Beside their lower specific resistances, the membranes **M8c** and **M11c** were very brittle which impedes their application to membrane fuel cells. Contrary to these membranes, the blend membranes **M5b** and **M9b** showed interesting properties: **M5b** blend membrane had a significantly reduced water uptake of 54.6%, compared to the water uptake of the pure ionomer membrane **5b** (207%), and an acceptable specific resistance of 10.53 Ω cm, while the **M9b** blend membrane exhibited an excellently low specific resistance of 3.82 Ω cm. However, the acidic component in **M9b** was water-soluble and is hence a polyelectrolyte, which is due to the higher hydrophilicity of the SO_2 bridge compared to the $C(CF_3)_2$ bridge. These findings have led us to the conclusion that it was advantageous to combine the beneficial properties of **5b** (good mechanical stability) and **9b** (excellent proton conductivity) *via* preparation of statistical copolymers from decafluorobiphenyl, BHPHFP, and BHPS. The synthesis and characterization of these statistical copolymers have been published elsewhere [20].

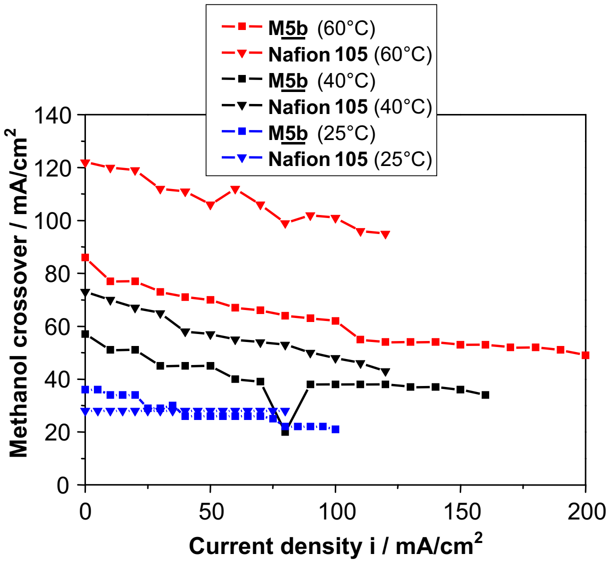


Fig. 13. Methanol crossover of M**5b** in DMFC in comparison to Nafion® 105, determined by measurement of the CO_2 concentration of the cathode off-gas *via* IR spectroscopy.

3.6. DMFC test of ionically crosslinked blend membranes

The characterization results presented in this chapter allow the conclusion that **M5b** shows the greatest perspectives for application in membrane fuel cells among all the investigated membranes. Therefore, this blend membrane was tested, together with other arylene main-chain ionomer membranes (ionically or covalently crosslinked, partially fluorinated or nonfluorinated), in a direct methanol fuel cell (DMFC) at various temperatures (25, 40 and 60 °C, air-breathing) and was compared with Nafion105® (Fig. 12, i/U polarization curves of **M5b** at 25, 40 and 60 °C; Fig. 13, methanol crossover of **M5b** in DMFC in comparison to Nafion105®). At all of the three temperatures and current densities the **M5b**-based MEA showed a better performance. The meOH crossover of the **M5b** MEA lies at 25 °C and small current densities slightly above that of a Nafion105® MEA. In contrast, at 40 and 60 °C the MEA crossover of the **M5b** MEA was markedly lower than that of the Nafion105® MEA. It is highly probable that the lower meOH permeability of the **M5b** MEA, compared to the Nafion105® MEA, led to the observed better DMFC performance of the **M5b** MEA, compared to the Nafion105® MEA [68]. For MEAs based onto other arylene main-chain-polymer-based covalently and/or ionically crosslinked ionomer membranes also reduced meOH crossover was observed [69], which in some cases led to improved DMFC performance.

4. Conclusion

Partially fluorinated poly(arylene ether) backbones with various combinations of different groups Z and L (cf. Schemes 1–3) were synthesized, characterized and evaluated in terms of suitability for postsulfonation and in terms of application as fuel cell membrane (component).

The development of membrane materials for polymer electrolyte membrane fuel cells means that all of the following requirements have to be met.

(i) Appropriate monomers yield soluble polymers in high conversion and molecular weight being high enough for good film-forming properties of their referring acid-base blend membranes with PBI (see (iii)).
(ii) The formed poly(arylene ether)s can be converted into their sulfonated analogues without loss of their film-forming properties.
(iii) Pure or ionically crosslinked (blend) membranes can be cast and their properties relevant for fuel cell applications are compared.

Among the investigated structure combinations of poly(arylene ether)s, only a few were able to fulfil these requirements. The group Z in the perfluorinated moiety of the corresponding monomers (when L is constant and equal to the hexafluoroisopropylidene group $C(CF_3)_2$) had a great influence on the achievable molecular weight and the related molecular weight distribution. Under the alkaline conditions of the polycondensation process and in the presence of trace amounts of water hydroxide ions can be formed which react with the carbon atom of the carbonyl bridge ($Z = CO$ in **6a**) or with the carbon atom next to the sulfur atom in the thioether bridge ($Z = S$ in **7a**), whereas the direct chemical bond ($Z =$ chemical bond in **5a**) turned out not to be susceptible in that way. Therefore, the structural moieties $Z = CO$ and $Z = S$ were disregarded for further polymer development. The influence of the group L at fixed group Z ($Z =$ bond) on the achievable molecular weight (distribution)s was rather low and correlated with the basicity/nucleophilicity of the bisphenolates used for the polycondensation reactions with decafluorobiphenyl ($Z =$ chemical bond). Bisphenolates with low pK_{b1} values ($pK_{b1} < 3.7$, $L = S$ (**10a**), $L =$ bond (**12a**)) yielded non-soluble and crosslinked polymers. All other bisphenolates that were reacted with decafluorobiphenyl ($L = C(CH_3)_2$ in **8a**, $L = SO_2$ in **9a** and $L =$ 9-fluorenyl in **11a**) led to high molecular weight polymers with similar molecular weight distributions. The poly(aryl)s **13a** and **14a** consisting of the non-fluorinated biphenylene instead of the octafluorobiphenylene moiety could not be obtained as high molecular weight and film-forming materials which was attributed to lack of activating groups within the biphenylene monomer.

Those poly(arylene ether) structures that passed the requirements of aspect (i) (**5a** – **9a**, **11a**) were subjected to conversion into their sulfonated forms by appropriate sulfonation reagents. As in the case of the polycondensation reactions, chemical groups Z in the perfluorinated moiety of the poly(aryl) structure should be avoided, since either gelation (**7a**) or side and degradation reactions (**6a**) finally led to brittle products. Among the various structures with fixed Z ($Z =$ bond), the poly(aryl)s **5a** ($L = C(CF_3)_2$) and **9a** ($L = SO_2$) turned out to be the structural units being most resistant to the strongly acidic conditions during the sulfonation process. Especially the brigde $L = C(CH_3)_2$ (**8a**) seems to be inappropriate for the intended application because of its sensibility to be cleaved by *ipso* substitution with H^+ and the resulting worse mechanical properties in comparison with the fluorinated analogue **5a** ($L = C(CF_3)_2$).

Membrane properties of each poly(aryl) ionomer (prerequisite (iii)) were evaluated on the basis of their ionical crosslinked blends (with PBI) in order to reduce the intrinsically high water uptake and swelling degree of the parent ionomers by sustaining a sufficiently low specific resistance comparable to that of Nafion®. A comparison between the four PBI blend membranes on the basis of **5b** ($L = C(CF_3)_2$), **8c** ($L = C(CH_3)_2$), **9b** ($L = SO_2$) and **11c** ($L =$ 9-fluorenyl) clearly confirmed the beneficial effects of the groups $L = C(CF_3)_2$ (**5b**) and $L = SO_2$ (**9b**) on the overall properties of the membrane. The blend membrane on the basis of **5b** was tested in a DMFC-MEA and showed superior U-i characteristics than Nafion®, which was mainly attributed to the observed lower methanol crossover.

Summarizing the findings of this study, among all the investigated ionomers the **5b** and **8b** structures showed the most advantageous properties for fuel cell application such as high molecular weight, high chemical, thermal and mechanical stability, and good film-forming properties (e. g. high proton conductivity, low water uptake/swelling) by blending with poly(benzimidazole)s (PBI). It could be proven that indeed the **5b**/PBI ionomer blend membrane comprises excellent direct methanol fuel cell (DMFC) performance.

In future work, we will design block copolymers using the most stable building blocks from the work presented here in order to fine-tune the membrane properties in terms of proton conductivity (as high as possible) by tailoring the length of the sulfonated, proton-conducting blocks, and in terms of swelling/water uptake by a reasonable selection of the type (degree of hydrophobicity) and/or length of the hydrophobic blocks which determines the extent of phase-separation and therefore the swelling of the block copolymer.

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