



Synthesis and characterization of novel (sulfonated) poly(arylene ether)s with pendent trifluoromethyl groups

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ABSTRACT

This paper reports the synthesis of four different trifluoromethyl-substituted poly(arylene ether)s on the basis of 2,2-bis(4-hydroxyphenyl)hexafluoropropane (bisphenol AF) and various difluoro- or dinitrophenyl or terphenyl monomers in the course of a step-growth polycondensation. Besides a comparison between the polymerisability of the different monomer combinations, a main focus of this work lies on the NMR characterization of these poly(arylene ether)s. Poly(arylene ether)s with sufficiently high number average molecular weights were sulfonated by fuming sulfuric acid or chlorosulfonic acid and investigated in terms of membrane properties relevant for fuel cell applications.

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1. Introduction

During the last few years, much effort in the further development of polymer electrolyte membranes for fuel cells has been made [1–7]. Current activities mainly focus on poly(perfluoroalkylsulfonic)acids (PFSA) and sulfonated arylene main-chain polymers. Since poly(perfluoroalkylsulfonic)acids (PFSA) were commercialized by Dupont de Nemours in 1962 (trademark Nafion®) there has been an enormous number of publications dealing with their properties in polymer electrolyte membrane fuel cells (PEMFC) [8]. In the last few years, PFSA ionomer membranes with a reduced number of reactive end groups have been developed [9] to minimize radical-induced depolymerisation reactions [10].

In the research field of sulfonated arylene main-chain polymers, growing interest in the preparation of partially fluorinated backbones is evident. Several backbone structures have been synthesized and evaluated in terms of applicability as polymer electrolyte membrane, among them are, for example, poly(arylene ether)s [11,12], poly(ether ketone)s [13,14], poly(arylene ether ether ketone)s [15], poly(ether sulfone)s [12,16–19], poly(arylene thioether sulfone)s [20], poly(arylene ether phosphine oxide)s [12] and

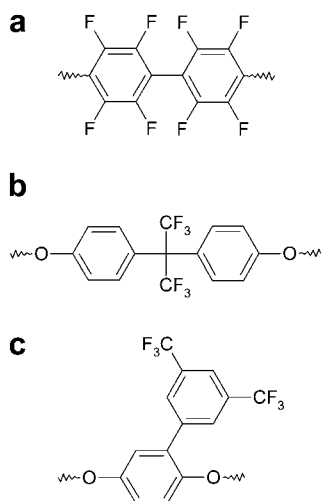
poly(arylene ether benzonitrile)s [21,22]. Holdcroft et al. have designed a comb-shaped structure consisting of a partially fluorinated poly(arylene ether) backbone with poly(α -methylstyrene sulfonic acid) side chains of well-defined length in order to mimic the principal architecture of PFSA [23]. The common features of these partially fluorinated structures are aromatic C–F bonds (by polycondensation with decafluorobiphenyl) (cf. Scheme 1a) or nonfluorinated phenylene/arylene rings bridged by the hexafluoroisopropylidene ($C(CF_3)_2$) group (by polycondensation with 2,2-bis(4-hydroxyphenyl)hexafluoropropane (bisphenol AF)) (cf. Scheme 1b). Guiver et al. recently reported on the incorporation of 3,5-bis(trifluoromethyl)phenyl hydroquinone into a poly(aryl ether ether ketone) leading to a structure with a strongly electron-deficient aromatic side chain (cf. Scheme 1c).

The limited number of partially fluorinated structural building blocks in sulfonated arylene main-chain polymers is probably due to a lack of appropriate and commercially available monomers and due to aggressive sulfonation conditions required to convert them into proton-conductive materials. On the other hand, poly(arylene ether)s with a high degree of pendent trifluoromethyl groups are known from other applications (for example from optical waveguides) and characterized by their excellent electrical insulating properties, high glass transition temperatures, good thermal stability and flame resistance with concomitant decreased crystallinity and water absorption [24–28].

The present paper makes an attempt to design ionomers on the basis of partially fluorinated poly(arylene ether)s having either only $C(CF_3)_2$ as further bridging moieties (**1a** in Scheme 2) and/or

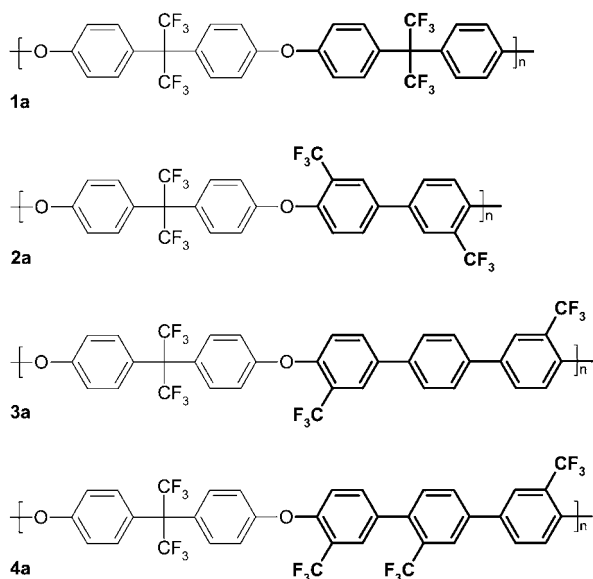
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Scheme 1. Overview of widely used (partially) fluorinated building blocks for the biphenyl moiety (as introduced by (a) decafluorobiphenyl) and for the bisphenol moiety (as introduced by (b) 2,2-bis(4-hydroxyphenyl)hexafluoropropane or by (c) 3,5-bis(trifluoromethyl)phenylhydroquinone).

trifluoromethyl groups attached to the main-chain (**2a–4a** in Scheme 2). Among these various structures, the most appropriate ones are identified by their properties relevant for fuel cell applications (ion-exchange capacity (IEC), specific resistance, water uptake, swelling degree, thermal stability, and weight loss in hydrogen peroxide solution at 60 °C). This heuristic approach was selected both from the standpoint of chemical stability and from morphological aspects. In order to obtain a chemical stability as high as possible, any structural elements apart from ether bridges with highly electron-deficient substituents were avoided in the targeted polymeric structures. As the membrane in a working fuel cell is exposed to many (potential) reactive species (such as H₂, O₂, H₂O, H⁺, HO[•], HOO[•]) under various conditions (e.g. change of temperature, of humidity, of load, etc.), the choice of bridging groups in the polymer backbone might be significant for its chemical stability [29]. It has further been reported in the literature that, for example,

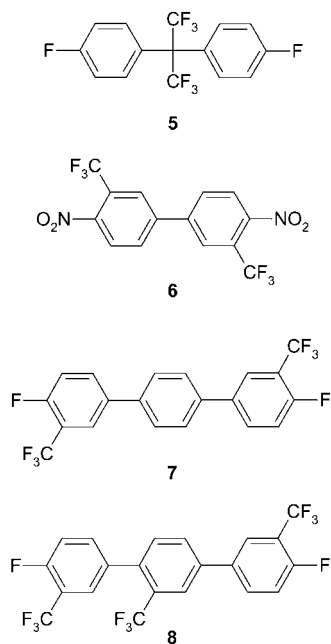


Scheme 2. Overview of the various synthesized poly(arylene ether)s: The bold structural elements were varied while the normal sketched one was fixed.

monomeric diaryl sulfone can be cleaved in concentrated sulfuric acid at elevated temperatures ($T > 120\text{ }^{\circ}\text{C}$) [30] via a nucleophilic substitution at the sulphur atom [31,32]. Such a degradation reaction could be relevant particularly during postsulfonation of poly(arylene ether sulfone)s (besides any acid-induced ether cleavages; see below for a further consideration of the stability of ether bridges). This cleavage might also occur in the presence of water in a working fuel cell under certain operating conditions. A further potentially reactive site for a nucleophilic species may be the electrophilic carbon atom of a carbonyl (C–CO–C) or a thio ether bridge (C–S–C) especially when they are substituted by electron-withdrawing neighbouring groups (as fluorine-containing ones). The following possible reactions at the sulphur atom in the monomer bis(pentafluorophenyl)sulphide may serve as examples: (i) One of the C–S bonds can be cleaved by appropriate (strong) nucleophiles [33] or (ii) the thio ether bridge can be oxidized to a sulfone under appropriate conditions [34,35]. The latter reaction proceeds via a sulfoxide intermediate (C–SO–C) so that any side reactions might be probable [36]. Since the highly electron-deficient character of the CF₃ groups attached to the arylene main-chain would enhance the susceptibility of any carbonyl or thio ether bridges in the polymer backbone toward nucleophilic attack (e.g. H₂O), the ether bond has been chosen as structural element in this contribution. The electron density at the oxygen atom in the C–O–C bridge decreases with the addition of any further electron-withdrawing (fluorine-containing) neighbour groups in the adjacent arylene rings. Such a substitution pattern would certainly minimize the tendency for an acid-induced ether bond cleavage. Since the electron density at the carbon atom next to the ether bridge is reduced as well, the HO[•] induced ether bond cleavage as proposed by Zhang and Mukerjee might also be impeded [37]. But this advantage might be accompanied by a higher susceptibility of this carbon atom toward nucleophiles. In order to hamper any possible reaction at this site, poly(arylene ether) backbones with a sterically demanding CF₃ group in *ortho*-position to the ether bridge have been chosen (**2a–4a**, cf. Scheme 2). The sulfonation of these polymeric backbones requires strong sulfonating reagents because the activation energy of the rate-determining step (formation of the *Wheland* complex) [38] is increased by the electron-withdrawing effects of the substituents relative to a non-substituted structure. However, the backward reaction (*ipso* substitution) is hampered as well which might be favourable for high thermal and hydrolytical stability [39,40]. It has been shown in the literature that the transport behaviour of an ionomer membrane strongly depends on its microstructure. Because of the enhanced acidity of the here presented sulfonated partially fluorinated poly(arylene ether)s over their nonfluorinated analogues, their morphological structure might possess more separated ion channels with less dead-end channels and a smaller separation between adjacent SO₃H groups than their nonfluorinated analogues [2].

For the synthesis of the targeted sulfonated partially fluorinated poly(arylene ether)s, the postsulfonation route has been chosen. In order to design appropriate structures the following requirements have to be met:

- Appropriate monomers (cf. Scheme 3) have to be synthesized according to the literature [25,26,41] (**5–7**) or have to be newly developed (**8**) as only 2,2-bis(4-hydroxyphenyl)hexafluoropropane (bisphenol AF) is commercially available.
- Appropriate monomer combinations have to yield soluble polymers in high conversion and with a number average molecular weight (M_n) above 10 kDa in a distribution typical for step-growth polymerizations. The polymerization has to proceed without or with only minor side or degradation reactions.



Scheme 3. Overview of the synthesized and newly developed monomers.

- (iii) The formed poly(arylene ether)s must be convertible into their sulfonated analogues without loss of their film-forming properties by a simple postsulfonation process.
- (iv) The sulfonated poly(arylene ether)s must be castable into mechanically stable membranes with proton resistances comparable to that of Nafion[®] 117.

2. Experimental

2.1. Materials

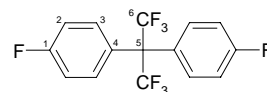
2,2-Bis(4-hydroxyphenyl)hexafluoropropane (bisphenol AF) was purchased from Sigma–Aldrich and dried at 65 °C in vacuum before use. All other monomers are not commercially available and were synthesized in-house. 2,2-Bis(4-fluorophenyl)hexafluoropropane was synthesized from 2,2-bis(4-aminophenyl)hexafluoropropane (ABCR) by Balz–Schiemann reaction [26]. The Ullmann biaryl synthesis [41] was used for the preparation of 4,4'-dinitro-3,3'-bis(trifluoromethyl)biphenyl starting from 5-bromo-2-nitrobenzotrifluoride (ABCR). 4,4''-Difluoro-3,3''-bis(trifluoromethyl)-*p*-terphenyl and 4,4''-difluoro-2',3,3''-tris(trifluoromethyl)-*p*-terphenyl were synthesized in-house by Suzuki coupling from 4-fluoro-3-trifluoromethylphenylboronic acid (self-prepared from 5-bromo-2-fluorobenzotrifluoride (ABCR) by Grignard reaction with trimethyl borate, magnesium (Fluka) and 1,4-dibromobenzene (Sigma–Aldrich) and 2,5-dibromobenzotrifluoride (ABCR) respectively) [25]. Solvents and other reagents were purchased either at Sigma–Aldrich, Fluka or ABCR.

2.2. Monomer preparation

2.2.1. Preparation of 2,2-bis(4-fluorophenyl)hexafluoropropane (5)

46.86 g (0.14 mmol) 2,2-bis(4-aminophenyl)hexafluoropropane were added to 180 g of tetrafluoroboric acid solution (48 wt.%) at 0 °C with intensive mechanical stirring. 19.35 g (0.28 mmol) sodium nitrite in 72 ml of water were slowly dropped into this suspension. Then the reaction mixture was stirred for 30 min. The resulting yellow precipitate was filtered, washed with 300 ml of cold water and 300 ml of diethyl ether. After the bis-diazonium

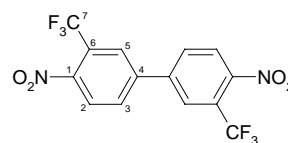
tetrafluoroborate was dried at room temperature under vacuum it was added to 600 ml anhydrous toluene at 50 °C. The temperature of the reaction mixture was slowly raised first to 90 °C, maintained for 1 hour and then increased to reflux temperature for 2 hours. After cooling down to room temperature, the reaction solution was successively washed with water, saturated NaHCO₃ solution and saturated NaCl solution. The organic layer was separated and dried over magnesium sulfate. Toluene was removed by rotary evaporation. The resulting viscous oil was distilled *in vacuo* to yield two fractions of which the second one was the desired product (0.042 mbar, 55 °C vapour temperature) that crystallized at room temperature (yield: 48%).



IR (KBr): $\nu = 1608, 1515, 1262, 1248, 1208, 1176, 1134, 968, 929, 898 \text{ cm}^{-1}$; ¹H NMR (200 MHz, CDCl₃, δ): 7.37 (m, 1H; H-3), 7.07 (m, 1H; H-2); ¹³C NMR (100 MHz, CDCl₃, δ): 162.88 (d, ¹J_{C-F} = 251 Hz; C-1), 132.14 (C-3), 124.07 (quartet, ¹J_{C-F} = 294 Hz; C-6), 119.14 (d, ⁴J_{C-F} = 3.8 Hz; C-4), 115.41 (d, ²J_{C-F} = 21.8 Hz; C-2), 63.79 (septet, ²J_{C-F} = 25.8 Hz; C-5); ¹⁹F NMR (235 MHz, CDCl₃, δ): -64.44 (s, 3F; F-6), -112.17 (m, 1F; F-1).

2.2.2. Preparation of 4,4'-dinitro-3,3'-bis(trifluoromethyl)biphenyl (6)

88.4 g (1.39 mol) activated copper powder [42] were added to a solution of 94.00 g (0.3495 mol) 5-bromo-2-nitrobenzotrifluoride in 200 ml *N,N*-dimethylformamide (DMF) and stirred under argon atmosphere at 155 °C for 72 hours. Then the solution was poured into 1.5 l of deionized water. The red precipitate was separated by filtration, washed with water and 1 M hydrochloric acid and dried *in vacuo* at 65 °C. Finally, the product was recrystallized twice from chloroform to yield a yellow product (yield: 78%).

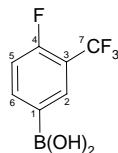


¹H NMR (250 MHz, Acetone-*d*₆, δ): 8.46 (m, 1H; H-5), 8.43 (dd, ³J_{H-H} = 8.5 Hz, ⁵J_{H-H} = 2.2 Hz, 1H; H-2), 8.25 (d, *J* = 8.25 Hz, 2H; H-3); ¹³C NMR (63 MHz, Acetone-*d*₆, δ): 148.92 (C-1), 143.14 (C-4), 134.14 (C-3), 128.45 (quartet, ³J_{C-F} = 5.1 Hz; C-5), 124.13 (q, ²J_{C-F} = 34.1 Hz; C-6), 123.11 (quartet, ¹J_{C-F} = 273.1 Hz; C-7).

2.2.3. Preparation of 4-fluoro-3-trifluoromethylphenylboronic acid for Suzuki coupling

2.399 g (98.74 mmol) magnesium turnings were activated by heating with a granule of iodine at 60 °C overnight and suspended in 300 ml of anhydrous diethyl ether after cooling down to ambient temperature. A solution of 21.9887 g (90.49 mmol) 5-bromo-2-fluorobenzotrifluoride in 100 ml THF was added dropwise and the reaction mixture was stirred overnight. This mixture was slowly dropped into a cooled (-78 °C) solution of 49.1824 g (473.29 mmol) trimethyl borate in 400 ml of anhydrous diethyl ether. After complete addition the mixture was allowed to warm to ambient temperature and stirred overnight at 25 °C. After 375 ml of 3 M HCl were added the organic layer was separated, and the aqueous layer was extracted twice with 150 ml diethyl ether. The combined organic phases were washed with water twice and dried over magnesium sulfate. After evaporating of the solvent the white

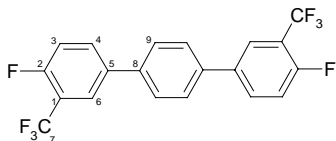
product was washed several times with *n*-hexane and dried at 60 °C under vacuum (yield: 69%).



^1H NMR (250 MHz, DMSO- d_6 , δ): 8.20–8.07 (m, 2H; H-2, H-5), 7.46–7.36 (m, 1H; H-6); ^{13}C NMR (50 MHz, DMSO- d_6 , δ): 160.25 (d, $^1J_{\text{C-F}} = 254.2$ Hz; C-4), 140.20 (m; C-2), 135.52 (m; C-1) 131.52 (m; C-6), 123.07 (quartet, $^1J = 271.9$ Hz; C-7), 116.49 (m; C-3), 116.10 (m; C-5); ^{19}F NMR (188 MHz, DMSO- d_6 , δ): –55.65 (s, 3F; F-7), –110.29 (s, 1F; F-4).

2.2.4. Preparation of 4,4''-difluoro-3,3''-bis(trifluoromethyl)-*p*-terphenyl (7)

8.6366 g (41.54 mmol) 4-fluoro-3-trifluoromethylphenyl and 4.830 g (17.31 mmol) 1,4-dibromobenzene, 130 ml toluene, 130 ml aqueous 1 M Na_2CO_3 solution and 0.60 g (3 mol%) $\text{Pd}(\text{PPh}_3)_4$ were intensively stirred at 115 °C for 5 days. The organic layer was separated and the aqueous phase extracted with toluene. The organic phases were combined, washed with water twice, dried over magnesium sulfate and concentrated by rotary evaporation. This solution was filtered over Al_2O_3 (type 100–125 mesh, activity 1, bed length 20 cm, diameter 2 cm) to remove the $\text{Pd}(\text{PPh}_3)_4$ catalyst. The column was washed with 1200 ml toluene. Finally, toluene was removed by rotary evaporation and the product was further purified by recrystallization from toluene/hexane (1/10) (yield: 75%).

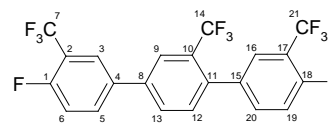


^1H NMR (200 MHz, Acetone- d_6 , δ): 7.29 (t, $J = 9.5$ Hz, 1H; H-3), 7.62 (s, 2H; H-9), 7.78–7.87 (signal heap, 2H; H-4, H-6); ^{13}C NMR (50 MHz, Acetone- d_6 , δ): 160.10 (dd, $^1J_{\text{C-F}} = 255$ Hz, $^3J_{\text{C-F}} = 2.1$ Hz; C-2), 139.04 (C-8), 138.00 (d, $^4J_{\text{C-F}} = 3.9$ Hz; C-5), 134.04 (d, $^3J_{\text{C-F}} = 8.7$ Hz; C-4), 128.61 (C-9), 126.33 (m; C-6), 123.64 (q, $^1J_{\text{C-F}} = 257$ Hz; C-7), 118.77 (dq, $^2J_{\text{C-F}} = 20.2$ Hz, $^2J_{\text{C-F}} = 12.5$ Hz; C-1), 118.54 (d, $^1J_{\text{C-F}} = 20.8$ Hz; C-2); ^{19}F NMR (235 MHz, Acetone- d_6 , δ): –56.91 (d, $^4J_{\text{F-F}} = 12.9$ Hz, 3F; F-7), –114.04 (m, 1F; F-2).

2.2.5. Preparation of 4,4''-difluoro-2',3,3''-tris(trifluoromethyl)-*p*-terphenyl (8)

6.6707 g (32.08 mmol) 4-fluoro-3-trifluoromethylphenylboronic acid and 4.0629 g (13.367 mmol) 2,5-dibromobenzotrifluorid, 130 ml toluene, 130 ml aqueous 1 M Na_2CO_3 solution and 0.4635 g (3 mol%) $\text{Pd}(\text{PPh}_3)_4$ were intensively stirred at 115 °C for 5 days. The working-up

procedure was similar to that for 4,4''-difluoro-3,3''-bis(trifluoromethyl)-*p*-terphenyl (yield: 71%).



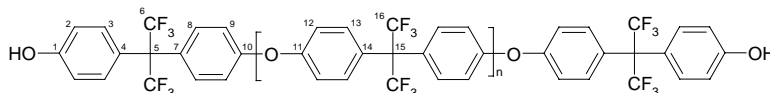
^1H , ^{13}C -HSQC NMR (250 MHz, 63 MHz, CDCl_3 , δ): 7.27 (m; 1H)/116.65 (H-19/C-19), 7.34 (m; 1H)/117.81 (H-6/C-6), 7.44 (d, $^3J_{\text{H-H}} = 8.2$ Hz; 1H)/132.87 (H-12/C-12), 7.55 (m; 1H)/134.48 (H-20/C-20), 7.61 (m; 1H)/127.80 (H-16/C-16), 7.78 (d, $^3J_{\text{H-H}} = 8.4$ Hz; 1H)/130.07 (H-13/C-13), 7.80 (m; 1H)/132.55 (H-5/C-5), 7.85 (m; 1H)/125.95 (H-3/C-3), 7.93 (s; 1H)/124.98 (H-9/C-9); ^{13}C NMR (63 MHz, CDCl_3 , δ): 159.87 (qd, $^1J_{\text{C-F}} = 259$ Hz (1F), $^3J_{\text{C-F}} = 2.0$ Hz (3F); C-18), 159.57 (qd, $^1J_{\text{C-F}} = 259$ Hz (1F), $^3J_{\text{C-F}} = 2.0$ Hz (3F); C-1), 139.17 (m; C-8), 138.33 (q, $^3J_{\text{C-F}} = 1.6$ Hz (3F); C-11), 135.71 (d, $^3J_{\text{C-F}} = 4.0$ Hz; C-15), 135.32 (d, $^3J_{\text{C-F}} = 4.3$ Hz; C-4), 134.48 (qqd, $^3J_{\text{C-F}} = 8.9$ Hz (1F), $^5J_{\text{C-F}} = 1.7$ Hz (3F), $^5J_{\text{C-F}} = 0.7$ Hz; C-20), 132.87 (m; C-12), 132.55 (qd, $^3J_{\text{C-F}} = 8.5$ Hz (1F), $^5J_{\text{C-F}} = 1.0$ Hz (3F); C-5), 130.07 (m; C-13), 129.60 (q, $^2J_{\text{C-F}} = 30.1$ Hz; C-10), 127.80 (dq, $^3J_{\text{C-F}} = 4.6$ Hz (3F), $^5J_{\text{C-F}} = 1.7$ Hz (3F), $^3J_{\text{C-F}} = 1.5$ Hz (1F); C-16), 125.95 (dq, $^3J_{\text{C-F}} = 4.6$ Hz (3F), $^3J_{\text{C-F}} = 2.0$ Hz (1F); C-3), 124.98 (q, $^3J_{\text{C-F}} = 5.0$ Hz; C-9), 123.71 (q, $^1J_{\text{C-F}} = 274$ Hz (3F); C-14), 122.46 (q, $^1J_{\text{C-F}} = 274$ Hz; C-7), 122.44 (q, $^1J_{\text{C-F}} = 274$ Hz; C-21), 119.34 (dq, $^2J_{\text{C-F}} = 33.1$ Hz (3F), $^2J_{\text{C-F}} = 12.8$ Hz (1F); C-2), 118.14 (dq, $^2J_{\text{C-F}} = 33.5$ Hz (3F), $^2J_{\text{C-F}} = 12.9$ Hz (1F); C-17), 117.81 (d, $^2J_{\text{C-F}} = 21.1$ Hz; C-6), 116.65 (d, $^2J_{\text{C-F}} = 20.8$ Hz; C-19); ^{19}F NMR (235 MHz, CDCl_3 , δ): –57.12 (s, 3F; F-14), –61.49 (d, $^4J_{\text{F-F}} = 7.8$ Hz, 3F; F-21), –61.54 (d, $^4J_{\text{F-F}} = 7.8$ Hz, 3F; F-7), –115.33 (m, 1F; F-18), –115.54 (m, 1F; F-1).

2.3. Polycondensation reactions

The polymers **1a–4a** were synthesized under typical aromatic nucleophilic polycondensation conditions, in a few cases with the help of toluene as water entrainer [12,25,28]. Equimolar amounts of the difluoro or dinitro monomer and of the bisphenol monomer were charged into a 100 ml three-neck flask equipped with an argon inlet, a mechanical stirrer, Dean–Stark trap, reflux condenser and mercury bubbler. Appropriate amounts of *N*-methyl-2-pyrrolidinone (NMP) or *N,N*-dimethylacetamide (DMAc) were added to obtain monomer concentrations of 8.6–22.0 wt.% (depending on the reactivity of the monomers). For deprotonation and dehydration of the system, potassium carbonate (2.35–8.00 equiv relating to the bisphenol monomer) and toluene were added and the reaction mixture was first heated to 145 °C for 3 hours to remove the toluene–water mixture and then to the reaction temperature (depending on the reactivity of the monomers) for 5–18 hours. Then the reaction mixture was slowly poured into water, washed several times with water and methanol. Finally the polymer was dried at 75 °C under vacuum.

2.3.1. Poly(arylene ether) **1a**

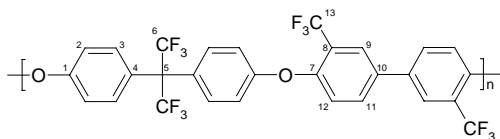
1.6812 g (5.00 mmol) 2,2-bis(4-hydroxyphenyl)hexafluoropropane (bisphenol AF); 1.7005 g (5.00 mmol) 2,2-bis(4-fluorophenyl)hexafluoropropane; 2.0732 g (15.00 mmol) K_2CO_3 ; 22 ml NMP/40 ml toluene reaction temperature: 180 °C, reaction time: 16 h; yield: 59%.



^1H NMR (200 MHz, CDCl_3 , δ): 7.40 (d, $^3J_{\text{H-H}} = 8.7$ Hz, 1H; H-8, H-13), 7.26 (d, $^3J_{\text{H-H}} = 8.7$ Hz, 0.06H; H-3), 7.03 (d, $^3J_{\text{H-H}} = 8.7$ Hz, 1H; H-9, H-12), 6.82 (d, $^3J_{\text{H-H}} = 8.7$ Hz, 0.06H; H-2); ^{13}C NMR (63 MHz, CDCl_3 , δ): 156.93 (C-11), 131.89 (C-13), 128.50 (C-14), 124.19 (quartet, $^1J_{\text{C-F}} = 287$ Hz; C-16), 118.53 (C-12), 63.85 (septet, $^2J_{\text{C-F}} = 25.6$ Hz; C-15). The carbon atoms of the end groups C-1–C-10 were not found in the spectrum probably due to the lower natural abundance of ^{13}C , ^{19}F NMR (235 MHz, CDCl_3 , δ): –64.06 (s, 1F; F-16), –64.13 (s, 0.12F; F-6).

2.3.2. Poly(arylene ether) **2a**

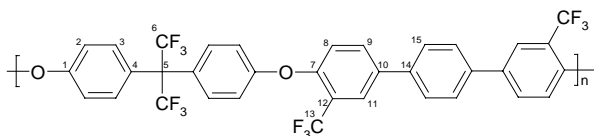
1.7686 g (5.26 mmol) 2,2-bis(4-hydroxyphenyl)hexafluoropropane (bisphenol AF); 2.0000 g (5.26 mmol) 4,4'-dinitro-3,3'-bis(trifluoromethyl)biphenyl; 5.8159 g (42.08 mmol) K_2CO_3 ; 13 ml NMP reaction temperature: 180 °C, reaction time: 18 h; yield: 76%.



^1H NMR (200 MHz, THF- d_6 , δ): 8.04 (s, 1H; H-9), 7.92 (dd, $^3J_{\text{H-H}} = 8.6$ Hz, $^5J_{\text{H-H}} = 1.5$ Hz, 1H; H-12), 7.50 (d, $^3J_{\text{H-H}} = 8.3$ Hz, 2H; H-3), 7.29 (d, $^3J_{\text{H-H}} = 8.8$ Hz, 1H; H-11), 7.17 (d, $^3J_{\text{H-H}} = 8.8$ Hz; 2H, H-2); ^{13}C NMR (63 MHz, THF- d_6 , δ): 159.41 (C-1), 155.98 (C-7), 137.09 (C-4), 134.26 (C-12), 133.96 (C-3), 130.53 (C-10), 127.77 (q, $^3J_{\text{C-F}} = 5.0$ Hz; C-9), 126.37 (q, $^1J_{\text{C-F}} = 288$ Hz; C-6), 125.35 (q, $^1J_{\text{C-F}} = 273$ Hz; C-13), 124.10 (q, $^2J_{\text{C-F}} = 31.4$ Hz; C-8), 122.87 (C-11), 120.36 (C-2), 65.93 (septet, $^2J_{\text{C-F}} = 24.8$ Hz; C-5); ^{19}F NMR (63 MHz, THF- d_6 , δ): –57.17 (s, 1F; F-13), –59.33 (s, 1F; F-6).

2.3.3. Poly(arylene ether) **3a**

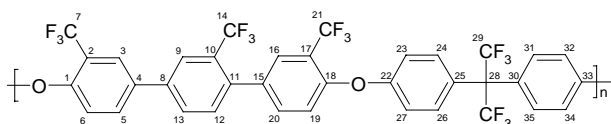
2.000 g (4.965 mmol) 4,4''-difluoro-3,3''-bis(trifluoromethyl)-p-terphenyl; 1.694 g (4.965 mmol) 2,2-bis(4-hydroxyphenyl)hexafluoropropane (bisphenol AF); 1.6143 g (11.68 mmol) K_2CO_3 ; 38 ml NMP/60 ml toluene reaction temperature: 180 °C, reaction time: 5 h; yield: 75%.



^1H NMR (400 MHz, CDCl_3 , δ): 7.95 (s, 1H; H-9), 7.76 (d, $^3J_{\text{H-F}} = 7.7$ Hz, 1H; H-11), 7.68 (s, 2H; H-15), 7.43 (d, $^3J_{\text{H-H}} = 7.7$ Hz, 2H; H-3), 7.15 (d, $^3J_{\text{H-H}} = 8.1$ Hz, 1H; H-8), 7.08 (d, $^3J_{\text{H-H}} = 8.1$ Hz, 2H; H-2); ^{13}C NMR (50 MHz, CDCl_3 , δ): 157.30 (C-1), 153.76 (C-7), 138.63 (C-14), 136.25 (C-10), 131.97 (C-9), 128.66 (C-3), 127.60 (C-15), 125.92 (C-15), 122.56 (quartet, $^2J_{\text{C-F}} = 31.8$ Hz; C-12), 120.77 (C-2), 118.33 (C-8). C-5, C-6 and C-13 are not found; ^{19}F NMR (188 MHz, CDCl_3 , δ): –60.62 (s, 1F; F-13), –62.79 (s, 1F; F-6).

2.3.4. Poly(arylene ether) **4a**

2.000 g (4.253 mmol) 4,4''-difluoro-2',3,3''-tris(trifluoromethyl)-p-terphenyl; 1.430 g (4.253 mmol) 2,2-bis(4-hydroxyphenyl)hexafluoropropane (bisphenol AF); 1.3828 g (10.005 mmol) K_2CO_3 ; 35 ml NMP/60 ml toluene reaction temperature: 180 °C, reaction time: 5 h; yield: 87%.



^1H , ^{13}C -HSQC NMR (250 MHz, 63 MHz, CDCl_3 , δ): 7.25 (m, 4H)/119.77 (H-23/C-23, H-27/C-27, H-32/C-32, H-34/C-34), 7.28 (d, $^3J_{\text{H-H}} = 9.2$ Hz; 1H)/120.76 (H-6/C-6), 7.33 (d, $^3J_{\text{H-H}} = 8.9$ Hz, 1H)/121.97 (H-19/C-19), 7.55 (m, 4H)/133.14 (H-24/C-24, H-26/C-26, H-31/C-31, H-35/C-35), 7.63 (d, $^3J_{\text{H-H}} = 8.1$ Hz, 1H)/134.22 (H-12/C-12), 7.70 (d, $^3J_{\text{H-H}} = 9.2$ Hz, 1H)/135.75 (H-20/C-20), 7.80 (s, 1H)/128.84 (H-9/C-9), 8.11 (d, $^3J_{\text{H-H}} = 8.1$ Hz, 1H)/131.54 (H-13/C-13), 8.11 (d, $^3J_{\text{H-H}} = 8.1$ Hz, 1H)/133.87 >(H-5/C-5), 8.18 (s, 1H)/125.81 (H-3/C-3), 8.20 (s, 1H)/127.13 (H-16/C-16); ^{13}C NMR (63 MHz, Acetone- d_6 , δ): 158.29 (C-22), 158.17 (C-33), 155.36 (q, $^3J_{\text{C-F}} = 1.6$ Hz; C-18), 155.12 (q, $^3J_{\text{C-F}} = 1.7$ Hz; C-1), 140.19 (C-8), 139.40 (q, $^3J_{\text{C-F}} = 1.89$ Hz; C-11), 136.08 (C-15), 135.94 (C-4), 135.75 (m; C-20), 134.22 (C-12), 133.87 (C-5), 133.14 (C-24, C-26, C-31, C-35), 131.54 (C-13), 129.75 (q, $^2J_{\text{C-F}} = 30.1$ Hz; C-10), 129.68 (C-25), 129.62 (C-30), 128.84 (q, $^3J_{\text{C-F}} = 5.0$ Hz; C-9), 127.13 (q, $^3J_{\text{C-F}} = 5.0$ Hz; C-16), 125.81 (q, $^3J_{\text{C-F}} = 5.35$ Hz; C-3), 125.38 (q, $^1J_{\text{C-F}} = 287$ Hz; C-29), 125.22 (q, $^1J_{\text{C-F}} = 274$ Hz; C-14), 124.46 (q, $^1J_{\text{C-F}} = 273$ Hz; C-7), 124.40 (q, $^1J_{\text{C-F}} = 273$ Hz; C-21), 122.88 (q, $^2J_{\text{C-F}} = 31.6$ Hz; C-2), 121.97 (C-6), 121.71 (q, $^2J_{\text{C-F}} = 31.5$ Hz; C-17), 120.76 (C-19), 119.81 (C-23, C-27), 119.73 (C-32, C-34), 64.96 (septet, $^2J_{\text{C-F}} = 25.8$ Hz; C-28); ^{19}F NMR (188 MHz, CDCl_3 , δ): –59.53 (s, 2F; F-29), –57.25 (s, 1F; F-21), –57.18 (s, 1F; F-7), –52.18 (s, 1F; F-14).

2.4. Heterogeneous sulfonation (procedure 1) [17]

2.00 g of polymer **3a** and 100 ml of fuming sulfuric acid H_2SO_4 (20% SO_3) or 0.25 g of polymer **4a** and 64 ml of H_2SO_4 (30% SO_3) were added into a 250 ml three-neck flask (equipped with mechanical stirrer, reflux condenser and a drying tube filled with phosphorus pentoxide) under vigorous stirring. After 30 min, the reaction mixture was slowly poured onto ice cubes. The resulting suspension was dialysed for 4 days to remove the excess sulfuric acid. Finally the water was removed by rotary evaporation and the sulfonated polymers (**3b** and **4b**) were dried at 90 °C under vacuum before characterization.

2.4.1. Homogeneous sulfonation (procedure 2) [43]

0.710 g (1.0157 mmol) of polymer **4a** was dissolved in 107 ml dichloromethane under argon atmosphere. 10.66 ml of 0.8 M chlorosulfonic acid in dichloromethane were dropped slowly to this solution under intensive stirring. This reaction mixture was stirred at room temperature until the dark brown product was precipitated (approximately 6 hours). The precipitation was filtered, washed with *n*-hexane twice and dissolved in 30 ml dimethylsulfoxide (DMSO). 60 ml of aqueous KOH solution (3 wt.%) were added and this solution was then stirred at room temperature for 6 hours. Finally the solution was acidified with 200 ml of hydrochloric acid (5 wt.%), stirred for 1 hour and dialysed for 2 days. The product was recovered after removing water and it was dried at 100 °C in a vacuum oven for 16 hours.

2.5. Membrane preparation

The membranes were cast into an aluminium bowl from their NMP solutions (10 wt.% concentration of sulfonated polymer) and dried at 130 °C at atmospheric pressure for 3 hours. The membranes were then soaked in 10 wt.% HCl at 90 °C for 48 hours and subsequently washed with deionized water in order to cleave any anhydrides which could be formed during the membrane preparation process by condensation of two sulfonic acid groups. Finally the membranes were immersed in deionized water at 60 °C for another 48 hours.

2.6. Polymer and membrane characterization

NMR spectra were recorded using a Bruker Avance 400 spectrometer at a resonance frequency of 400 MHz or 250 MHz for ^1H ,

188 MHz for ^{19}F and 250 MHz for ^1H , ^{13}C -HSQC (heteronuclear single quantum coherence) experiments.

The molecular weight distributions of the polymers and ionomers (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), a refractive index detector (Shodex RI71) and a static light-scattering detector (PSS SLD 7000). 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 through 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 has been estimated qualitatively in terms of their relative film-forming properties in the following way:

- 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 ($T_{5\text{wt.}\% \text{ loss}}$). 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 ($T_{\text{SO}_3\text{H onset}}$) for which the asymmetric stretching vibration of the S=O group at 1352–1342 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 hours before determination of their thermal properties by TGA and DSC.

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

The specific conductivity (κ^T with T = temperature in °C) of the membranes was determined in the temperature range from 25 °C to 70 °C in 0.5 M HCl by electrochemical impedance spectroscopy (EIS) using a method described in the literature [44] on an IM6 Model of Zahner Elektrik.

The values for the water uptake (WU) of the membranes were determined after equilibrating in water of defined temperatures (25 °C, 40 °C, 60 °C, 90 °C). After 48 hours the samples were removed from the water solution, quickly dry wiped and immediately weighed (m_{wet}). Then the samples were dried to weight constancy at 90 °C and weighed once again (m_{dry}). The water uptake can be obtained from the following equation.

$$\text{WU}[\%] = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \cdot 100[\%] \quad (1)$$

The number of water molecules per sulfonic acid group λ is defined as the quantity of H_2O molecules ($n(\text{H}_2\text{O})$) related to the number of sulfonic acid groups of the polymer [40] ($n(\text{SO}_3\text{H})$) and is calculated according to Equation (2):

$$\lambda = \frac{\text{WU}[\%]}{\text{M}(\text{H}_2\text{O}) \left[\text{g mol}^{-1} \right] \cdot \text{IEC} \left[\text{mmol g}^{-1} \right]} \cdot 10 \quad (2)$$

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.

$$\text{Swelling Degree}[\%] = \frac{l_{\text{wet}} - l_{\text{dry}}}{l_{\text{dry}}} \cdot 100[\%] \quad (3)$$

3. Results and discussion

3.1. Synthesis and characterization of monomers

The monomeric building blocks **5–8** (Scheme 3) for the preparation of the model polymers **1a–4a** could be synthesized by using well known organic reactions (Balz–Schiemann reaction, Ullmann biaryl synthesis, Suzuki coupling) and characterized by ^1H , ^{13}C and ^{19}F NMR spectroscopies. The NMR signals of the monomers **5–7** could be assigned to the corresponding nuclei by comparing with literature data [25,26,41]. However, no reference data for monomer **8** are available in the literature. In addition, the relatively high number of chemically non-equivalent nuclei and the lower symmetry of the molecule in comparison to **7** cause complicated ^1H and ^{13}C NMR spectra. ^{19}F , ^{13}C spin–spin coupling and the resulting typical fine structure give the basis for the analysis of the ^{13}C NMR spectrum of **8**. An additional ^1H , ^{13}C -HSQC NMR experiment serves for the definite assignment of the corresponding ^1H signals.

Fig. 1 shows a section of the ^{13}C NMR spectrum of **8**. The principal procedure for the structure elucidation is pointed out at the example of the ^{13}C NMR signals of the carbon atoms C-3, C-9 and C-16 in the following. The ^{19}F , ^{13}C spin–spin coupling of C-9 with F-14 causes the quartet at 124.98 ppm. As the chemical environments of the carbon atoms C-3 and C-16 are rather similar and a distinction between the two signals only by the chemical shift would be ambiguous, the multiplet structure of the signals helps to assign the signals properly. The nuclear spin at C-3 can interact with those at F-1 (1F) and F-7 (3F), causing the doublet of the quartet at 125.95 ppm whereas a coupling of C-3 with F-14 (at the median phenylene ring) of the molecules is not observed due to the long distance between the two nuclei (the resultant coupling constant $^6J_{\text{C-F}}$ would be expected to be very low and might not be resolved). The situation is different for the coupling behaviour of C-16, from which the three F-14 atoms are only five bonds away and the coupling can be resolved in the ^{13}C NMR spectrum. Considering the other four neighbouring fluorine atoms (F-18 (1F) and F-21 (3F)), the signal at 127.80 ppm can be interpreted as a doublet of a quartet of a quartet with the ^{19}F , ^{13}C coupling constants given in Fig. 1 in good accordance with simulation of such a multiplet (done with the software ACD/SpecManager Version 10.02). The remaining signals of the ^{13}C NMR spectrum were elucidated by this principal procedure and the results are summarized in Experimental section. All the other signals in the ^1H , ^{13}C -HSQC NMR spectrum could then be assigned doubtlessly (Fig. 2). After their complete characterization the monomers **5–8** were then converted into the polymeric structures given in Scheme 2.

3.2. Polycondensation reactions

The polymers **1a–4a** were synthesized by step-growth polycondensation of 2,2-bis(4-hydroxyphenyl)hexafluoropropane with

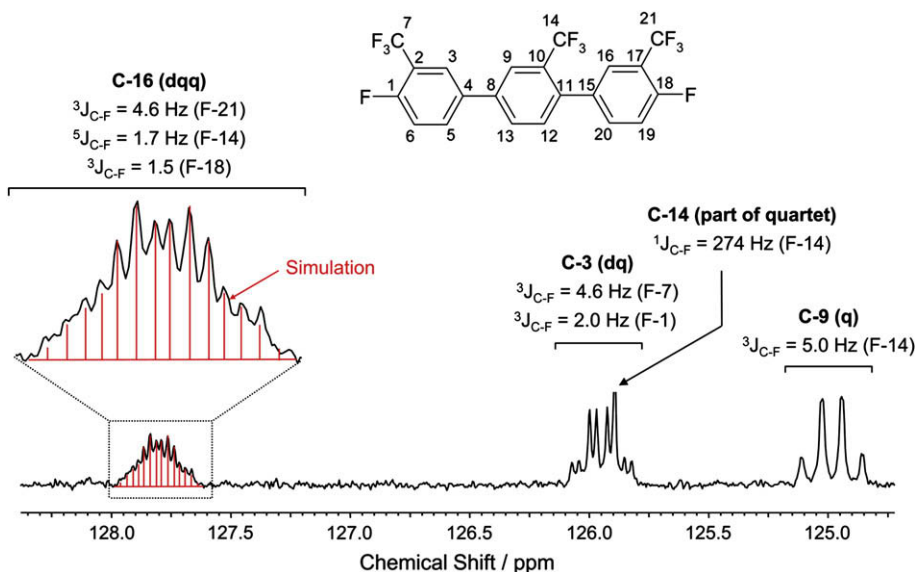


Fig. 1. Section of the ^{13}C NMR spectrum of monomer **8**.

the dihalo- or dinitrophenyl (**5**, **6**) or terphenyl (**7**, **8**) monomers. Gel permeation chromatography (GPC) has been used to characterize the polymeric products in terms of their molecular weight distribution (Table 1). Table 1 also summarizes their film-forming properties. The comparison between the number average molecular weights M_n^{GPC} reveals that the terphenyl monomers **7** and **8** are more activated for nucleophilic displacement polycondensation than the biphenyl monomers **5** and **6**. This difference in the reactivity might be attributed to the additional phenylene ring with its capability to stabilize the negative charge developed at the 4- and 4'-position of the adjacent aryl moiety in the transition state (Meisenheimer complex) of the nucleophilic displacement reaction [45]. The additional CF_3 group at the median phenylene ring of **8** activates the monomer once more compared to monomer **7** and explains the very high molecular weight of poly(arylene ether) **4a**. The polymers **1a** and **2a** have relatively poor film-forming properties, most probably because of their low-molecular weight and, in the case of **2a**, also because of the high polydispersity. The latter one could be consequence of the high initial monomer concentration that was necessary to obtain a coagulating polymer [46].

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the poly(arylene ether)s **1a–4a** (Table 1) demonstrate their high thermal stability as it can be expected for fluorine-containing arylene main-chain polymers [25,28]. Only the glass transition temperature of **1a** is comparatively low which, however, can be explained by the lower molecular weight and thus enhanced flexibility of the polymer chains [47]. The glass transition temperatures of the terphenylene based poly(arylene ether)s **3a** and **4a** are higher than those of the biphenylene-based ones **1a** and **2a**. This might be, firstly, due to the lower molecular weight of **1a** and **2a** and, secondly, due to the higher rigidity of the polymer backbone of **3a** and **4a**. When $T_{5\text{wt}\% \text{ loss}}$ and T_g of the terphenylene based poly(arylene ether)s **3a** and **4a** are compared, a slight decrease in the thermal stability can be observed for **4a** (with the additional CF_3 group) although its molecular weight is about three times higher. This effect could be caused by repulsive interactions between the sterically demanding CF_3 groups.

The chemical structures of the polymers **1a–4a** were additionally investigated by NMR spectroscopy. Fig. 3 shows the ^1H

and ^{19}F NMR spectra of **1a**. By neglecting any possible cyclization reactions during the polycondensation process (which might be justified for the relatively high monomer concentration and the low conversion) [48], the polymerization degree and thus the number average molecular weight (M_n^{NMR}) can be estimated from the NMR signal ratios. As no fluorine nuclei bound to an aromatic ring are detectable in the ^{19}F NMR spectrum of **1a** and as the ^1H NMR spectrum does not show any $^1\text{H},^{19}\text{F}$ spin–spin coupling it can be assumed that the end groups are essentially OH groups. On basis of the calculated stoichiometry used for the polycondensation one would expect a 1:1 ratio of F and OH end groups. This discrepancy might be explained by any impurities in the self-prepared monomers that were not detectable by the applied characterization methods. Such impurities would distort the stoichiometric imbalance of the polymerization reaction and explain the excess of HO end groups. The polymerization degree n for **1a** can be estimated from the NMR signal ratios to roughly 16 (from ^1H NMR) or 17 (from ^{19}F NMR) corresponding to $M_n^{\text{NMR}}(^1\text{H}) = 6018$ Da or $M_n^{\text{NMR}}(^{19}\text{F}) = 6352$ Da according to the following equations.

$$n(^1\text{H NMR}) = \frac{I(\text{H-12}, \text{H-9})}{I(\text{H-2})} - 1 = 15.83 \approx 16 \quad (4)$$

$$n(^{19}\text{F NMR}) = 2 \cdot \frac{I(\text{F-16})}{I(\text{F-6})} = 16.67 \approx 17 \quad (5)$$

If one considers the relative error in the GPC analysis (which is normally 10–15%) [49] and the assumption (made for the determination of M_n by NMR spectroscopy: see above), the correlation between these methods is relatively good.

While the polymers **1a–3a** could be fully characterized by one-dimensional NMR methods the definite characterization of **4a** required $^1\text{H},^{13}\text{C}$ -HSQC NMR as in the case of the corresponding monomer **8**. A detailed assignment of the $^1\text{H},^{13}\text{C}$ -HSQC NMR spectrum is depicted in Fig. 4. It can be seen by comparing this spectrum with that of monomer **8** (Fig. 2) that all signals are downfield-shifted as expected whereas the strongest effect is observed for the signals H-3/C-3 and H-16/C-16. The detailed understanding of this NMR spectrum gives the basis for the

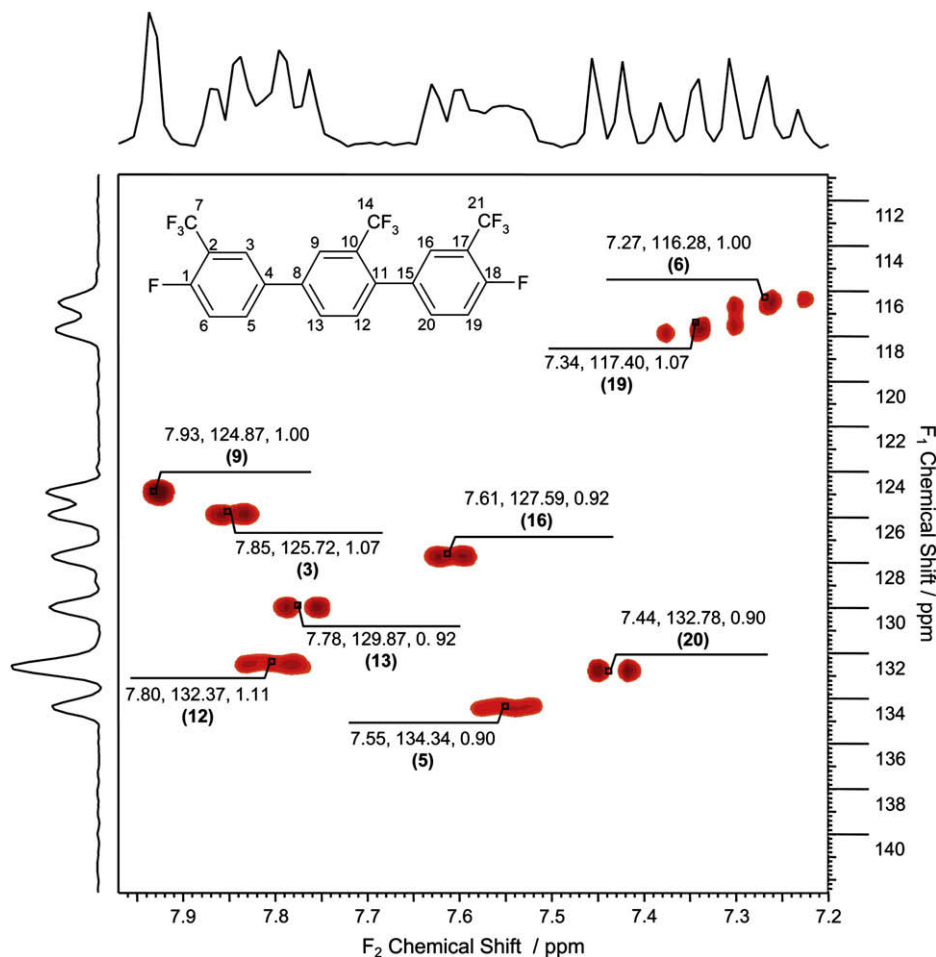


Fig. 2. ^1H , ^{13}C -HSQC NMR spectrum of monomer **8**.

evaluation of the corresponding sulfonated poly(arylene ether)s in the next section.

In order to sum up the suitability of the various poly(arylene ether)s **1a–4a** as potential ionomer backbones, the following interim status can be given: The synthesis of suitable monomers (and their characterization) could be realized successfully, i.e. requirement (i) could be passed for all targeted structures. However, the conversion of the synthesized monomers with 2,2-bis(4-hydroxyphenyl)hexafluoropropane into the corresponding poly(arylene ether)s with the requirements mentioned above under (ii) was only satisfactory for the terphenylene based polymers **3a** and **4a**. Methods for the sulfonation of these structures and the issues connected with the postsulfonation will be outlined in the next section.

3.3. Sulfonation reactions

The sulfonation reaction of a polymer is a trade-off between the desired introduction of the SO_3H group (and the control over its number) and any side or degradation reactions (that could finally result in a decrease of the molecular weight). As the basic poly(arylene ether)s **1a** and **2a** show only poor membrane-forming properties (cf. Table 1), they were disregarded for converting into their sulfonated analogues. Therefore, the details for appropriate sulfonation processes have only been worked out for the poly(arylene ether)s **3a** and **4a**. Table 2 summarizes the applied sulfonation conditions. While **3a** could be sulfonated with fuming sulfuric acid (20% SO_2) ending up in a sulfonation degree of $\text{SD} = 0.92$ (**3b**), the poly(arylene ether) **4a** yielded only a low

Table 1

Overview of the initial monomer concentration used for polycondensation, of the molecular weight distribution of the resulting polymers **1a–4a** determined by GPC (using polystyrene for calibration), of their relative membrane-forming properties, and of their thermal properties (temperature at which the sample has lost 5 wt.% of its initial weight $T_{5\text{wt.}\% \text{ loss}}$, glass transition temperature T_g).

Polymer	Initial monomer concentration [wt.%]	M_n^{GPC} [g mol^{-1}]	PDI	Relative film-forming properties	$T_{5\text{wt.}\% \text{ loss}}$ [$^{\circ}\text{C}$]	T_g [$^{\circ}\text{C}$]
1a	13.0	5,000	2.14	–	493	134.9
2a	22.0	7,200	10.63	–/+	496 (500) ^a	169.4 (167.0) ^a
3a	8.6	16,900	1.98	++	508 (500) ^b	187.2 (197.0) ^b
4a	8.7	45,900	3.42	++	501	179.7

^a Values taken from the literature [28].

^b Values taken from the literature [25].

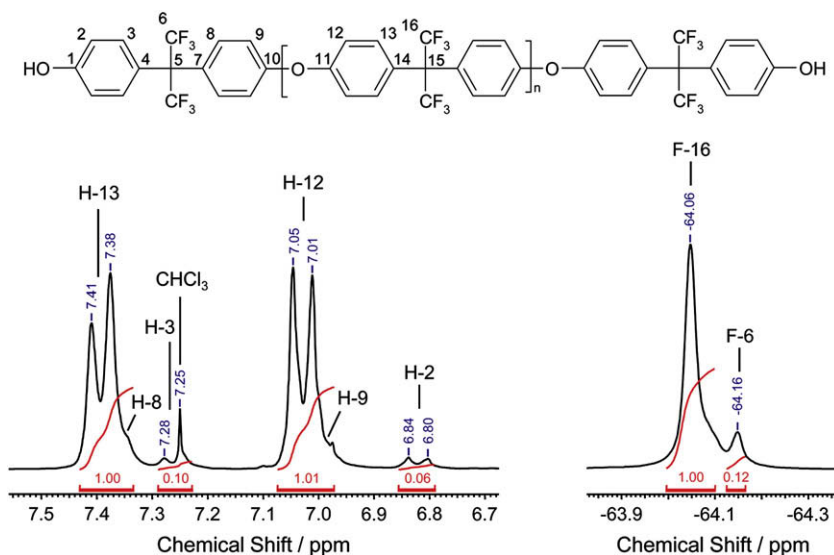


Fig. 3. ^1H and ^{19}F NMR spectra of the poly(arylene ether) **1a**.

sulfonated product even by using a higher concentration of the electrophilic species (SO_3) in the fuming sulfuric acid (**4b**). In order to achieve a higher sulfonation degree for this extremely electron-poor poly(arylene ether), sulfonation in CH_2Cl_2 (in which the polymer is initially soluble) with chlorosulfonic acid has been conducted (**4c**).

As it can be expected from the literature [50,51], the film-forming properties of the resulting ionomers are affected by the method used for sulfonation. The relative film-forming properties of the ionomers synthesized (Table 2) via the heterogeneous method (**3b** and **4b**) are worse than in the case of the milder conditions during homogeneous sulfonation (**4c**) indicating stronger degradation reactions during the heterogeneous sulfonation route.

Structural characterization by NMR spectroscopy is focussed on **4c**. In the following part of this section the ^1H , ^{13}C -HSQC NMR spectrum of the sulfonated poly(arylene ether) **4c** will be discussed in order to get an insight into the preferred sulfonation site (Fig. 5). The broader spots in the spectrum of **4c** in comparison to the nonsulfonated polymer **4a** (Fig. 4) rule out an explicit elucidation of the spectrum. These line broadening effects are probably caused by the presence of exchangeable protons in the sulfonated species **4c** and the higher viscosity of its solution compared to that of **4a** [52]. Another reason for some broad spots in the spectrum of **4c** might be a non-uniform distribution of the sulfonic acid groups along the ionomer chain causing signals with similar chemical shifts both of the ^1H and the ^{13}C nuclei and the overlapping of these signals in the spectrum. Such an overlapping of peaks might be the reason for the observed high signal intensity, for instance, at around 8.05/130.71. The chemical structure in Fig. 5 shows only one (albeit the most likely) possibility for the structure with $\text{SD} = 1.30$ where 70% monosulfonated and 30% disulfonated moieties are statistically distributed over the polymer chain. For instance, a sulfonation degree of $\text{SD} = 1.3$ could also be realized by a structure consisting of 65% disulfonated and 35% nonsulfonated moieties. Another uncertainty is the position of the sulfonic acid group which, in principle, could also be at C-6 and C-19 respectively.

A clear assignment is not possible, but there are indications that the sulfonic acid groups are preferably attached at the bisphenoxy moiety. No overlapping is obviously observed for the NMR signals caused by the nuclei 5, 9, 12 and 20 so that a sulfonation at these

positions can be excluded. The comparison between the spectrum of **4c** and **4a** indicates that the signals of 3, 16 and 6, 19 and 13 are most likely at 8.09/125.13 ppm and 7.01/121.92 ppm and 8.05/130.71 ppm. The high signal intensities at 8.09/125.13 ppm and 8.05/130.71 ppm suggest an overlapping which could be interpreted as done in Table 3 and Fig. 5 and would indicate that sulfonation took place in the bisphenoxy moiety. However, a more detailed structure elucidation of this novel ionomer would necessitate fractionating of the ionomer sample and subsequent MALDI-TOF mass spectroscopy analysis [53,54], which were unfortunately not available for this study.

As mentioned above the sulfonation process could be accompanied by partial degradation of the polymer backbone. In order to estimate the relative stability of the novel polymer backbone **4a** in the two different sulfonation media (fuming sulfuric acid for **4b** and chlorosulfonic acid in CH_2Cl_2 for **4c**) GPC measurements have been made. As discussed in a previous paper [55], the addition of lithium halides to the sample solution represses electrostatic forces among the chains of low sulfonated polymers which could alter the coil dimensions and which would distort the obtained molecular weight. In addition, it cannot be excluded completely that any intermolecular electrostatic (such as ion exchange, ion exclusion, ion inclusion) or intramolecular electrostatic interactions and adsorption effects due to hydrogen bonding may occur [56]. In order to minimize such effects, lithium bromide was added to the eluent (0.06 M LiBr in DMAc) and the sample concentration was chosen to be relatively low (2 g/l). The molar mass distributions of **4a–4c** determined from universal calibration with polystyrene as a standard are depicted in Fig. 6, the number average molecular weights (M_n) and polydispersity indices (PDI) are gathered in Table 1 for the nonsulfonated polymer and in Table 2 for the sulfonated ones. Obviously there is a considerable shift to lower molecular weights during the heterogeneous sulfonation reaction ($M_n = 45.9 \text{ kDa}/M_w = 157.0 \text{ kDa}$; for **4a** and $M_n = 30.0 \text{ kDa}/M_w = 120.9 \text{ kDa}$ for **4b**) while the shape of the chromatograms (with the shoulder on the low-molecular side) and the polydispersity indices remain unchanged (PDI = 3.42 for **4a** and PDI = 3.39 for **4b**). The molecular weight distribution of the product of the homogeneous sulfonation (**4c**) is less shifted vs. **4a** ($M_n = 50.0 \text{ kDa}/M_w = 135.0 \text{ kDa}$ for **4c**) and the shoulder at $M = 20\text{--}40 \text{ kDa}$ – present in the starting material (**4a**) – disappears resulting in

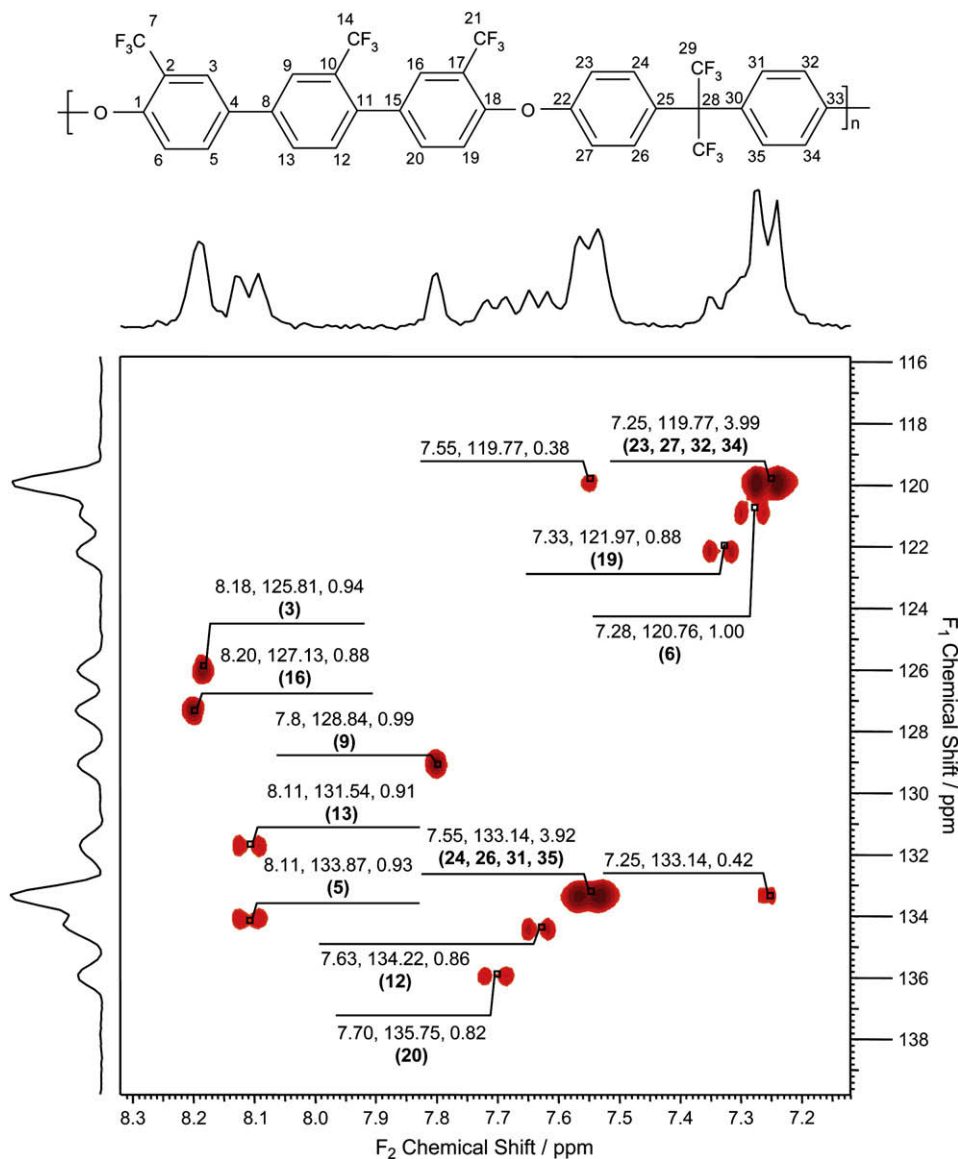


Fig. 4. ^1H , ^{13}C -HSQC NMR spectrum of the poly(arylene ether) **4a**.

a narrower distribution (PDI = 2.70). Presumably this shoulder is caused by any cyclic or branched macromolecules which are not soluble in water or methanol (that were used in the purification process of the polymeric product **4a**) [17]. With introducing a certain amount of sulfonic acid groups onto the polymer backbone, the solubility of these structures is enhanced and they are removed predominantly in the working-up procedure of the sulfonation reaction.

Partial molecular weight degradation caused by acid-induced ether cleavage under the harsh sulfonation conditions [29] cannot be excluded for both sulfonation routes. The molecular weight of the sulfonated polymer should be larger than that of the non-sulfonated polymer by the molecular weight of the attached sulfonic acid groups if no degradation took place. It can be stated, however, that the effect of molecular weight degradation is less pronounced in the case of the homogeneous sulfonation route.

Table 2

Overview of the conditions for the sulfonation of the poly(arylene ether)s **3a** and **4a** and the properties of the resulting ionomers in comparison to Nafion[®] 117.

Ionomer	Sulfonation reagent/ time [hour]	Relative film-forming properties	M_n [kDa]	Polydispersity index (PDI)	IEC _{total} [mmol/g]	SD ^a	$T_{\text{SO}_3\text{H}}$ onset [°C]	$\kappa^{25^\circ\text{C}}$ [mS/cm]	E_a [kJ/mol]
3b	H ₂ SO ₄ (20% SO ₃)/0.5	+	16.7	2.80	1.19	0.92	198	99	17.4
4b	H ₂ SO ₄ (30% SO ₃)/0.5	+	31.0	3.39	0.83	0.64	260	36	17.7
4c	HSO ₃ Cl in CH ₂ Cl ₂ /6	++	50.0	2.70	1.48	1.29	214	167	29.2
Nafion [®] 117	–	++	–	–	0.90 (0.91) ^b	–	229	133 (97) ^c	17.5

^a SD = Degree of sulfonation, calculated from IEC_{total}.

^b Taken from the literature [2,5].

^c Specific conductivity under similar conditions, but in 0.1 M HCl as an electrolyte (value taken from the literature [66]).

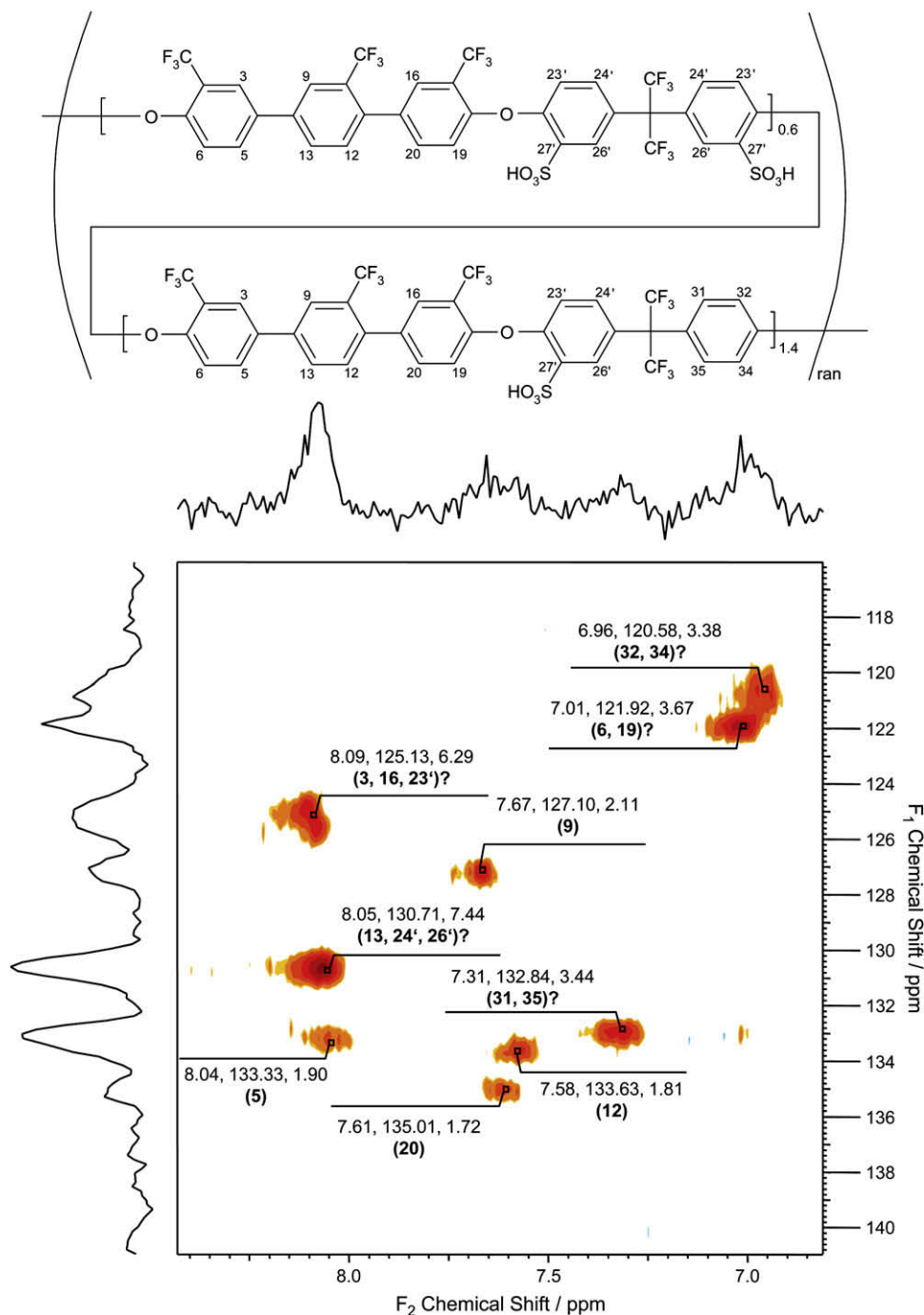


Fig. 5. $^1\text{H},^{13}\text{C}$ -HSQC NMR spectrum of the sulfonated poly(arylene ether) **4c**.

Fig. 7 shows the GPC chromatograms for **4a–4c**, recorded with a light-scattering and a refractive index detector. While the refractive index detector does not show any signals at very high elution volumes (ca. 30–34 ml) for all the three polymers, a light-scattering signal can be observed for **4b** at 30–32 ml elution volume indicating particles with a high scattering power in a very low concentration. This signal is probably caused by the presence of microgel particles. Such microgel particles have a large molecular weight but they are also very compact (because of their crosslinked nature). As the separation mechanism of GPC is based on the hydrodynamic radius of the sample molecules, the corresponding signal of such a microgel particle appears at high elution. They

strongly scatter the laser light when passing the static light-scattering detector. However, they are hardly detectable in the RI detector due to their low concentration. The worse mechanical properties of **4b** compared to **4c** (cf. relative film-forming properties in Table 2) can thus be explained by the more pronounced polymer degradation (probably by an acid-induced ether cleavage) and the presence of microgel particles. Therefore, the homogeneous sulfonation method can be regarded as the smoother one. The observed microgel particles could be formed as a result of crosslinking under the extremely acidic conditions at the interface between the polymer surface and the fuming sulfuric acid. A certain fraction of the sulfonic acid groups might be protonated by the

Table 3

Comparison between the experimental and theoretical integral intensities of **4c** (cf. also Fig. 5).

Chemical shift $\delta_{\text{H}}/\delta_{\text{C}}$ [ppm]	Atom number(s)	Experimental intensity	Theoretical intensity ^a
8.09/125.13	3, 6, 23'	6.29	6.60
8.05/130.71	13, 24', 26'	7.44	7.20
8.04/133.33	5	1.90	2.00
7.67/127.10	9	2.11	2.00
7.61/135.01	20	1.72	2.00
7.58/133.63	12	1.81	2.00
7.31/132.84	31, 35	3.44	2.80
7.01/121.92	6, 19	3.67	4.00
6.96/120.58	32, 34	3.38	2.80

^a Calculated from the structure with 70% mono- and 30% disulfonated moieties in Fig. 5.

fuming sulfuric acid. The hygroscopic nature of the sulfuric acid could facilitate the elimination of water and form a strongly electrophilic species which could then attack another aromatic ring of an adjacent polymer or ionomer chain. The result would be a sulfone bridge which has been reported in the literature for thermally crosslinked sulfonated poly(ether ether ketone)s [57].

3.4. Membrane characterization

Besides the synthesis and the structural characterization of appropriate sulfonated arylene main-chain polymers, the evaluation of membrane properties in terms of fuel cell applications is of great importance for the development and further optimization of alternative membrane materials (cf. Table 2). A direct comparison between the various membranes **3b**, **4b** and **4c** is rather difficult since the experimental ion-exchange capacities range from $\text{IEC}_{\text{total}} = 0.83 \text{ mmol/g}$ (for **4b**), over $\text{IEC}_{\text{total}} = 1.19 \text{ mmol/g}$ (for **3b**) and $\text{IEC}_{\text{total}} = 1.48 \text{ mmol/g}$ (for **4c**) corresponding to different sulfonation degrees and entailing different transport properties. However, tendencies for the most appropriate structure(s) can be drawn from the data presented in Table 2 and in Figs. 8–11. They further could serve as starting point for future development and optimization.

A comparison between the degradation temperature of the sulfonic acid groups in **4b** and **4c** (Table 2) reveals that the thermal stability decreases with increasing ion-exchange capacity or degree of sulfonation. Such effects have been observed earlier for sulfonated poly(ether ether ketone)s (sPEEK) and attributed to

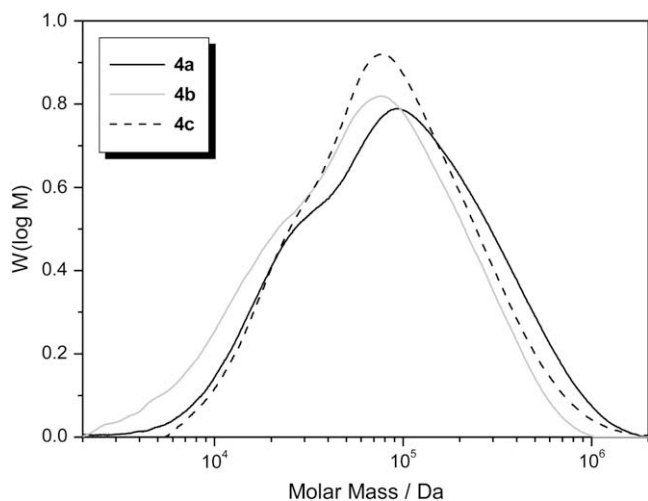


Fig. 6. Molar mass distribution of poly(arylene ether) **4a** and of its sulfonated forms **4b** and **4c**.

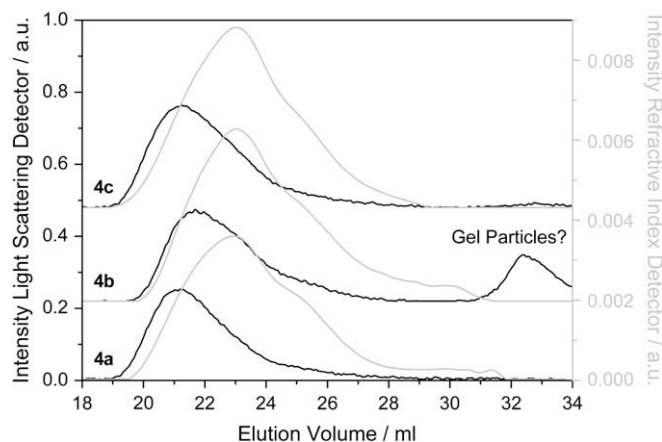


Fig. 7. GPC elograms of poly(arylene ether) **4a** and its sulfonated forms **4b** and **4c**, recorded with a light-scattering and a refractive index detector.

a degradation mechanism initiated at the sulfonic acid sites [58]. By comparing **3b** with $\text{IEC}_{\text{total}} = 1.19 \text{ mmol/g}$ and **4c** with $\text{IEC}_{\text{total}} = 1.48 \text{ mmol/g}$, the beneficial effect of the additional CF_3 substituent in **4c** can be seen. Despite having the higher ion-exchange capacity, **4c** is thermally more stable than **3b** and only slightly less stable than the reference material Nafion[®] 117. Table 2 also summarizes the specific conductivities in 0.5 M HCl at 25 °C. The measured value of the Nafion[®] 117 membrane in the present study is higher than that reported in the literature [59] which could be due to some differences in the experimental conditions and in the thermal history of the Nafion[®] membrane [60]. It has further been shown in the literature that the measured conductivity of Nafion[®] is also influenced by the ionic strength of the external solution [60]. Therefore, only the values of proton conductivity obtained at the same experimental conditions are compared. The proton conductivity of the new ionomer **4c** exceeds that of the Nafion[®] 117 membrane which can be traced back to its higher sulfonation level and higher water uptake respectively (cf. Figs. 9 and 10). This higher content of sulfonic acid groups in **4c** compared to Nafion[®] 117 also entails a stronger swelling due to the weaker relaxation forces in the polymer backbone (cf. Fig. 11) which is usually observed for

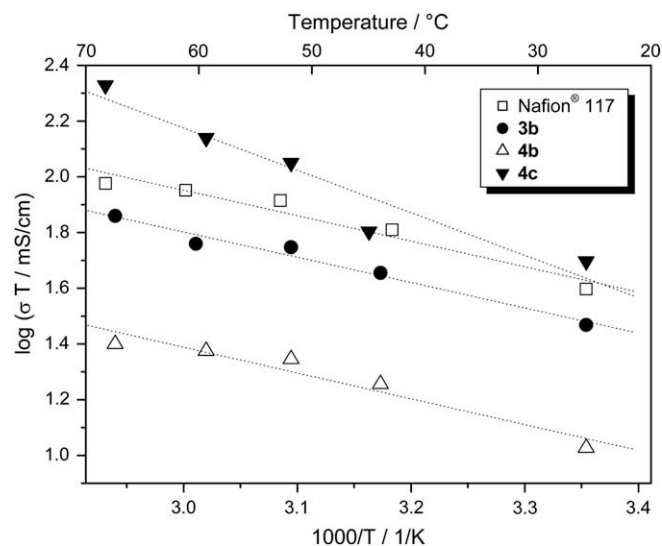


Fig. 8. Temperature dependence of the specific conductivities for the synthesized membranes and for Nafion[®] 117 (measured in 0.5 M HCl).

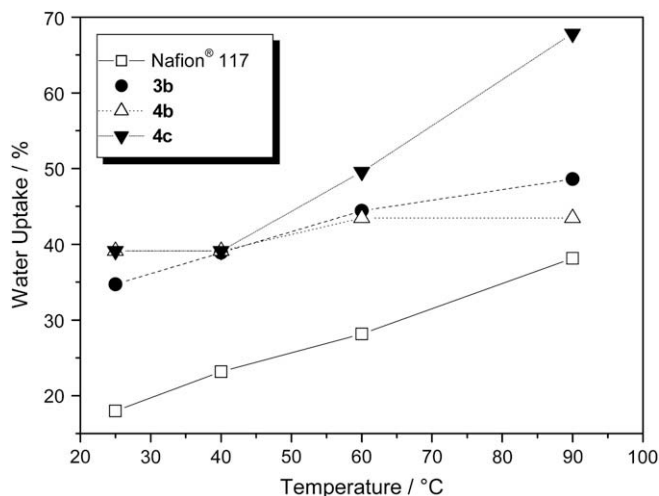


Fig. 9. Water uptake of the membranes **3b**, **4b** and **4c** in comparison to that of Nafion® 117 in dependence of temperature.

poly(aryl) based ionomers [61,62]. However, it can be deduced from a comparison of the proton conductivities of **4b** and **4c** as well as of their water uptake (Fig. 9) and swelling degree (Fig. 11) that a reasonable window for optimization for this system exists. The activation energies for proton transport – listed in Table 2 – are determined from the slope of the linear fit in the Arrhenius plot depicted in Fig. 8. While the value for Nafion® 117 lies in the same range as reported in the literature [63], the activation energy for proton conduction in **4c** is significantly higher than that for the other membranes **3b** and **4b**. Although no definite explanation for these findings can be given on the basis of the presented data, one could assume a change in the proton transport mechanism with increasing sulfonation degree. An increased number of sulfonic acid groups on the backbone of structure **4** could further enhance the rigidity of the system which then could influence the ratio between structural and molecular diffusion of protons [64].

In order to clarify the reasons for these findings and in order to get some more insight into the transport properties of these novel poly(arylene ether) ionomers (including fuel cell and methanol permeability tests), a series of various sulfonated poly(arylene ether) ionomers (preferably of structure **4**) will be part

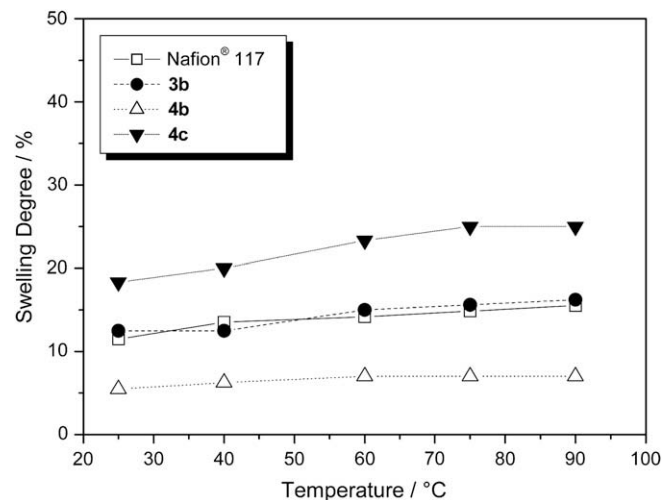


Fig. 11. Swelling degree for the synthesized membranes and for Nafion® 117 in dependence of temperature.

of future work in our group. The homogeneous sulfonation method is thought to be the most promising way to introduce the sulfonic acid group into this highly electron-deficient poly(arylene ether). Albeit synthetically challenging, the sulfonation of 4,4''-difluoro-2',3,3''-tris(trifluoromethyl)-*p*-terphenyl (**8**) and its subsequent co-polycondensation with the nonsulfonated one and with 2,2-bis(4-hydroxyphenyl)hexafluoropropane is considered as an attractive way to accomplish a better control over the sulfonation degree. It can be expected that the water uptake (Figs. 9 and 10) and the swelling behaviour (Fig. 11) of **4c** might be reduced by lowering its sulfonation degree while retaining sufficient proton conductivity.

The oxidative stabilities of the membranes **3b** and **4c** are estimated from their weight loss in hydrogen peroxide solution (5 wt.%) at elevated temperature (60 °C) [12]. As depicted in Fig. 12, membrane **3b** has lost 35% of its initial weight already after 6 hours incubation time. A clear improvement is detected for membrane **4c** with the additional CF₃ group which is stable for 24 hours. However, after 48 hours, severe degradation takes place and a sudden weight loss is detectable. In principle, the further improvement of the oxidative stability of the sulfonated poly

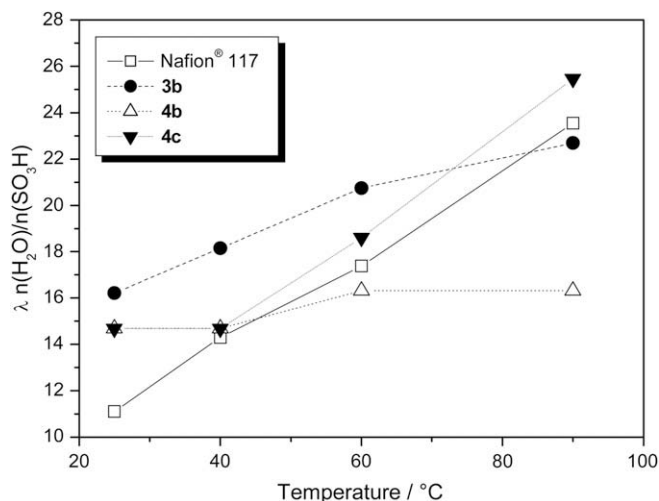


Fig. 10. Water uptake per sulfonic acid group for the synthesized membranes and for Nafion® 117 in dependence of temperature.

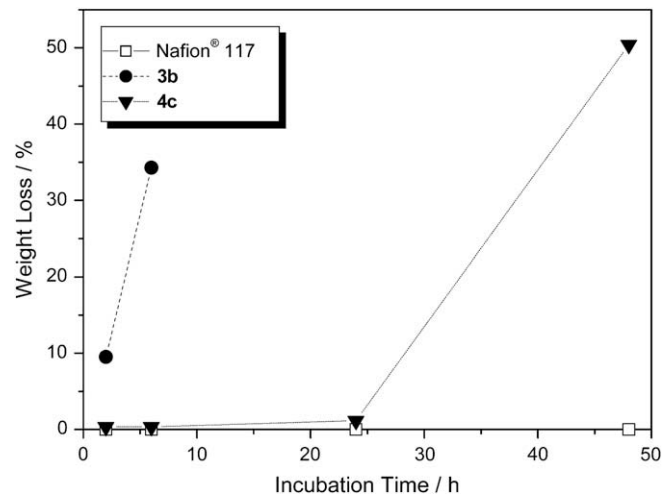


Fig. 12. Oxidative stability of **3b** and **4c** in comparison with Nafion® 117.

(arylene structure) **4** should be possible, for example, by reducing the sulfonation degree or by ionic crosslinking of a higher sulfonated species [65].

4. Conclusions

A series of partially fluorinated poly(arylene ether)s with pendent trifluoromethyl groups and/or with arylene rings bridged by hexafluoroisopropylidene groups in their backbones have been prepared and characterized. They have further been evaluated as potential candidates for postsulfonation provided the basic polymers had high molecular weights and sufficient film-forming properties. A clear dependence of polymerisability could be detected whereof the terphenyl monomers turned out to be the more activated toward aromatic nucleophilic substitution, leading to higher molecular weight polymers than the corresponding biphenyls.

The polymerization degrees of the two poly(arylene ether)s **1a** and **2a** are rather low, resulting in highly brittle polymer films and disqualifying these structures for any postsulfonation experiments. Unlike these biphenylene-based polymers, the two film-forming polymers **3a** and **4a** could be converted into their sulfonated forms by fuming sulfuric or chlorosulfonic acid. The sulfonated polymers **3b**, **4c** and **4b** were characterized in terms of possible fuel cell applications. Ionomer **4c** turned out to be a very promising candidate in terms of low specific resistance, moderate water uptake and relatively high oxidative stability which is attributed to the stabilizing effects of the CF₃ substituents at each aromatic ring of the terphenyl in combination with the C(CF₃)₂ bridge in the bisphenol moiety of the sulfonated poly(arylene ether). Such a material is thought to be interesting for the development of polymer electrolyte membranes since it offers broad leeway for further optimization including crosslinking [1], incorporation of inorganic particles [66] or formation of multi-block-co-ionomers [67]. Further sulfonation experiments on **4a** will be carried out in the future in our group in order to get a deeper understanding about the proton conductivity, the water uptake, the swelling degree and the oxidative stability. These experiments will also include the sulfonation of 4,4'-difluoro-2',3,3'-tris(trifluoromethyl)-*p*-terphenyl (monomer **8**) and its subsequent polycondensation.

Apart from any possible fuel cell applications, the highly trifluoromethyl-substituted, poly(arylene ether) **4a** might also be a good candidate as optical waveguide material due to the high content of fluorine [68].

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