ABSTRACT: In this contribution a series of novel multiblock-co-ionomers consisting of hydrophobic (partially fluorinated) and hydrophilic (sulfonated) domains has been prepared and characterised in terms of their applicability as fuel cell membranes. The synthesis of these multiblock-co-ionomers is a four-step procedure including (1) the sulfonation of the monomer 4,4'-difluorodiphenylsulfone, (2) the preparation of hydrophilic telechelic macromonomers by molecular-weight controlled step-growth polycondensation of the sulfonated monomer with various bis(thio)phenols, (3) the preparation of a hydrophobic telechelic macromonomer and (4) the coupling of both telechelic macromonomers to yield microphase-separated block-co-ionomers. This study focuses on the investigation of the influence of various linkage groups and atoms within the hydrophilic domains of the multiblock-co-ionomers. Both the telechelic macromonomers and the multiblock-co-ionomers were structurally investigated by $^1$H- and $^{19}$F-NMR spectroscopy and gel permeation chromatography (GPC). All multiblock-co-ionomers of this series could be cast into membranes and their membrane properties (ion-exchange capacity, specific resistance, swelling ratio, water uptake, thermal and oxidative stability) were measured and discussed in dependence of the various linkage groups within the hydrophilic domains. © 2007 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 45: 5237–5255, 2007

Keywords: Carother’s equation; direct methanol fuel cell; gel permeation chromatography (GPC); macromonomers; multiblock-co-ionomers; NMR; polymer electrolyte membrane fuel cell; step-growth polycondensation

INTRODUCTION

Polymer electrolyte membranes (PEMs) have been on focus of research and development for many years as one of their applications is the use in polymer electrolyte membrane fuel cells (PEMFCs) or direct methanol fuel cells (DMFCs), which are promising, environmentally friendly and efficient power sources. The membrane material has to fulfil a number of criteria to withstand the harsh conditions during operation and to ensure an economically reasonable running of the system. Beside high protonic and zero electronic conductivity, the membrane has to possess low permeability to fuel and oxidant, low water transport through diffusion and electro-osmosis, oxidative and hydrolytic stability, good mechanical properties in both the dry and the hydrated state, and finally economically reasonable production and maintenance costs.\(^1,\!^2\) The current state-of-the-art PEM material is polyperfluoroalkylsulfonic acid\(^3\) (e.g., Nafion\(^R\), Flemion\(^R\), or Dow\(^R\)) having good mechanical, thermal, and chemical stability as well as good protonic conductivity at temperatures below 80 °C.\(^4\) However, major drawbacks of this material are the high methanol-crossover that significantly lowers the efficiency of a DMFC system, the reduction in conductivity at higher temperatures and the relatively low glass transition temperature (ca.
110 °C in the dry state and considerably lower in the hydrated state) limiting the operation temperature of fuel cells. Additionally the complicated production process, which includes strongly hazardous intermediates, demands for high safety and environment precautions. During the last decades much effort in designing alternative PEM materials has been made and reviewed in literature by a lot of different authors. Many different families of polymers and different strategies of introducing ionogenic groups (sulfonic and/or phosphonic acids) have been explored. Sulfonated poly(arylene ether)s and poly(arylene ether sulfone)s are considered as good candidates in terms of high thermal, oxidative, hydrolytic, and mechanical stability as well as reduced methanol permeability. An evident trend in the design of novel PEM materials and thus the tailoring of properties is the control of polymer architecture, including the number and position of sulfonic acid groups as well as the morphology. Beside the preparation of statistical co-ionomers starting from a mixture of sulfonated/unsulfonated difluoromonomers and appropriate bisphenol monomers there are a few examples for designing morphologically controlled and microphase-separated sulfonated polymers. An interesting approach on this kind of polymers has recently been done by Holdcroft et al. who reported on highly fluorinated comb-shaped copolymers and ionic graft polymers to mimic the principal architecture of polyperfluoroalkysulfonic acids with improved mechanical integrity at higher temperatures and lower to moderate glass transition temperatures compared with Nafion. The preparation of sulfonated multiblock-co-ionomers for fuel cell membranes consisting of hydrophilic (sulfonated) and hydrophobic segments, in which the first one serves for proton transport and the latter one for increasing mechanical stability in comparison with the respective homo-ionomers [by lowering the water uptake (WU)] is sparsely reported in literature. Nonfluorinated sulfonated multiblock-co-poly(arylene ether ketone)s were synthesised and characterized with respect to fuel cell applications by Scherer and coworkers. Meier-Haack and coworkers delved into the synthesis of nonfluorinated sulfonated multiblock-co-poly(ether sulfone)s.

Recently, Miyatake and coworkers could demonstrated that sulfonated multiblock-co-polymides have superior proton conductivity, especially at low humidity, when compared with the corresponding sulfonated statistical co-polymides. McGrath’s group published the synthesis and characterization of a multiblock-co-poly(arylene ether sulfone) consisting of highly hydrophobic partially fluorinated segments and sulfonic acid groups in the hydrophilic segment being located meta to a sulfone bridge. The electron-withdrawing effects (-M and -I effects) of the sulfone bridge guarantee a high acid strength of the ionogenic groups, whereas the highly fluorinated hydrophobic segments in the multiblock architecture counteract the inherent tendency of the sulfonic acid group to attract water molecules, which should be favorable for high proton conductivity and mechanical stability.

In this contribution a series of novel partially fluorinated multiblock-co-ionomers has been synthesised and the influence of the chemical bridging groups (E and X) in the hydrophilic block has been comparatively investigated (cf. Scheme 1 for notations). The multiblock architecture was synthetically built up by combining F-terminated hydrophobic (5) and OH- or SH-terminated hydrophilic telechelic macromonomers (1a–4a), which were prepared from the corresponding monomers in the course of a nucleophilic aromatic polycondensation. Macromonomer 5 was chosen to provide highest possible hydrophobicity for the hydrophobic block and to avoid disadvantages raised from other activated partially fluorinated monomers (like carboxyl groups in a highly fluorinated environment). The length and thus the degree of polymerization (DP) of both the hydrophobic (m) and the hydrophilic (n) block, respectively, was fixed to m = 8 and n = 4, respectively, to achieve ion-exchange capacities (IEC) comparable to that of Nafion. The DP for those step-growth polymerisations was adjusted by the stoichiometric imbalance r of the two monomers according to Carother’s Equation. The calculation of this stoichiometric imbalance r is exemplified for the synthesis of the F-terminated hydrophobic telechelic macromonomer 5 in the following. It should be noted that—unlike a system with bifunctional monomers with different functional groups (A–B, e.g., hydroxyl- or amino acids)—a difference between the number average DP (Xn) and the DP in a system with two bifunctional monomers of the type A–A and B–B exists. For the considered case of the bifunctional monomer 2,2-bis(4-hydroxyphenyl)hexafluoroisopropane (A–A) and decasfluorobiphenyl (that can be regarded as bifunctional monomer because of the much higher reactivity of the fluorines in 4,4′-position than in 2,2′- or 3,3′-position, B–B)}
this difference between $\langle X_n \rangle$ and the DP ($m$) follows the simple correlation given in the following equation.

$$\langle X_n \rangle = 2DP = 2m = 16 \quad (1)$$

The DP and the targeted molecular weight ($M_{\text{target}}$) are related by eq 2 ($M_{\text{ru}} =$ molecular weight of the repeating unit)

$$M_{\text{target}} = DP \times M_{\text{ru}} = 8 \times 630.34 \text{ Da} \approx 5043 \text{ Da} \quad (2)$$

Finally the stoichiometric imbalance $r$, which is the ratio of monomer A–A to monomer B–B, can be calculated by the following equation.

$$r = \frac{n_A-A}{n_B-B} = \frac{\langle X_n \rangle - 1}{\langle X_n \rangle + 1} = \frac{15}{17} = 0.882 \quad (3)$$

EXPERIMENTAL

Instrumentation

Ion-exchange capacities ($IEC_{\text{direct}}$ and $IEC_{\text{total}}$) 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 ($IEC_{\text{direct}}$). After that a defined excess of NaOH was added and this solution was back-titrated with 0.1 M HCl ($IEC_{\text{total}}$). The specific resistance of membranes was determined by electrochemical impedance spectroscopy, using a method described in literature, using 0.5 M HCl as electrolyte at 25 °C on IM6 Model of Zahner Elektrik. The WU of the samples was determined after equilibrating in water of defined temperatures (25, 40, 60, and 90 °C). After 48 h the sample was removed from the water solution, quickly dry wiped, and immediately weighed ($m_{\text{wet}}$). Then the sample was dried to weight constancy at 90 °C and weighed once again ($m_{\text{dry}}$). The WU can be obtained from these two values according to the following equation.

$$\text{WU(\%)} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100 \% \quad (4)$$

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

$$\text{Swelling degree(\%)} = \frac{l_{\text{wet}} - l_{\text{dry}}}{l_{\text{dry}}} \times 100 \% \quad (5)$$

Thermal stability of the 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% O2, 35–30% N2). The decomposition gases were further examined in a coupled FTIR spectrometer (Nicolet Nexus FTIR spectrometer) to identify the splitting-off temperature of the sulfonic acid group ($T_{\text{SO3H onset}}$), for which the asymmetric stretching vibration of the S=O group at 1352–1342 cm$^{-1}$ was used.

Isothermal TGA measurements (at 200, 220, and 240 °C) were done on the same machine (Netzsch, model STA 449C) and under the same oxygen-enriched atmosphere. Membrane pieces
were dried in a vacuum oven at 90 °C for 16 h before measurement.

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

The morphology of the multiblock-co-ionomers was determined by transmission electron microscopy (TEM), using a Philips CM10 TEM. To have a better contrast in the images, membranes were pretreated in 1 M Pb(NO₃)₂ at 90 °C for 24 h. The further preparation of sample for TEM has already been described earlier.31

Gel permeation chromatography (GPC) was carried out with an Agilent Technologies GPC system (Series 1200), using the universal calibration method and a refractive index detector (Shodex RI71).

Materials

4,4’-Dihydroxydiphenylsulfide, 4,4’-sulfanediyldi-thiophenol, 2,2-bis(4-hydroxyphenyl)sulfone, 2,2-bis(4-hydroxyphenyl)hexafluoroisopropylmethyldiether, decafluorobiphenylester, and anhydrous potassium carbonate were purchased at Aldrich and were used in excess. Disodium-4,4’-difluorodiphenylsulfone-3,3’-disulfonate is not commercially available and was synthesised from 4,4’-difluorodiphenylsulfone (ABCR). All other reagents were supplied by Aldrich and used as received.

Disodium-4,4’-difluorodiphenylsulfone-3,3’-disulfonate

This monomer was synthesized from 4,4’-difluorodiphenylsulfone following a procedure from literature,32,33 which was optimized in terms of the recrystallization reagent.

About 25.71 g (98.33 mmol) 4,4’-difluorodiphenylsulfone were dissolved in 60 mL of fuming sulphuric acid (30% SO₃) and stirred for 6 h at 110 °C. The solution was allowed to cool to room temperature and then poured into 400 mL of ice water. Then 180 g sodium chloride was added to precipitate a white product. The raw product was filtered, dried at 90 °C in a vacuum oven and redissolved in 600 mL of deionized water. After the pH value of this solution was adjusted to pH = 8 by 2 M NaOH, another 180 g were added to isolate the product. This product was recrystallized from methanol/water (8/1) first and then from methanol/water (8/2). The product was dried at 90 °C in a vacuum oven before characterisation. Yield: 82%.

1H NMR (200 MHz, DMSO-d₆, δ): 8.19 (dd, J₁ = 6.33 Hz, J₂ = 2.52 Hz, 3H, 1H), 8.02 (m, 5H, 1H), 7.46–7.50 (m, 6H, 1H), 3.44 (s, 7H, 2H). 13C NMR (100 MHz, DMSO-d₆, δ): 161.25 (d, 1JC-F = 259.5 Hz, 3C), 136.48 (d, 3JC-F = 18.6 Hz, 3C), 136.25 (d, 3JC-F = 3.3 Hz, 5C), 131.29 (d, 3JC-F = 9.9 Hz, 2C), 128.46 (d, 3JC-F = 4.6 Hz, 3C), 118.61 (d, 3JC-F = 24.3 Hz, 6C).

Preparation of the OH-Terminated Hydrophilic Telechelic Macromonomers 1a–4a

The hydrophilic telechelic macromonomers 1a–4a were synthesised from disodium-4,4’-difluorodiphenylsulfone-3,3’-disulfonate and the respective bisphenols according to a standard nucleophilic displacement polymerisation whereof the DP was adjusted to n = 4 by using a stoichiometric imbalance of r = 0.778.

About 33.653 mmol of the bisphenol compound (7.3454 g 4,4’-dihydroxydiphenylsulfide for 1a, 8.4267 g 4,4’-sulfanediyldi-thiophenol for 2a, 8.4223 g 2,2-bis(4-hydroxyphenyl)sulfone for 3a and 11.3151 g 2,2-bis(4-hydroxyphenyl)hexafluoroisopropylmethyldiether for 4a) were dissolved in NMP (62.5 mL for 1a, 66 mL for 2a and 3a, 72.5 mL for 4a) in a 250-mL three-neck flask equipped with magnetic stir bar, argon inlet, reflux condenser, and mercury bubbler. After the monomer had been dissolved completely, 13.82 g (0.100 mol) potassium carbonate were added and the mixture was heated to 80 °C for 7 h. Then a solution of 12.0000 g (26.182 mmol) of disodium-4,4’-difluorodiphenylsulfone-3,3’-disulfonate in NMP (same amounts as aforementioned) was added into the reaction mixture and the temperature was raised to 130 °C for further 24 h. The reaction mixture was poured into 1 L iso-propanol to precipitate the product, which was then separated and dissolved in...
hydrochloric acid (10 wt %) at 60 °C for 4 h. Finally this solution was dialyzed for 48 h and the desired product was recovered after the water was evaporated. The product was dried at 110 °C for 16 h in a vacuum oven before characterization and further use.

**Telechelic 1a**

![Telechelic 1a Diagram]

\[^1^H\text{NMR (DMSO-}d_6,\text{ 400 MHz,} \delta\):} 8.29 (s, \(^5^H, \(^8^H, \(^{13}^H, 1.25 \text{ H})\), 7.86 (d, \(^3^J_{H-H} = 8.3 \text{ Hz,} \)^9^H, \(^{15}^H\)), 7.83 (d, \(^3^J_{H-H} = 6.9 \text{ Hz,} \)^7^H\), 7.36 (d, \(^3^J_{H-H} = 7.9 \text{ Hz,} \)^{12}^H, 2.00 H), 7.29 (d, \(^3^J_{H-H} = 8.3 \text{ Hz,} \)^3^H, 0.44 H), 7.15 (d, \(^3^J_{H-H} = 8.2 \text{ Hz,} \)^{1}^H, 0.43 H), 7.04 (d, \(^3^J_{H-H} = 7.8 \text{ Hz,} \)^{11}^H), 7.01 (d, \(^3^J_{H-H} = 8.8 \text{ Hz,} \)^{10}^H, \(^{14}^H\)), 6.97 (d, \(^3^J_{H-H} = 8.2 \text{ Hz,} \)^2^H\), 6.91 (d, \(^3^J_{H-H} = 8.5 \text{ Hz,} \)^6^H, 0.24 H), 6.82 (d, \(^3^J_{H-H} = 8.4 \text{ Hz,} \)^2^H, 0.41 H). Integral values for the overlapping signals: cf. Figure 2.

**Telechelic 2a**

![Telechelic 2a Diagram]

\[^1^H\text{NMR (DMSO-}d_6,\text{ 400 MHz,} \delta\):} 8.17 (s, \(^5^H, \(^8^H, \(^{13}^H, 1 \text{ H})\), 7.62 (fine structure not recognizable, 7\(^H, \)^9^H, \(^{15}^H, 1 \text{ H})\), 7.53–7.42 (signal heap, \(^2^H, \)^3^H, \(^4^H, \)^{11}^H, \(^{12}^H, 4.18\text{H})\), 7.30 (d, \(^3^J_{H-H} = 7.7 \text{ Hz,} \)^7^H, 0.57H\), 6.90–6.82 (fine structure not recognizable, \(^6^H, \)^{10}^H, \(^{14}^H, 1 \text{ H})\).

**Telechelic 3a**

![Telechelic 3a Diagram]

\[^1^H\text{NMR (DMSO-}d_6,\text{ 400 MHz,} \delta\):} 8.32 (s, \(^5^H, \(^8^H, \(^{13}^H, 1 \text{ H})\), 7.97–7.83 (superposition of peaks, \(^3^H, \)^7^H, \(^{12}^H, \(^{15}^H, 3.30\text{H); doublet of}^{12}^H\text{ can still be seen at 7.90 with} \(^3^J_{H-H} = 8.4 \text{ Hz}\), 7.73 (d, \(^3^J_{H-H} = 8.7 \text{ Hz,} \)^2^H, 0.34H\), 7.23 (d, \(^3^J_{H-H} = 8.4 \text{ Hz,} \)^{10}^H, \(^{14}^H, 1.00\text{H})\), 7.16–7.01 (superposition of peaks, \(^{11}^H, \)^4^H, 2.36H; doublet of \(^{11}^H\text{ can still be seen at 7.10 with} \(^3^J_{H-H} = 8.6 \text{ Hz}\), 6.91 (d, \(^3^J_{H-H} = 8.7 \text{ Hz,} \)^{1}^H, 0.36H).

**Telechelic 4a**

![Telechelic 4a Diagram]
Preparation of the F-Terminated Hydrophobic Telechelic Macromonomer 5

The hydrophobic telechelic macromonomer 5 was synthesised under similar conditions as the corresponding polymer. Divergent from that procedure, the stoichiometric ratio was fixed to $r = 0.882$ to obtain $m = 8$ and the reaction time was reduced to 3 h.

About 26.6900 g (79.38 mmol) 2,2-bis(4-hydroxyphenyl)hexafluoropropane and 30.0708 g (90.00 mmol) decаfluorobiphenyl were dissolved in 420 mL N,N-dimethylacetonitrile (DMAc) in a 1000-mL three-neck flask equipped with an argon inlet, a mechanical stirrer, a reflux condenser and a mercury bubbler. 30.68 g (0.222 mol) of potassium carbonate were added after the monomers had been dissolved completely and the reaction mixture was stirred at 80 °C for 3 h. Then the reaction mixture was poured into 2 L of stirred water, the precipitation was filtered, washed twice with water and methanol and dried at 75 °C in a vacuum oven for 16 h.

1H NMR (200 MHz, CDCl3, $\delta$): 7.07 (d, $3J_{H-H} = 8.4$ Hz, 1H), 7.43 (d, $3J_{H-H} = 8.8$ Hz, 1H). 13C NMR (50 MHz, CDCl3, $\delta$): 157.60, 145.03 (d, $1J_{C-F} = 253$ Hz), 141.80 (d, $1J_{C-F} = 253$ Hz), 135.03–134.41 ($^6C$, $n \geq 2$, not further analysable), 132.04, 128.97, 115.51, 103.57–102.91. 13C NMR signals of the hexafluoroisopropylidene group are not visible because of the strong coupling with 19F (quartet, septet). 19F NMR (188 MHz, CDCl3, $\delta$): $-64.35$ (6.00 F), $-137.74$ (4.46 F), $-150.19$ (0.25 F), $-152.65$ (4.06 F), 160.64 (0.50 F).

Polycondensation of the Telechelic Macromonomers

The nucleophilic displacement polycondensation reactions for the preparation of 1b–4b were carried out with the same starting concentrations of monomers (13 wt% in N-methylpyrrolidinone (NMP)), the same threefold excess of potassium carbonate related to the OH-terminated telechelic hydrophobic macromonomer (1a–4a) and the same starting temperature. Since the increase in viscosity of the different reaction mixture was dramatically different indicating various reactivities of the four macromonomers 1a–4a, there was a need to adapt the dilution and temperature for each reaction batch individually. The individual reactions conditions are summarized in Table 5. An explicit procedure is given in the following for the preparation of the multiblock-co-ionomer 2b.

About 8.5090 g (13.499 mmol) of the hydrophobic telechelic macromonomer 5 and 8.0000 g (13.449 mmol) of the hydrophilic telechelic macromonomer 2a were dissolved in 108 mL NMP under argon atmosphere and intensive stirring. This mixture was heated to 80 °C for 2 h. Then 5.5971 g (40.497 mmol) potassium carbonate was added. The reaction mixture was stirred at 80 °C and diluted by 20 mL NMP after 90, 135, 150, 180, 210 min, and by further 80 mL NMP after 225 min. Then it was stirred for further 15 min and then poured into 2 L of distilled water. The product was separated by filtration, digested in 500 mL of hydrochloric acid (10 wt%) at 60 °C for 4 h. Finally the product was filtered and dried at 90 °C in a vacuum oven for 16 h.

Multiblock-co-Ionomer 1b

19F NMR (188 MHz, DMSO-d6, $\delta$): $-59.01$ ($^5F$, 6 F), $-133.59$ ($^5F$, $^4F$, $^3F$, $^2F$, $^1F$, $^1F$, 4.53 F (calculated with m = 8: 4.50 F)), $-149.05$ ($^5F$, $^4F$, $^3F$, 4.53 F (calculated with m = 8: 4.50 F)). 1H NMR (250 MHz, DMSO-d6, $\delta$): 8.26 (s, $^3H$, 1H), 7.83 (d, $3J_{H-H} = 8.1$ Hz, $^4H$, 1H), 7.37–7.34 [signal heap, $^2H$, $^3H$, $^6H$, 6.13H (calculated for n = 4 and m = 8: 7.50 H)], 7.04–6.97 [signal heap, $^1H$, $^6H$, $^9H$, 3.50H (calculated for n = 4 and m = 8: 6.50 H)].
Multiblock-co-ionomer 2b

\[ \text{1H NMR (250 MHz, DMSO-}d_6, \delta) : 8.17 \text{ (s, 3H, 1H), 7.65–7.37 [signal heap, 1H, 2H, 4H, 6H, 7H, 8H, 9H, 10H, 11H, 10.02H (calculated for } n = 4 \text{ and } m = 8 : 14.00 \text{ H}), 6.89–6.83 \text{ (d, } 3 \text{J}_{H-H} = 7.90 \text{ Hz, 5H, 1H).} \]

Multiblock-co-ionomer 3b

\[ \text{19F NMR (188 MHz, DMSO-}d_6, \delta) : -59.00 \text{ (5F, 6 F), -133.47 [2F, 3F, 7F, 8F, 4.57 F (calculated with } m = 8 : 4.50 F] , -148.97 [1F, 4F, 9F, 5F, 4.63 F (calculated for } m = 8 : 4.50 F).} \]

Multiblock-co-ionomer 4b

\[ \text{19F NMR (188 MHz, DMSO-}d_6, \delta) : -58.80 - -59.02 \text{ (1F, 2F, 7F, 1 F), -133.59 [4F, 5F, 6F, 10F, 0.44 F (calculated for } m = 8 : 0.46 F] , -149.03 [3F, 6F, 8F, 11F, 0.45 F (calculated for } m = 8 : 0.46 F)]. \]

Preparation of Model Polymer 8

About 12.3197 g (49.20 mmol) of 4,4'-sulfanediyldi-thiophenol and 16.7060 g (50.00 mmol) of decafluorobiphenyl were dissolved in 140 mL NMP under argon atmosphere and intensive stirring. Then 19.32 g (0.140 mmol) potassium carbonate was added and the reaction mixture was stirred at room temperature for 6 h (considerable increase in viscosity). This mixture was poured into 2 L of methanol under stirring and the polymer was filtered, washed with methanol twice and finally dried at 90 °C in a vacuum oven for 16 h.

\[ \text{1H NMR (250 MHz, CDCl}_3, \delta) : 7.38 \text{ (d, } 3 \text{J}_{H-H} = 8.30 \text{ Hz, 1H), 7.27 \text{ (d, } 3 \text{J}_{H-H} = 7.27 \text{ Hz, 1H).} \]

\[ \text{19F NMR (188 MHz, CDCl}_3, \delta) : -131.88 \text{ (1 F), -138.97 (1 F).} \]
Membrane Preparation

Membranes were cast into aluminium bowls from their NMP/DMAc solutions (10 wt %) and dried at 130 °C at atmospheric pressure for at least 3 h. All membranes were soaked in 10 wt % HCl at 90 °C for 48 h and subsequently washed with deionized water. After that, the membranes were immersed in deionized water at 60 °C for another 48 h.

RESULTS AND DISCUSSION

Characterization of the Telechelic Macromonomers and Multiblock-co-Ionomers

Both the hydrophilic and the hydrophobic telechelic macromonomers were synthesised by step-growth polycondensation, using the respective calculated stoichiometric imbalance \( r \). \(^1\)H NMR and \(^1\)H,\(^{13}\)C-HSQC-NMR (heteronuclear single quantum coherence nuclear magnetic resonance) spectroscopy was used as characterisation tool in the case of the OH-terminated hydrophilic macromonomers (1a–4a) whereas \(^19\)F NMR spectroscopy served for the elucidation of the F-terminated hydrophobic macromonomer 5. NMR spectroscopy could also be used for the estimation of the number average molecular weight \( M_n \) which is exemplified for the end group analysis of 1a (\(^1\)H NMR) and 4a (\(^1\)H,\(^{13}\)C-HSQC-NMR) as representatives for the hydrophilic telechelic macromonomers and of 5 (\(^19\)F NMR). The number average molecular weight \( M_n^{\text{NMR}} \) values are compared with the calculated ones and those (\( M_n^{\text{GPC}} \)) obtained from GPC in Table 1. Figure 2 shows the \(^1\)H NMR spectrum of the OH-terminated hydrophilic telechelic macromonomer 1a. Signals were assigned by comparing the chemical shifts of the monomer and of the corresponding homo-ionomer. The polymerization degree \( n \) (\( n = x + 1 \), \( x \) is the polymerization degree chosen in Figure 2 for the peak assignment, the real polymerization degree \( n \) is higher for one repeating unit) was estimated from the ratio of signal intensities to be 3.33 according to the following equations.

\[
x = \frac{I(\text{H})}{2I(\text{H})} = \frac{2}{2 \cdot 0.43} = 2.33 \quad (6)
\]

\[
n = x + 1 = 3.33 \quad (7)
\]

In case of the OH-terminated hydrophilic macromonomer 4a the one-dimensional \(^1\)H NMR spectrum could not reveal the chemical structure in detail because of an over-lapping of peaks. The determination of the chemical struc-

Table 1. Comparison of the Calculated Number Average Molecular Weight (\( M_n \)) with the Experimental Values Obtained from End Group Analysis by NMR (\( M_n^{\text{NMR}} \)) or from GPC (\( M_n^{\text{GPC}} \))

<table>
<thead>
<tr>
<th>Telechelic Macromonomer</th>
<th>( M_n^{\text{Target}} ) [Da]</th>
<th>( M_n^{\text{NMR}} ) [Da]</th>
<th>( M_n^{\text{GPC}} ) [Da]</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>2,549</td>
<td>2,101</td>
<td>2,990</td>
<td>1.71</td>
</tr>
<tr>
<td>2a</td>
<td>2,677</td>
<td>2,443</td>
<td>4,275</td>
<td>1.30</td>
</tr>
<tr>
<td>3a</td>
<td>2,677</td>
<td>2,490</td>
<td>6,063</td>
<td>1.28</td>
</tr>
<tr>
<td>4a</td>
<td>3,022</td>
<td>3,240</td>
<td>7,405</td>
<td>1.54</td>
</tr>
<tr>
<td>5</td>
<td>5,043</td>
<td>5,270</td>
<td>2,990</td>
<td>2.50</td>
</tr>
</tbody>
</table>

\( M_n^{\text{Target}} \), calculated number average molecular weight; \( M_n^{\text{NMR}} \), number average molecular weight determined by end group analysis using NMR spectroscopy; \( M_n^{\text{GPC}} \), number average molecular weight determined by GPC; PDI, polydispersity index determined by GPC.

Figure 1. Molecular weight distribution of multiblock-co-ionomer 3b in comparison with the corresponding macromonomers 3a and 5, determined by GPC. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ture was carried out by $^{1}$H, $^{13}$C-HSQC. Figure 3 shows the assignment of the peaks together with the chemical shifts and the integrals. The number average molecular weight was calculated by the ratio of signal intensities as described earlier for 1a.

$^{19}$F NMR spectroscopy gave information on the end groups and thus the number average molecular

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**Figure 2.** $^{1}$H NMR spectrum of the hydrophilic telechelic macromonomer 1a.

**Figure 3.** $^{1}$H-, $^{13}$C-HSQC spectrum of the OH-terminated telechelic hydrophilic macromonomer 4a.
weight of macromonomer 5 as depicted in Figure 4. The peaks at -64.35, -137.78, and -152.65 ppm can be assigned to the chain fluorine atoms 3F, 2F, and 1F in accordance with the observed chemical shift for the corresponding homo-polymer.26 The little fronting observed for all those peaks and thus the increased integrals of the peak at -137.78 and -152.65 ppm might be attributed to the modified chemical environment at the end of the chains and caused from the fluorine atoms 2F, 4F, and 6F. Finally the remaining two signals at -150.19 and -160.64 ppm were attributed to be caused by the fluorine atoms 7F and 8F, which is supported by the reported chemical shift values of decafluorobiphenyl.35 Using this assignment the polymerization degree can be calculated to \( m = 8.36 \) corresponding to a number average molecular weight of \( M_n = 5270 \text{ Da} \), which is in good accordance with the calculated value \( M_n = 5043 \text{ Da} \) for the used stoichiometric imbalance.

The comparison in Table 1 between the experimental \( M_n^{NMR} \) and \( M_n^{GPC} \) values with the calculated \( M_n^{target} \) reveals a certain discrepancy for these two methods in the characterization of the telechelic macromonomers 1a–4a and 5. Obviously the calculations of \( M_n \) from the NMR spectra match the \( M_n^{target} \) values quite well whereas those obtained from GPC analysis show a broader variation. It can be further seen from Table 1 that the \( M_n^{GPC} \) values for the hydrophilic telechelic macromonomers (1a–4a) are higher but for the hydrophobic one (5) lower than the calculated value \( M_n^{target} \). This variation might be associated with deviations from the Mark–Houwink relation for polymers with molar masses below 10–20 kDa (depending on the polymer class). The validity of the applied universal calibration is based on the Mark–Houwink coefficient, which are derived by assuming a Gaussian distribution for the polymer coils.36–39 This assumption might not necessarily be fulfilled for all polymer classes below a certain molecular weight. Therefore NMR spectroscopy is thought to be more precise for the determination of \( M_n \) for the telechelic macromonomers. It can be concluded from Table 1 that both the hydrophilic telechelic macromonomers 2a–4a and the hydrophobic telechelic macromonomer 5 were formed in the desired and afore calculated number average molecular weight \( M_n^{target} \). Only 1a shows a slightly higher \( M_n^{NMR} \) value as calculated, which corresponds to a block length of \( n = 5.5 \) instead of \( n = 4 \). Despite a relatively good accordance between the presented \( M_n^{NMR} \) values and the calculated \( M_n^{target} \) one has to consider that the applied classical theory of step-growth polymerisation, which is mainly based on Carother’s and Flory’s work does not consider contributions of cyclization reactions and does not differentiate between kinetically and thermodynamically controlled step-growth polymerisations.40,41 Figure 1 reveals at the example of the hydrophilic telechelic macromonomer 3a and the hydrophobic telechelic macromonomer 5 that oligomeric impurities (shoulder and/or little peaks) are present, which might also include cyclic oligomers apart from linear ones. However the interfering effect of eventually existent cyclic oligomers on
the coupling reaction between the hydrophilic and the hydrophobic telechelic macromonomer is thought to be rather low because of the lower reactivity of fluorine atoms in 2,2'- and 3,3'-position in cyclic oligomers compared with the 4,4'-position in linear oligomers. The possible physical incorporation of cyclic oligomers in the growing chain network during the coupling reaction would influence the morphological structure but it might also contribute to an enhanced mechanical stability due to the entanglement of these cyclic oligomers among each other and with the growing chain. Since the scope of this work is not the precise investigation of the step-growth polymerization by itself, which would require more powerful analysis tools, such as matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI/TOF-MS),\textsuperscript{42,43} the following sections deal with the characterization of multiblock-co-ionomers.

The coupling products 1b–4b of the polycondensation between the hydrophilic and hydrophobic macromonomers were investigated both by GPC analysis and NMR spectroscopy (\textsuperscript{1}H, \textsuperscript{19}F NMR). The molecular weight distribution of multiblock-co-ionomer 3b is depicted in Figure 1 together with the distributions of the corresponding macromonomers 3a and 5. The coupling reaction was obviously successful although there is still some need for further optimization in terms of the broad distribution. Table 2 lists the GPC results of the coupling products. Assuming that the ideal composition is comprised of alternating hydrophilic A and hydrophobic B blocks with block lengths \(n(A) = 4\) and \(m(B) = 8\) the number of repeating AB units can be estimated (p, Scheme 1). With the exception of ionomer 2b the corresponding values lie in the range between 6 and 8. Further information on the structural composition was gained from

<table>
<thead>
<tr>
<th>Multiblock-co-Ionomer</th>
<th>(M_n^{GPC}) [Da]</th>
<th>PDI</th>
<th>(M_n^{calculated}) per AB-Block [Da]</th>
<th>Number of Repeating AB-Blocks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b</td>
<td>59,992</td>
<td>2.86</td>
<td>7,592</td>
<td>7.90</td>
</tr>
<tr>
<td>2b</td>
<td>9,924</td>
<td>2.46</td>
<td>7,720</td>
<td>1.29</td>
</tr>
<tr>
<td>3b</td>
<td>46,388</td>
<td>2.99</td>
<td>7,720</td>
<td>6.01</td>
</tr>
<tr>
<td>4b</td>
<td>61,281</td>
<td>4.19</td>
<td>8,065</td>
<td>7.60</td>
</tr>
</tbody>
</table>

\(M_n^{calculated}\) per repeating AB-Block, calculated number average molecular weight of a repeating unit [AB-block with A = hydrophilic block (assuming \(n = 4\)) and B = hydrophobic block (assuming \(m = 8\)).

Figure 5. \textsuperscript{19}F NMR spectrum of multiblock-co-ionomer 1b. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
the $^{19}$F NMR spectra of the products 1b–4b. As expected the $^{19}$F-NMR signals of the end group atoms ($^4$F–$^8$F, Fig. 4) of the telechelic hydrophobic macromonomer 5 disappear after reaction with the telechelic hydrophilic macromonomers 1a, 3a, and 4a, which is exemplified in Figure 5 for 1b as representative for this group. In contrast to all other ionomers 2b is an exception in terms of a consistent and clearly interpretable $^{19}$F NMR spectrum (Fig. 6). The signal at $-63.52$ ppm can be assigned to the fluorine atoms of the hexafluoroisopropylidene bridging group. To understand this spectrum more clearly the effects of substitution in 4,4'-position of the octafluorobiphenylene moiety (Scheme 2) on the chemical shift were studied by comparison with literature$^{26,35}$ and by preparing the polymeric model compound 8 from decafluorobiphenyl and 4,4'-sulfanediyl-bis-thiophenol. Scheme 3 reveals that the chemical shifts of the fluorine nuclei $^2$F and $^3$F are very similar for the both different poly(arylene ether)s 6 and 7.$^{2,34}$ By substituting the ether bridge by a thioether bridge (8) a downfield shift of the corresponding signals is observed. Using this information the two major groups of signals ($-138.16$, $-153.59$ ppm, and $-132.24$, $-137.17$ ppm) in Figure 6 can be attributed to be caused by fluorine atoms of the differently (O or S) substituted octafluorobiphenylene moieties. The origin of the signals at $-141.50$ and $-160.51$ ppm as well as the shoulders of the main peaks at $-136.16$ and $-153.59$ ppm is a bit dubious. Although the position and intensity of four peaks ($^8$F, $^9$F, $^{10}$F, and $^{11}$F) fit

Figure 6. $^{19}$F NMR spectrum of multiblock-co-ionomer 2b. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Scheme 2. Definition of terms used in the text.

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quite well to the end group fluorine atoms there is a little doubt since the peak at -141.50 ppm (\(7\text{F}\)) would have been downfield-shifted for about 8.5 ppm relative to the signal observed for decafluorobiphenyl and the macromonomer \(5\). A little difference in the chemical shift in dependence of the solvent (CDCl\(_3\), DMSO-\(d_6\)) were reported in the literature for decafluorobiphenyl in the order of magnitude of 1 ppm\(^{34}\) (Scheme 3). However, dipole–dipole or van der Waals interactions of the solvent with the multiblock-co-ionomer especially with its end groups could lead to sterically preferred orientations and could thus cause the observed shift in the resonance frequency of \(7\text{F}\) in \(1b\).

By using this assignment of peaks (with the intensities given in Fig. 6) the realized \(A_nB_m\) structure would differ from the ideal repeating structure (where \(A\) is the hydrophobic multiblock with \(n = 4\) and \(B\) the hydrophobic multiblock with \(m = 8\)) that is expected by assuming a statistically controlled course of the polycondensation reaction between the two most encountered macromonomers (\(A\) with \(n = 4\) and \(B\) with \(m = 8\)). Table 3 summarizes the theoretical intensities for the first \(A_4B_8\) multiblock structures and compares them with the experimentally obtained values. The experimental integrals of \(1\text{F}\) and \(2\text{F}\) are considerably higher when compared with the intensities of \(6\text{F}\) and \(7\text{F}\) as expected for an \(A_4B_8\) multiblock structure. It can be concluded from Figure 6 and Table 3 that the ideal and most likely \(A_4B_8\) composition is formed to a much lower extent than expected, which might have one or both of the following reasons:

1. The reactivity of the shorter \(B\) (\(m < 8\)) macromonomers is higher than for \(m \geq 8\)
2. Trans(thio)etherification occurs between OH-or SH-terminated macromonomers with (thio) ether bridges in the growing chain: \(R-O-R^1 + R^2-OH \rightarrow R-O-R^2 + R^1-OH\).

Transetherification is usually used for the synthesis of polyethers\(^{45-48}\) and may occur during step-growth polycondensations leading to

**Scheme 3.** Influence of the effects of substitution in 4,4'-position of the octafluorobiphenylene moiety on the chemical shift in CDCl\(_3\) and in DMSO-\(d_6\) (in brackets). Values are taken from literature\(^{25,34,44}\) (for \(6, 7,\) and \(9\)) and measured for the model polymer \(8\).

**Table 3.** Theoretical Intensity in the 19F NMR Spectrum of 1b for the First \(A_4B_8\) Block Structures

<table>
<thead>
<tr>
<th>Signal At</th>
<th>Caused By</th>
<th>Experimental Intensity</th>
<th>Theoretical Intensity(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-63.52</td>
<td>(5\text{F})</td>
<td>6.00</td>
<td>AB 6.00</td>
</tr>
<tr>
<td>-132.24</td>
<td>(2\text{F})</td>
<td>0.70</td>
<td>ABA 0.25</td>
</tr>
<tr>
<td>-137.17 to</td>
<td>(1\text{F}, 3\text{F}, 7\text{F}, 9\text{F}, 10\text{F})</td>
<td>5.68</td>
<td>BABAB 4.50</td>
</tr>
<tr>
<td>-138.78</td>
<td></td>
<td></td>
<td>ABAB 4.50</td>
</tr>
<tr>
<td>-141.50</td>
<td>(12\text{F})</td>
<td>0.23</td>
<td>ABABA 4.50</td>
</tr>
<tr>
<td>-153.59</td>
<td>(4\text{F}, 6\text{F}, 8\text{F})</td>
<td>4.54</td>
<td>BAB 4.00</td>
</tr>
<tr>
<td>-160.51</td>
<td>(11\text{F})</td>
<td>0.45</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Calculated by assuming \(n = 4\) for the hydrophilic A-Block and \(m = 8\) for the hydrophobic B-Block.
the observed microstructure. However, a more
detailed study on the microstructure would re-
quire more powerful characterization tools espe-
cially (MALDI/TOF-MS)\(^{42,43}\) which is not an in-
house technique.

Further evidence of deviations from the ideal
A\(_4\)B\(_8\) structure could be obtained from the \(^1\)H
NMR spectra. As shown for ionomer 1\(b\) in Fig-
ure 7 and listed for the other ionomers 2\(b\)–4\(b\) in
the Experimental Section there are discrepan-
cies between the calculated and the experimen-
tal integral values. These discrepancies might
be caused by the same reasons as discussed
before for the \(^1\)\(^9\)F NMR spectrum of 1\(b\).

**Membrane Characterisation**

TEM was used to stress the formation of multi-
block-co-ionomers with a microphase-separated
morphology. Figure 8 represents the TEM
images of 3\(b\) in two different magnifications. At
52,000\(\times\) magnification a more or less homoge-
ous surface is visible (Fig. 8, left). The cavity
probably arises from a nonideal evaporation of
the solvent during the membrane casting pro-
cess. A more structured morphology is observed
at the magnification of 145,000\(\times\) (Fig. 8, right),
where the dark regions can be interpreted as
lead sulfonate groups and the light domains
might correspond to the hydrophobic multi-
blocks of the multiblock-co-ionomer.

The series of these multiblock-co-ionomers
was fully characterized in terms of suitability
for application as proton exchange membrane in
fuel cells. Table 4 gives an overview of IEC, the
specific resistance and the thermal stability of
the synthesised multiblock-co-ionomers in com-
parison to the corresponding values of Nafion\(^{46}\).

Figure 7. \(^1\)H NMR spectrum of multiblock-co-ionomer 1\(b\). [Color figure can be
viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 8. TEM images of membrane 3\(b\) with a magnification of \(\times\)52,000 (left) and
\(\times\)145,000 (right).
117. It clearly can be seen from Table 4 that the experimental IECdirect and IECtotal values are almost identical among each other (which is expected for a non-crosslinked membrane\textsuperscript{26}) and that they slightly differ with the calculated IEC value (IECcalculated) for the proposed structure (\(n = 4\) and \(m = 8\)) which might be connected with the reasons discussed in the previous section. The specific resistance of all multiblock-co-ionomer membranes is in the same order of magnitude with that of Nafion\textsuperscript{117}. Ionomer 4b shows a slightly lower calculated IEC value and therefore a decreased number of proton conductive groups per weight unit so that a little higher proton resistance for this ionomer is expected when compared with the other three ones which is indeed in accordance with the presented data. The specific resistance of the remaining ionomers 1b–3b varies with the electronic effects (-I and -M effects) of the bridging groups as expected. The lowest specific resistance is measured for ionomer 3b, which has the most electron-withdrawing bridging groups (X = O, E = SO\textsubscript{2}), followed by ionomer 1b with X = O and E = S and ionomer 2b with X = S and E = S. Thermal stability of these multiblock-co-ionomers is estimated from TGA/FTIR coupling by using the asymmetric S=O stretching vibration at 1352–1342 cm\textsuperscript{-1} in the FTIR spectrum as detection for the onset of the splitting-off temperature of the sulfonic acid group. The TGA traces of the multiblock-co-ionomers 1b–4b are depicted in Figure 9 and compared with the corresponding one for Nafton\textsuperscript{117}. All synthesised multiblock-co-ionomers show the typical and expected course for sulfonated arylene main-chain ionomers and exhibit two distinct thermal degradation steps, of which the first weight loss step at around 220 °C is mainly attributed to the loss of sulfonic acid groups and the second weight loss step at roughly 480 °C, which refers mainly to the decomposition of the main chain. In case of Nafton\textsuperscript{117} a seamless transition between these two degradation steps takes place. Because of the similarity of all TGA traces and the detected onset of the splitting-off temperature of the SO\textsubscript{3}H group in this series of multiblock-co-ionomers a reliable trend for the preferred bridging groups E and X can not be recognized. It can be assumed that the influence of the bridging groups on the stability of the SO\textsubscript{3}H group is rather low. To estimate the relatively thermal stability of the novel multiblock-co-ionomers in comparison to Nafton\textsuperscript{117} more precisely, isothermal TGA measurements were carried out for Nafton\textsuperscript{117} and membrane 2b at three different temperatures (200, 220, and 240 °C, cf. Fig. 10). The initially steep weight loss within the first hour of isothermal heating can be led back to the release of residual absorbed water and is observed for all investi-

<table>
<thead>
<tr>
<th>Multiblock-co-Ionomer</th>
<th>IEC\textsubscript{direct} [mmol/g]</th>
<th>IEC\textsubscript{total} [mmol/g]</th>
<th>IEC\textsubscript{calculated} [mmol/g]</th>
<th>Specific Resistance (\rho) [(\Omega) cm]</th>
<th>(T_{SO_3H\text{ onset}}) [°C]\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b</td>
<td>1.13</td>
<td>1.20</td>
<td>1.05</td>
<td>4.02</td>
<td>226.0</td>
</tr>
<tr>
<td>2b</td>
<td>0.92</td>
<td>0.92</td>
<td>1.04</td>
<td>4.17</td>
<td>225.4</td>
</tr>
<tr>
<td>3b</td>
<td>1.07</td>
<td>1.07</td>
<td>1.04</td>
<td>3.56</td>
<td>218.5</td>
</tr>
<tr>
<td>4b</td>
<td>0.87</td>
<td>0.87</td>
<td>0.99</td>
<td>5.26</td>
<td>214.1</td>
</tr>
<tr>
<td>Nafion\textsuperscript{117}</td>
<td>0.90</td>
<td>0.90</td>
<td>–</td>
<td>6.59</td>
<td>228.7</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Obtained from TGA/FTIR coupling (first traces of SO\textsubscript{2} in the IR spectrum were used for evaluation).

Figure 9. TGA traces of the multiblock-co-ionomers in comparison with Nafton\textsuperscript{117}. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
gated samples. There is a clear dependence of thermal stability of the applied temperature, which is more pronounced in case of Nafion® 117. While Nafion® 117 is very stable at 200 °C, the gradient of the isotherms at 220 and 240 °C becomes more negative indicating an increased thermal decomposition at these higher temperatures under the oxidising atmosphere. Thermal degradation of Nafion® 117 has already been investigated in air by Savinell et al. who proposed a decomposition mechanism commencing at the sulfonic acid end groups with the loss of SO₂ and HO radicals under the formation of perfluoroalkyl radicals, which initiate further reactions.49 These authors reported a decomposition temperature of 270 °C in air. The earlier decomposition in our experiments might be attributed to the stronger oxidising conditions (65–70% O₂) in the TGA measurements. In contrast to Nafion® 117 the investigated multiblock-co-ionomer 2b does not show such a distinct change in the gradient of the isotherms indicating a higher thermal stability of the sulfonic acid group attached at the aromatic phenylene rings when compared with that of Nafion®. Figure 11 highlights the isotherms of the novel multiblock-co-ionomers 1b–4b and Nafion® 117 and verifies the behaviour, observed and discussed before for 2b, for the entire series.

Mechanical properties of proton exchange membranes are closely related to the WU and swelling ratio; the WU of 1b–4b in comparison with Nafion® 117 is shown in Figure 12 and the swelling degree in Figure 13. Although the hydration behavior of all synthesised membranes is higher than that of Nafion® 117, a systematic dependence on the type of bridging atoms or groups can be seen. Both the WU and the swelling ratio of the membrane with the thio ether bridges E = S and X = S (2b) are the highest within this series. Lower WU and lower swelling ratio can be realized by substituting one of the thio ether bridges (E = S) by an ether bridge (E = O). Membrane 1b exhibits a clearly decreased WU and swelling ratio compared with 2b in spite of having the lower specific resistance. The substitution of the second thio ether bridging group (X = S) in 1b by the sulfone bridging group (X = SO₂) in 3b seems to have only minor impact on the hydration behaviour. These observations might be explained by the different electronic environments of E and X in the hydrophilic multiblock of the multiblock-co-ionomer. The bridging group X is part of a symmetrically 4,4′-disubstituted bisphenol moiety whereas E is the linkage group between the bisphenol and the biphenyl moiety and is therefore adjacent to chemically different neighbouring groups with distinct electronic effects. In case of the linkage group E the strongly electron-deficient sulfonic acid group in meta-position to E causes a higher polarity of bonds in the nearer environment of this bridging group in comparison to those in the neighbouring of X. Additionally the polarisability of C—S is higher than that of C—O, which explains the higher
susceptibility of 2b to water in comparison to 1b and 3b. As shown by means of ionomer 4b the incorporation of the highly hydrophobic bridging group X = C(CF₃)₂ can further improve the WU and swelling degree.

To be able to estimate the oxidative stability of these novel membranes in comparison to Nafion® 117 the weight loss in hydrogen peroxide solution (5 wt%) at 60 °C in dependence of time was determined. The results are graphed in Figure 14. Although there is still a need for improving the oxidative stability of the synthesised multiblock-co-ionomers in general (e.g.,

Table 5. Overview of the Reaction Conditions for the Preparation of the Different Multiblock-co-Ionomers

<table>
<thead>
<tr>
<th>Block-co-Ionomer</th>
<th>Reaction Temperature [°C]</th>
<th>Reaction Time [h]</th>
<th>Degree of Dilution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b</td>
<td>80</td>
<td>18</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>80</td>
<td>3</td>
<td>1.67</td>
</tr>
<tr>
<td>3b</td>
<td>80</td>
<td>21</td>
<td>0.94</td>
</tr>
<tr>
<td>4b</td>
<td>80</td>
<td>4</td>
<td>3.20</td>
</tr>
</tbody>
</table>

* The degree of dilution is defined as the ratio of the volume of NMP added during reaction to the starting volume of NMP.
dation after 6 h. After that time the weight loss of 4b increases from nearly 0 to 30% and remains at this value up to the end of the test after 48 h. This simple test can admittedly not be used for an accurate study of degradation, but it can serve as a preselection for the most promising membranes in terms of oxidative stability. Using the results of this test a series with a rough estimation of oxidative stability of the prepared membranes can be given as follows: 4b > 3b > 1b > 2b. Finally it can be stated that the membranes 1b, 3b, and 4b are promising candidate for the use in a PEMFC or DMFC.

CONCLUSIONS

In this contribution the influence of the chemical nature of bridging atoms or groups in the hydrophilic segments of multiblock-co-ionomers has been comparatively investigated in terms of their properties as fuel cell membranes. It turned out that not only the chemical nature of the bridging atoms or groups is crucial for the properties of the membranes, but also their position and electronic environment. The thio ether linkage group (E in Scheme 2) between two asymmetrically substituted arylene rings seems to be a weak point in the polymer architecture. Ionomers with symmetrically substituted thio ether linkages on the other hand (X in Scheme 2) entail similar properties as corresponding ionomers with sulfone linkages although their oxidative stability seems to be slightly lower. But the alleged infeasibility of the synthesized ionomer with the highest possible set of thio ether linkages might be compensated by the selective oxidation of the thio ether bridges to sulfone bridges provided that the crystallinity of the ionomer does not change dramatically and causes brittleness. The principal possibility of selective oxidation of this kind of bridges has already been discussed in literature and patents. Further membrane development in our group will also be done by the variation of multiblock length of the hydrophilic and hydrophobic multiblock for the most promising systems.

The authors would like to thank the Landesstiftung Baden-Württemberg for financial support of this research effort in the project “Direktmethanol-Mikrobrennstoffzellenstack mit neuen MEA.”

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