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Side-chain sulfonated random and multiblock poly(ether sulfone)s for PEM applications

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ABSTRACT

Copoly(arylene ether sulfone)s from 4.4'-difluorodiphenyl sulfone, 4.4'-dihydroxydiphenyl sulfone bistrimethylsilylether, and 2,5-diphenylhydroquinone bis-trimethylsilylether were obtained by nucleophilic displacement polycondensation with high molecular weights. While the random copolymers were obtained with narrow molecular weight distributions, the molecular weight distributions of the multiblock copolymers were much broader, probably indicating branching reactions. Random as well as multiblock copolymers showed a single glass transition temperature (T_g) at around 230 °C. Upon sulfonation with concentrated sulfuric acid, the $T_{e^{S}}$ (from samples in the protonated form) were shifted to higher temperatures. NMR spectra and the determined ion-exchange capacities, which were close to the theoretical values, indicated that the pendant phenyl rings of the 2,5-diphenylhydroquinone moieties in the polymer backbone were sulfonated selectively. Membranes prepared from N-methyl-2-pyrrolidone solutions were transparent and soft. The water uptake at room temperature increased from 30% to 80% with increasing IEC. Samples with an IEC \ge 1.8 mmol/g swell to a high extend (sMBC) or even dissolve in water (sRC) at elevated temperatures. While the proton conductivities of the low IEC samples were lower than or close to that of Nafion[®], the conductivities of the high IEC samples were superior to that of Nafion[®]. In general membranes from block copolymers showed similar water uptake and similar dimensional changes but higher proton conductivities as compared to samples from random copolymers with similar monomer composition and ion-exchange capacities.

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1. Introduction

Fuel cells are considered to be attractive and clean alternatives to the widely employed internal combustion engines for power production. Among the various types of fuel cells the low temperature acidic polymer electrolyte membrane fuel cells (PEMFC) possess the broadest area of (possible) application, ranging from power supply for small electronic devices over power source in electrical cars to electrical and heat supply in household. One key-component in PEMFC is the membrane which enables the charge (proton) transport from the anode to the cathode side. Furthermore the membrane should prevent the reactants from diffusing to the opposite electrode. Despite intensive research activities in the past decades, fuel cells are used to date only in nichemarkets. The reasons for not having reached the breakthrough in mass-markets, are on one hand the costs for the membrane, the standard is still Nafion[®] or similar poly(perfluoroalkyl sulfonic acid)s, as well as for the catalyst and on the other hand an operation temperature below 100 °C. However, an operation temperature well above 100 °C would be preferred, because (a) the catalytic activity is increased with increasing temperature, (b) the catalysts are less susceptible to poisoning (faster desorption of e.g. CO), both allowing the use of less amounts of catalysts, and (c) water management is much easier due to the absence of liquid water [1]. Nowadays research in materials for ion-exchange membranes is focused on sulfonated fully aromatic polymers such as polyimides [2–5], poly(ether sulfone)s, polysulfones, poly(ether ether ketone)s (for sulfonated poly(arylene ether)s see for example the review [6] and references therein), or recently, poly(phenylene sulfone)s [7–9]. The sulfonic acid group can be introduced into the polymer chain either by the use of already sulfonated monomers or by a post-sulfonation step. Regardless of the method employed for the introduction of the sulfonic acid group, most often the polymer main chain is sulfonated. As outlined e.g. by Iojoiu et al. [10], the sulfonation step is the crucial step in the preparation of ionexchange membranes. Moreover sulfonation of the main chain might have a negative impact on the mechanical as well as the chemical properties of the polymer materials [11]. In order to cir-





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cumvent these drawbacks, several research groups have prepared side-chain sulfonated poly(arylene ether)s [12–20].

The Jannasch group for example introduced sulfophenyl sidegroups directly to the polymer backbone by the reaction of lithiated PSU with 2-sulfobenzoic acid cyclic anhydride [12,13]. In order to enhance the sulfonation degree, the lithiated polymer was reacted in a first step with 4-fluorobenzoyl chloride. In a second step the fluorine moiety in the side-chain was converted by a nucleophilic displacement reaction with highly sulfonated molecules like 2-naphthol-6,8-disulfonic acid or 8-hydroxy-1,3,6-pyrenetrisulfonic acid [14]. Kim et al. [15], Liu et al. [16] and our group [17] reported on side-chain sulfonated poly(arylene ether)s based on 2,5-dihydroxybiphenyl [15,17] and alkylated phenyl side-chains [16], recently. Unlike the results reported in [15,16], we observed sidechain as well as main-chain sulfonation when using 2.5-dihydroxybiphenvl as sulfonable monomeric unit. These different results can be addressed to the electron withdrawing effects of monomers used in Refs. [15,16] (decafluorobiphenyl, 2,6-difluorobenzonitrile, 4,4'difluorobenzophenone) instead of 4,4'-difluorodiphenyl sulfone used in Refs. [17]. Random copoly(ether sulfone)s with 2,5-diphenylhydroquinone in the polymer backbone showing enhanced thermo-oxidative stabilities have been recently described by Liu et al. [18]. On treatment with conc. sulfuric acid only sulfonation of the side-chain was observed. Tian et al. reported on poly(ether sulfone)s with highly sulfonated nanoclusters consisting of hexaphenylbiphenol units in the main chain [19,20]. Moderate water-uptake and proton conductivities comparable to or even higher than Nafion[®] were reported. Promising results in single fuel cell tests were obtained with the new membrane materials.

Vogel et al. reported on an unexpected high hydrolytic stability of poly(styrene sulfonic acid) up to 200 °C in water [21] but poly(styrene sulfonic acid) is not suitable for use in fuel cells due to its low electrochemical and chemical stability. A fast degradation occurs during fuel cell operation on the cathode side due to reactions at the tertiary carbon of the polymer backbone [22].

Due to the higher ion-exchange capacity that is needed for nonfluorinated membrane materials compared to poly(perfluoroalkyl sulfonic acid)s like Nafion[®] to achieve a similar performance, these membranes have a much higher water uptake combined with a much lower dimensional stability. As shown by the McGrath group, block copolymers have in this context superior properties over random copolymers with similar chemical composition and ion-exchange capacities [23–25].

In this contribution we report on poly(ether sulfone)s based on 2,5-diphenyl hydroquinone, which are sulfonated at the side-chain only. These polymers are mimicking on one hand poly(styrene sulfonic acid) (side chain sulfonation) but possessing on the other hand a thermally, chemically and mechanically stable polymer backbone. The degree of sulfonation and thus the ion-exchange capacities are determined by the amount of 2,5-diphenylhydroquinone moieties in the polymer backbone. Two different types of polymers, namely random copolymers (RC) and multiblock copolymers (MBC), were synthesized and their structure and composition was evaluated by NMR spectroscopy. The effect of molecule architecture and ion-exchange capacity on thermal properties, water-uptake, dimensional stability and proton conductivity will be discussed.

2. Experimental

2.1. Materials

4,4'-Difluorodiphenyl sulfone (DFDPhS) was purchased from FuMaTech GmbH (Germany). 4,4'-dihydroxydiphenyl sulfone (DHDPhS), 1,4-benzoquinone and sodium dithionite were obtained from Aldrich (Germany). N-methyl-2-pyrrolidone (NMP), benzene and calcium carbonate were purchased from Merck (Germany). Potassium carbonate and hexamethyl disilazane (HMDS) were purchased from Fluka (Germany) and decafluoro biphenyl (DFBP) from FluoroChem (UK). Concentrated sulfuric acid (min. 96%) and toluene were obtained from Acros (Belgium). Aluminum trichloride was purchased from ABCR (Germany).

All chemicals were used as received except 4,4'-difluorodiphenyl sulfone which was purified by vacuum distillation and NMP which was distilled twice under reduced pressure from CaH₂. K_2CO_3 and CaCO₃ were dried in vacuum at 150 °C for 24 h.

2.2. Characterization

Solution viscosities were measured in NMP with c = 2 g/L, using an automated Ubbelohde viscosimeter thermostated at 25 °C. Inherent viscosities were calculated from Eq. (1) where c is the polymer concentration in g/dL and t and t_0 are the running time of the polymer solution and the pure solvent, respectively.

$$\eta_{inh} = \frac{\ln\left(1 + \frac{t - t_0}{t_0}\right)}{c} \tag{1}$$

Differential scanning calorimetry (DSC) measurements were carried out with a Netzsch DSC Phoenix 408 at a heating rate of 20 K/min in nitrogen atmosphere using aluminum pans. The second heating scan was used to determine the $T_{\rm g}$.

Detection of T_g of humidified samples was carried out in stainless steel high pressure pans at a heating rate of 5 K/min.

Mechanical properties of thin films were determined at room temperature on a Zwick Z010 instrument. Samples were cut from films into strips of 10 mm width and 100 mm length. The sample length between clamps was set to 50 mm and a strain rate of 50 mm/min was applied. Before measurements samples were equilibrated at 25 °C and 50% r.h. (dry samples) or were stored in water at 25 °C (wet samples). The latter samples were taken from the water just before the measurements.

NMR spectra were recorded on a Bruker DRX 500 spectrometer operating at 500.13 MHz for ¹H, 125.76 MHz for ¹³C and 470.59 MHz for ¹⁹F. 5 mm o.d. sample tubes were used. DMSO- d_6 , chloroform- d_1 or CDCl₃/trifluoroacetic acid (TFA-d) mixtures served as solvent and internal chemical shift reference (CHCl₃: ¹H 7.26 ppm, ¹³C 77.0 ppm; DMSO: ¹H 2.50 ppm; ¹³C 39.6 ppm). Hexafluorobenzene was used as external chemical shift reference (-163 ppm) for ¹⁹F NMR spectra.

Molecular weights were obtained from GPC measurements on a Knauer GPC equipped with Zorbax PSM Trimodal S columns and a RI detector. A mixture of DMAc with 2 vol.% water and 3 g/L LiCl was used as eluent. Poly(4-vinyl pyridine) samples served as standards for molecular weight calibration.

The ion-exchange capacities of sulfonated samples were determined by the titration method as described elsewhere [26].

The water uptake WU was measured by soaking a piece of dry membrane in water for 24 h at 25 °C, 50 °C and 80 °C, respectively. After removing the sample, excess water is wiped off gently with a tissue, and the sample is weighed immediately to get the value m_{wet} . Subsequently the sample is dried in vacuum at 100 °C to constant weight (m_{dry}). The water uptake is calculated using Eq. (2) and is given in percentage increase in weight, where m_{wet} and m_{dry} are weights of the water-swollen and dry membrane sample, respectively.

$$WU = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100\%$$
⁽²⁾

For evaluation of swelling properties, the dimensions (length, width and thickness) of the membrane samples were determined in the dry and wet state. The swelling is expressed in percentage increase in dimensions (ΔL change in length and width; Δd change in thickness).

The proton conductivities were measured in a temperature and humidity controlled chamber using a four-point probe (FuMaTech GmbH, Germany). The membrane conductivities (in-plane) were calculated from cell geometry and membrane resistance (Eq. (3)), which was obtained at the frequency that produced the minimum imaginary response (phase angle close to zero). A Gamry Reference 600 potentiostat, operated over a frequency range from 1 Hz to 1 MHz, was used for the conductivity measurements.

$$\sigma = \frac{l}{w \cdot d \cdot R} \, (S/cm) \tag{3}$$

where l is the distance between electrodes (1 cm), w the width (1.5 cm) and d the thickness of the sample and R the measured resistance. The relative humidity (r.h.) in the sample compartment was calculated from the saturated water vapor pressure in the water compartment and in the sample compartment, at the adjusted temperatures and ambient pressure (1013 hPa), respectively using the following equation:

$$r.h. = \frac{SWV_{Tsample}}{SWV_{Twater}} \cdot 100\%$$
(4)

where r.h. is the relative humidity in %, $SWV_{Tsample}$ the saturated water vapor pressure in the sample compartment at sample temperature and SWV_{Twater} the saturated water vapor pressure in the water reservoir at water temperature. The values for the saturated water vapor pressure were taken from Ref. [39].

2.3. Preparation of 2,5-diphenylhydroquinone

2,5-Diphenylhydroquinone (DPhHQ) was prepared by a slightly modified procedure described by Shildneck and Adams [27]. A 1L three-necked flask, equipped with a reflux condenser, a thermometer and a 500 mL dropping funnel was charged with a suspension of 150 g (1.125 mol) finely powdered aluminum chloride in 250 mL dry benzene. A solution of 50 g (0.46 mol) 1,4-benzoquinone in 500 mL dry benzene was slowly added to the suspension via the dropping funnel under stirring with a magnetic stirrer. The rate of addition was regulated to maintain the temperature at 35-40 °C. The stirring was continued overnight (17 h) while the temperature was allowed to drop to room temperature. The Friedel-Crafts-complex was decomposed by pouring the reaction mixture slowly onto a mechanically stirred mixture of 1 kg ice and 125 mL of conc. hydrochloric acid. Stirring was continued until a brown emulsion was formed. The benzene was removed by steam distillation and the solid raw product was separated by filtration. The filter cake was washed with hot water to obtain a green powder (mixture of guinones, hydroquinones and guinhydrones). For further work-up the product was dissolved in 500 mL diethyl ether. Undissolved material was removed by filtration. The filtrate was treated three times with a saturated sodium dithionite solution in a separating funnel for reduction of the quinones and quinhydrones. The ether layer was washed twice with water and finally dried over sodium sulfate. After filtration and removal of diethyl ether 23 g of a brownish solid remained. This powder was stirred again with 100 mL diethyl ether. A white solid remained undissolved and was removed by filtration. The product was obtained by removal of the diethyl ether and final drying in vacuum at 70 °C over night.

Yield: 20.4 g (78 mmol; 17%); melting point (DSC): 225.5 °C (Lit. 225 °C Ref. [27]). ¹H NMR (DMSO- d_6): δ (ppm): 6.86 (s, 2H); 7.29 (t, 4H); 7.40 (t, 2H); 7.56 (d, 4H); 8.89 (s, 2H; OH).

2.4. Silylation of bisphenols

A 2L round-bottomed flask, equipped with a reflux condenser and a drying tube (KOH), was charged with 1 mol of the respective bisphenol, 1.1 mol of HMDS and 1 L toluene. The reaction mixture was refluxed until the evolution of ammonia ceased. Toluene and excess of HMDS were removed under reduced pressure and the purified products were finally obtained in quantitative yield by vacuum distillation (Table 1).

2.5. Synthesis of random copolymers

10 mmol of DFDPhS, 10-x mmol of bis-TMS-DHDPhS and x mmol of bis-TMS-DPhHQ were weighed into a 50 mL threenecked flask equipped with a magnetic stirr bar, gas-inlet and gas-outlet to which 30 mL of anhydrous and argon-saturated NMP was added. After complete dissolution of the monomers a 1:5 mixture of anhydrous potassium carbonate and calcium carbonate (20 mmol with respect to carbonate) was added. The reaction mixture was heated under stirring and argon purging for 24 h to 175 °C and finally for 2 h at 190 °C. After cooling to room temperature the viscous solution was diluted with 20 mL of NMP and subsequently filtered for the removal of insoluble material. The products were isolated by precipitation in methanol and filtration. The solids were intensively washed with water at rt and methanol at 50 °C. Finally the products were dried in vacuum at 100 °C to constant weight.

2.6. Synthesis of hydroxy endgroup functionalized oligomers

Two different types of end-group functionalized oligomers were prepared in this study. One type was prepared from 4,4'-difluorodiphenyl sulfone and 2,5-diphenyl hydroquinone bis-trimethylsilylether, which will be sulfonated later to introduce hydrophilicity (oligo-DP-PES; diphenylated oligo-PES) and the other (oligo-PES) from 4,4'-difluorodiphenyl sulfone and 4,4'-dihydroxydiphenyl sulfone bis-trimethylsilvlether. The molecular weight and the endgroup functionality are predetermined by a stoichiometric offset of the monomer feed ratios. In this study the molecular weight (M_n) of the 2,5-diphenylhydroquinone containing oligomer was set to approx. 10,000 g/mol. Molecular weights of the PES oligomers, were designed to be approx. 5000 g/mol, 10,000 g/mol and 15,000 g/ mol, in order to make the ion-exchange capacities comparable to those of the random copolymers. The molecular weights were determined by ¹H NMR spectroscopy from the hydroxy-terminated oligomers using the integrals of the diphenylsulfone main chain protons

 Table 1

 Properties of silvlated bisphenols.

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Silylated bisphenol	Yield (%)	b.p. ^a /m.p. ^b	Literature
4,4'-Dihydroxydiphenyl sulfone	99	230 °C 6 \times 10 ⁻³ mbar 89 °C	90 °C [28]
2,5-Diphenyl hydroquinone	99	250 °C 2.5 x 10 ⁻³ mbar 148.6 °C	-

^a Distillation via short-pass distillation: oil bath temperature.

^b The melting points were determined by DSC as maximum of the melting endotherm.

in *ortho*-position to the ether linkage (δ = 7.27 ppm (oligo-PES, solvent: DMSO-*d*₆); δ = 6.99 ppm (oligo-DP-PES, solvent: CDCl₃/ TFA-*d* 4:1 v/v)) and the signal of the corresponding protons in the *ortho*-position to the phenolic end-group (δ = 6.92 ppm (oligo-PES)) and in *ortho*-position to the terminal diphenyl hydroquinone group (δ = 6.94 ppm (oligo-DP-PES)), respectively. The synthetic procedure was the same as for the random copolymers.

2.7. Endcapping of hydroxy-terminated oligomers with decafluoro biphenyl (DFBP)

For end-capping the hydroxy-terminated oligomers, the method described by Lee et al. was employed [23]. 1 mmol of the oligo-PES and 6 mmol of DFBP were weighed into a 100 mL three-necked flask, equipped with a magnetic stirr bar, a gas-in-



Scheme 1. Synthetic pathway to random copoly(arylene ether sufone)s by nucleophilic displacement polycondensation (TMS = trimethylsilyl); residual trimethylsilyl ether groups are hydrolyzed during precipitation.



Scheme 2. Synthetic pathway to block copoly(arylene ether sufone)s by nucleophilic displacement polycondensation (TMS = trimethylsilyl); residual trimethylsilyl ether groups are hydrolyzed during precipitation.



Fig. 1. ¹H NMR spectra of hydroxy-terminated oligo-PES (A) before end-capping with decafluoro biphenyl and (B) after end-capping (solvent: DMSO-d₆).

let and a gas-outlet. 50 mL of anhydrous and argon-saturated NMP was added to the flask. After complete dissolution of the reactants 4 mmol of anhydrous K₂CO₃ was added to the reaction mixture and the temperature was raised to 100 °C under stirring and argon purging for 24 h. After cooling to room temperature the reaction mixture was filtered and the product was coagulated in a 10-fold excess of methanol. The product was isolated by filtration and washed intensively with water and methanol. Finally the end-capped product was dried in vacuum at 100 °C to constant weight. The molecular weight of end-capped oligomers was determined bv the NMR spectroscopy.

2.8. Synthesis of multiblock copolymers

0.3 mmol of the end-capped oligo-PES and 0.3 mmol of the respective oligo-DP-PES were weighed into a 100 mL three-necked round-bottomed flask, equipped with a magnetic stirr bar, a gas-inlet and a gas-outlet. 50 mL of anhydrous and argon-saturated NMP was added to the flask. After complete dissolution of the reactants 2 mmol of anhydrous K_2CO_3 was added to the reaction mixture and the temperature was raised to 100 °C under stirring and argon purging for 24 h. After cooling to room temperature the reaction mixture was filtered and the product was coagulated in a 10-fold excess of methanol. The product was isolated by filtration and washed intensively with water and methanol. Finally the product was dried in vacuum at 100 °C to constant weight.

2.9. Sulfonation of copolymers

The sulfonation of random as well as multiblock copolymers was achieved by treatment with concentrated sulfuric acid (96–98 wt.%) at room temperature. Approximately 3 g of the respective polymer and 30 mL of conc. sulfuric acid were placed in a 50 mL round-bottomed flask and the reaction mixture was stirred for 24 h. During the reaction time the polymer dissolves in the sulfonating agent and the color changes from slightly yellow to brown-ish-green. The sulfonated product was isolated by pouring the reaction mixture into a large excess of isopropanol. The precipitated product was filtered off and washed thoroughly with methanol until neutral. The product was finally dried in vacuum at 110 °C to constant weight.

2.10. Membrane preparation

The sulfonated samples (in H⁺ form) were dissolved in NMP (~15% wt./vol.) and stirred to give a homogeneous solution. Prior to the casting process the solution was filtered through glass wool, in order to remove undissolved matter. 3 mL of this solution was poured in an aluminum frame (4 × 1.5 cm²) and dried at 80 °C in vacuum for 24 h. The membrane samples were released by immersing the frame into water. Remaining NMP was removed by intensive washing with water and soaking the samples for at least 24 h in 0.5 M sulfuric acid. The samples are washed thoroughly with DI water and finally stored in DI water at room temperature until further characterization.

3. Results and discussion

3.1. Preparation and properties of random and multiblock copolymers

Random as well as multiblock copoly(arylene ether sulfone)s from 4,4'-difluorodiphenyl sulfone and different ratios of the bistrimethylsilylethers of 4,4'-dihydroxydiphenyl sulfone and 2,5-diphenyl hydroquinone were successfully prepared by the so-called "silyl method" in solution using a 5:1 mixture of CaCO₃ and K₂CO₃ as base. It has been reported that the use of calcium or magnesium salts in combination with small amounts of potassium carbonate facilitates the nucleophilic displacement polycondensation [29–32]. This effect has been attributed to the removal of the highly reactive fluoride ions, especially in the presence of trace amounts of water, by the formation of insoluble earth alkali fluorides [30,31]. The synthetic pathways for the two different types of polymers prepared in this study, random copolymers and multiblock copolymers, are shown in Schemes 1 and 2. While the synthesis of the random copolymers (RC-1-RC-3) is conducted by simply heating of the respective amounts of monomers in NMP at 175 °C (Scheme 1), the synthesis of the block copolymers is more sophisticated (Scheme 2). In this case the individual blocks with hydroxy endgroups were prepared and characterized concerning their molecular weights (M_n) followed by conversion of the hydroxy end-groups of the finally oligo-PES with decafluoro biphenyl. The complete conversion of phenoxy endgroups was checked by ¹H as well as ¹⁹F NMR spectroscopy (Figs. 1 and 2). The ¹H NMR spectrum of the hydroxyl-terminated oligo-PES (Fig. 1A) shows the expected signals of the protons in ortho-position to the hydroxy end-group (b') at 6.92 ppm, in meta-position to the hydroxy end-group (a') at 7.77 ppm. The signals assigned to the corresponding main chain protons (b and a) appear at 7.27 ppm (ortho to the ether group) and at 7.99 ppm (ortho to the sulfone group). The signals of the protons attached to the second benzene ring of the terminal diphenylsulfone moiety appear at 7.25 ppm (b") and 7.92 ppm (a"). Upon conversion of the hydroxy end-groups with decafluoro biphenyl, the signals of the protons associated with the hydroxy end groups disappear completely in the ¹H NMR spectrum (Fig. 1B). The two signals of lower intensity (b''' and a''') in this spectrum are assigned to the protons in *ortho-* and *meta-*position to the newly formed ether linkage with decafluoro biphenyl. The ¹⁹F spectrum (Fig. 2) shows in addition to the signals of the nonafluoro biphenyl endgroup (assignment see figure) at least one signal (d') appearing at -138.3 ppm. From the ¹⁹F-19F 2D NMR spectrum (not shown) this signal and a second one (e'), which is superimposed by the signal e, are attributed to the formation of a symmetrical 4,4'-substituted decafluoro biphenyl structure (dimer formation). The dimer content is approx. 10% as estimated from the ¹⁹F NMR spectrum.



Fig. 2. ¹⁹F NMR spectrum of oligo-PES end-capped with decafluoro biphenyl (solvent: DMSO-d₆).

In the next step the hydroxy-terminated oligomers are reacted with the decafluoro biphenyl-terminated oligomers to give the different multiblock copolymers (MBC-1-MBC-3). All polymers, random as well as multi block copolymers, were obtained in almost quantitative yield and with molecular weights up to 70.000 g/mol (M_n) (Table 2). The high molecular weights are expressed by the high inherent viscosities (up to 0.93 dl/g) as well. However, one feature is striking when taking a closer look at the polydispersities (PD) of random and multiblock copolymers (Table 2). While the random copolymers show relatively narrow PD in the range from 2.3 to 2.9, the PD of the multiblock copolymers are in the range from 6 to 8, although starting from oligomers with a PD of around 2. Examples of gpc curves are given in Fig. 3 (random copolymer RC-2) and Fig. 4 (multiblock copolymer MBC-2). The broadening of the molecular weight distribution of multiblock copolymers is explained by branching reactions at the decafluoro biphenyl unit (Scheme 3). Some broadened ¹⁹F NMR signals of low intensity were observed in the MBC spectra which might be assigned to branching points. However, a conclusive proof of such branching units is not straightforward because the intensity of these signals is low and the substitution pattern of the branching point result in a complex spectrum. However, the significant signal broadening compared to the signals of the linear main chain suggests a restricted mobility as expected for the branching units.

However, crosslinking was not observed since all multiblock copolymers were soluble in dipolar aprotic solvents like NMP, DMAc or DMSO. It should be noted, that the solubility of multiblock copolymers is much better in amidic solvents like NMP or DMAc than in DMSO, while the random copolymers dissolve readily in all the above mentioned solvents.

On sulfonation with conc. sulfuric acid the molecular weights of the polymers did not decrease as indicated by the viscosity data and the gpc data (Table 3). On the contrary, the data suggest higher molecular weights than the starting material. This effect is attributed firstly to the formation of aggregates due to the formation of hydrogen bonds between the sulfonic acid groups of different polymer chains. Such aggregation of ionic polymers has been reported by several groups in the past [33–36]. Secondly, the solubilities as well as interactions between the sulfonated polymer and the solvent change, which leads to different chain conformations (hydrodynamic radii), giving rise to the observed effect. However, the molecular weight distribution keeps almost constant after the sulfonation process, indicating that no degradation occurred during the sulfonation step. The water uptake (WU) of sulfonated random copolymers is increasing with increasing ion-exchange capacity and increasing temperature. The values found in this study are slightly higher but still comparable to those reported by Liu et al. [18]. Even at 80 °C the samples sRC-2 and sRC-3 retained their shape and showed moderate water uptake especially when taking the relatively high IEC into account. Only the sample



Fig. 3. gpc curves of samples RC-2 (a, dashed line) and sRC-2 (b, solid line).

sRC-1, possessing an IEC of 2.05 mmol/g, dissolved at 80 °C. The sulfonated multiblock copolymers showed a slightly higher water uptake as compared to their random copolymers. This may result from the fact that the sulfonic acid groups are distributed over the whole polymer backbone in the case of the randon copolymers. The non-sulfonated as well as the sulfonated sequences are much shorter than in the blockcopolymers, leading to smaller respective domains. These smaller domains prevent on one hand a high water uptake due to a lower number of sulfonic acid groups. On the other hand the resistive forces against swelling of the non-sulfonated domains at high temperatures are also smaller than for the multiblock copolymers. The sulfonic acid groups are incorporated as highly sulfonated clusters (blocks) into the polymer chain of the multiblock copolymers. Such clusters (blocks) might result in the formation of larger sulfonated but also non-sulfonated domains as compared to the random copolymers. These larger domains favor the water uptake while the larger non-sulfonated domains prevent the sample from dissolving in water at high temperatures. From this argumentation it is not surprising that the sample with the highest IEC (sMBC-1) shows a high water uptake but does not dissolve in water at 80 °C.

Upon water uptake the membrane materials show a dimensional change. The in-plane swelling (length and width) is increasing with increasing ion-exchange capacity and increasing temperature as outlined in Table 4. In the case of the random copolymers the determined values are in good agreement with the values reported by Liu et al. [18]. All samples with low to medium IEC showed good dimensional stability at temperatures up to 50 °C. There are no differences between the random and multi-

Table 2

Composition and properties of random copolymers (RC) and multiblock copolymers (MBC).

Sample	Feed ratio		Product ratio ^a		$\eta_{inh} (dl/g)$	M_n (g/mol)	M_w (g/mol)	PD	$T_{\rm g}~(^{\circ}{\rm C})$
	DHDPhS	DPhHQ	DHDPhS	DPhHQ					
RC-1	4	6	4	6.1	0.65	39,000	91,000	2.3	233
RC-2	5	5	5	5.0	0.43	44,000	105,000	2.4	232
RC-3	6	4	6	3.9	0.93	70,000	206,000	2.9	229
	M _n oligo-DP-PES ^{a,b} (g/mol)		M _n oligo-PES ^e	M _n oligo-PES ^{a,c} (g/mol)					
MBC-1	9000		4600		1.08	44,000	285,000	6.5	224
MBC-2	9200		10,600		1.15	31,800	244,000	7.7	-
MBC-3	9200		14,500		1.64	55,000	316,000	5.8	233

^a Determined from ¹H NMR spectra.

^b Composed of DPhHQ and DFDPhS.

^c Composed of DHDPhS and DFDPhS.



Fig. 4. gpc curves of samples MBC-2 (d, open symbol) and sMBC-2 (e, solid symbol) together with gpc curves of the starting oligomers (a, oligo-PES (dashed-dotted line); b, oligo-DP-PES (dotted line); c, end-capped oligo-DP-PES (solid line)).

block copolymers within the error margin. Only the high IEC samples showed a much higher swelling (sMBC-1) or even dissolve in water at 80 $^{\circ}$ C (sRC-1).

The swelling in z-direction (perpendicular to the surface) shows the same trend as the swelling in x-y-direction: the higher the IEC, the higher the swelling. However, due to the smaller dimensions (µm instead of mm) and the determination procedure (micrometer screw) a high deviation of the values is observed. Contrary to the findings reported by Lee et al. [23] the random copolymers investigated in this study showed an "asymmetric" swelling, meaning that the dimensional change in thickness is more pronounced than the dimensional change in length and width. This effect is less pronounced or even reversed for the multiblock copolymers. This might be a result of the relatively short oligomers used for the preparation of block copolymers, but this does not explain the properties of the random copolymers. Furthermore, the choice of solvent for the membrane preparation (NMP) might play a role, which has a strong effect on the morphology and hence on the membrane properties [37].

3.2. Thermal and mechanical properties

The non-sulfonated random copolymers possess a single glass transition temperature (T_g) around 230 °C (Table 2). These values are in good agreement with the values reported by Liu et al. [18]. On sulfonation the T_g of dry samples is shifted to temperatures around 260 °C, due to the interactions (formation of hydrogen bonds) between the sulfonic acid groups.

The glass transition temperatures of the oligomers used for the preparation of the multiblock copolymers are 206 °C (4600 g/mol), 212 °C (10,600 g/mol) and 225 °C (14,500 g/mol) for the oligo-PES blocks and 205 °C (9000 g/mol) for the oligo-DP-PES block. The multiblock copolymers prepared from the oligomers show in the non-sulfonated form only a single T_g , which is increasing with increasing length of the oligo-PES block (224 °C (MBC-1); 227 °C (MBC-2); 233 °C (MBC-3)). This result is not surprising since the T_g s of the building blocks are quite similar. Furthermore, a phase separation between the two different blocks and therefore the

appearance of two T_{gs} in the dsc curves is not expected due to the quite similar chemical composition of the two building blocks of the polymer backbone.

Interestingly no T_g could be detected for the two sulfonated multiblock copolymers sMBC-1 and sMBC-2 in the temperature range up to 300 °C. Only the sulfonated multiblock copolymer with the lowest IEC (sMBC-3) showed a single T_g at 255 °C. It is supposed, that the high number of sulfonic acid groups in the samples sMBC-1 and sMBC-2 leads to such a high number of hydrogen bonds between the polymer chains, that the T_g is shifted to temperatures close to or even above 300 °C. Further studies on the thermal properties of these materials will be performed and reported in a forthcoming publication.

The thermal properties of the sulfonated materials change dramatically in the hydrated state. The $T_{\rm g}$ of the high IEC random copolymers (sRC-1and sRC-2) drops to ca. 110 °C at high humidification levels and is thus in the same range as observed for Nafion[®] under fully hydrated conditions [38]. It is obvious from Fig. 5, that from a certain water content on (ca. 15-20 mol water per mol sulfonic acid group), only a minor or no change in $T_{\rm g}$ occurs. This is attributed to the fact that the water molecules are more or less tightly bound by hydrogen bonds to the sulfonic acid groups hence disturbing the hydrogen bonds between sulfonic acid groups. Thus this water acts as plasticizer in these materials. Further adsorbed water shows no interaction with the polymer and behaves like bulk water and has therefore no influence on the thermal properties of the material. A more detailed discussion on the effect of water on the thermal properties of ion-exchange materials will be published in a forthcoming paper.

Contrary to the perfluoroalkyl sulfonic acids, which show cold drawing behavior, all sulfonated samples prepared in this study showed a brittle fracture behavior on applied tensile stress in the nominally dry state (conditioned at 25 °C, 50% r.h.). The Young's moduli are in the range of 1.5 to ca. 2.0 GPa (see Table 4). Perfluoralkylsulfonic acids like Nafion[®] have a Young's modulus of ca. 0.2 GPa under the same test conditions. On the other hand the elongation at break is for the Nafion[®]-type samples much higher



Scheme 3. Possible chain growth reaction during synthesis of multiblock copolymers: (A) linear chain growth and (B) branching.

Table 3 Composition and properties of sulfonated random copolymers (sRC) and multiblock copolymers (sMBC).

Sample	$\eta_{inh} (dl/g)$	M_n (g/mol)	M _w (g/mol)	PD	T_g (°C)	IEC _{theo} (mmol/g)	IEC _{titr.} (mmol/g)	WU (%)		
								25 °C	50 °C	80 °C
sRC-1	1.74	50,000	155,000	3.1	260	2.12	2.05	69	97	dis. ^b
sRC-2	0.78	64,000	174,000	2.7	251	1.82	1.71	48	57	111
sRC-3	3.71	120,000	340,000	2.8	264	1.50	1.45	22	26	35
sMBC-1	6.31	29,000	345,000	11.9	n.d. ^a	2.24	1.95	80	114	473
sMBC-2	4.16	34,000	218,000	6.4	n.d.	1.73	1.53	51	65	128
sMBC-3	3.29	62,000	407,000	6.6	255	1.49	1.39	38	47	60

^a Not detected up to 300 °C.

^b Dissolved.

Table 4

Mechanical properties of sulfonated random and multiblock copolymers in nominally dry and humidified state.

Sample	IEC (mmol/g)	Dimensional change $\Delta L imes \Delta d$ (%)		Young's modulus		Elongation at break		
		25 °C	50 °C	80 °C	Dry (GPa)	Wet (GPa)	Dry (%)	Wet (%)
sRC-1	2.05	17 imes 34	27 imes 36	_ ^a	1.56	0.40	5.9	6.1
sRC-2	1.71	17 imes 21	20 imes 22	33 imes 36	n.d. ^b	n.d.	n.d.	n.d.
sRC-3	1.45	3×15	4×7	6×17	1.93	1.12	5.7	7.1
sMBC-1	1.95	14 imes 22	22 imes 32	88 imes 73	n.d.	n.d.	n.d.	n.d.
sMBC-2	1.53	17 imes 16	18 imes 15	34 imes 31	1.98	0.88	3.3	6.0
sMBC-3	1.39	8×20	10×14	13 imes 25	1.82	1.25	6.0	10.0

^a Dissolved.

^b n.d. = not determined.

(>100%) than for the aromatic polymers (<10%). The plasticization effect of water in the ion-exchange membranes is also reflected by the mechanical properties of humidified samples. The Young's moduli of the random as well as multiblock copolymers drop significantly on humidification and a clear trend is obvious. Samples with high IEC possess a lower Young's modulus than samples with low IEC due to the higher water uptake. However, the Young's moduli of ion-exchange materials introduced in this study in the wet state are still higher than that of Nafion[®]-type materials.

Furthermore the type of respond on the tensile stress changes for the aromatic polymers. While the dry samples show a brittle fracture behavior, the wet ones showed a cold draw behavior like the perfluoroalkyl sulfonic acids.

3.3. NMR spectroscopic characterization

The chemical composition of the various copolymers prepared in this study was determined from ¹H NMR spectra. Fig. 6 shows



Fig. 5. Glass transition temperature of humidified ion-exchange membranes as function of hydration number. Data for Nafion were adapted from Ref. [38].

the spectra of the non-sulfonated random copolymers together with the signal assignment. The spectra show five well-separated groups of signals appearing at 8.1–7.7, 7.45, 7.35, 7.3–7.15 and, 7.15–7.0 ppm. The assignment of the signals as outlined in Fig. 6 was deduced from 2D NMR spectra. As an example, the 2D spectrum of sample RC-3 is shown in Fig. 7. The splitting of the signals a and b of the diphenylsulfone unit into four doublets, which is more pronounced for the proton a, is assigned to the three different diphenylsulfone-centered triads I–III which are formed in the polymer backbone (Scheme 4). The doublet at 7.98 ppm is assigned to

the proton a in ortho-position to the sulfone groups in substructure I, whereas the doublet at 7.75 ppm can be assigned to proton a'" of substructure III. The nonsymmetric triad II with protons a' and a" results in two doublets of same intensity located between these signals at 7.90 and 7.83 ppm. The corresponding signals b-b'" could be identified by 2D NMR (Fig. 7). The intensities of the signals assigned to the different substructures correspond very well with the theoretical values from probability calculations, indicating the formation of real random copolymers. Overall, a very good correlation between monomer ratio in the feed and monomer ratio in the polymer backbone was found (Table 2). The ¹H NMR spectrum of the multiblock copolymers (Fig. 8) is much simpler than that of the random copolymers, because only the symmetric substructures I (from the PES-block) and III (from the DP-PES-block) of Scheme 4 can occur in this type of polymer neglecting the terminal units of each block. As for the random copolymers, the composition determined by NMR spectroscopy fits very well with composition calculated from the educts. With increasing relative content of the still unsulfonated "hydrophilic" block, which is poorly soluble in DMSO, a line broadening is observed. The ¹H NMR spectra of sulfonated random and multiblock copolymers (Figs. 9 and 10) show the same changes, compared to the spectra of the non-sulfonated samples. The signals d-f of the pendant phenyl ring disappear and two doublets of same intensity appear at 7.46 and 7.56 ppm (Fig. 10). The signal pattern, intensities and the down-field shift compared to signals d and e in the non-sulfonated samples clearly indicate selective sulfonation of the pendant phenyl rings in para-position. The signals of the diphenylsulfone units remain unchanged and show the different pattern for RC and MBC as discussed before. In the case of similar copolymers having phenylhydroquinone units instead of 2,5-diphenyl hydroquinone units in the polymer backbone, the sulfonation of the pen-



Fig. 6. ¹H NMR spectra of random copoly(arylene ether sulfone)s (solvent: DMSO-d₆).



Fig. 7. 2D-NMR spectrum ($^{1}H-^{1}H$ COSY) of sample RC-3 (solvent: DMSO- d_{6}).



Scheme 4. Possible diphenylsulfone-centered triads occurring in the random copoly(arylene ether sulfone)s giving rise to the splitting of the proton signals of this unit.

dant phenyl ring as well as of the hydroquinone ring resulted in a change of the splitting pattern of signal a [18]. Thus, within the limits of the NMR method there is no indication that the sulfonation occurs at other positions than the pendant phenyl rings. It

should be mentioned that the signal of proton c shows a splitting in three signals due to pentad effects for the sRCs. Furthermore, sulfonation results in an improved solubility of the hydrophilic block and so the line broadening observed for MBCs is significantly



Fig. 8. ¹H NMR spectra of multiblock copoly(arylene ether sulfone)s (solvent: DMSO-*d*₆).



Fig. 9. ¹H NMR spectra of sulfonated random copoly(arylene ether sulfone)s (solvent: DMSO-d₆).



Fig. 10. ¹H NMR spectra of sulfonated multiblock copoly(arylene ether sulfone)s (solvent: DMSO-*d*₆).



Fig. 11. 2D NMR spectrum (¹H–¹H COSY) of sample sRC-3 (solvent: DMSO-*d*₆).

reduced for sMBcs. The assignment of signals was again supported by 2D NMR spectra recorded from random copolymers (Fig. 11).

3.4. Conductivity measurements

The proton conductivities, measured in plane, of the membranes were studied over a temperature range from 30 °C to 100 °C at 100% relative humidity (sample and water reservoir have the same temperature) and above 100 °C at 1 atm water vapor pressure, meaning that the relative humidity decreases with increasing temperature (the relative humidity at temperatures above 100 °C was calculated from the temperature of the water reservoir (100 °C) and the sample temperature [39]). The proton conductivities as function of temperature are displayed in Fig. 12 (random copolymers) and 13 (multiblock copolymers). The conductivity curve of Nafion[®] 115 is given in these plots as reference. The conductivities of the random copolymers increase with increasing ion-exchange capacity and increasing temperature. Although the ion-exchange capacity of sRC-3 exceeds that of Nafion[®] by at least 50%, the proton conductivity is much lower than that of the reference. The samples sRC-1 and sRC-2 having IECs of 2.05 and 1.71 mmol/g, respectively showed proton conductivities comparable to that of Nafion[®]. At temperatures above 100 °C and at reduced humidification the same trend for the conductivities is observed as for measurements at fully hydrated conditions, the higher the IEC the higher the conductivities. However, the conductivities decrease much stronger with increasing temperature (decreasing humidity) than that of Nafion[®]. The sample with the lowest IEC (sRC-3) shows the lowest conductivity and the steepest decrease. With increasing IEC the loss of conductivity with temperature is less steep but still more pronounced than that of Nafion[®].

Although having comparable ion-exchange capacities, the multiblock copolymers showed a completely different behavior than the random copolymers. Even the samples with the lowest IEC (sMBC-2, sMBC-3) possess at 100% r.h. a proton conductivity similar to Nafion[®], while the sample with highest IEC (sMBC-1) exceeds that of Nafion[®] by ca. 100% in the temperature range up to 100 °C under fully hydrated conditions. As already observed for the random copolymers, the loss of conductivity is much more severe compared to Nafion[®]. However, the inflection point is shifted to temperatures above 100 °C. As an example, sMBC-1 (IEC: 1.95 mmol/g) shows a higher conductivity than Nafion[®] up to ca. 120 °C.



Fig. 12. Proton conductivities of sulfonated random copolymers as function of temperature and relative humidity (at T > 100 °C).



Fig. 13. Proton conductivities of sulfonated multiblock copolymers as function of temperature and relative humidity (at T > 100 °C).

The differences in proton conductivities can be explained when taking the water uptake (Table 3) of the samples into account. The hydration numbers λ of the random copolymers sRC-1–sRC-3 are 57.6, 31.2 and 16.5, respectively. In the same order as the λ -value increases an increase in the proton conductivity of these membrane materials is observed. Due to the higher water uptake (at 20 °C) the hydration numbers of the multiblock copolymers are substantially higher than those of the random copolymers at comparable ion-exchange capacities (Fig. 14), which leads to the observed higher conductivities at fully hydrated conditions. The loss of conductivity with increasing temperature might be a result of a faster desorption of the water compared to Nafion[®], due to the lower acid strength of aromatic sulfonic acids. A second reason for the higher water uptake on one hand and the faster desorption of water on the other hand may be due to differences in the morphology of hydrocarbon-based membranes and perfluoroalkyl sulfonic acids-based like Nafion[®]. The latter shows a strong phase separated morphology between the highly hydrophobic backbone and the hydrophilic side chains. The differences in hydrophilic and hydrophobic properties are not that pronounced in hydrocarbonbased membranes, resulting in a less-ordered (phase-separated) morphology, even in the multiblock copolymers.



Fig. 14. Hydration number λ as function of ion-exchange capacity after storage in water at 20 °C.

4. Conclusions

Random as well as multiblock copolymers were successfully prepared from 4.4'-difluorodiphenvl sulfone. bis-(4-hvdroxy phenyl) sulfone and 2,5-diphenyl hydroquinone by nucleophilic displacement polycondensation reaction using the silyl-method. While the random copolymers had a linear structure with low PD values, it turned out that during preparation of the multiblock copolymers branching reactions occurred at the decafluoro biphenyl unit. Nonetheless the multiblock copolymers were still soluble in dipolar aprotic solvents. Contrary to the findings with monophenylated polymers (using phenyl hydroquinone instead of 2,5-diphenyl hydroquinone) reported earlier by our group, a selective sulfonation of the side-chain was achieved with conc. sulfuric acid. Membranes prepared from both types of polymers were transparent and flexible. Although having comparable ion-exchange capacities, the sulfonated multiblock copolymers showed higher proton conductivities than the sulfonated random copolymers and at high IEC (\ge 1.95 mmol/g) even higher than Nafion[®] at 100% relative humidity, which was attributed to the relatively high water uptake of the membranes prepared from the multiblock copolymers. On the other hand, membranes prepared from random copolymers with an IEC \ge 1.8 mmol/g tend to soften to a high extend or even dissolve in water at elevated temperatures.

Due to their high proton-conductivity and good dimensional stability at elevated temperatures sulfonated multiblock copolymers turned out to be promising candidates for membrane materials in PEM fuel cells operated at temperatures up to 120 °C.

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