

## Sulfonated poly(ether sulfone)s for fuel cells by solvent-free polymerization\*

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**Abstract:** Poly(ether sulfone)s from 4,4'-difluorodiphenylsulfone (DFDPhS), 4,4'-bis-trimethylsiloxy-diphenylsulfone, and 2,5-bis-trimethylsiloxy-biphenyl were obtained by melt polycondensation with high molecular weights ( $\eta_{inh} > 0.4$  dl/g). The nonsulfonated samples showed a single glass-transition temperature ( $T_g$ ) in the range from 180 to 230 °C depending on the monomer composition in the polymer backbone. The  $T_g$  of sulfonated samples could not be detected by differential scanning calorimetry (DSC). Membranes with a theoretical ion-exchange capacity (IEC) ranging from 0 to 2.08 mmol/g should be obtained, assuming only a sulfonation of the pendant phenyl ring. However, the sulfonation with concentrated sulfuric acid always led to the introduction of two sulfonic acid groups into the phenylhydroquinone (PhHQ) moieties in the polymer backbone; one at the desired position at the pendant phenyl ring and one at the phenyl ring in the polymer backbone. Membranes prepared from *N*-methyl-2-pyrrolidone (NMP) solutions of nonsulfonated and sulfonated samples were transparent and soft to slightly brittle. The water uptake at room temperature increased with increasing IEC from 4 to 50 % (IEC ~ 1.50 mmol/g). On further increase of the IEC, a strong water uptake until dissolution was observed. Methanol diffusion coefficients for samples with an IEC up to 1.10 mmol/g were one order of magnitude lower than that reported for Nafion<sup>®</sup>.

**Keywords:** ion-exchange membranes; fuel cells; poly(arylene ether); sulfonation; melt polycondensation.

### INTRODUCTION

Polymer electrolyte membranes and, in particular, cation exchange membranes are used in a broad field of applications such as low fouling membranes in water and wastewater treatment, solid polymer electrolytes in electrochemical processes, or as ion-selective membranes in sensors.

The fuel cell technology has been recognized as one of the key technologies for future clean energy conversion and production systems for mobile as well as stationary applications such as consumer electronics, automotives, in-house heat and power supply, or decentralized power and heat generation. The advantage of fuel cells over conventional energy conversion systems like combustion is their high efficiency. Especially for automotive applications, membrane-based fuel cells are favored. Additionally, an environmentally friendly production process of the membrane and membrane materials is of certain interest in the sense of a “green product”.

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Despite some drawbacks, today poly(perfluoroalkylsulfonic acid)s such as Nafion<sup>®</sup> and similar materials are still the standard membrane materials for polymer electrolyte fuel cells (PEMFCs). The disadvantages of these materials and the demand for new and clean energy conversion/production systems have initiated world-wide research activities on the development of alternative membrane materials for PEMFCs. Among the various materials suggested, sulfonated poly(arylene ether)s are seen as the most promising ones due to their outstanding chemical and thermal stabilities, high glass-transition temperature ( $T_g$ ), as well as their good solubility in dipolar aprotic solvents such as *N*-methyl-2-pyrrolidone (NMP), dimethylsulfoxide (DMSO), or *N,N*-dimethylacetamide (DMAc) and film-forming properties.

Sulfonated poly(arylene ether)s are generally attained by two different routes. The most suitable and most often applied way to obtain functionalized and, in particular, sulfonated polymers is the post-treatment (sulfonation) of a given polymer [1]. Depending on the chemical composition of the polymer backbone and the desired degree of sulfonation, various sulfonating agents with different reactivities can be selected and are commercially available. Although easy to carry out, this method bears some risks and disadvantages over the synthesis of the same type of polymer using sulfonated monomers. These are mainly degradation of the polymer backbone and the inhomogeneous and uncontrolled distribution of the sulfonic acid groups along the polymer backbone. Iojoiu et al. studied the influence of various processing parameters of sulfonation of different poly(arylene ether sulfone)s on the degree of sulfonation as well as the material properties recently [2]. Most attractive seems to be the sulfonation in concentrated sulfuric acid (i.e., 98 %) [3–6] or chlorosulfonic acid [7–17] acting both as solvent and as sulfonating agent since both reagents are inexpensive and readily available. As reported by Blanco et al. [16], a rapid degradation occurs during the sulfonation of polysulfone (PSU), which makes this method at least questionable for a number of poly(ether sulfone)s (PES).

The second route to obtain functionalized polymers is given by the use of monomers already bearing functional groups, e.g., sulfonic acid groups. This method has the advantage that (a) the site of functionalization; (b) the number of functional groups; and (c) the distribution of functional groups, either randomly or blockwise, in the polymer chain can be easily controlled. Furthermore, the risk of side reactions such as degradation or crosslinking connected with the post-functionalization route can be overcome. Several research groups have focused their work in this area. Most often, a sulfonated 4,4'-dichlorodiphenyl sulfone or 4,4'-difluorodiphenyl sulfone, or, in the case of poly(arylene ether ketone)s, sulfonated 4,4'-dihalobenzophenone is used together with the nonsulfonated monomer and various types of bisphenols such as bisphenol A, 4,4'-dihydroxy biphenyl, phenolphthalein, and others [18–34]. The sulfonated monomer is easily obtained by sulfonation of the dihalogeno sulfone with fuming sulfuric acid (30 % SO<sub>3</sub>) at 90 °C for 6 h [18].

Other groups used the commercially available sodium salt of hydroquinone sulfonic acid as sulfonated monomer in the synthesis of sulfonated poly(arylene ether sulfone)s [20,35–37]. Kozłowski mentioned in a patent the incorporation of 3,3'-sulfonyl-bis-(6-hydroxybenzene sulfonic acid) (sulfonated bisphenol S) into polymers [38]. However, in these cases, the sulfonic acid group is attached to the activated ring, which enhances the risk of desulfonation in fuel cell applications.

Another method to functionalize poly(arylene ether sulfone)s is given with the metalation (lithiation) route, which has been intensively employed by several research groups [39,40–55], and has been the subject of a recently published review by Jannasch [56]. The activation is usually achieved by the treatment of the respective polymer with a strong base such as butyllithium or alkali hydrides (NaH, LiH) at low temperatures (–78 to –30 °C) in an inert solvent like tetrahydrofuran (THF). Further reaction of the activated polymers with, for example, derivatives of a carboxylic acid, sulfuric acid, or a phosphonic acid, leads to carboxylated, sulfonated, or phosphonated polymers, respectively.

When dealing with sulfonated aromatic systems, one has to keep in mind that sulfonated aromatic rings are susceptible to desulfonation, depending on the electron density at the sulfonated site and on the conditions in the medium, such as elevated temperatures and the presence of acid. Since the direct

sulfonation is an electrophilic reaction, the sulfonation occurs at electron-rich sites of the polymer backbone, which is in PSUs the *ortho*-position to the ether linkage. The advantage of the metalation method over the direct sulfonation is that the activation takes place at electron-poor sites of the polymer backbone, in general, in *ortho*-position to the electron-withdrawing sulfone-linkage. Thus, these sulfonated PSUs are expected to be less sensitive to desulfonation than those obtained by the direct sulfonation method.

Recently, Vogel et al. reported on a surprisingly high hydrolytic stability of poly(styrene sulfonic acid) [57]. First indications of hydrolysis were found only after treatment in water at 200 °C for 24 h. On the other hand, poly(styrene sulfonic acid) is not suitable for applications in fuel cells due to its chemical instability arising from the tertiary carbon in the polymer backbone.

These results led us to the idea to prepare chemically stable poly(arylene ethers) with a pending phenyl ring, which can be sulfonated selectively, in order to mimic poly(styrene sulfonic acid). Having the sulfonic acid group in the side chain has further advantages as has been described in the literature, for example, by McGrath or Lafitte [51,53].

Secondly, an alternative synthetic route should be evaluated in this work, which involves a limited use of solvents. For this purpose, all PESs were prepared by a melt polycondensation process, first described by Kricheldorf et al. [58,59]. For comparison, some poly(ether ether ketone)s were prepared by conventional polycondensation in solution. All polymers are characterized in terms of molecular weight [inherent viscosity, gel permeation chromatography (GPC)], thermal properties, ion-exchange properties, as well as transport properties.

## EXPERIMENTAL

### Materials

4,4'-difluorodiphenylsulfone (DFDPhS) was purchased from Lancaster and was used as received. 2,5-Dihydroxybiphenyl (phenylhydroquinone; PhHQ) was purchased from Acros. Hexamethyl diisilazane (HMDS), 4,4'-dihydroxydiphenylsulfone (DHDPhS) were products of ABCR. Toluene, dichloromethane, and NMP were all obtained from Merck. Cesium fluoride and trifluoroacetic acid were purchased from Aldrich.

### Silylation of bisphenols

0.5 mol of the respective bisphenol was refluxed in a mixture of 0.5 l toluene and 0.6 mol of HMDS. After the evolution of ammonia had ceased, toluene and excess HMDS were removed under reduced pressure. The purified products were finally obtained in quantitative yield by vacuum distillation (Table 1).

**Table 1** Properties of silylated bisphenols.

| Silylated bisphenol           | Yield (%) | b.p. °C   | Literature         |
|-------------------------------|-----------|---|--------------------|
| 4,4'-Dihydroxydiphenylsulfone | 99        | 230–240 <sup>a</sup> at $6-9 \times 10^{-3}$<br>m.p. 89 | m.p. 90 °C<br>[60] |
| 2,5-Dihydroxybiphenyl         | 99        | 118 ( $6.5 \times 10^{-2}$ mbar)                        |                    |

<sup>a</sup>Distillation via short-pass distillation equipment; oil bath temperature.

## POLYMERIZATION IN BULK

30 mmol of DFDPhS, and in total 30 mmol of bis-TMS-DHDPhS and bis-TMS-PhHQ were weighed into a 100-ml 3-necked round-bottom flask, equipped with a gas-inlet and a gas-outlet tube and a me-

chanical stirrer. The reaction mixture was heated to 130 °C in a metal bath under a slow stream of dry argon. After complete melting of the components, 100 mg of CsF were added and the temperature was raised gradually to 300 °C over a period of 8 h. After cooling to room temperature, the reaction products were dissolved in a mixture of dichloromethane and trifluoroacetic acid (4:1 v/v). After complete dissolution, the polymers were precipitated into a large excess of ethanol, filtered off, washed intensively with hot ethanol, and dried finally to constant weight at 80 °C in vacuum.

The compositions and molecular weights of samples prepared in this work are listed in Table 2.

**Table 2** Composition and basic polymer properties of PESs.

| Sample  | PhHQ | DHDPhS | DFDPhS | $\eta_{inh}$ (dl/g) <sup>a</sup> | $M_w^b$ | $M_n^b$ | DP  |
|---------|------|--------|--------|----------------------------------|---------|---------|-----|
| PES-I   | 0    | 8      | 8      | 0.37                             | 44 000  | 20 000  | 2.2 |
| PES-II  | 2    | 6      | 8      | 0.63                             | 111 000 | 48 000  | 2.3 |
| PES-III | 3    | 5      | 8      | 0.44                             | 67 000  | 29 000  | 2.3 |
| PES-IV  | 4    | 4      | 8      | 0.43                             | 72 000  | 35 000  | 2.1 |
| PES-V   | 5    | 3      | 8      | 0.39                             | 58 000  | 24 000  | 2.3 |
| PES-VI  | 6    | 2      | 8      | 0.41                             | 71 000  | 30 000  | 2.4 |
| PES-VII | 8    | 0      | 8      | 1.17                             | 230 000 | 81 000  | 2.8 |

<sup>a</sup> $c = 2$  g/l in DMAc at 30 °C.

<sup>b</sup>From GPC measurements; eluent DMAc containing 2 vol % water and 3 g/l LiCl, poly(4-vinyl pyridine) standards were used for molecular weight calibration.

## Sulfonation

The sulfonation was achieved by treatment of the respective polymer sample with concentrated sulfuric acid (96–98 %) at room temperature. Approximately 2 g of polymer and 20 ml of conc. sulfuric acid were placed in a 50-ml round-bottom flask. The reaction mixture was stirred until the polymer was completely dissolved (4 h). For isolation of the sulfonated product, the respective reaction mixture was poured into a large excess of water. The precipitate was filtered off and washed thoroughly with water until neutral. The products were dried in vacuum at 80 °C to constant weight.

## Measurements

The viscosities were measured in DMAc with  $c = 2$  g/l using an automated Ubbelohde viscosimeter thermostatted at 25 °C.

Differential scanning calorimetry (DSC) measurements were carried out with a Netzsch DSC Phönix 408 at a heating rate of 20 K/min. The second heating scan was used to determine the  $T_g$ .

<sup>1</sup>H spectra were recorded on a Bruker AMX 500 spectrometer operating at 500.13 MHz for <sup>1</sup>H. DMSO-*d*<sub>6</sub> served as the solvent and internal chemical shift reference (2.5 ppm for <sup>1</sup>H).

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

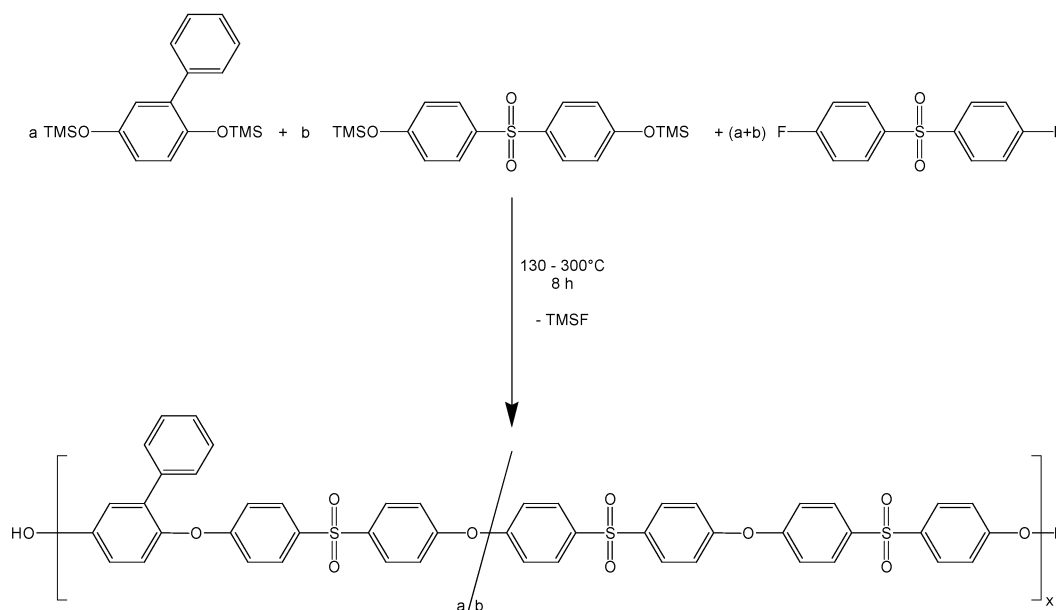
The ion-exchange capacities of sulfonated samples were determined by the titration method as described elsewhere [63].

The water uptake was measured by soaking a piece of dry membrane in water for 24 h at 25 °C. The excess water is wiped off gently with a tissue, and the sample is weighed immediately. Subsequently, the membranes were dried at 80 °C in vacuum to constant weight. The water uptake is calculated using eq. 1 and is given in percentage increase in weight, where  $m_{wet}$  and  $m_{dry}$  are the weights of the water-swollen and dry membrane sample, respectively.

$$W = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100 \% \quad (1)$$

## RESULTS AND DISCUSSION

The “silyl method” has been successfully applied for the preparation of PESs by nucleophilic displacement reaction in the melt from DFDPhS and trimethylsilylether derivatives of PhHQ and DFDPhS. The general chemical structure of the synthesized PESs is given in Fig. 1.



**Fig. 1** General structure of PESs prepared in this study. The ratio  $a/b$  was varied between 1:0 and 0:1 (see also Table 2).

In general, the silyl method has the advantage that the silylated bisphenols have a much lower melting point and/or boiling point than their non-silylated counterparts. Secondly, water and hydrohalic acid as reaction products are avoided, thus minimizing the risk of side reactions. Thirdly, the combination of silylation and distillation is an effective method for the purification of many monomers. Contrary to the standard nucleophilic displacement reaction in solution, polycondensation using the “silyl method” carried out in the melt has the advantage that only a very small amount of catalyst (e.g., cesium fluoride or potassium fluoride) is needed to run the reaction. The only by-product is the highly volatile trimethylsilyl fluoride, which distills off during the reaction. The disadvantage of this method is that only highly reactive fluoro compounds can be used as monomers hence limiting the number of available polymer structures. Moreover, reaction temperatures up to 300 °C are needed to keep the polymer in the molten state and to obtain polymers of high molecular weight (Table 2). For the reaction of *O,O'*-bis-TMS-PhHQ with DFDPhS, a temperature as low as 150–170 °C was sufficient to start the reaction, while for the reaction of *O,O'*-bis-TMS-DHDPhS with DFDPhS at least 200 °C were needed. From the reaction course the formation of a block-like structure of the polymer backbone might be deduced. However, no evidence for a block-like structure was found neither in the NMR spectra nor in the DSC traces.

### NMR spectroscopic characterization

The composition of copolymers was determined from  $^1\text{H}$  NMR spectra (Fig. 2). These show four well-separated groups of peaks appearing in the spectra at 8.1–7.7, 7.45–7.35, 7.35–7.1, and 7.05–6.95 ppm. The peak assignment to structural units in the polymer backbone is given in Fig. 2. The splitting of peaks “a” into four doublets is assigned to the relative position of the pendant phenyl ring to the diphenylsulfone unit. A detailed NMR spectroscopic characterization will be published in a forthcoming paper. For the calculation of the copolymer composition, the integral of the peaks a and a' was fixed to the value of the theoretical composition. The results are listed in Table 3. Except for samples PES-II and PES-III, the compositions determined from the NMR spectra coincide well with the theoretical values within the error margin of the method (10 %).

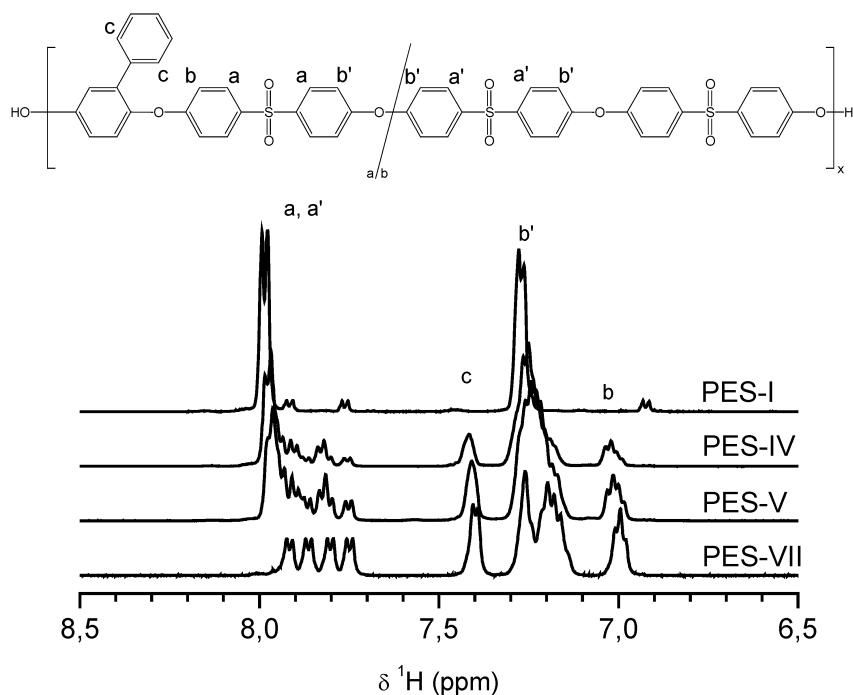


Fig. 2  $^1\text{H}$  NMR spectra of PES-I, PES-IV, PES-V, and PES-VII.

Table 3 Quantitative evaluation of NMR spectra.

| Sample  | Theoretical integral peaks a, a'* | Integral peak c |             | Total integral |             |
|---------|-----------------------------------|-----------------|-------------|----------------|-------------|
|         |                                   | Determined      | Theoretical | Determined     | Theoretical |
| PES-I   | 8                                 | 0               | 0           | 16             | 16          |
| PES-II  | 28                                | 2               | 2           | 59             | 64          |
| PES-III | 52                                | 4               | 6           | 111            | 128         |
| PES-IV  | 12                                | 2               | 2           | 31             | 32          |
| PES-V   | 44                                | 10              | 10          | 129            | 128         |
| PES-VI  | 20                                | 6               | 6           | 63             | 64          |
| PES-VII | 4                                 | 2               | 2           | 16             | 16          |

\*This integral has been taken as internal calibration for integration.

### Thermal properties

The nonsulfonated samples are amorphous polymers and show a single  $T_g$  in the DSC traces, ranging from 180–230 °C (2. heating trace). As expected, the  $T_g$  of the copolymers drops with increasing content of PhHQ moiety in the polymer backbone (Fig. 3). The physical mixture of PES-II and PES-III shows two distinct  $T_g$ s, demonstrating a phase separation between the two different polymers. As a result from the higher reactivity of PhHQ over 4,4'-DHDPHS, a block-like structure of the polymer was expected which should in the case of a phase-separated morphology lead to two  $T_g$ s in the DSC curves. The single  $T_g$  of the copolymers indicates the random incorporation of the different monomers into the polymer backbone or at least the formation of small miscible blocks.

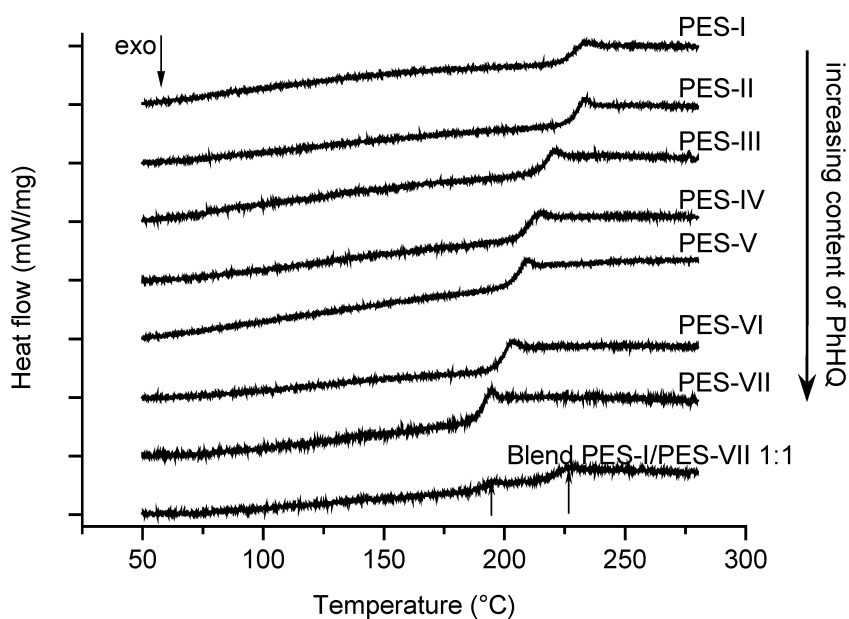
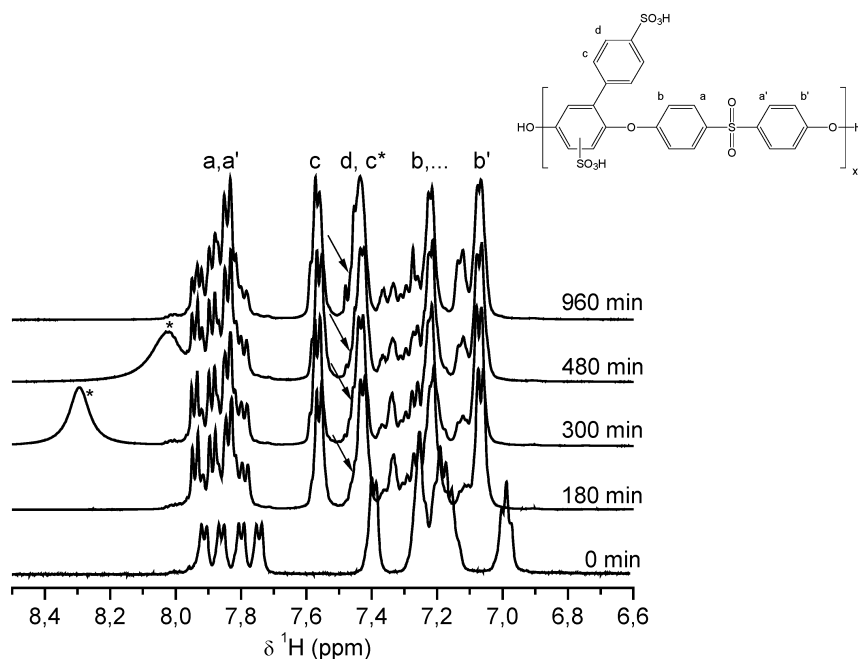


Fig. 3 DSC thermograms of nonsulfonated PES samples (2. heating trace).

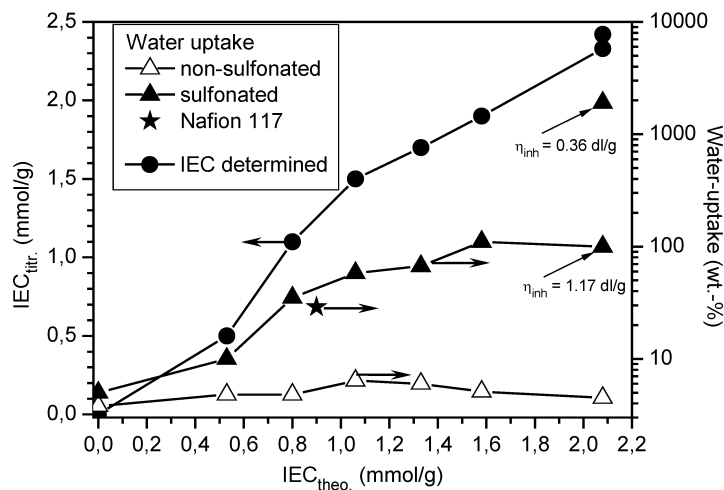
### Sulfonation

The sulfonation of the PES samples was performed by dissolving an appropriate amount of polymer in a large excess of conc. sulfuric acid (96–98 %) at room temperature. The progress of sulfonation with time was followed by  $^1\text{H}$  NMR spectroscopy (Fig. 4). For a PEEK derivative having PhHQ moieties in the polymer backbone it has been shown that only single sulfonation at the pendant phenyl ring occurs [62]. Contrary to the sulfonation of that PEEK derivative the NMR spectra of sulfonated PES indicate a double sulfonation of the phenyl hydroquinone moieties. After 3 h treatment time, ca. 80 % of the pendant phenyl rings were sulfonated, while the total degree of sulfonation was approximately 150 %. The sulfonation rate increases only slightly with time, resulting in a total degree of sulfonation of 180 % and a degree of sulfonation of the pendant phenyl ring of 90 % after 16 h reaction time.



**Fig. 4**  $^1\text{H}$  NMR spectra of PES-VII after different treatment times with conc. sulfuric acid. The arrows assign the signal from sulfonation of the polymer backbone;  $c^*$  = signal from nonsulfonated pendant phenyl ring, \* = water.

The nonsulfonated PES membranes showed a very low water uptake around 5 wt %, while the water uptake of the sulfonated samples increase with increase of the ion-exchange capacity (IEC) as depicted in Fig. 5. Membranes with an IEC up to 1.50 mmol/g had an acceptable water uptake of 50 wt %. The effect of the molecular weight on the membrane properties is clearly demonstrated for the sample with the highest IEC (PES-VII). The “low-molecular-weight” sample ( $\eta_{\text{inh}} = 0.36 \text{ dl/g}$ ) swells 10-fold higher than the “high-molecular-weight” sample ( $\eta_{\text{inh}} = 1.17 \text{ mmol/g}$ ).

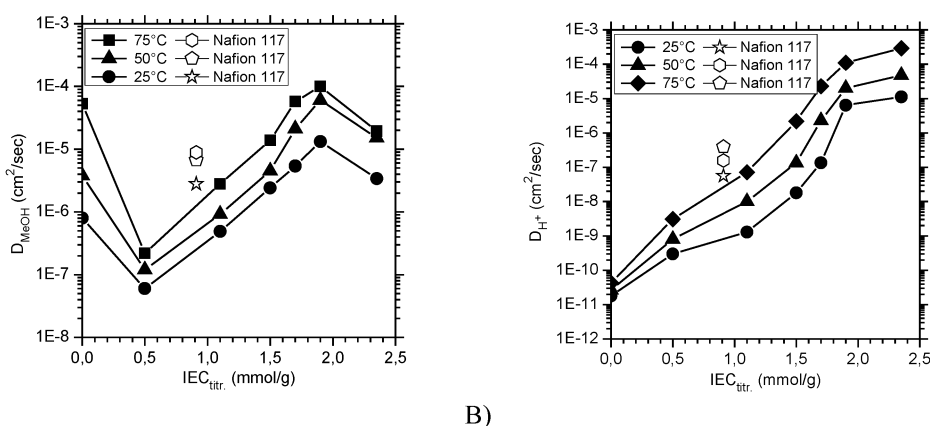


**Fig. 5** Water uptake of nonsulfonated ( $\Delta$ ) and sulfonated ( $\blacktriangle$ ) PES samples at 20 °C and determined IECs of sulfonated PES membranes ( $\bullet$ ).



## Transport properties

The diffusion coefficients for methanol and protons in sulfonated PES membranes together with the values for a Nafion membrane are displayed in Fig. 6. The procedures for the measurement and the calculation of the diffusion coefficients were adopted from the literature [63]. As expected, the diffusion coefficients are increasing with increasing IEC and increasing temperature, due to higher hydrophilicity and an enhanced swelling of the membranes (Fig. 5). Up to an IEC of 1.5 mmol/g, the methanol diffusion coefficient for the PES membranes is lower than or comparable to that for Nafion 117 (Fig. 6A). The differences in methanol diffusion between Nafion and PES samples diminish with increasing temperature due to a higher swelling of the PES samples. The decrease of methanol diffusion coefficient at an IEC of  $\sim 2.40$  mmol/g is related to the high molecular weight of the polymer sample, which has a tremendous effect on the swelling (Fig. 5A). On the other hand, IECs higher than 1.50 mmol/g are needed to achieve a proton diffusion comparable to that of Nafion (Fig. 6B).



**Fig. 6** Methanol (A) and proton (B) diffusion coefficients in sulfonated PES membranes at 25, 50, and 75 °C;  $c_{\text{MeOH}} = 10$  wt %;  $c_{\text{HCl}} = 0.5$  mol/l.

## CONCLUSION

This study describes the first step toward a solvent-free preparation of ion-exchange membranes for fuel cell applications. The silyl method has been successfully applied for the synthesis of high-molecular-weight PES from 2,5-bis-trimethylsiloxy-biphenyl, 4,4'-bis-trimethylsiloxy-diphenylsulfone and DFDPPhS. This special method avoids large amounts of solvent and catalysts during the synthesis step. Contrary to the findings from the sulfonation of similar PEEK, the post-sulfonation of PES samples with sulfuric acid leads to an undesired double sulfonation of the PhHQ moieties in the polymer backbone. Despite that over-sulfonation, samples with an IEC up to 1.50 mmol/g showed promising properties concerning future application, for example, as ion-exchange membranes in fuel cells.

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