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Sulfonated Aromatic Polymers for Fuel Cell Membranes

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Abstract Aromatic and heteroaromatic polymers are well known for their often excellent thermal and chemical stability as well as their good mechanical properties and high continuous service temperatures. Therefore, they have long been considered promising candidates for the development of proton-conducting membranes for fuel cells, especially for applications above 80 °C. Typically, sulfonic or phosphonic acid groups are introduced to provide acidic sites. While it is possible to introduce these groups by post-modification of the preformed polymers, the preferred method in many cases is modification of the monomers and subsequent polymer synthesis, because this allows better control of the number, distribution, and position of the acidic sites. Compared to perfluorosulfonic acid polymers, such as Nafion, proton-conducting membranes based on aromatic hydrocarbon polymers tend to exhibit excellent conductivities in the fully hydrated state and significantly reduced crossover, especially of methanol in DMFC applications. However, this often comes at the expense of a higher degree of swelling and a greater loss of conductivity with decreasing water content, which is considered a severe drawback e.g., for automotive applications. Recent approaches to improving the property profile of hydrocarbon membranes include block copolymers, rigid rod polymers, and the attachment of acidic groups via side chains.

Keywords Block copolymers · Hydrocarbon membranes · Proton exchange membranes · Sidechain functionalized polymers · Sulfonated poly(arylene ether)s · Sulfonated rigid rod polymers

1
Introduction

Aromatic polymers are generally considered to be well suited as a basis for polymer electrolyte membranes in Polymer Electrolyte Membrane Fuel Cell (PEMFC) or Direct Methanol Fuel Cell (DMFC). Many aromatic polymers are used for technical applications under very demanding conditions and, depending on the exact chemical structures, their property profiles can be adjusted to a wide range of requirements. Polyimides (PI), polyaramides (PA), polyamidimides (PAI), polyarylates (often liquid crystalline fully aromatic polyesters) (LCP), poly(arylene ether ketone)s (PAEK), poly(arylene ether sulfone)s (PAES), poly(ether imide)s (PEI), polycarbonates (PC), poly(phenylene oxide) (PPO), poly(phenylene sulphide) (PPS), and poly(benzimidazole) (PBI) are examples of engineering and high performance polymers which are being used commercially for technical applications. In addition to the commercially available materials, a huge variety of aromatic polymers with high thermal stability, including poly(*para*-phenylene) derivatives (PPP) and heteroaromatic polymers, such as poly(quinoline)s (PQ), poly(phenylquinoxaline)s (PPQ), poly(oxadiazole)s, poly(benzoxazole)s (PBO), and many others, has been prepared in many labs. Some of the most prominent properties, which many classes of aromatic polymers have in common, are high thermal stability, including high heat distortion temperature, high continuous service temperature, and/or high decomposition temperature, as well as excellent mechanical properties, including high elastic modulus and high tensile and impact strengths.

High decomposition temperature is often identified with high oxidative stability, and, in combination with good mechanical properties, this is considered a desirable starting point for the development of a proton conducting membrane. However, the conditions the membrane must endure in a fuel cell are quite different from the conditions for which these polymers were originally intended. In addition to oxidizing conditions at the cathode, the membrane is also exposed to reducing conditions at the anode, both in the presence of active catalysts, and aqueous acidic hydrolyzing conditions, in a situation where the membrane is swollen in water or methanol/water mixtures. As a proton conductor, the polymer is substituted with acidic groups, and – with very few exceptions – proton transport requires considerable amounts of water to be present within the membrane. The acidic groups ensure swelling of the polymer membrane in water, and at the same time they provide a high number of charge carriers (protons) within the membrane by dissociation. In contrast, engineering or high performance polymers swell very little in water, often significantly less than 1%. Thermal stabilities are typically studied in dry air, and under such conditions where decomposition temperatures as high as 600 °C can be found, e.g., for polyimides or certain heteroaromatic polymers such as polyquinolines. However, these stabilities do not appear to translate into similar stabilities under wet conditions. Figure 1 shows decomposition temperatures of selected polymers in dry air compared with those determined in the presence of water vapor [1].

Two observations are obvious from the graphs in Fig. 1: first, the decomposition temperatures in dry atmosphere are much higher than those under wet conditions; second, they also vary much more under dry conditions than under wet conditions. Consequently, the potential stability of a polymer under fuel cell conditions can probably not be judged with sufficient confidence from studies of the dry polymer.

Besides thermal stability, the introduction of acidic groups into the parent polymer structure dramatically changes the chemical and physical properties. Absorption of water in PEMFC applications or water methanol mixtures in DMFC applications was mentioned already: it is undesired and very small in most engineering plastics and high performance polymers, but it is essential and can amount to several hundred percent in proton conduct-

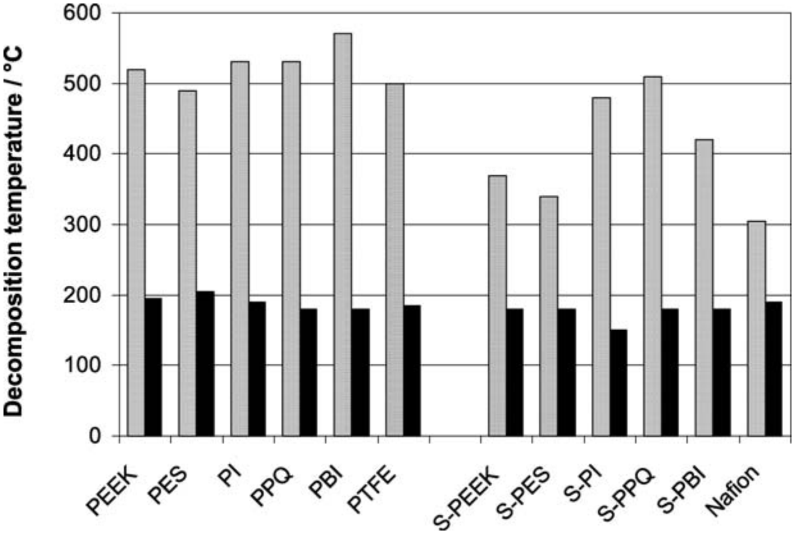


Fig. 1 Decomposition temperature (defined as 5% weight loss) of various sulfonated and non-sulfonated polymers in Helium (*cross hatched columns*) and saturated water vapor (*closed columns*); data from [1]

ing membranes. Also, crystallinity can be reduced partially or completely by sulfonation, resulting in dramatic changes of mechanical properties and loss of stability against solvents. Depending on the number of acidic groups per polymer chain, the polymers can even become soluble in water, water methanol mixtures, or other polar solvents. While this is partly desirable, because some polymers such as poly(arylether ketone)s (e.g., PEEK) would otherwise be difficult to process into membranes, it needs to be controlled in order not to loose the mechanical integrity of the membranes. It is also immediately clear that any polymer which is swollen to a significant extent in a solvent (e.g., water) is more prone to chemical attack than if it were present as a bulk injection molded article.

Besides hydrolysis, degradation by free radicals is a concern in fuel cell applications. These issues must be considered when selecting suitable polymer structures for membrane materials. Ideally, during operation of a PEMFC, no free radicals should be present. In reality, however, there are several possibilities for the formation of radicals. The membrane is never completely impermeable for oxidant (oxygen) and fuel (hydrogen, methanol). Thus, there is always the possibility of the presence of a small amount of oxygen at the anode, and hydrogen or methanol at the cathode. Direct reaction could proceed through one-electron processes, involving free radical intermediates, such as hydroxyl or hydroperoxy radicals, which could then attack the membrane polymer. Crossover of oxidant and fuel through the membrane also results in non-zero concentration of both within the membrane, resulting in the possibility of direct reaction and again formation of free radicals throughout the membrane. An interesting paper on this subject was published recently by a group of Chinese researchers [2]. In order to identify the origin of the radicals which decompose the membrane, the following set of experiments was performed: the polarization curve of a fuel cell with a sulfonated polystyrene membrane was followed over time, while it was run continuously with hydrogen/oxygen at 80 °C, and fully humidified at a current density of 1 A/cm^2. Degradation was very strong after 228 h, as shown by a decrease of the cell voltage at 300 mA/cm^2 from over 700 mV to approximately 150 mV. After disassembly of the cell, the membrane thickness was found to have decreased from 160 μm to 137 μm. The analysis of the sulphur content along a cross-section of the membrane by energy dispersive X-Ray analysis (EDAX) showed a homogeneous distribution in a virgin membrane, while, after the fuel cell test, the sulphur content was strongly reduced at the cathode side of the membrane. In addition, the infrared (IR) spectroscopy showed a loss of aromatic groups. The authors concluded that the degradation begins at the cathode side and then progresses inwards, consuming the polymer. In order to prove this, another membrane was prepared from sulfonated polystyrene coated with recast Nafion® on the cathode side. A fuel cell experiment with this membrane performed under the same conditions as before did not show any indications of degradation for 240 hours. This allows several conclusions:

Firstly (and obviously), the degradation does indeed start at the cathode, probably by the formation of free radicals by imperfect reaction at the catalyst. Secondly, formation of radicals at the anode or within the membrane is very low or absent. This is quite interesting, since in the steady state of operation, the concentration of fuel which permeates from the anode through the membrane to the cathode should exhibit a linear profile, with the lowest concentration at the cathode. If the degradation does start at the cathode side of the membrane despite the low concentration of fuel there, it is likely that the catalyst is in some way involved in the formation of the undesired radicals, as assumed by the authors of the paper discussed above [2]. Consequently, improving the performance of the catalyst for the cathode reaction may also reduce the formation of radicals, possibly resulting in significantly enhanced membrane lifetimes. Thirdly, radicals which are formed at the cathode do not diffuse quickly throughout the membrane, at least not on the time scale of a few hundred hours. Otherwise, degradation would not be located at one side of the membrane, and it would not be possible to prevent it by simply coating this side with a non-degrading polymer. It is clear that these considerations deserve more investigation, since, if the observations can be confirmed and generalized, they could point to ways to significantly improve the lifetime of non-fluorinated membranes.

Long-term stability is a major concern, but there is also a long list of other properties which are required for successful use of a membrane electrolyte in a fuel cell. Depending on the intended use of the fuel cell, the importance of the various properties changes. For instance, the use in automotive applications requires very high performance at low catalyst loading (for cost), no loss of performance at reduced or even absent humidification, and a lifetime above 5000 h under quickly and constantly changing power levels, including many start-stop cycles, even under freezing conditions. Operation at elevated temperatures, i.e., in the range of 110–130 °C, has been cited as important as well, but may not be the immediate focus of the automakers anymore [3] because of other problems associated with high temperature operation, which do not originate from the membrane. Also, while the current price of commercially available membranes, such as Nafion®, is prohibitive for use in automobiles, projections by General Motors (GM), based partly on data from DuPont, indicate that, at amounts required once a significant number of automobiles is built with fuel cells as power source, it is likely that the price target can be met [3]. Thus, the present high cost of perfluorinated proton conducting materials is not necessarily a fundamental problem that needs to be solved by science, but rather an economical issue. Potential low cost or operation at high temperatures alone should not be a sufficient justification for membrane work. For successful alternative membrane materials, proton conductivity (fully humidified as well as under dry conditions) must not be less than that of Nafion®, and water absorption must not be higher than that of Nafion®.

The situation is different when the use in DMFC is concerned. Here, one of the main issues is low methanol crossover, and, related to this, low swelling of the membrane in methanol/water mixtures. In this field, membranes based on aromatic polymers have an advantage over Nafion® due to their generally low methanol crossover rate. In addition, the chemical structure of hydrocarbon polymers can be adjusted relatively easily (at least in the lab), allowing for optimization of swelling in methanol/water mixtures. Humidification, operation under dry conditions, and freezing are not as much of a problem, since methanol/water mixtures can be used as fuel. If the intended use is for portable electronic devices, cost per kW power is less critical (compare your laptop battery: it delivers probably approximately 20 W for 3 h at a price of 150 \$, amounting to 7500 \$/kW). The system complexity and, hence, the size are much more of a problem.

The third application for fuel cells, which is often suggested in the literature, are small power plants for decentralized generation of electrical power and heat. Such systems would likely be operating continuously, under constant conditions. Size and weight are not the most important concerns, but cost is important. For the membrane, the positive side is probably operation under constant conditions. However, the demands for lifetime are probably extreme, amounting to much more than 10 000 h and up to 50 000 h.

2

Aromatic Polymers for Proton Conducting Membranes

Considering all this, almost all classes of high performance polymers have been used as basis for the development of proton conducting polymers for fuel cell applications. Figure 2 shows an overview of the structures.

The most common approach for the synthesis is sulfonation of a preformed, often commercially available, polymer. Sulfonic acid groups are selected as the source of protons for three simple reasons: they are easy to introduce into aromatic rings; they dissociate more readily than typical carboxylic acids, resulting in a larger number of charge carriers; and, unlike phosphonic acids, they do not easily form anhydrides on dehydration, resulting in easy and quick rehydration of sulfonated polymers in contrast to phosphonated ones.

Synthesis of the polymers by post-sulfonation is straightforward whenever there are electron-rich phenyl rings present in the polymer backbone or in side chains. This is, for example, the case in many poly(arylene ether ketone)s and poly(arylene ether sulfone)s, poly(phenylene oxide), poly(phenylene sulphide), certain poly(*para*phenylene)s, poly(phenylquinoxaline)s, and others. However, the exact chemical structure, such as the exact level of activation or deactivation of the aromatic groups, or the presence of acid labile groups, as well as the solubility of the starting material and the end product, deter-

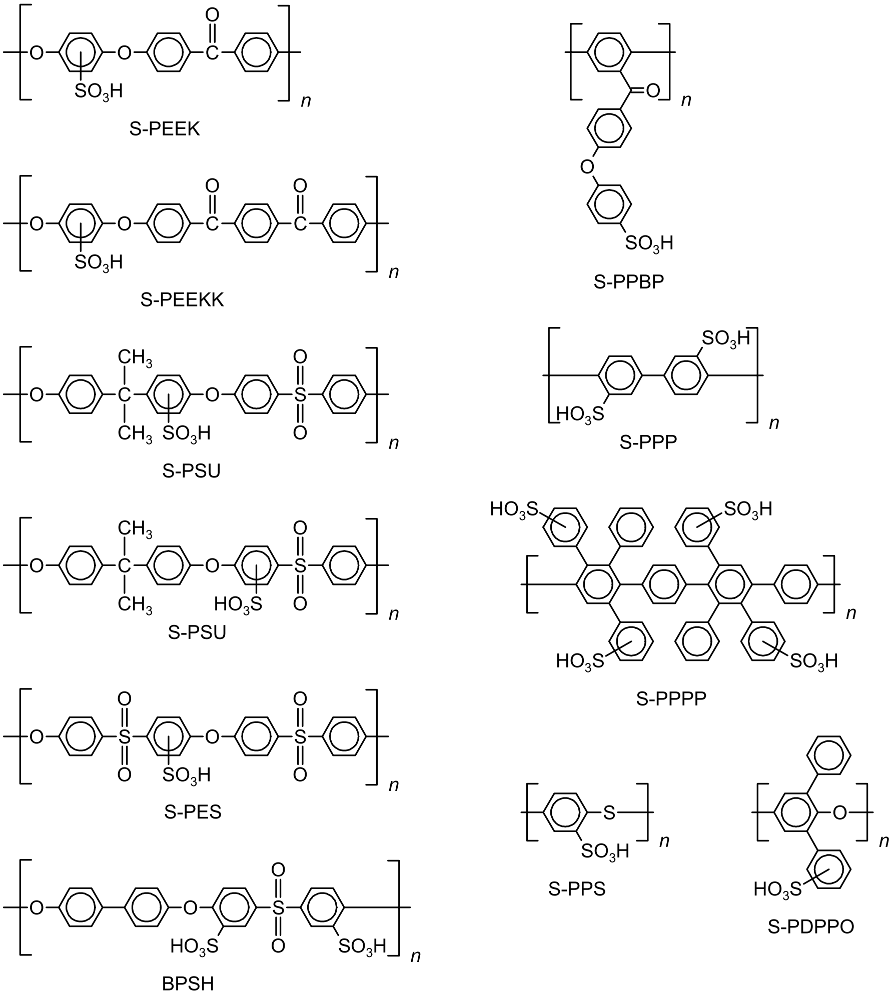


Fig. 2 Chemical structures of proton-conducting aromatic polymers

mine the type of sulfonating agent which is required, and to some degree also the extent of sulfonation. Concentrated sulphuric acid, oleum (SO_3 dissolved in sulphuric acid), and chlorosulfonic acid are the most commonly used reagents. In ideal cases, reaction time and temperature allow to control the degree of sulfonation. Aromatic polyethers, such as PEEK, are examples for this kind of behavior, a general representation of which is shown in Fig. 3. The plot in Fig. 3 is based on data from various authors summarized in [1].

Sometimes, when the aromatic groups of the polymer are too activated, simple post sulfonation can lead to crosslinking. The arylsulfonic acid groups formed by sulfonation are then able to act as sulfonating agent themselves,

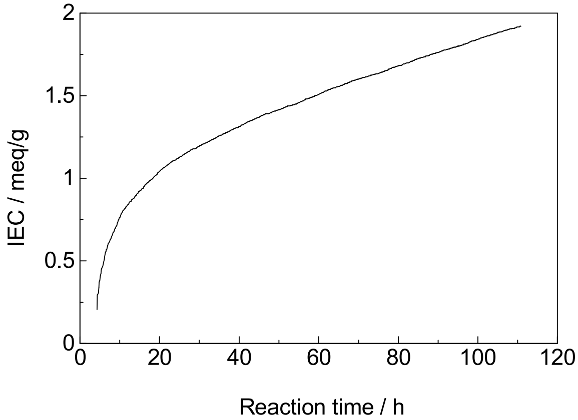


Fig. 3 Degree of sulfonation of PEEK in dependence of time. Sulfonation by concentrated sulphuric acid at room temperature (curve taken from [1])

and some of them can form sulfone bridges between different polymer chains. Thus, very activated polymers can be sulfonated only to relatively low degrees of sulfonation before crosslinking begins. Higher sulfonation of these polymers requires alternate routes which proceed via less activated systems. One example is the sulfonation of poly(phenylene sulphide) via the sulfonium salt, which sufficiently deactivates some of the phenyl rings to allow sulfonation of the others without crosslinking (see section 3.7).

Another example is the sulfonation of poly(ether sulfone)s via lithium organic intermediates, which creates special sites for sulfonation [4, 5]. Although this latter technique was developed for a different reason, it offers the possibility to create sites that are active for sulfonation but not for crosslinking (Fig. 4).

Sulfonation of preformed polymers will always lead to sulfonation of the most activated sites, typically in electron-rich phenyl rings which are substituted by ether or thioether groups. Carbonyl or sulfone groups, fluorinated groups, and some heteroaromatic groups (six-membered rings with one or more heteroatoms, or five-membered rings with two or more heteroatoms) typically deactivate. Unfortunately, sulfonation is reversible. Under acidic conditions, especially at higher temperatures, sulfonic acid groups are lost from activated sites. Therefore, long-term stability of several thousand hours of operation requires sulfonation in less activated, preferably deactivated sites. In principle, this is possible with the common sulfonating agents. However, it requires more drastic conditions (e.g., oleum at temperatures above 150 °C), which can often not be tolerated by the polymer chains. If electron-rich and electron-poor phenyl rings are present in the same polymer, as in poly(arylene ether sulfone)s and poly(arylene ether ketone)s, sulfonation of

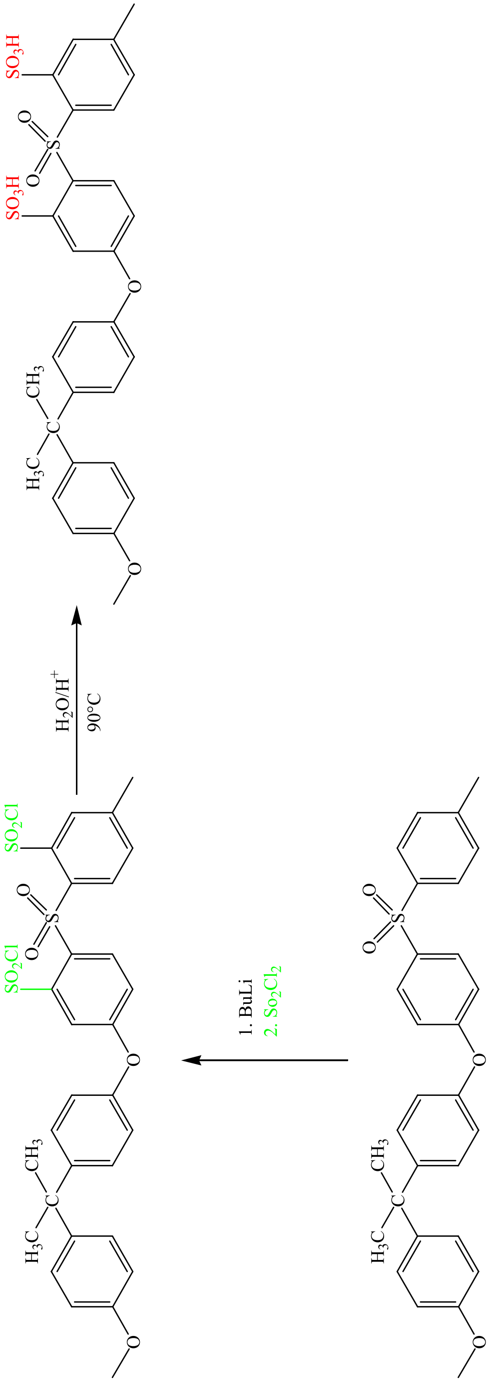


Fig. 4 Sulfonation via lithiation [4, 5]

the deactivated ketone or sulfone sites requires conditions which lead to partial degradation of the polymer chain.

There are two approaches to introduce sulfonic acid groups in deactivated positions. One was developed by Kerres [4, 5] and is the one shown in Fig. 4. It proceeds via organometal intermediates, because these groups are more easily introduced into the electron-poor sites than into electron-rich ones. An exchange of the metal for sulfonic acid groups then introduces sulfonation in those electron-poor sites that were originally occupied by metal atoms.

The other approach is to move the sulfonation step from the polymer stage to the monomer stage. Its most prominent disadvantage is obvious: if the sulfonation is to be achieved at the monomer stage, no preformed commercially available polymers can be used. Rather, the polymer must be synthesized using sulfonated monomer(s). While synthesis of the aromatic polymers shown in Fig. 3 is well established, sulfonation of the monomers often changes the properties. Solubilities, tolerance of the sulfonic acid (or salt) groups towards polymerization conditions, and/or tolerance of any catalysts towards the sulfonic acid or salt groups must be considered. Despite the difficulties this can cause sometimes, this route is very attractive, since it allows more control over position and degree of sulfonation than post-sulfonation of preformed polymers. For example, it has been used very successfully for the synthesis of poly(arylene ether)s and poly(*para*-phenylene)s.

The following chapters give an overview of the most recent developments in the field of aromatic proton conducting membranes. Additional information, especially on previous literature, can be found in a number of preceding reviews [1, 6–12].

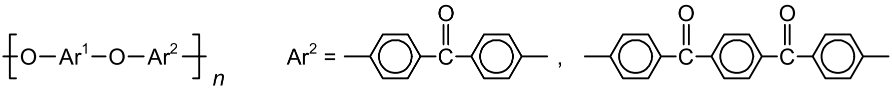
3

Poly(Arylene Ether Ketone)s

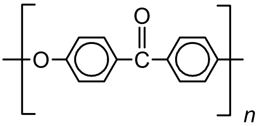
3.1

General

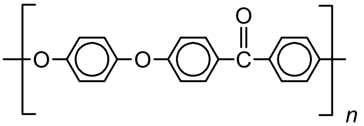
Poly(arylene ether ketone)s are polymers which consist of aromatic units, joined together by ether and ketone groups. All aromatic groups, e.g., 1,4-phenylene, 1,3-phenylene, 1,2-phenylene, biphenylene, naphthylene, heteroaromatic rings, polycyclic ring systems, can be included, and actually have been included at least in laboratory samples. In addition to ether and ketone groups, other linking groups are also possible, e.g., alkylene, perfluoroalkylene, thioether, cyclic groups, etc. Until about ten years ago, there was quite a selection of different commercially available poly(aryl ether ketone)s. All of them consisted exclusively of 1,4-phenylene rings, joined by ether and ketone groups. Figure 5 shows examples of the structures.



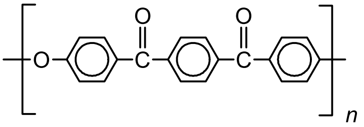
General structure



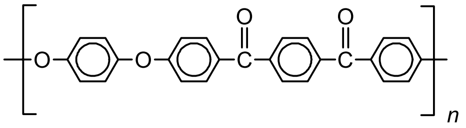
PEK; e.g. Victrex PEEK P22 (Victrex); Stilan (Raychem)



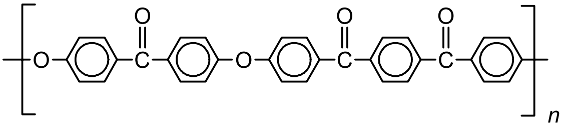
PEEK; e.g. Victrex PEEK (Victrex), Gatone PEEK (Gharda), Kadel (Solvay), CoorsTek PEEK (CoorsTek), Ketron (Quadrant)



PEKK; e.g. CoorsTek PEKK (CoorsTek)



PEEKK; e.g. Hostatec (Hoechst)



PEKEKK; e.g. Ultrapek (BASF)

Fig. 5 Examples of structures of poly(aryl ether ketone)s which are or were commercially available. Ar^1 is typically a *para*-substituted bisphenol, but can in principle be any aromatic system. Many more structures have been prepared in the lab, e.g., PEEEK, PEEKEK, etc.

All commercially available poly(arylene ether ketone)s follow the same scheme of composition as those shown above. They are semicrystalline, and since the only difference between these structures is the sequence of ether and ketone groups, they are often not only miscible, but some of them also cocrystallize. The crystallinity of the poly(arylene ether ketone)s is their most important feature, since it determines their physical properties, especially the high melting temperature (around 330–400 °C) and resulting high heat distortion temperature and high continuous service temperature, the excellent chemical stability and ESC-resistance, and the superior mechanical properties. Within the subgroup of poly(aryl ether ketone)s which follow the structural principles shown in Fig. 5, an unofficial but widely used nomenclature has been established. It assumes that all aromatic units in the polymer chain are 1,4-phenylene groups, and that there are no substituents. Then, the ether and ketone groups are simply listed in their order of appearance along the polymer chain, as indicated in Fig. 5, for example, "poly(ether ether ketone) (PEEK)" or "poly(ether ketone) (PEK)". This does not work with biphenyl, 1,3-phenylene, and heteroaromatic groups present.

Presently, however, only three types of poly(arylether ketone)s are still produced commercially: PEEK, PEK, and PEKK. Most work for proton conducting membranes has been done based on PEEK, but the others have been used as well [1, 6, 7, 13–32].

Sulfonated PEEK (S-PEEK) becomes water soluble above an ion exchange capacity of 1.8 mmol/g [1], corresponding to a degree of sulfonation of approximately 60% (60% of all repeating units have one sulfonic acid group). For application in fuel cell systems, especially those which are intended for intermittent use with start-stop cycles and varying load, the water level in the membrane will vary. Strong changes in swelling under changing humidity levels would result in strongly varying stress within the cell (or rather stack of cells) and may damage the membrane electrode assembly, e.g., by compressing the gas diffusion layer and/or delamination of membrane and catalyst layer. Therefore, swelling of the membrane in water must be relatively low (preferably not more than that of Nafion®: 16% at 80 °C and 100% r.h. by weight, 32% by volume). Consequently, a membrane based on S-PEEK would have to have an IEC considerably lower than 1.8 mmol/g in order to avoid excessive swelling. However, this results in relatively low proton conductivity even in the fully hydrated state. Figure 6 shows a comparison of the conductivites of Nafion® 117 and S-PEEK with an IEC of 1.6 mmol/g at 100 °C in dependence of the relative humidity. Even at 100% relative humidity, the conductivity of the S-PEEK membrane is lower than that of Nafion® 117 by a factor of 5. Pre-treatment of the membrane at higher temperatures in water or sulphuric acid can decrease this difference to a factor of about 2. As the humidity is reduced, the gap increases, since the conductivity of the S-PEEK drops much faster than that of Nafion® (Fig. 6).

Water uptake was studied by Kreuer [7, 31] and compared to Nafion®. For an interpretation of these data, one needs to consider that the sulfonic acids involved are strong acids, which will dissociate when possible. This requires a certain amount of water, depending on the degree to which the ions after

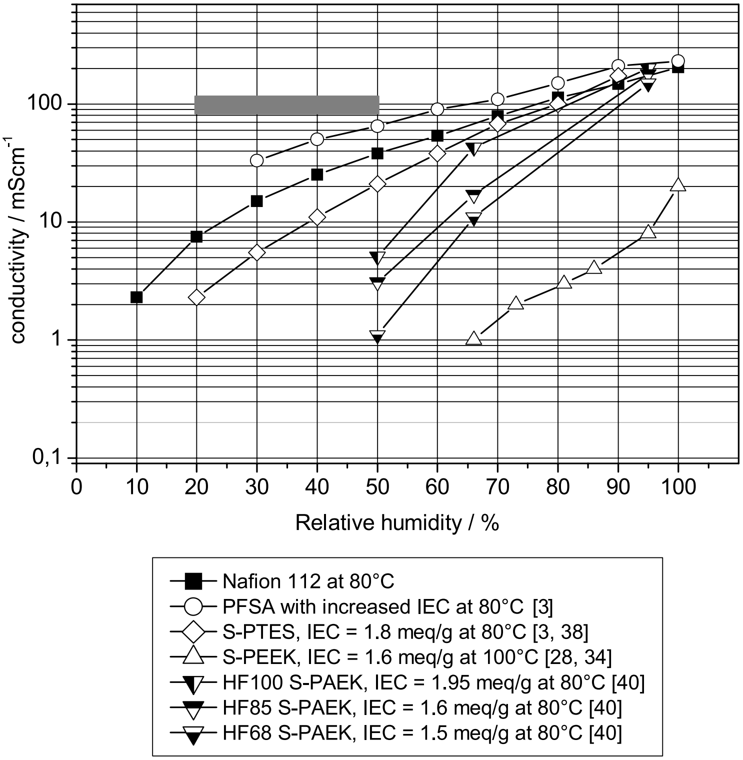


Fig. 6 Humidity dependence of the conductivities of Nafion® and aromatic hydrocarbon membranes [3, 28, 34, 38, 40]

dissociation need to be hydrated for stabilization, or, in other words, the acid strength. Thus, water in the membrane has different "functions", resulting in different "states" of water: water required for the primary hydration of the dissociated acid, loosely bound water, and "bulk" water as a second phase [7, 24]. In order to correct for different degrees of sulfonation, the ratio λ of moles of water per mole of sulfonic acid groups is introduced. A plot of λ versus temperature for S-PEEKK of different IEC and Nafion® 117 is shown in Fig. 7.

Nafion® 117 in liquid water takes up more water per sulfonic acid group than S-PEEKK of IEC values between 0.78 mmol/g and 1.78 mmol/g up to a certain temperature, which depends on the IEC value of the S-PEEKK. At this temperature, which is 65 °C for IEC = 1.78 mmol/g, 80 °C for IEC = 1.4 mmol/g, 100 °C for IEC = 0.78 mmol/g, the water content of the S-PEEKK membranes increases tremendously. Nafion® shows similar behavior only at a temperature of 140 °C. Until this temperature is reached, its molar water content is almost constant at $\lambda = 20$. The excess swelling of S-PEEKK at temperatures of 100 °C or less causes severe problems in using these materials as membranes in fuel cells.

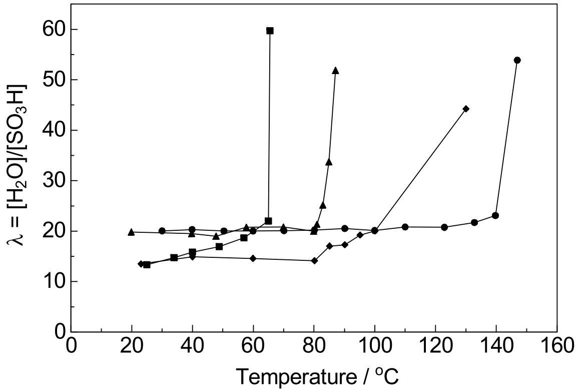


Fig. 7 Molar water uptake of different polymers vs. temperature [7,24], ● Nafion, ■ S-PEEKK (IEC = 0.78 mmol/g), ▲ S-PEEKK (IEC = 1.4 mmol/g), ◆ S-PEEKK (IEC = 1.78 mmol/g)

Since the densities of Nafion® and S-PEEKK are different, data should be compared based on volume (mmol/mL) rather than weight (mmol/g). Table 1 compares values of λ with weight-based and volume-based water uptakes for Nafion® and S-PEEKK.

A value of $\lambda = 10$ for Nafion® 117 shows that Nafion® takes up only 16% (w/w) of water at room temperature, corresponding to an estimated volume increase of 32% (w/v). This remains constant up to more than 120 °C (Fig. 7). In comparison, S-PEEKK with an IEC = 1.78 mmol/g takes up 32% (w/w) of water based on weight, corresponding to an estimated volume increase of 43% (w/v) at $\lambda = 10$. This increases to $\lambda = 20$ (64% water uptake based on weight, 86% volume increase) at 65 °C, and shoots up to $\lambda = 60$ (192% water uptake based on weight, 260% volume increase) at 70 °C (Fig. 7). This difference in swelling behavior has been attributed to the lower hy-

Table 1 Water uptake for Nafion® and S-PEEKK at room temperature[a]

		Nafion® 117	S-PEEKK		
IEC mmol/g		0.89	0.78	1.4	1.78
IEC mmol/mL		1.75	1.05	1.88	2.39
Density g/mL		1.97	1.34	1.34	1.34
Water uptake %	$\lambda = 10$	16	14	25	32
per weight	$\lambda = 20$	32	28	50	64
Water uptake %	$\lambda = 10$	32	19	34	43
per volume	$\lambda = 20$	64	38	68	86

[a] Data based on DuPont Product Information (Nafion®) and [7,31] (S-PEEKK)

drophobicity of the PEEKK polymer chains as compared to the perfluorinated chains of Nafion®, and the resulting less strict microphase separation into hydrophilic aqueous domains dispersed in a hydrophobic continuous phase of sulfonated poly(aryl ether ketone)s in contrast to sulfonated perfluoropolymers [7].

S-PEEKK with a degree of sulfonation of 70% (IEC = 1.69 mmol/g) [31] and S-PEEK with a degree of sulfonation of 65% (IEC = 2.13 mmol/g) [33] can supposedly match or even surpass the conductivity of Nafion® at 80 °C in the fully hydrated state. In another source [26], however, the conductivity of S-PEEK with 65% sulfonation is reported to be about a factor of 10 lower than that of Nafion® [6, 26]. A S-PEEK with a degree of sulfonation of 88% (IEC = 2.48 mmol/g) is reported to show a conductivity which is lower than that of Nafion® by a factor of approximately 3 at 100 °C and 85% r.h., but does meet or beat that of Nafion® at 160 °C and 75% r.h. [28, 34]. However, the water uptake of this polymer is so high that no conductivities could be measured above 90% relative humidity. Yet another source claims a conductivity of 400 mS/cm at 80 °C and 90% r.h. for a S-PEEK with 85% sulfonation [6]. At a degree of sulfonation of 11% (IEC = 1.6 mmol/g), S-PEEK was reported to have a conductivity up to 45 mS/cm at 20 °C in the fully hydrated state, depending on pre-treatment conditions. In another study, a sulfonated poly(ether ketone) (S-PEK) with an IEC = 1.71 mmol/g was found to have a conductivity of 100 mS/cm at 90 °C and full hydration, while Nafion® 112 was measured at 88 mS/cm in the same study. Variations in post-treatment of the same membrane can also lead to large differences in conductivity and water uptake [35]. Apparently, conductivity data vary strongly, even under presumably similar conditions. Thus, data can only be compared safely within a study, while a comparison between studies may lead to misinterpretations. As shown above, the values of conductivity reported for S-PEEK under similar conditions can vary by up to three orders of magnitude. Rozière and Jones [1] attribute this to the solvent used for casting, with large differences found between those data reported by authors casting from NMP [28, 31, 34] and those casting from DMF or DMAc [26, 29]. The effect was studied by Kaliaguine et al. [36]. It is related to the stability of the solvents. DMF and DMAc may decompose, producing dimethylamide, which then may be protonated, resulting in dimethylammonium counter ions for the sulfonic acid groups. This is likely to change the solubility characteristics significantly, which can change the transport properties of the membranes, even if the ammonium ions are afterwards exchanged for protons. A strong influence of the casting conditions on transport characteristics has also been frequently found in gas separation membranes, where the distribution of free volume and the relaxation of the polymer chains plays a role for transport properties. A look at the thermodynamics [37] of the interaction between polymer and solvent and the resulting implications for film formation by solvent casting with subsequent drying shows that solvent, starting concentration, and temperature profile cannot be chosen at random. Under unfavourable conditions, phase separation may occur, resulting in films with so much internal stress that they do not even have good mechanical properties. Swelling properties and even transport properties may be affected as well if polymer chains are not relaxed within the film. The same polymer, cast under different conditions or from a different solvent, may exhibit excellent properties. However, such influences should be transient (aging is often observed for gas separation membranes). Therefore, it should be possible to find pre-treatment conditions for proton conducting membranes which eliminate all influences of history.

Nevertheless, simple sulfonated poly(aryl ether ketone)s do not appear to be a challenge for the commercially available perfluorosulfonic acid polymers when swelling behavior at desired operating temperatures is considered besides conductivity. Swelling is important for technical applications, e.g., in fuel cell powered cars. Based on considerations concerning stack design, swelling of the membrane in the presence of liquid water at the operating temperature (80–100 °C) must probably be less than 100% by volume [3]. Considerations such as internal pressure and the resulting requirements of strength of the stack components, potential damage to the gas diffusion media by swelling membranes, and fatigue issues due to swelling-deswelling cycles during the typical operation cycles of a car seem to indicate an expected limit in this range. At the same time, the need to reduce system complexity leads to the desire to operate the fuel cell without external humidification. Therefore, the conductivity of the membrane is ideally no less than 100 mS/cm at humidities between 20% r.h. and liquid water [3]. So far, no membrane can satisfy these requirements. Unfortunately, for many materials the humidity dependence of the conductivity is not reported in the literature. Some exceptions are shown in Fig. 6.

It can be seen that with decreasing humidity the proton conductivity drops much more dramatically for S-PEEK than for Nafion®. Figure 7 also shows data for a sulfonated poly(thioether sulfone) S-PTES [3, 38] (see Fig. 8 for the chemical structure), which exhibits much higher conductivities than the S-PEEK. Its conductivity even surpasses that of Nafion® 112 at humidities above 85%, but then drops off more steeply with decreasing humidity. However, it should be noted that the S-PTES shown here with an IEC of 1.8 mmol/g dissolves in boiling water within two hours [3] and is therefore not suitable for operation in a fuel cell under conditions with strongly varying load, where liquid water at high temperatures can be present. Still, this comparison shows

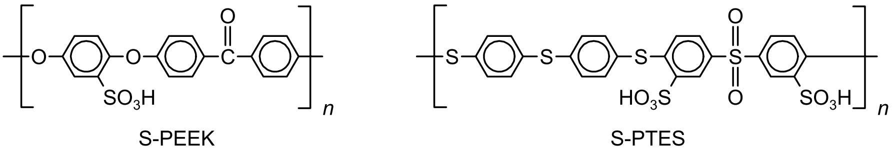


Fig. 8 Chemical structures of S-PEEK and S-PTES

that the chemical structure of polymer chains has a strong effect on proton conductivity. One obvious difference between the S-PEEK and the S-PTES is the position of the sulfonic acid groups (Fig. 8).

The S-PEEK of this example was prepared by sulfonation of PEEK (post-sulfonation) [28, 34]. Its sulfonic acid groups are therefore attached to the most electron-rich phenyl rings of the polymer chain: those between the ether groups. Apart from the fact that the sulfonic acid groups are somewhat labile in this position, their position on electron-rich phenyl rings also reduces their acidity because sulfonation is reversible under certain conditions. In contrast, the sulfonic acid groups of the S-PTES were introduced into the monomer dichlorodiphenylsulfone before polymerization [38]. They are in the less electron-rich phenyl rings attached to sulfone groups, and hence they are more acidic than those of the post-sulfonated S-PEEK. Molecular modelling [39] indicates that the acidity governs the number of water molecules required for an acid group to dissociate and release a proton (as a hydrated $H_3O^{\oplus}$ ion). This is one of the reasons cited for the high conductivity of Nafion® and other perfluorosulfonic acid polymers in comparison with hydrocarbon polymers: perfluoroalkyl sulfonic acids are more acidic than aromatic sulfonic acids. This can be observed in a plot of conductivity versus water content (Fig. 9a).

While at a water uptake of 30% (corresponding to a relative humidity of 85%) the conductivity of S-PTES meets that of Nafion® 112, it is only half of that of Nafion® at smaller water contents (lower relative humidity). Unfortunately, similar data are often not available for other polymers described in the literature to compare and confirm any interpretation for different chemical structures. Some data are available, although these were not obtained in the same way. (The data shown in Fig. 9a) were obtained by determination of the water uptake of a film when exposed to an atmosphere with controlled moisture content at 80 °C and measurement of the conductivity under the same conditions. The data shown in Fig. 9b), taken from the literature for various sulfonated hydrocarbon polymers, were obtained by swelling the polymer films in water (varying times and temperatures, unfortunately) and measuring the conductivity in water (varying temperatures, unfortunately). Nevertheless, it would be really interesting to have data which are really comparable for many different polymer systems, because the information from the plots in Fig. 9 could be interpreted as an "efficiency" with which the polymer can "use" the water present in the film to transport protons, i.e., how much water is required for a desired conductivity in different systems? For technical applications, there is a maximum degree of swelling of the membrane which can be tolerated. From plots as in Fig. 9 one could conclude which polymer system will offer the highest conductivity under this limitation.

Other modifications of the chemical structure of the repeating units of poly(aryl ether ketone)s also show potential for significant improvement. For example, the introduction of fluorinated aromatic rings and bulky groups re-

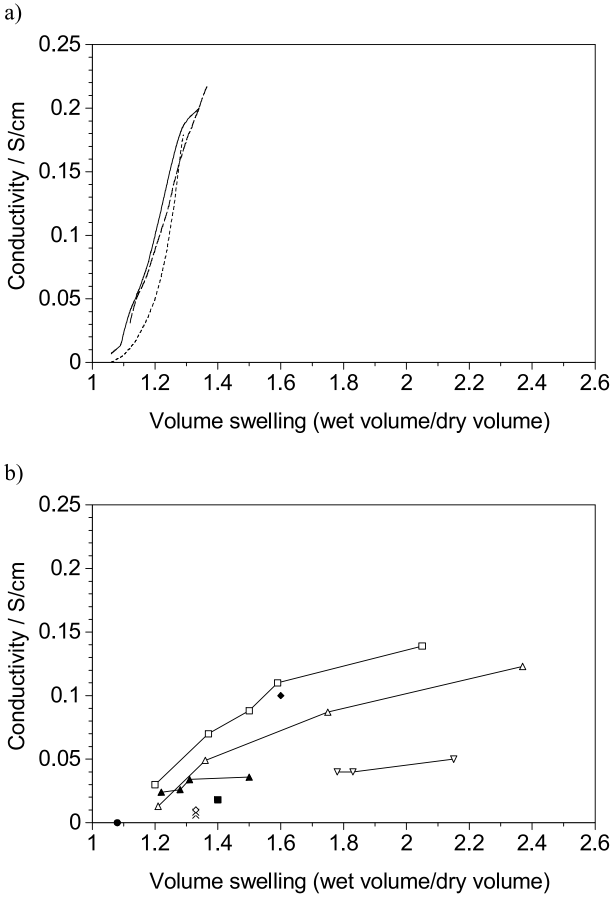


Fig. 9 Conductivity in dependence of water content. **a** – – – Nafion® 112, — a modified poly(perfluoro sulfonic acid), and - - - S-PTES [3]; **b** various hydrocarbon polymers: -◆- sulfonated poly(phosphazene) [1, 192], -◇- benzylsulfonated PBI (80% sulfonation) [1], -□- BPSH [166], -■- sulfonated polyimide blockcopolymer [61, 64], -●- S-PEEK (65% sulfonation) [6]; sulfonated poly(*para*-phenylene)s: -x- sulfonated poly(2-(4′-phenoxy)benzoyl-1,4-phenylene (65% sulfonation) [6], -▽- sulfonated poly(2-benzoyl-1,4-phenylene) (IEC/mmol/g = 2.6; 2.8; 4.0) [79], -▲- sulfonated poly(2-(4′-phenyl)benzoyl-1,4-phenylene) blockcopolymers (IEC/mmol/g = 0.7; 0.75; 0.94; 1.2) [78], -△- sulfonated phenylated poly(*para*-phenylene) (IEC/mmol/g = 0.98; 1.4; 1.8; 2.2) [77]

sults in membranes with much higher conductivity at reduced humidity [40] than conventional sulfonated PEEK or PEEKK (Figs. 6, 10).

The degree of sulfonation was varied by incorporation of varying amounts of 6F-bisphenol instead of 9,9-bis(4′-hydroxyphenyl)fluorene, and sulfonation under conditions where only the fluorene units were sulfonated, not the 6F-bisphenol units. HF100 S-PAEK contains no 6F-bisphenol. HF85

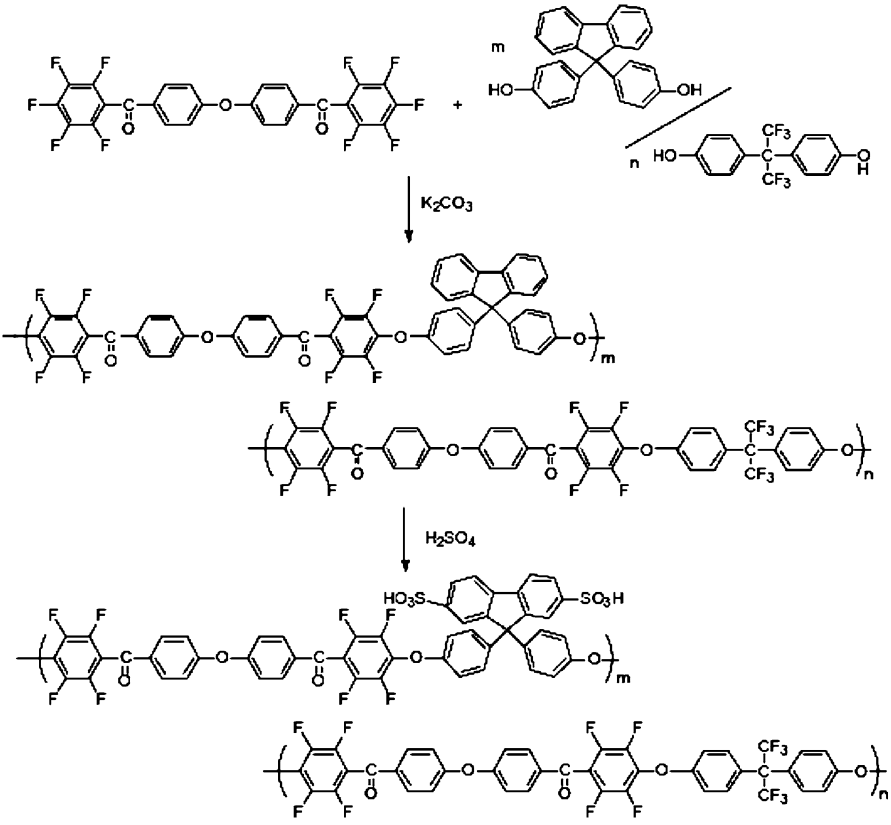


Fig. 10 Poly(aryl ether ketone)s with modified chemical structure [40]

S-PAEK and HF68 S-PAEK contain 15% and 32% 6F-bisphenol, respectively (Fig. 10). Especially, the polymer with the highest degree of sulfonation (HF100 S-PAEK) exhibits good conductivity at 50% relative humidity. However, it swells excessively [40]. Within the series described here, the polymer with 15% 6F-bisphenol appears to be the best compromise between swelling and low r.h. conductivity.

Instead of sulfonated fluorenone units as bulky groups, sulfonated naphthalene can also be used [41]. To this end, 6,7-dihydroxy-2-naphthalene sulfonic acid is used as building block to introduce the sulfonic acid groups (Fig. 11).

Although these materials do not exhibit the outstanding conductivities reported for the fluorine-based polymers described above, they do match or exceed the conductivity of Nafion® 117 at temperatures above 110 °C [41]. Interestingly, the water uptake of the polymer with IEC = 1.6 mmol/g and a conductivity of 60 mS/cm at 110 °C (comparable to Nafion® 117) is no more than 63% on immersion in liquid water at 80 °C for 24 h.

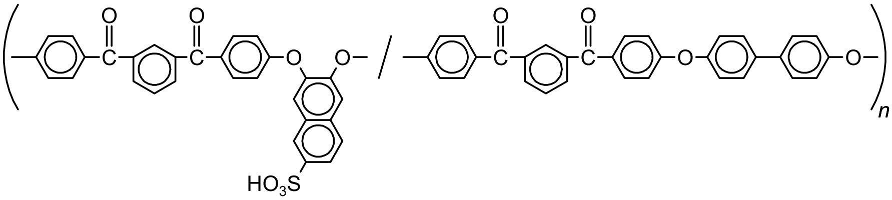


Fig. 11 Poly(aryl ether ketone)s with bulky groups [41]

3.2
Sulfonated Poly(Arylene Ether Ketone)s in DMFC

Sulfonated poly(aryl ether ketone)s appear to have their merits especially in DMFC, where one of the problems of current commercially available perfluorinated membranes is the relatively high methanol permeability, which translates to a reduced power efficiency of the fuel cell.

Sulfonated poly(arylene ether ketone)s have been shown to possess lower methanol permeability than Nafion® by a factor of 3–4 (corrected for membrane thickness) [42]. Incorporation of inorganic proton conductors, such as heteropolyacids, can reduce methanol permeability further to a factor of more than 20 (corrected for thickness) [42] compared to plain Nafion® 117, while maintaining almost the same proton conductivity as Nafion® 117 at room temperature (fully hydrated). Some results are shown in Table 2.

S-PEEK with tungstophosphoric acid (TPA) alone exhibits a higher methanol flow than unfilled S-PEEK, and the TPA is also extracted to a significant extent by liquid water. Interestingly, both methanol flow and bleeding of TPA are strongly decreased by the addition of ZrO_2. The zirconium oxide was not added as a preformed powder, but was prepared in situ by hydrolysis of zirconium tetra propoxide in the casting solution [42]. In the case

Table 2 Reduction of methanol crossover in S-PEK by the addition of inorganic additives (data from [42])

Polymer	D (μm)	MeOH flow (g/hm^2)	Reduction of MeOH flow	Conductivity[a] (mS/cm)
Nafion® 117	175	658	–	94
S-PEK, 1.71 mmol/g	70	411	4×	54
S-PEK:TPA[b] 90:10	75	978	1.6×	82
S-PEK:ZrO_2:TPA 64:8:28	108	47	23×	86

[a] fully hydrated, 25 °C, in 0.333 M H_2SO_4

[b] TPA: Tungstophosphoric acid, $H_3PW_{12}O_{40}$

of highly sulfonated S-PEEK (85% sulfonation, IEC = 2.4 mmol/g), which is soluble at room temperature in water/methanol (80/20), the incorporation of 14% of ZrO_2 stabilizes the membrane, so that even at 55 °C it does not dissolve [43].

A strong reduction in water uptake of S-PEEK can also be achieved by the addition of layered silicates (nano-clays, such as laponite and montmorillonite) [44]. The addition of 10% (w/w) of laponite or montmorillonite to S-PEEK (IEC = 1.7 mmol/g) reduces water uptake at 80 °C from more than 400% (w/w) to less than 50% (w/w). Methanol permeability is reduced by a factor of 2 to 3 as compared to the neat S-PEEK. The proton conductivity of the untreated composite membrane is reduced by a factor of more than 10, but a treatment of the composite membrane with 1 M sulphuric acid for 10 h brings the conductivity back up to the original value of $\approx$50 mS/cm at room temperature (fully hydrated). This is attributed to an exchange of the sodium ions in the layered silicate for protons [44].

3.3
Block Copolymers

A relatively recent approach to improve the property profile of sulfonated poly(aryl ether ketone)s is the use of block copolymers. It is clear that high conductivity of S-PAEK, especially at low relative humidity (and, hence, low water content), can only be achieved at very high sulfonation levels. However, such polymers take up excessive amounts of water, or are even water soluble (see sections above). A potential solution to this dilemma is crosslinking. Unfortunately, at crosslinking densities which suppress swelling sufficiently, the materials typically become brittle. In general, this is not surprising, since both effects are closely related to the length of the chain segments between two crosslinks. In order to significantly reduce the swelling, the segments must be so short that they cannot coil up significantly in the relaxed state. Otherwise, in the presence of water, uncoiling would allow for a large change in macroscopic volume and, hence, swelling. If the segments are so short that they can no longer coil up significantly, they will be mechanically fixed by the crosslinks, resulting in reduced mobility and, hence, loss of the ability to dissipate mechanical energy, causing brittleness.

Separate optimization of mechanical strength, high proton conductivity (i.e., high IEC), and low water uptake may be possible if the functions are separated in a block copolymer structure. The hydrophobic blocks can serve as matrix for mechanical strength and limited swelling, and the hydrophilic blocks with acidic groups can serve as proton transport pathways, comparable to the microphase separated morphology of Nafion®. While a large part of the literature deals with sulfonated block copolymers based on styrene (proton transport related: [45, 46]), there has also some work been done on block copolymers based on poly(arylene ether ketone)s [47–49], poly(arylene ether sulfone)s [50–58], polyimides [59–65], and even poly(*para*-phenylene)s [66].

The block architecture of the polymer chains significantly changes the physical properties. In the case of poly(arylene ether ketone)s, for instance, it was shown that, while randomly sulfonated copolymers with IEC >1.6 mmol/g

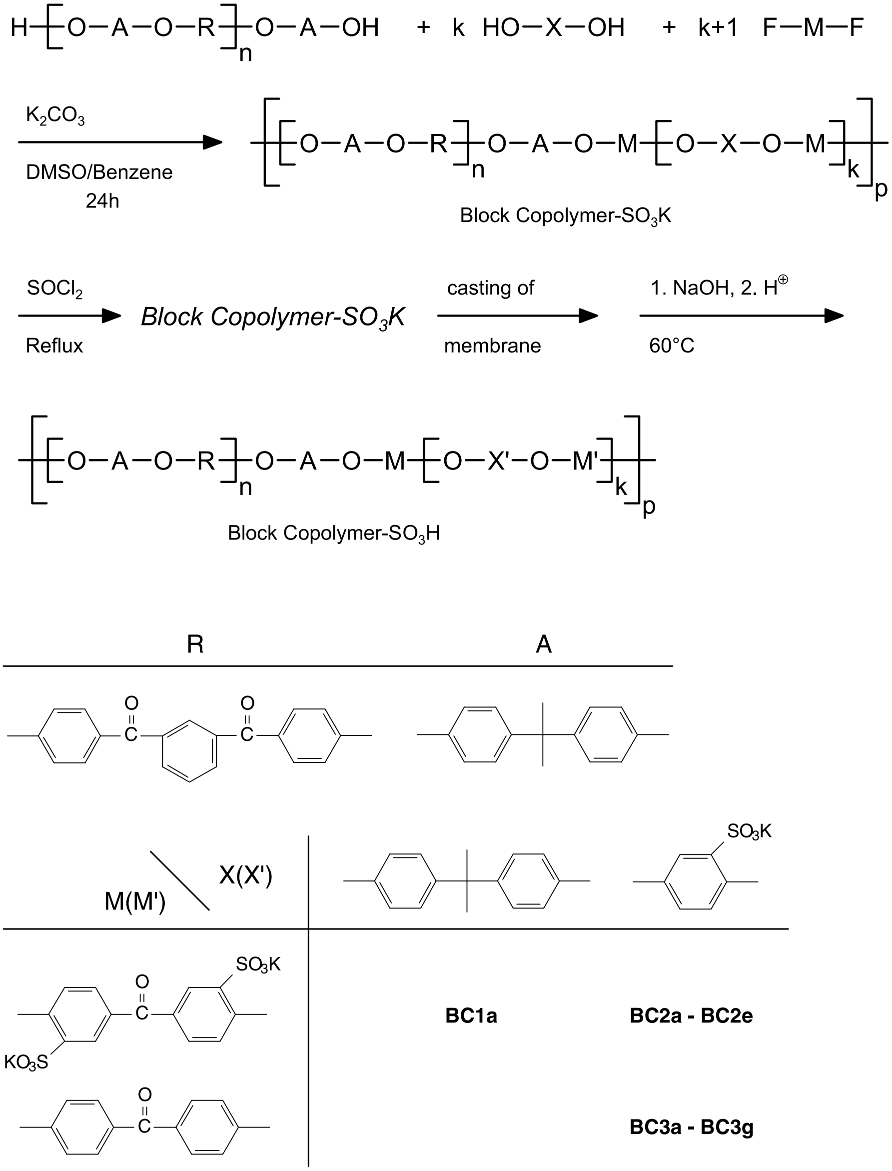


Fig. 12 Sulfonated poly(arylene ether ketone) block copolymers [48, 49]

Table 3 Sulfonated poly(arylene ether ketone) block copolymers [48, 49]

Polymer	IEC (titration) (mmol/g)	Water uptake (%) at 60 °C	Water uptake (%) at 100 °C	Conductivity (mS/cm) r.t.	Conductivity (mS/cm) at 60 °C
1	1.86	53	250	95	166
2	1.48	18	230	81	129
3	1.36	15	210	66	116
4	0.68	4	11	10	24

were completely or at least partly soluble in water even at room temperature [67], sulfonated block copolymers consisting of the exact same components were insoluble even in boiling water, even at IEC values up to 1.86 mmol/g [48, 49]. Figure 12 shows the general structure of these block copolymers.

The block copolymers exhibit conductivities up to 166 mS/cm at 60 °C, fully hydrated, at a water uptake up to 250% in boiling water. Table 3 shows some properties of these materials.

Even higher conductivities were found for block copolymers consisting of sulfonated poly(aryl ether sulfone) blocks alternating with fluorinated aromatic polyether blocks (Fig. 13), although they had relatively high water uptake even at room temperature. Table 4 shows conductivites and water uptake data.

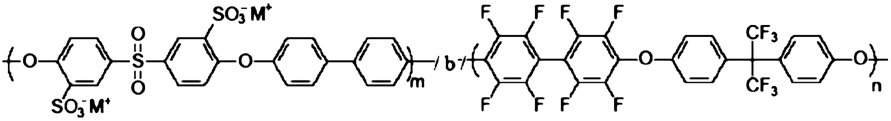


Fig. 13 Block copolymers with aryl ether sulfone hydrophilic and fluorinated aryl ether hydrophobic blocks [56]

Table 4 Conductivities and water uptake of partly fluorinated aromatic block copolymers [56]

Polymer	Molar mass hydrophilic block (g/mol)	Molar mass hydrophobic block (g/mol)	IEC (mmol/g)	Conductivity at room temperature (mS/cm)	Water uptake at room temperature (%)
1	5000	2800	2.3	320	470
2	5000	5000	1.5	120	130
3	15 000	15 000	1.46	160	260

Clearly, separation of the requirements of "high IEC" and "good mechanical properties" in different blocks by combining segments with high degree of sulfonation with totally unsulfonated, hydrophobic segments is an attractive concept, despite the increased synthesis effort.

3.4
Blends of S-PAEK with Inert Polymers

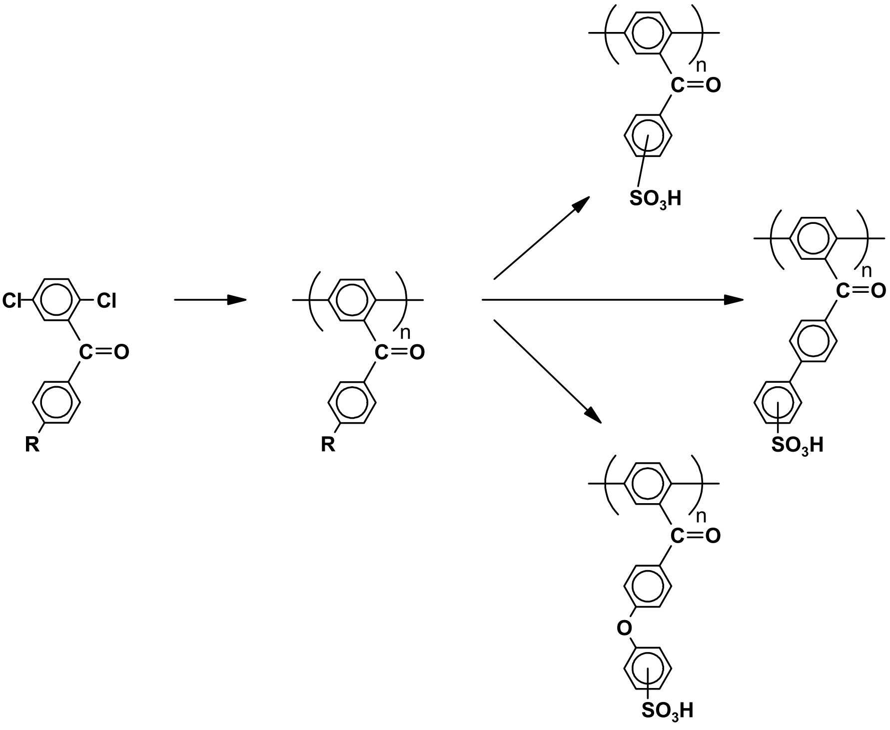
Blending sulfonated proton conducting polymers with non-sulfonated inert polymers is another approach to separate the requirements for high proton conductivity on one hand and good mechanical properties on the other. Recently, sulfonated poly(arylene ether ketone)s have been blended with various elastomers [68], PVdF [69] [70], polyacrylonitrile [71], polyethylene [72, 73], and phenolic resins [74]. In most cases, it is possible to approach the conductivity of Nafion® type materials under fully hydrated conditions, and at the same time reduce the water uptake and swelling in comparison to the sulfonated parent polymers. Also, mechanical properties can be improved. However, in order to achieve high conductivities, a high degree of sulfonation of the parent polymer is necessary, raising the issue of long-term durability and potential extraction of soluble fractions.

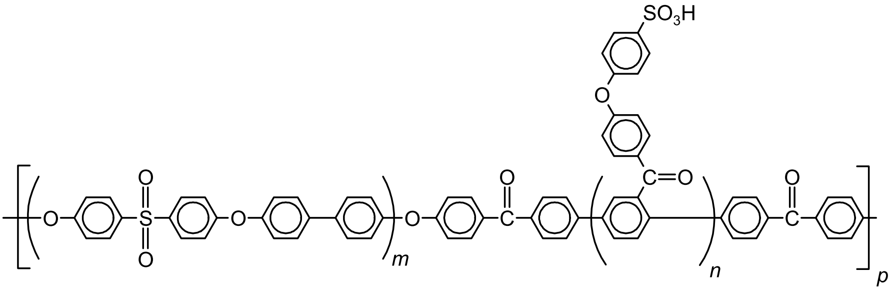
3.5
Poly(*para*-phenylene)s

Another class of chemically exceptionally stable polymers are the poly(*para*-phenylene)s. In addition, they are stiff, rod-like polymers. This feature usually tends to cause insolubility of polymers, which is an attractive approach: rod-like polymers can be expected to be insoluble in water at much higher IEC values than polymers consisting of flexible chains, such as poly(arylene ether)s. Since proton conductivity depends on IEC, such polymers have the potential to form membranes with high conductivity at relatively low degrees of swelling and good dimensional and mechanical stability.

Derivatives which are soluble in organic solvents can be prepared from substituted monomers. Considering the very demanding conditions in fuel cells, fully aromatic structures are preferred. An attractive system is based on the coupling of substituted dichlorophenyl monomers using a Nickel catalyst, with the most popular monomer being 2,5-dichlorobenzophenone. The resulting polymers are typically soluble in dipolar aprotic solvents and can be sulfonated similar to poly(arylene ether ketone)s and poly(arylene ether sulfone)s [6, 26, 75–82]. Figure 14 shows the chemical structures involved.

The poly(*para*-phenylenes)s can be considered rigid rod polymers, which distinguishes them from all other types of polymers typically used for proton conducting membranes, possibly with the exception of certain polyimides. A striking consequence of the rigid rod structure is the fact that the poly(*para*-





S-P1

Fig. 14 Structures and synthesis of poly(*para*-phenylene)s for proton transport membranes

phenylenes)s can be sulfonated to very high IECs without rendering them soluble in water. For example, poly(2-benzoyl-1,4-phenylene) is still insoluble in water at an IEC of 4.0 mmol/g. Its water uptake at room temperature in liquid water is 115%. Sulfonation up to IEC of 6.5 mmol/g is possible, although at this extreme degree of sulfonation the polymer does become water soluble.

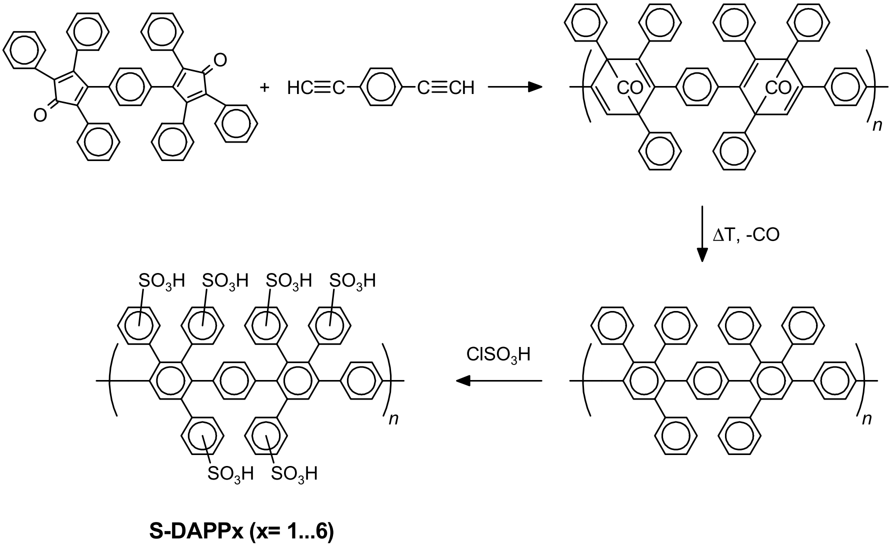


Fig. 15 Poly(*para*-phenylene)s by Diels–Alder reaction [77]

Probably because of limited molar mass, the brittleness of these poly(*para*-phenylene)s can be compensated by incorporating them as sulfonated segments into block copolymers with poly(aryl ether sulfone)s [78]. As for the poly(aryl ether ketone) block copolymers, water uptake is reduced while relatively high conductivity (considering the IEC) is maintained [78].

Another method [77] for the synthesis of poly(*para*-phenylene)s utilizes a reaction which was already successfully used by Stille [83–85] in the 1960s: Diels-Alder reaction (Fig. 15).

Diels-Alder additions are generally regioselective, resulting in predominantly *para* linkages of the polymer chain. However, in sterically crowded systems regioselectivity may be lost to some degree, which introduces some *meta* linkages. Thus, these polymers may not be as strictly rod-like as the polymers prepared by catalytic aryl coupling. Their phenyl substituents provide a large number of potential sites for sulfonation, which can be achieved with chlorosulfonic acid. Above an IEC of 2.2 mmol/g, corresponding to approximately two sulfonic acid groups per repeating unit, they were reported to undergo excessive swelling and form a hydrogel in water [77].

A third pathway to soluble poly(*para*-phenylene)s is Ullmann coupling of sulfonated dibromo biphenyl monomers [80] (Fig. 16).

For the coupling reaction, it is useful to exchange the protons of the sulfonic acids for organic cations, such as pyridinium or trimethyl benzylammonium. In order to modify the polymer properties, some of the sulfonic acid groups can be used to introduce aromatic substituents by sulfone formation.

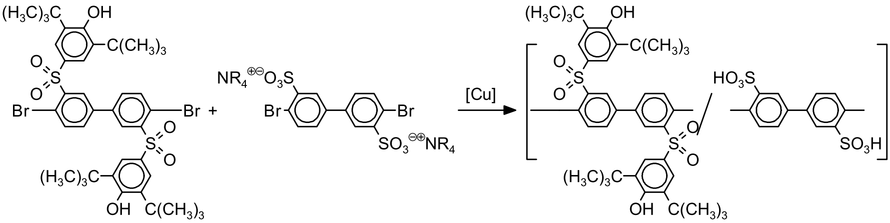


Fig. 16 Poly(*para*-phenylene)s by Ullmann coupling [80]

Table 5 IEC, water uptake and conductivity of selected poly(*para*-phenylene)s [77–80]

Polymer	IEC (mmol/g)	Water uptake at 30 °C in liquid water % (w/w)	Conductivity at room temperature in liquid water (mS/cm)
Nafion® 112	0.91	25	100
S-DAPP4 (Fig. 15)	2.2	137	123
S-DAPP3 (Fig. 15)	1.8	75	87
S-DAPP2 (Fig. 15)	1.4	36	49
S-P1 (Fig. 14)	4.0	115	50
S-P1 (Fig. 14)	2.8	83	40
Copolymer 5% di-*tert.*butylphenol (Fig. 16)	5.7	(50% v/v from 22% r.h. to 100% r.h.)	250
Copolymer 5% di-*tert.*-butylphenyl (Fig. 16)	6.1	(87% v/v from 22% r.h. to 100% r.h.)	700

Table 5 summarizes characterization data of some poly(*para*-phenylene)s. Values for Nafion® are added for comparison.

An interesting comparison was drawn between sulfonated PEEK and sulfonated poly(2-(4-phenoxy)benzoyl-1,4-phenylene) (Fig. 17). They are almost structural isomers, except for one more ether bridge in PEEK. Yet, at comparable degrees of sulfonation, the poly(*para*-phenylen) derivative showed up to 2 orders of magnitude higher proton conductivity when measured under the same conditions [6], and the proton conductivity did not drop off at temperatures up to 110 °C (Fig. 17).

3.6
Non-Rigid Rod Polyphenylenes

In principle, all dichloro aromatics can be coupled with the same Nickel based system which has been used for the synthesis of the poly(2-benzoyl-

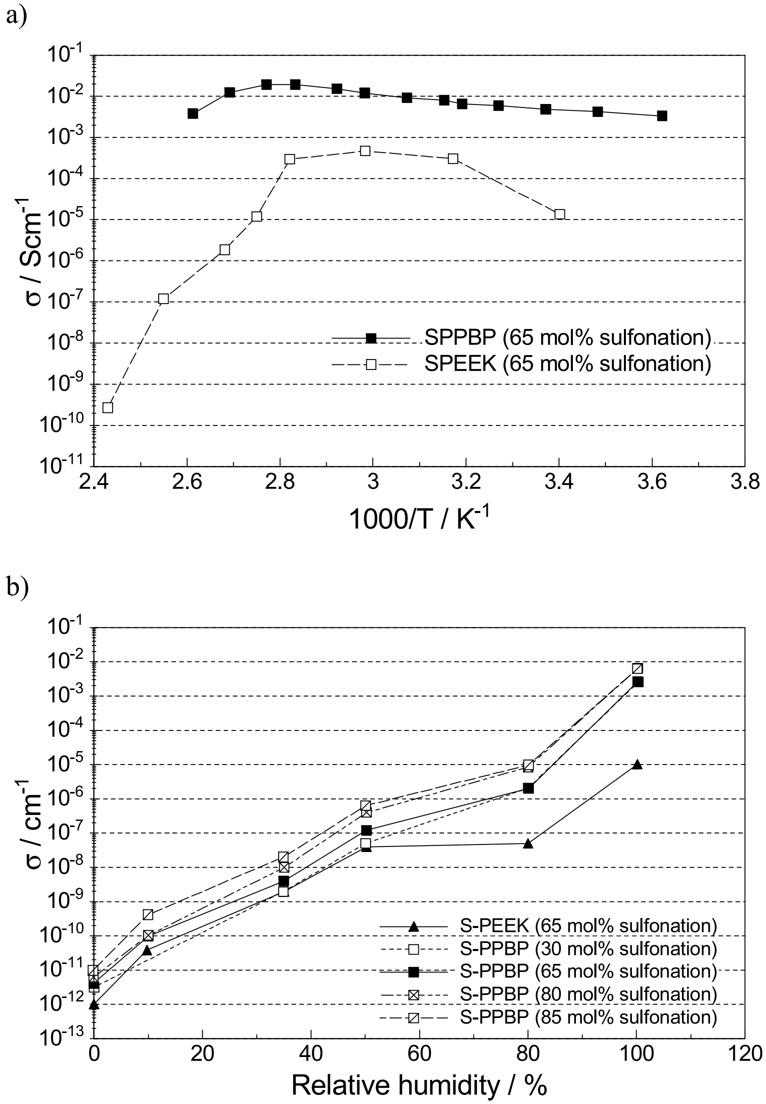


Fig. 17 Comparison of the proton conductivity of S-PEEK and S-PPBP **a** vs. temperature and **b** vs. relative humidity [6]

1,4-phenylene) described above. However, whenever the coupling is not exclusively *para*, the resulting polymers are no rigid rods.

For example, Frey and Mülhaupt et al. [86] studied copolymers from 1,3-dichlorobenzene and 4,4′-dichlorodiphenyl sulfone, which had either carboxylic or sulfonic acid side groups. Figure 18 shows the structures.

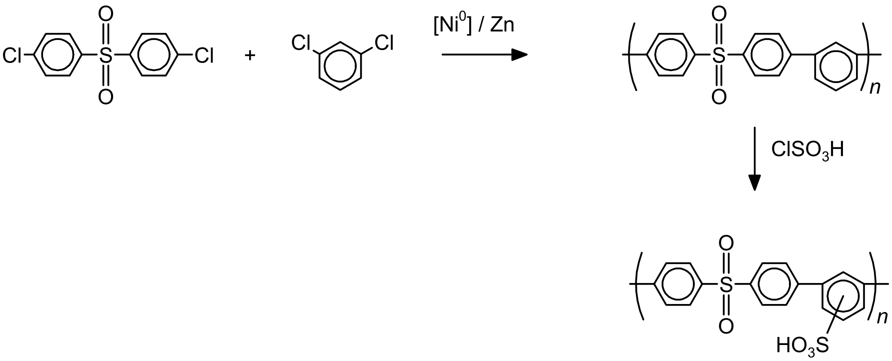


Fig. 18 Non-rigid rod sulfonated polyphenylenes [86]

With sufficiently high IEC, these polymers had higher proton conductivity than Nafion® 117 over a temperature range from 20–110 °C (fully hydrated, in a gas-tight sample holder). Water uptake was very high: more than 500% at 90 °C. Interestingly, a blend of a carboxylated and a sulfonated polymer of this type with an overall IEC value of 4.8 mmol/g still showed a conductivity comparable to that of Nafion® 117, but had a water uptake of only 132% at 90 °C.

3.7
Poly(Phenylene Sulphide)

Poly(phenylene sulphide) itself is a semicrystalline material with excellent mechanical properties and good chemical stability. Due to its electron-rich structure, it can be sulfonated relatively easily up to a degree of sulfonation corresponding to 0.85 sulfonic acid group per phenyl ring (IEC = 4.5 mmol/g) [87]. Even higher sulfonation, up to two sulfonic acid groups per phenyl ring (IEC = 7.4 mmol/g), cannot be achieved directly due to crosslinking, but is accessible though a cationic intermediate, which prevents crosslinking [88, 89]. The proton conductivity of this material was found to be 20 mS/cm at 20 °C and 95% relative humidity [89].

4
Polysulfones

Over the past three decades, several aromatic poly(arylene ether sulfone)s have been commercialized. These polymers show unique combinations of chemical and physical properties, including high stability against hydrolysis, high thermal stabilty, high stability against oxidation and UV-light, high glass transition temperature, and good transparency, when amorphous. First


A)
x
2 x ClO₂S
SO₂Cl
FeCl₃
120°C - 190°C
- HCl
x
B)
x Cl
Cl
x NaO
ONa
CH₃
DMAc/Toluene
160°C 24h
- 2x NaCl
K₂CO₃
DMAc/Toluene
160°C 24h
- 2x KCl
x HO
OH
C)
TMSO
OTMS
2 CsF
- 2 Me₃SiF
CsO
OCs
F
F
- 2 CsF

◀ **Fig. 19** Synthesis of poly(ethersulfone)s by **A** Friedel–Crafts sulfonylation and **B** by nucleophilic polycondensation in solution using phenolates and **C** melt polycondensation using trimethylsilyl derivatives of bisphenols

attempts to synthesize polysulfones were succesfully carried out by a Friedel-Crafts sulfonylation reaction of arylene disulfonyl chlorides, e.g., diphenyl ether-4,4′-disulfonyl chloride with diaryl ethers, e.g., diphenyl ether, or by self-condensation of 4-phenoxy benzene sulfonyl chloride in the presence of $FeCl_3$ [90, 91] (Fig. 19A). While the former reaction bears the risk of side reactions, namely, sulfonylation not only in *para* but also in *ortho* position, the latter gives only the desired linear all-*para* product.

Meanwhile, most commercial polysulfones (PSU) and poly(ether sulfone)s (PES) are obtained from conversion of suitable aromatic dihalides with bisphenols by nucleophilic displacement polycondensation (Fig. 19B). Generally, 4,4′-dichlorodiphenyl sulfone (DCDPS) is reacted with alkali salts of bisphenols [92, 93]. The reaction is carried out in solution using *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethyl acetamide (DMAc), or dimethyl sulfoxide (DMSO) as the solvent. Occasionally, the more reactive, but also more expensive, 4,4′-difluorodiphenyl sulfone might be used for experimental purposes. Usually, the electronegativity of the sulfone linkage is sufficient to increase the reactivity of the aromatic chloride in DCDPS (Fig. 19).

Alternatively, the bistrimethylsilyl ethers of the bisphenols can be used instead of the alkali salts. This approach has the advantage, since the formation of water and, thus, the risk of a hydrolytic cleavage of C–F bonds is avoided. Furthermore, the purification of the silylated bisphenols can be achieved by simple vacuum distillation. The use of silylated bisphenols also allows for the preparation of poly(arylene ether)s in the melt (T 130–300 °C) in the presence of catalytic amounts of CsF or KF, thus, avoiding the removal of large amounts of inorganic salts and solvents [94–96] (Fig. 19C).

Polysulfones (PSU) and poly(ether sulfone)s (PES) have been widely used as membrane materials for ultrafiltration, pervaporation [97–99], or electrodialysis [100], due to their chemical und thermal stability, high glass transition temperature (T_g), which is in the range of 180 °C to values well above 200 °C, as well as their good film-forming properties and solubility in dipolar aprotic solvents, such as NMP, DMAc, or DMSO.

Besides the classical polyethersulfone (Fig. 19A) derived from the reaction of 4,4′-dihalodiphenyl sulfone and 4,4′-hydroxydiphenyl sulfone or self-condensation of 4-halo-4′-hydroxydiphenyl sulfone and polysulfone (Fig. 19B) derived from the reaction of bisphenol A (2,2-*bis*-(4-hydroxyphenyl) propane) and 4,4′-dihalodiphenyl sulfone, a large number of polysulfones have been either commercialized or prepared for research purpose by variation of the bisphenol moieties.

5

Functionalization of Poly(Ether Sulfone)s

Functionalized (e.g., sulfonated or phosphonated) poly(arylene ether sulfone)s can be 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 [101]. While sulfonated poly(arylene ether sulfone)s are easily accessible by electrophilic or nucleophilic substitution at the aromatic ring, the phosphonation is much more complicated and is described in the literature less often than the sulfonation [102–104]. Phosphonic acids and, in particular, arylphosphonic acids are not of such strong interest as proton conducting membrane materials in fuel cells, because of their lower acidic activity compared to the corresponding sulfonic acids. Therefore, a much higher concentration of phosphonic acid groups in the polymer is required in order to get a high proton conductivity. Furthermore, synthetic routes for the preparation of phosphonated polymers are rather limited as compared to sulfonic acid derivatives. On the other hand, arylphosphonic acids show a higher thermostability and are not susceptible to "dephosphonation". In addition, phosphonated polymers are considered to be promising candidates for membranes with sufficient proton conductivities at low humidification levels or even in the absence of humidity.

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, can be easily controlled in the polymer chain.

Both methods, the post-sulfonation of preformed poly(arylene ether sulfone)s and the preparation of functionalized polymers by the use of sulfonated monomers, have been widely described in the literature and will be discussed in the following sections.

5.1

Post-Sulfonation and Post-Phosphonation of Polysulfones

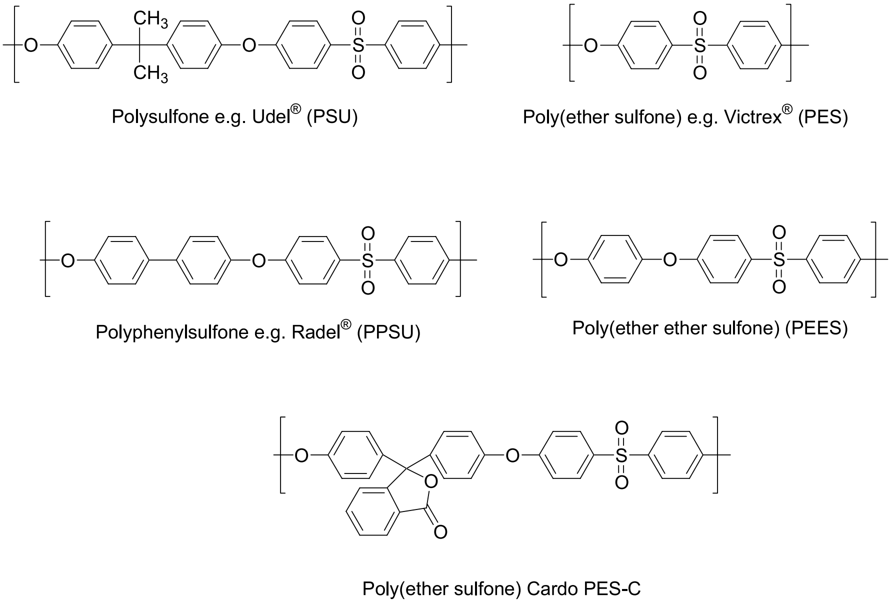
Depending on the chemical composition of the polymer backbone and the desired degree of sulfonation, various sulfonating agents with different reactivities can be selected and are commercially available (Table 6).

Although easy to carry out, post-sulfonation of poly(arylene ether sulfone)s 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 homogeneity. Iojoiu et al. studied the influence of various processing paramaters of sulfonation of different poly(arylene ether sulfone)s on the degree of sulfonation as well as on the material properties

Table 6 Sulfonating Agents

Sulfonating Agent	Reactivity	Reaction site	Comments
Chlorosulfonic acid	High	Electron-rich ring	Inexpensive, side-reactions (degradation, crosslinking)
Fuming sulfuric acid (Oleum)	High	Electron-rich ring	Inexpensive, crosslinking
Sulfuric acid	High	Electron-rich ring	Inexpensive, lowering of reactivity by reaction product water
Sulfur trioxide/ triethylphosphate (TEP)	Medium to high	Electron-rich ring	Inexpensive, reactivity might be controlled by TEP content
Trimethylsilylsulfonyl chloride	Medium	Electron-rich ring	Relatively expensive
Acetylsulfate	Low	Aliphatic double bonds	Inexpensive
BuLi + SO_2 or SO_3	High	Electron-poor ring	Expensive
BuLi + sultones, halogenoalkylsulfonic acids...	High	Electron-poor ring	Expensive

in a recent paper [105] (the reader is also referred to the literature cited in this paper for more detailed information). Most attractive seems to be the sulfonation in concentrated sulfuric acid (i.e. 98%) [78, 106–108] or chlorosulfonic acid [97, 99, 109–117], acting both as solvent and as sulfonating agent since both reagents are inexpensive and readily available. As reported by Blanco et al. [116], a rapid degradation occurs when sulfonating PSU, which makes this method at least questionable for a number of poly(ether sulfone)s. They proposed a degradation mechanism which involves the protonation of the ether oxygen [116]. A much higher stability was observed for PES-C (for chemical structure see Fig. 20). Furthermore, when using sulfuric acid for the sulfonation the byproduct water dilutes the reaction medium, thus decreasing its reactivity. The effect of acid concentration on the sulfonation kinetics has been studied for a poly(ether ether ketone), for example, by Huang et al. [118]. On the other hand, PES, which is not soluble in concentrated sulfuric acid, or PPSU are both soluble in halogenated solvents, which are well adapted to electrophilic substitution. Although the starting materials are perfectly soluble in these solvents, the sulfonated products obtained by the reaction with chlorosulfonic acid [18, 74, 97, 117, 119] or SO_3 (PPSU, [120]) are not, and they precipitate during the reaction, which leads to inhomogeneously sulfonated products and the degree of sulfonation is uncontrolled. To overcome this problem, Genova-Dimitrova et al. [30] suggested to add small amounts of DMF to the reaction mixture in order to keep the polymer in solution.



Polysulfone e.g. Udel® (PSU)

Poly(ether sulfone) e.g. Victrex® (PES)

Polyphenylsulfone e.g. Radel® (PPSU)

Poly(ether ether sulfone) (PEES)

Poly(ether sulfone) Cardo PES-C

Fig. 20 Commercially available poly(ether sulfone)s

In other studies, the sulfonation with SO_3-triethylphosphate complex in dichloromethane has been proposed and was described to be more reliable with a minimum risk of side reactions [101, 121–123]. The disadvantage of using SO_3-triethylphosphate complex is its toxicity and high reactivity of SO_3, as well as the exothermic reaction with triethylphosphate which makes it difficult to use.

An alternative approach to carry out the sulfonation reaction under homogeneous conditions is based on the use of trimethylsilyl chlorosulfonate as sulfonating agent and dichloromethane or dichloroethane as solvents [27, 30, 50, 120, 124, 127]. The reaction mixture remains homogeneous when kept anhydrous, due to the trimethyl silylester formed during the reaction. The ester further reduces the risk of side reactions, namely, crosslinking or degradation, as reported from sulfonation reactions with chlorosulfonic acid. Dyck et al. [120] reported a much more homogeneous reaction product and a much better control of the degree of sulfonation when using trimethylsilyl chlorosulfonate instead of SO_3-TEP complex for the sulfonation of PPSU. The sulfonation with the SO_3-TEP complex always led to the formation of two fractions: a water-soluble one with a high degree of sulfonation (>2.88 mmol/g) and a water-insoluble fraction with a degree of sulfonation <1.5 mmol/g). The degree of sulfonation was controlled by either reaction time or by the amount of trimethylsilyl chlorosulfonate added to the reaction mixture. The inhomogeneity is also reflected in the membrane properties as, for example, the methanol permeability. The SO_3-TEP sulfonated membranes showed a methanol permeability comparable to Nafion®, which are ca. two-fold higher than that of the more homogeneously sulfonated products yielded from the reaction with trimethylsilyl chlorosulfonate. While generally dense symmetric membranes are employed in fuel cell applications, Dyck et al. [120] described the preparation of an asymmetric membrane with a thin dense top layer and a support layer exhibiting a closed-cell structure. An asymmetric membrane with an IEC of 2.08 mmol/g showed a four-fold higher proton conductivity (ca. 55 mS/cm at 80 °C) compared to a symmetric membrane from the same material and of the same thickness. Park et al. [124] investigated the effect of thermal treatment of sulfonated membranes (sPSU) on membrane properties, such as water uptake, proton conductivity, and methanol permeability. The sulfonation was achieved by treatment of PSU with a 1:1 molar mixture of chlorosulfonic acid/chlorotrimethylsilane in 1,2-dichloroethane. The degree of sulfonation was controlled by the amount of sulfonating agent added to the reaction mixture. A maximum degree of sulfonation of 75%, corresponding to an IEC of 1.45 mmol/g was achieved. Thermal treatment of the membranes for 2 h at 150 °C, which is well below the glass transition temperatures (T_g) of the membrane materials (193–225 °C, depending on the degree of sulfonation) resulted in a pronounced lowering of the methanol permeability but it only slightly affected the water uptake and the proton conductivities, especially for membranes with low ion-exchange capacities (0.55–0.85 mmol/g).

Yang et al. reported on the preparation of polysulfone-*block*-PVDF copolymers [50, 51]. Again, the sulfonation of the polysulfone was conducted with trimethylsilyl chlorosulfonate and the degree of sulfonation was controlled by the amount of sulfonating agent added to the reaction mixture. As a result, the block copolymers showed higher proton conductivities at IECs <1.4 mmol/g than sulfonated homopolymers with comparable IECs. For lowest IEC polymers (ca. 0.8 mmol/g) the conductivity was enhanced by a factor of 4 over a temperature range from 30 °C up to 80 °C. With higher IECs no differences between the two different types of membranes were found. Since the λ-values (mol H_2O/mol SO_3H) were nearly identical for the two membrane types, the conductivity differences could not be associated with differences in λ. TEM micrographs revealed that in both polymers with low IEC ionic aggregates exist, being larger in the block copolymer (50–200 nm) than in the homopolymer. It was proposed that the presence of the hydrophobic block promotes the phase separation between sulfonated and non-sulfonated domains and thus the formation of ionic aggregates and an ionic network, leading to the observed conductivity enhancement. In high IEC membranes with fully developed ionic network, the relatively small hydrophobic blocks have only little or no effect on the conductivity.

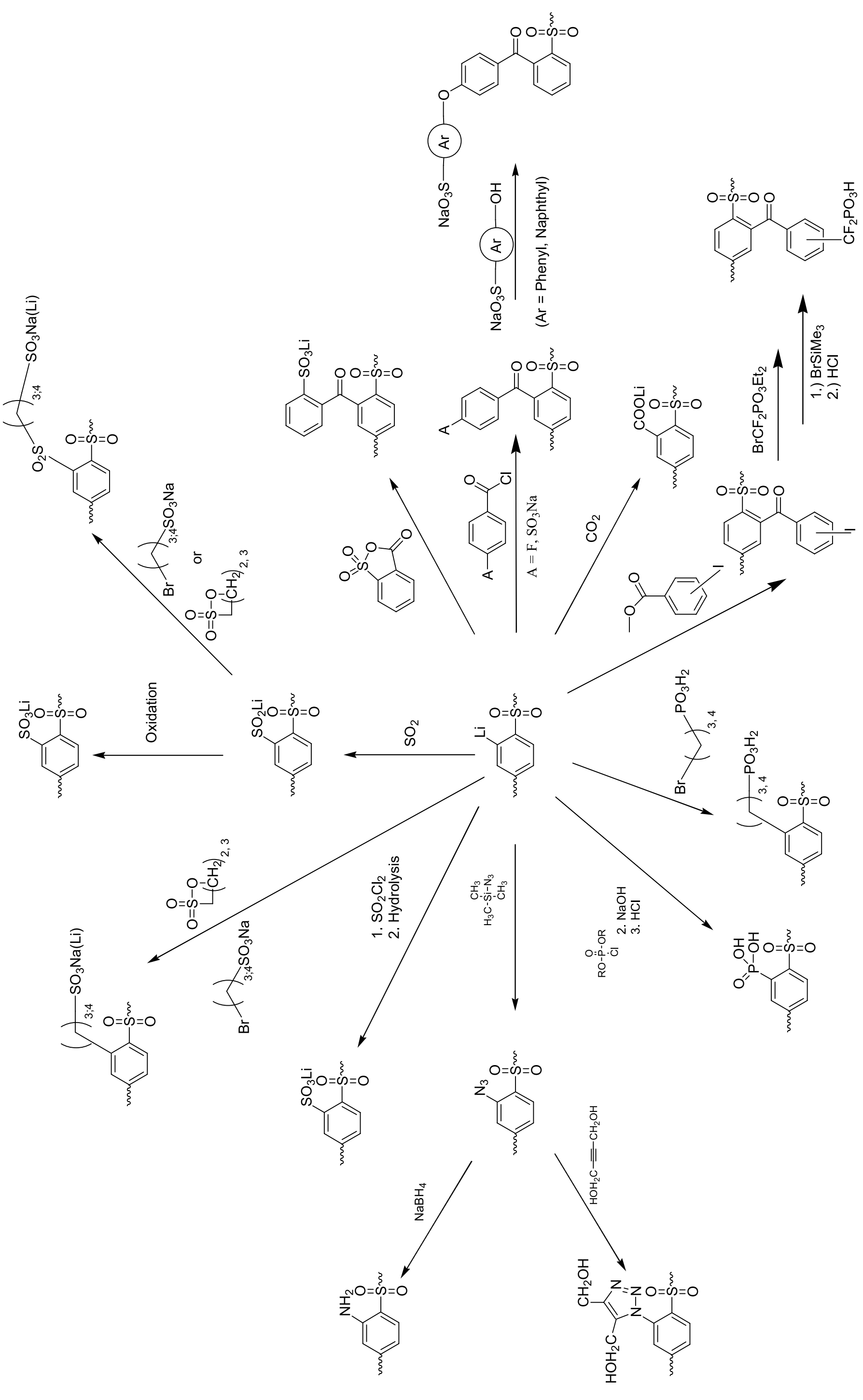
An interesting approach to obtaining sulfonated poly(arylene ether sulfone)s was reported by Zhang et al. [52, 125]. They prepared poly(arylene ether sulfone)-*block*-polybutadiene copolymers and achieved a selective sulfonation of the remaining double bonds in the flexible polybutadiene block-segments by using acetylsulfate. Although IECs were only in the range from 0.107 mmol/g to 0.624 mmol/g, relatively high proton conductivities up to 30 mS/cm (IEC 0.624 mmol/g) at 25 °C were recorded. This was attributed to the fixation of the proton conducting groups to the flexible polybutadiene segments (T_gs ranging from – 37.7 °C to – 4.5 °C), which provides greater mobility and allows for easier formation of ionic pathways. In a second attempt to enhance the ion-exchange capacity of the block copolymers, both the poly(arylene ether sulfone) (PAES) segments as well as the polybutadiene segments were sulfonated. While the former were obtained by polymerization of sulfonated and non-sulfonated DCDPS with bisphenol A, the latter were obtained by selective sulfonation with acetylsulfate. The degree of sulfonation of the PAES segments were controlled by the ratio of DCDPS to SDCDPS. Double bonds, which still remained in the flexible block after the sulfonation process, were epoxidized to further reduce the gas permeability. The introduction of the sulfonated PAES segments resulted in a remarkable increase in intramolecular and intermolecular chain interactions, leading to higher T_g and T_m of the membranes. Furthermore, the microstructure of the membranes were found to correspond to DS of the PAES segments, as the size of polybutadiene domains increased with increasing DS up to 40 mol % SDCDPS (IEC = 0.622 mmol/g) of sulfonated PAES segments. The latter sample showed the highest proton conductivity (0.108 S/cm at 90 °C) of all samples under investigation in this study due to the formation of an interpenetrating ionic network. Further increase of the DS of sPAES resulted in a demixing of the different blocks. In order to get sulfonated polysulfones with the functional groups in the side-chain and a predefined degree of sulfonation, Meier-Haack et al. prepared polysulfones with phenylhydroquinone moieties in the backbone [126–128]. The sulfonation was conducted with various sulfonating agents, such as concentrated sulfuric acid or chlorosulfonic acid trimethylsilylester. Contrary to the sulfonation of similar poly(ether ether ketone)s [129, 130], the sulfonation of the poly(ether sulfone)s occurred always at the side-chain as well as at the main-chain. Despite the mixed and partly "oversulfonation" ($IEC_{titr.} > IEC_{theo.}$) samples with an IEC up to 1.5 mmol/g, (water uptake of 25 mol water/mol SO_3H) showed promising properties (proton diffusion, methanol diffusion) concerning future applications, e.g., in fuel cells. Furthermore, these materials showed no hydrolytic cleavage of the sulfonic acid group and no backbone degradation upon heating in water for 168 h at 130 °C.

5.2
Functionalization by Chemical Grafting Reactions

A promising alternative to the direct functionalization (sulfonation; phosphonation) of high performance polymers is offered by the chemical grafting reaction. This synthetic route involves first an activitation step, e.g., by irradiation (UV, ion beam, electron beam, γ-ray) or chemical treatment followed by conversion of the activated sites.

Belfort and co-workers, for example, described the photochemical modification of poly(ether sulfone) and sulfonated poly(sulfone) nanofiltration membranes for the control of fouling [131, 132]. Irradiation of sPES or PSU with UV light of a wavelength of 254 nm led to scission of the S–C bond in the polymer backbone, thus, forming a radical at that position. In the presence of *N*-vinyl pyrrolidone,for example, grafting occurs. With no vinyl monomer present, the radical terminates with a hydroxyl group. In both cases more hydrophilic membranes with lower fouling tendency were obtained. However, since the activation is realized by bond breaking within the polymer main-chain, the molecular weight and, therefore, the mechanical properties of the membrane material might be negatively influenced. This might also be the reason why this method has not so far been applied in the production of ion-exchange membranes for 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 [4, 5, 32, 102, 133–145], and has been the subject of a recently published review by Jannasch [146]. 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 °C to – 30 °C) in an inert solvent, such as THF. Further reaction of the activated polymers with, for example, carboxylic acid, sulfuric acid, or phosphonic acid derivatives, leads to carboxylated, sulfonated, or phosphonated polymers, respectively. This method is not limited to the introduction of acidic groups. The activated polymers can be treated with numerous electrophilic substances, many of which are commercially available (Fig. 21). Amination and hydroxylation, for example, have been reported in the literature by Guiver and co-workers [135] and Kerres and co-workers [32]. Phosphonation of poly(arylene ether sulfone)s via the metalation route has been recently described by Jannasch and co-workers [102, 147]. The phosphonic acid group was linked directly to the polysulfone main-chain by the lithiation method. In the second work, Lafitte and Jannasch described the phosphonation of benzoyl-modified polysulfones in the side-chain. In the first step, the polysulfone was reacted with methyl iodobenzoat by the lithiation method to give iodobenzoyl-PSU. This product was further converted into benzoyl-difluoromethylphosphonate via a CuBr mediated cross-coupling reaction with diethyl(bromodifluoromethyl)phosphonate and subsequent hydrolysis with bromotrimethylsilane (Fig. 21). Membranes with an IEC of 1.79 mmol/g showed a very low water uptake of less than 10 wt. % in the range from 20 °C to 100 °C and a reasonable proton conductivity of 5 mS/cm at 100 °C.


Li
SO2
SO2Li
Oxidation
SO3Li
or
SO3Na(Li)
CO2
COOLi
A = F, SO3Na
(Ar = Phenyl, Naphthyl)
NaO3S
Ar
OH
BrCF2PO3Et2
1.) BrSiMe3
2.) HCl
CF2PO3H
PO3H2
3, 4
2. NaOH
3. HCl
1. SO2Cl2
2. Hydrolysis
N3
NaBH4
NH2
HOH2C
CH2OH

◀ **Fig. 21** Possible reactions leading to sulfonated or phosphonated polymers via lithiation route

Since the polymers to be activated need to have at least one acidic proton in the main chain and must be soluble in suitable solvents, the number of polymers which can be modified by this particular method is limited. So far only the modification of poly(arylene ether sulfone)s and polybenzimidazoles as suitable materials for fuel cell membranes has been reported in the literature [4, 5, 32, 102, 136–146, 148–151]. The attempt to lithiate poly(ether sulfone) under homogeneous conditions failed so far, due to poor solubility and the alternating electron-donating and electron-withdrawing linkages present in poly(ether sulfone), which result in an overall unfavorable balance in the polymer chain.

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 the *ortho*-position to the ether linkage in polysulfones. The advantage of the metalation method over the direct sulfonation is that the activition takes place at electron-poor sites of the polymer backbone, in general, in *ortho*-position to the electron-withdrawing sulfone-linkage. Thus, these sulfonated polysulfones are expected to be less sensitive to desulfonation than those obtained by the direct sulfonation method. However, the site of conversion can be shifted from the electron-poor (*ortho*-position to the sulfone linkage) site to the electron-rich site (*ortho*-position to the ether linkage) by introduction of bromine atoms into the polymer main chain either by bromination or by using brominated monomers. At low temperatures, lithium-bromine rather than lithium-hydrogen exchange occurs exclusively [133]. While Guiver and co-workers used the lithiation method to modify NF, RO, and UF membranes, Kerres and co-workers employed this method for the preparation of ion-exchange membranes for electrochemical applications, such as fuel cells, by the introduction of sulfonic acid groups. This was accomplished by conversion of the lithiated species, for example, with SO_2, followed by oxidation of the obtained sulfinic acid giving the sulfonic acid. The sulfinic acid derivatives were also subject to further reaction with dihalogenoalkyls, e.g., diiodobutane, to achieve a covalent crosslinking (Fig. 22A) in order to reduce extensive swelling of highly sulfonated membrane materials [32].

Besides the covalent crosslinking, Kerres et al. investigated the properties of fuel cell membranes of ionically crosslinked polysulfonic acids. This type of crosslinking was achieved by blending sulfonated poly(arylene ether sulfone)s and poly(arylene ether ketone)s with basic polymers, such as polybenzimidazole, poly(ethylene imine), poly(vinyl pyridine), or amino functional-

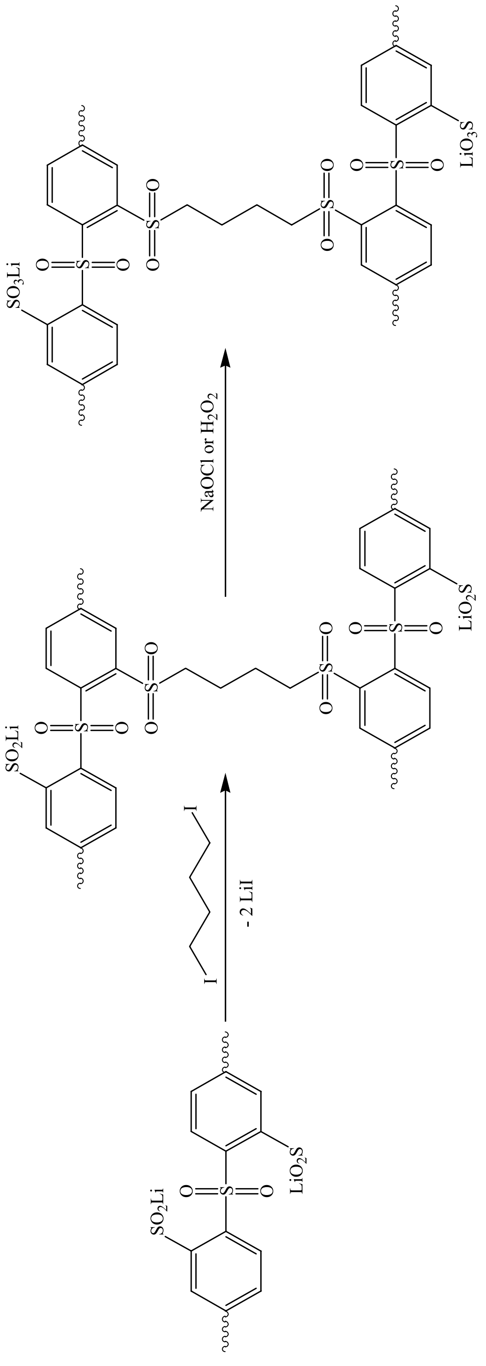


Fig. 22 Crosslinking of poly(ether sulfone)s by conversion of lithium sulfinate groups with diiodobutane

ized polysulfone [138, 140, 141]. The latter was obtained by conversion of the lithiated PSU, for example, with 4-acetylpyridine or *bis*(diethylamino)benzophenone. Ionically, covalently, and both ionically and covalently crosslinked membranes with IECs in the range from 1.1 to 1.25 mmol/g showed low swelling (40–45%) in water up to temperatures of 60 °C [141]. At higher temperatures the covalently crosslinked membrane showed highest dimensional stability, followed by the ionically crosslinked membrane, which was explained with the breakdown of the ionic crosslinks. Surprisingly, at least dimensionally stable was the "double crosslinked" sample. Due to incompatibilities between the sulfonated PEK and the sulfinated PSU, a phase separated morphology occurs in the resulting membrane with the ionically crosslinked polymers as continuous phase. Therefore, the swelling of this membrane is mainly determined by the weaker ionically crosslinked phase rather than by the dispersed covalently crosslinked particles. Both the covalently and the ionically crosslinked membranes showed in DMFC tests at temperatures ranging from 25 °C up to 110 °C quite similar behavior to Nafion® 105, but with much lower methanol crossover [141].

Jannasch and co-workers used the lithiation route to place the sulfonic acid groups into the side-chain rather than the main-chain. The activated polysulfone was reacted with either 2-sulfobenzoic acid anhydride [142] or 4-fluorobenzoyl chloride. The latter was further reacted with hydroxyaryl sulfonic acids, such as 4-sulfophenol sodium salt or 2-naphthol-7-sulfonic acid sodium salt [144] (Fig. 23). In another approach, lithiated PSU or PPSU were first reacted with SO_2, then further converted with a bromoalkyl sulfonic acid sodium salt, or with 1,3-propane sultone, or 1,4-butane sultone [143] (Fig. 21). Thus, the alkyl sulfonic acids are bonded to the polymer backbone via a sulfone linkage, which, in contrast to a phenyl-alkyl ether linkage, should be resistant towards acidic hydrolysis. The latter can be obtained by reacting sultones with hydroxyl groups in the polymer backbone as described, for example, by Kricheldorf and co-workers [152] and Orugi and co-workers [153, 154]. The introduction of the sulfonic acid group into the side-chains might have some advantages over the "traditional" main-chain sulfonation. Separating the ionic sites from the main-chain opens up the opportunity to manipulate and influence the phase separation into hydrophilic and hydrophobic domains, which occurs in the membranes while in contact with water. This may give rise to the formation of more stable morphologies, despite the presence of a highly swollen phase. Thus, the introduction of the ionic group into the side-chain may allow for higher IEC without compromising the resistance towards swelling. Sulfo-alkylated and sulfo-phenylated poly(arylene ether sulfone)s showed thermostabilities up to 300 °C, as revealed by TGA measurements. The proton conductivities of the sulfoalkylated poly(arylene ether sulfone)s were reported to be 77 mS/cm at 70 °C and 100% relative humidity for PSU carrying 0.9 sulfopropyl groups per repeating unit. The major drawback of these polymers is their high water uptake at temperatures above 75 °C, which was assigned to the plasticization effect of the alkyl chains on the PSU main chain. More promising with respect to swelling seems to be the grafting of arylsulfonic acids onto the PSU main-chain. Jannasch and co-workers reported a moderate swelling (15–18 H_2O/SO_3H) of sulfophenylated PPSU membranes (0.9 side chains/repeat unit; IEC = 1.63 mmol/g)

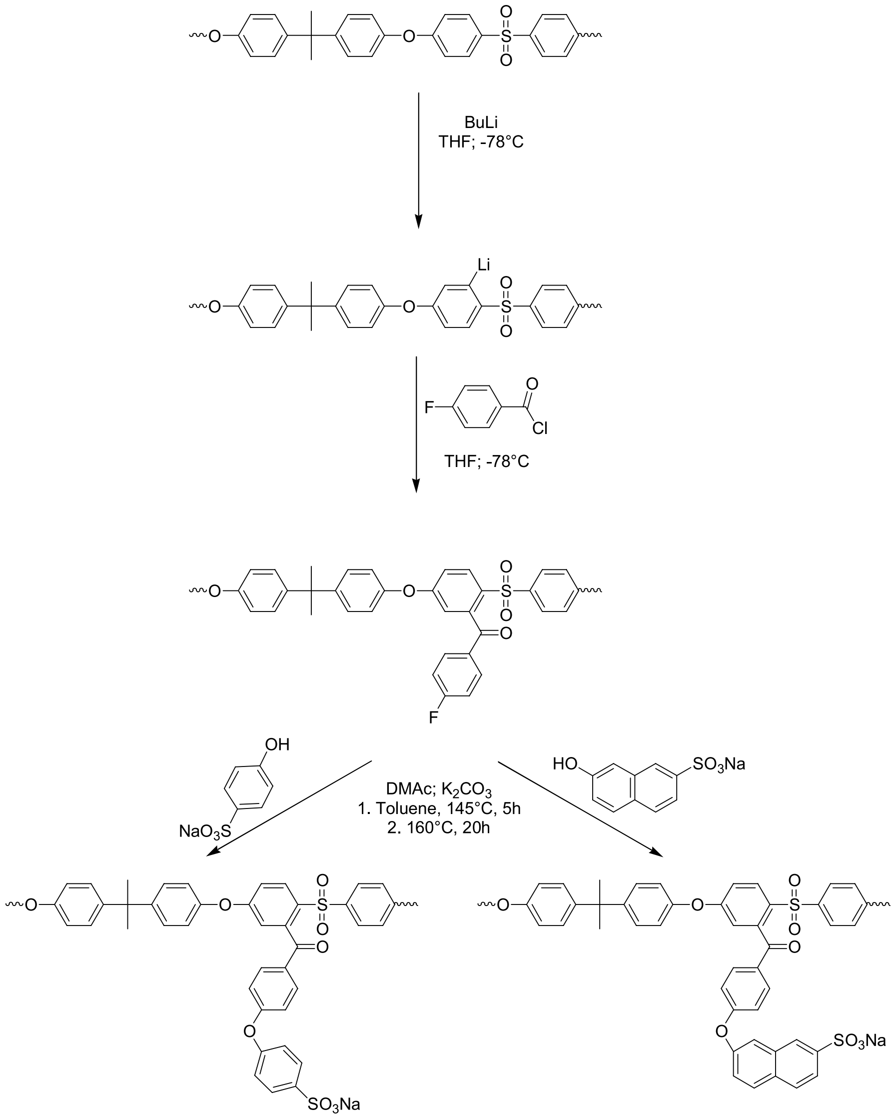


Fig. 23 Introduction of functionalized side groups into poly(ether sulfone) by lithiation and subsequent nucleophilic addition

at temperatures up to 140 °C. A PSU membrane, having the same degree of grafting (IEC = 1.51 mmol/g) was dimensionally stable up to 120 °C. The proton conductivities of PPSU membranes (degree of grafting of 0.9) were in the range from 37 mS/cm at 30 °C to 42 mS/cm at 140 °C. Increasing the length and stiffness of the sulfonated side-chain by grafting of 4-sulfophenoxy benzoyl leads to lower proton conductivities at 120 °C, 11 mS/cm, and 32 mS/cm for a degree of grafting of 0.5 and 0.9, respectively. The introduction of 7-sulfo-2-naphthoxy benzoyl groups resulted in very brittle membranes, which were, therefore, not further characterized in terms of electrochemical properties [144] (Fig. 23). The same authors introduced side-chains consisting of higly sulfonated naphthoxybenzoyl (double sulfonated) or pyrenoxybenzoyl groups (3-fold sulfonated) to a polysulfone backbone [155]. This chemical structure leads to the formation of larger and more uniform ionic clusters than conventionally sulfonated polysulfones with sulfonic acid groups distributed along the main-chain. This particular architecture allows the formation of networks of water-filled nanopores, which facilitated high levels of proton conductivity up to 300 mS/cm at 100 °C (exceeding commercial Nafion®) at moderate levels of water uptake. Recently, Lafitte and Jannasch reported on the fuel cell performance of a 2-sulfobenzoyl-PSU membrane (IEC 1.2 mmol/g) in the temperature range from 60 to 110 °C [156]. A lifetime of at least 300 h at the operation temperature of 60 °C was stated for this membrane. The comparatively lower performance to Nafion® 117 was explained with non-optimized Nafion ®-containing electrodes.

5.3
Functionalized Poly(Arylene Ether Sulfone)s from Sulfonated Monomers

An alternative approach to the post-functionalization route is the use of functionalized monomers. This method has the advantage of overcoming the risks of side reactions, such as degradation or crosslinking connected with the post-functionalization route. Furthermore, it provides an easy route to control the degree and site of functionalization as well as the distribution of functional groups along the polymer chain. Several research groups have focused their work on 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 non-sulfonated monomer and various types of bisphenols, such as bisphenol A, 4,4′-dihydroxy biphenyl, phenolphthalein, and others [67, 100, 157–171]. The sulfonated monomer can be easily obtained by sulfonation of the dihalo sulfone with fuming sulfuric acid (30% SO_3) at 90 °C for 6 h [157] (Fig. 24A). Here, the sulfonated monomer was used for the preparation of more hydrophilic polysulfones, but for no specific application. Other groups used the commercially available sodium salt of hydroquinone sulfonic acid as sulfonated monomer in the synthesis of sulfonated poly(arylene ether sul-

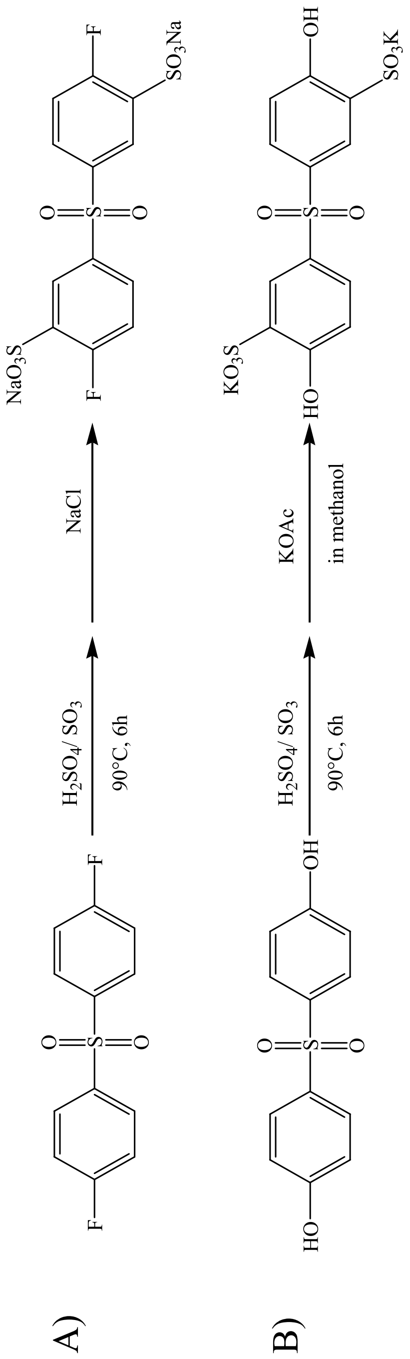


Fig. 24 Synthesis of **A** sulfonated 4,4′-difluorodiphenyl sulfone and **B** 3,3′-sulfonyl-*bis*-(6-hydroxybenzene sulfonic acid) (sulfonated bisphenol S)

fone)s [58, 67, 172, 173]. Kozlowski mentioned in a patent the incorporation of 3,3′-sulfonyl-*bis*-(6-hydroxybenzene sulfonic acid) (sulfonated bisphenol S; Fig. 24B) into polymers [174].

The sulfonation of the dihalide monomer has the advantage that the deactivated ring in *ortho*-position to the halogene is sulfonated, giving rise to higher stability with respect to desulfonation, and second two sulfonic acid groups are incorporated into the repeating unit. Furthermore, the reactivity of these monomers to nucleophilic displacement reactions is enhanced due to the electron-withdrawing effect of the introduced sulfonic acid groups. Although in *ortho*-position to the ether linkage in the polymer, the sulfonic acid groups should be more stable against desulfonation than in the hydroquinone units due to the electron-withdrawing and therefore deactivating effect of the sulfone or ketone linkage. In the hydroquinone sulfonic acid based poly(arylene ether)s, the sulfonic acid groups are positioned at an activated benzene ring with two ether linkages. However, as reported by Vogel et al., poly(arylene ether sulfone)s sulfonated at the hydroquinone moiety showed a high resistance against desulfonation at 130 °C in water [175].

Takeuchi [176] reported on the self-condensation of 2,6-*bis*(*p*-sodium sulfophenoxy)benzonitrile at 140 °C in phosphorous pentoxide/methane sulfonic acid, giving sulfonated hyperbranched polymers (Fig. 25). This product with an equivalent weight of 436 g/mol was soluble in DMSO and water and showed no film-forming properties. Membranes with an IEC ranging from 0.31–1.20 mmol/g were obtained by blending various amounts of the hyperbranched polymer with poly(vinyl alcohol). Although the matrix was crosslinked with glutaraldehyde, the membranes had a high water uptake between 59% and 101%. Interestingly, the membrane with the highest content of the hyperbranched polymer showed the second least water uptake (62%) of all samples under investigation.

Xiao et al. [177] reported on sulfonated poly(arylene ether ketone)s based on bisphenol S and 4,4′-difluorobenzophenone and sulfonated 4,4′-difluorobenzophenone (sodium salt). The ion-exchange capacity was varied between 1.23 mmol/g (30 mol % sulfonated monomer) and 1.73 mmol/g (45 mol % sulfonated monomer). These polymers were amorphous in nature and showed an increasing T_g ranging from 268 °C to 317 °C, with increasing amount of the sulfonated moiety in the polymer backbone. The water uptake of the membranes was reported to be much lower than that of Nafion® 115.

The electrochemical properties of cation-exchange membranes based on sulfonated poly(arylene ether sulfone)s (s-PES) were described in a paper by Kang et al. [100]. The intended applications for these membranes were general electro-membrane rather than fuel cell applications. The properties of the membranes prepared in this work were compared to commercially available ion-exchange membranes (Neosepta® CM-1, CMX, and CMB), as well as to sulfonated polysulfones obtained by post-sulfonation of Udel® 1700 with chlorosulfonic acid (s-PSU) (Fig. 26). The s-PES membrane materials were

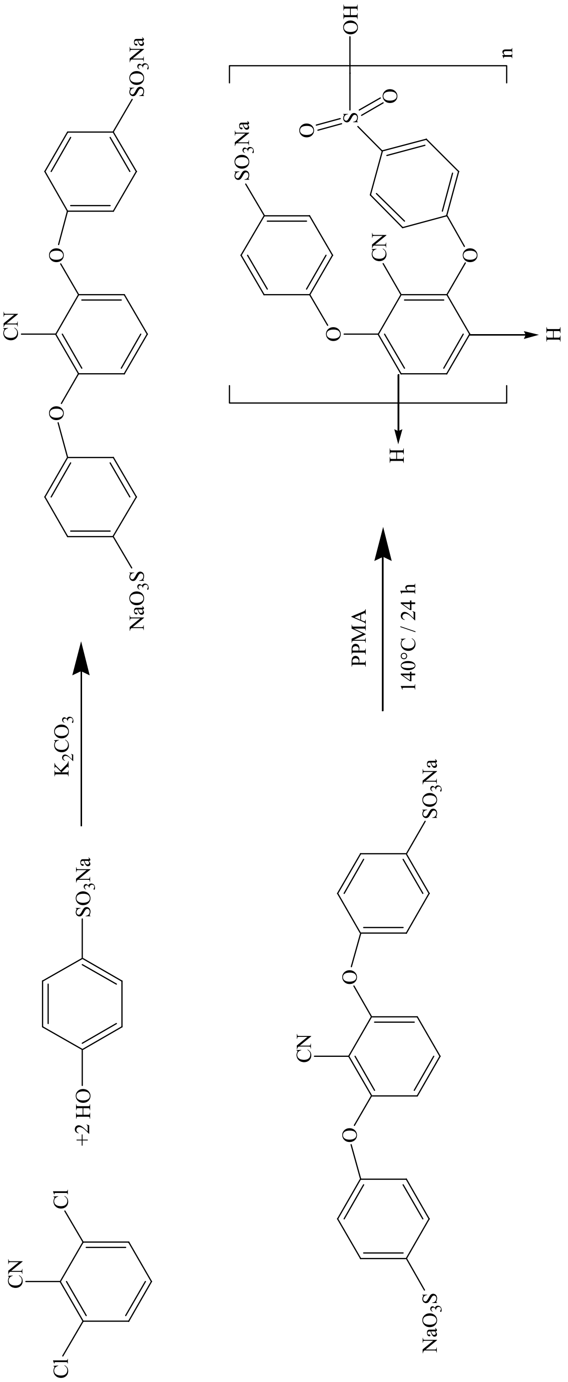


Fig. 25 Synthetic route towards a hyperbranched sulfonated poly(ether sulfone)

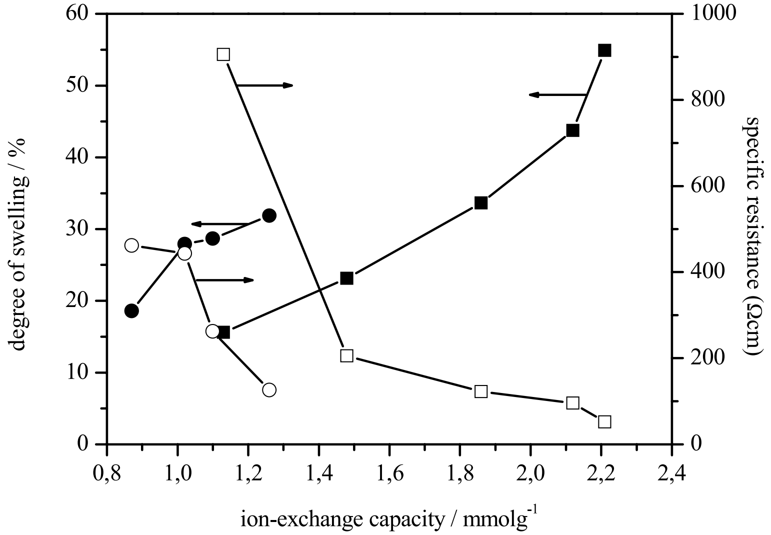


Fig. 26 Comparison of sulfonated poly(arylene ether sulfone) membranes prepared by post-sulfonation and direct polymerization (●, ○: s-PSU; ■, □: s-PES; *open symbols*: specific resistance, *filled symbols*: swelling). Data taken from [100]

composed of 4,4′-dichlorodiphenylsulfone, 4,4′-dihydoxybiphenyl, and varying amounts of sulfonated 4,4′-dichlorodiphenylsulfone, in order to adjust the ion-exchange capacity between 1.13 and 2.21 mmol/g. By variation of the sulfonation time, ion-exchange capacities of s-PSU between 0.87 mmol/g and 1.26 mmol/g were achieved. These values correspond to degrees of sulfonation ranging from 50% to 72%, taking into account that only one sulfonic acid group is introduced to the bisphenol A unit. Furthermore, it should be mentioned that the s-PSU material was sulfonated at the electron-rich bisphenol A moiety in the polymer backbone.

Despite having higher IEC, s-PES samples swelled much less than the s-PSU samples. Contrary to these findings, the specific resistances of s-PSU samples were significantly higher. The s-PES membranes with an IEC ranging from 1.86 mmol/g up to 2.21 mmol/g exhibited electrical properties comparable to the commercial membranes. The electrical resistances of these membranes were below 1.0 Ωcm^2. However, the mechanical properties were drastically weakened when the IEC exceeded 2 mmol/g. These findings were rationalized with the lower molecular weight of these polymers due to the low reactivity of the sulfonated monomer, which prevents the formation of high molecular weight samples. In these membranes the plasticizing effect of absorbed water is more pronounced than in a high molecular weight sample of lower IEC. However, no molecular weights for the prepared polymers were given in the paper. Chronopotentiometric measurements indicated excellent electrochemical properties, making the s-PES membranes suitable for electro-membrane application at high current ranges, especially electro-dialysis.

Shin et al. reported on sulfonated poly(arylene ether sulfone)s prepared from 4,4′-difluorodiphenylsulfone, hydroquinone, and hydroquinone sulfonic acid [67]. The degree of sulfonation was controlled by variation of the hydroquinone/hydroquinone sulfonic acid ratio. The IECs calculated from the monomer composition were in the range from 0.59 mmol/g to 2.47 mmol/g (determined 2.13 mmol/g). Despite the high IEC the water uptake was very low, corresponding to 8.8 to 10 water molecules per sulfonic acid group. Due to their good mechanical and thermal properties, these polymers are considered to be promising candidates for fuel cell applications. However, neither proton conductivities nor fuel cell test data were reported.

Lakshmi et al. [173], Meier-Haack et al. [172], and Taeger et al. [58] used the silyl-method for the preparation of sulfonated poly(arylene ether sulfone)s. Like Shin et al. [67], these authors used hydroquinone sulfonic acid as source for the proton exchange group. Polymers were prepared from the more reactive 4,4′-difluorodiphenyl sulfone rather than 4,4′-dichlorodiphenyl sulfone and various silylated bisphenol comonomers, such as hydroquinone, phenolphthalein, 2,6-dihydroxynaphthalene, bisphenol A [173], or 4,4′-dihydroxybiphenyl [58, 172, 173]. The use of silylethers and difluoro aromates allows for lower reaction temperatures (150 °C), as in the case of dichloro aromates and free bisphenols (180–190 °C). In the latter case, the water formed has to be removed by azeotropic distillation and the lower reactivity of the dichloro compound has to be taken into account.

Polymers with 75 or 60 mol % of hydroquinone sulfonic acid were prepared, resulting in membranes with theoretical IECs ranging from 1.32 mmol/g to 1.95 mmol/g [173]. The water uptake of the samples varied with the IEC as well as with the chemical structure of the polymer backbone. Samples with the highest IEC showed the highest water uptake. It was found that the water uptake could be reduced when bulky bisphenols, such as 2,6-dihydroxynaphthalene, phenophthalein, or 4,4′-dihydroxybiphenyl, were incorporated into the polymer backbone. On the other hand, the highest proton conductivities were detected for membranes derived from polymers with hydroquinone (3.3 mS/cm at 25 °C (IEC 1.95 mmol/g)) or bisphenol A (3.05 mS/cm at 25 °C (IEC 1.81 mmol/g)).

It is well accepted that the superior properties of Nafion® membranes result from a phase separation between the hydrophobic perfluorinated polymer backbone and the sulfonic acid bearing side-chains. This phase separation leads to the formation of ion-conducting channels in the nm-range. Also ion-exchange membranes derived from sulfonated styrene-ethylene/butylene-styrene triblock copolymers (s-SEBS) exhibit a phase-separated morphology, which led to proton conductivities similar to Nafion® but with a much lower methanol crossover [178].

Table 7 Ion exchange capacity and water uptake of poly(ether sulfone) membrane samples (taken from [58])

Sample[a]	Water/ uptake (%)	H_2O/SO_3H mol/mol	Ion exchange capacity (mmol/g) calculated from monomer comp.	titration	NMR
HPA	1.4	–	0	–	–
HPB	n.d.[a]	–	2.48	–	–
PAE-MBC 5/5	34.4	19	1.24	0.83	0.99
PAE-MBC 10/5	21.7	14	0.83	0.67	0.86
PAE-MBC 15/5	12.6	12	0.62	0.46	0.59
PAE-MBC 20/5	9.5	9	0.51	0.35	0.59
PAE-MBC 10/10	28.3	14	1.24	0.84	1.14
PAE-MBC 20/20	34.8	16	1.24	0.90	1.19
PAE-RC 1/1	33.2	16	1.24	1.15	1.14
PAE-RC 2/1	16.9	12	0.83	0.85	0.81
PAE-RC 3/1	11.8	11	0.62	0.45	0.61
PAE-RC 4/1	8.4	10	0.50	0.08	0.48
Nafion® 117	28.9	21	0.91[b]	0.77	–

[a] not determined due to solubility in water
[b] [27]

Taeger et al. [58] and Meier-Haack et al. [172] investigated the properties s-PES block copolymers and the corresponding random copolymers. The aim of this work was to provide fully aromatic ion-exchange membranes with a phase-separated morphology. Both, block and random copolymers were prepared from 4,4′-difluorodiphenylsulfone, hydroquinone sulfonic acid, and 4,4′-dihydroxybiphenyl. The theoretical IECs were adjusted by monomer composition between 0 mmol/g (homopolymer from 4,4′-dihydroxybiphenyl and 4,4′-difluorodiphenylsulfone) and 2.48 mmol/g (homopolymer from hydroquinone sulfonic acid and 4,4′-difluorodiphenylsulfone).

The water uptake and ion-exchange capacities for poly(ether sulfone) membranes are given in Table 7. The ion-exchange capacities, determined by ^{1}H NMR spectroscopy are in good agreement with the values calculated from the initial monomer composition. However, using the titration method, the values are somewhat lower, which is rationalized by the fact that only a part of the sulfonic acids groups is accessible to the sodium ions. On the other hand, with NMR spectroscopy, all sulfonic acid groups are detected, regardless of whether they play an active role in the ion-exchange process or not. Therefore, the IEC determined by the titration method gives a more realistic value than that obtained from NMR spectroscopy concerning the behavior of the membrane in the fuel cells.

The water uptake shows a nearly linear dependence from the ion-exchange capacity of the membranes. It is in the same range as observed for the Nafion®

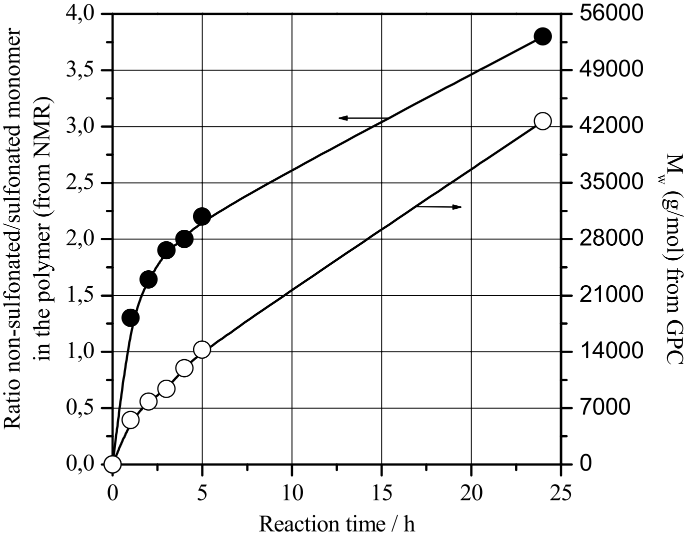


Fig. 27 Influence of reaction time on the monomer ratio in the polymer followed by NMR spectroscopy as illustrated by the preparation of PAE-RC 4/1 (taken from [58])

membranes. Unexpectedly, no difference between the water uptake of random and multiblock copolymers was observed in contrast to sulfonated polyaramide membranes [179]. From studies following the polymerization process of a random sulfonated copoly(ether sulfone), it was deduced, that during the preparation of random copolymers, a block-like structure is obtained due to differences in the reactivity of the monomers (Fig. 27). Therefore, it is likely that the morphology of the membranes prepared from random or block copolymers is very similar, resulting in a similar behavior of the membranes.

As expected, the diffusion coefficients increased with increasing IEC, due to higher hydrophilicity resulting in an enhanced swelling of the membranes. At comparable IEC, the methanol diffusion coefficients for poly(ether sulfone) membranes are one to two orders of magnitude lower than those of the Nafion® membrane, indicating improved barrier properties for methanol (lower methanol crossover) of poly(ether sulfone) membranes. Still, for most membranes the proton diffusion coefficients were also lower than those of the Nafion® membrane. The proton conductivities (Fig. 28A) are reflecting the findings of the diffusion coefficient measurements. Although by a factor of two lower than that of Nafion® 117, the fuel cell performances of the s-PES membranes were comparable to that of Nafion® (Fig. 28B).

The McGrath group [159–171] extensively studied the use of sulfonated 4,4′-dichlorodiphenylsulfone in combination with various bisphenols, such as bisphenol A, bisphenol 6F, hydroquinone, biphenol, and 4,4′-dichlorodiphenylsulfone, for the preparation of ion-exchange materials. The main results of this work were recently published in a review [170]. In general, the

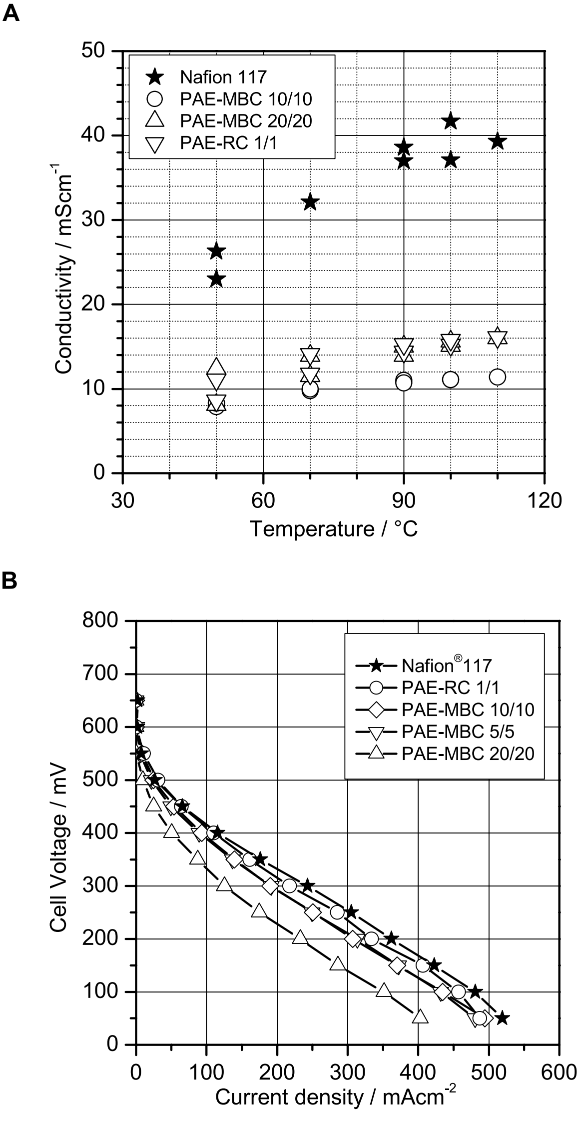


Fig. 28 Electrical properties of poly(ether sulfone) membranes compared to Nafion® 117 membrane; **A** conductivity at 100% relative humidity; **B** polarization curves from DMFC tests at 110 °C (1.5 mol/l MeOH; 2.5 bar air) (taken from [58])

free bisphenols were reacted with the dichloro compounds in NMP at 190 °C, in the presence of K_2CO_3. The prepared materials showed thermo stabilities up to temperatures of 400 °C (weight loss 5%) in nitrogen atmosphere and up to 220 °C in air (30 min). Polymers (BPSH) based on biphenol and DCDPS with up to 60 mol % of the sulfonated monomer (sDCDPS) gave stable membranes, while those with 100 mol % sulfonated monomer (IEC 3.6 mmol/g) were water soluble. The sodium salt form of the sulfonated polymers swelled less in water than in the acid form. Furthermore, the thermo stability of the sodium form was much better than that of protonated membranes. High proton conductivities were achieved with biphenol as the phenolic component. For example a polymer with 40 mol % of the sulfonated monomer (IEC = 1.72 mmol/g) showed a proton conductivity of 110 mS/cm at 25 °C, whereas a polymer with 60% sulfonated monomer (IEC = 2.42 mmol/g) had a conductivity of 170 mS/cm [160]. The value for Nafion® 1135 (IEC = 0.91 mmol/g) given in this paper was 120 mS/cm. A phase separated morphology was reported with hydrophilic domains with a size ranging from 10 to 25 nm, depending on the degree of sulfonation. At sulfonation levels higher than 50% (50 mol % of sulfonated monomer) a phase inversion was observed using AFM. These findings correlated very well with an immense increase of water uptake. Furthermore, samples with more than 50 mol % sDCDPS showed two Tgs in the DSC curves, indicating a well organized phase separation in these systems [165]. Such poly(arylene ether sulfone) membranes showed similar or even better performance in both hydrogen/air and especially direct methanol fuel cell tests than Nafion® 117 membranes [170]. The long-term tests in a hydrogen/air fuel cell (800 h at 80 °C, 0.5 V, and 100% r.h.) revealed a high stability of the poly(arylene ether sulfone) under these conditions.

In a further study, Kim et al. [164] reported on the properties of sulfonated poly(arylene ether sulfone) membranes (BPSH) blended with heteropolyacid (HPA). The blend membrane composed of 70 wt. % of an sulfonated poly(arylene ether sulfone), having an IEC of 1.72 mmol/g and 30 wt. % HPA, showed much higher conductivities than non-blended membranes and even Nafion® 1135 (Fig. 29). After treatment, the weight loss of the blend membranes increased with increasing degree of sulfonation of the polymer matrix, but was only 2% after 48 h in liquid water at 30 °C and ca. 1% after 15 h at 100 °C in water vapor. In a recent paper, Kim et al. reported on poly(arylene ether sulfone)s based on sDCDPS, bisphenol 6F, and 2,6-difluorobenzonitrile [169]. These partly fluorinated membranes with an IEC of 1.32 mmol/g exhibited a 33% higher current density at 0.5 V than that of the above discussed poly(arylene ether sulfone) membranes (IEC 1.72 mmol/g) and a recasted Nafion® 1100 membrane with comparable thicknesses. Similar proton conductivities were detected for all membranes discussed in this paper. Although having a slightly higher water uptake, the fluorinated membrane exhibited an approximately 2-fold lower methanol permeability when compared to Nafion®.

In more fundamental works, Kim et al. studied the influence of (hydro)-thermal pre-treatment and the state of water in sulfonated polymers on the membrane performance [166–168]. Again, BPSH samples with different degree of sulfonation were used for the investigations. Kim indicated three

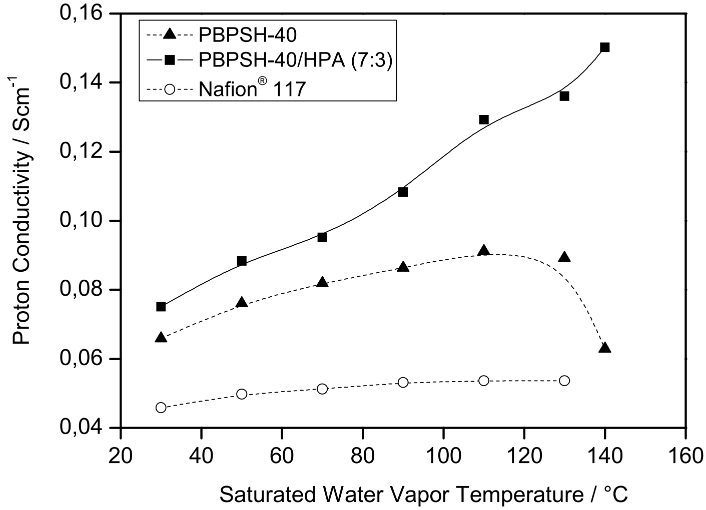


Fig. 29 Proton conductivities of sulfonated poy(arylene ether sulfone) membrane and its blend with a heteropolyacid in comparison with Nafion® 117 (data taken from [164])

irreversible morphological states (regimes, borders indicated by arrows in Fig. 30), which can be controlled by the copolymer composition, and the pretreatment parameters (temperatures). Regime 1 describes the morphology of the as-casted membrane with isolated hydrophilic domains. Within this regime the water absorption increases only slightly with the temperature. In regime 2, where interconnection between hydrophilic domains occurs, the water absorption increases steadily (linear) with treatment temperature, while in regime 3 a rapid water absorption with temperature is observed (Fig. 30). In this regime, the hydrophilic/hydrophobic domain structure was no longer well defined. But not only the water uptake is influenced by the morphological changes. The mechanical properties (Fig. 31) and the proton conductivities (Fig. 32) also show dependencies on hydro-thermal treatment.

The transition temperatures of poly(arylene ether sulfone)s and Nafion® 1135 are given in Table 8. The formation of destinct morphological regimes on thermal treatment allows to adjust the membrane properties in terms of proton conductivity, water uptake, and mechanical strength at an optimum, by treatment at an appropriate temperature. On the other hand, the knowledge of the transition temperatures could be used to predict the upper operation temperature of ion-exchange membranes in fuel cells. These findings also demonstrated that the performance loss of ion-exchange membranes at elevated temperatures might not only be based on dehydration but also on morphological changes as indicated by comparison of the ion conductivities at elevated temperature and the regime transition temperatures of the respective polymer membranes. The morphological changes can be

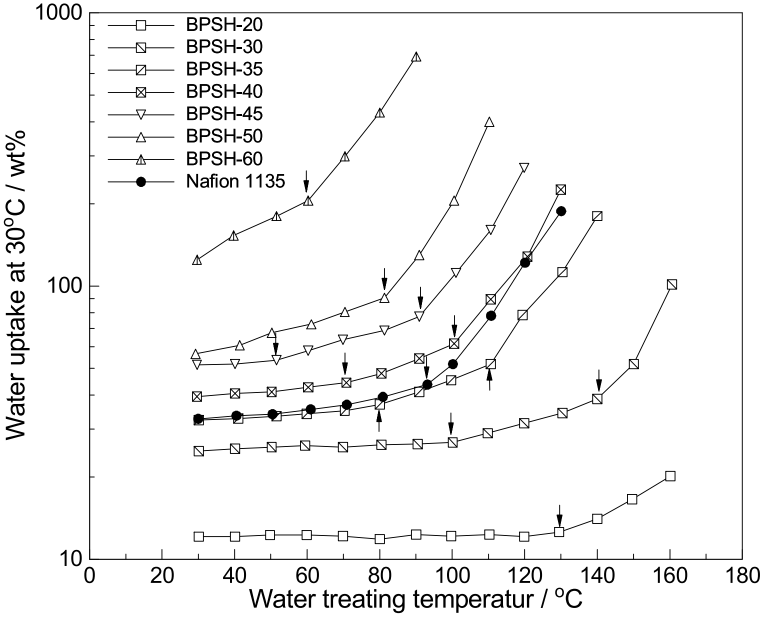


Fig. 30 Water absorption of sulfonated poy(arylene ether sulfone) membranes as a function of water treatment temperature (data taken from [166]). The regime transition temperatures are indicated by *arrows*

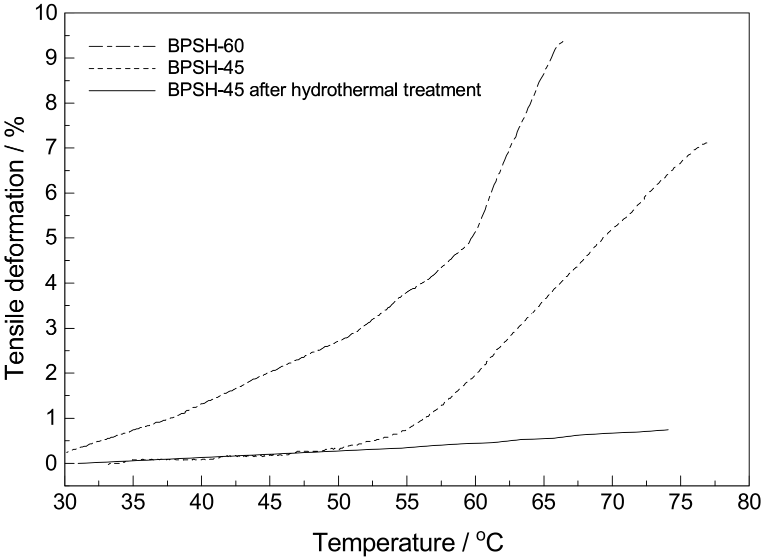


Fig. 31 Tensile deformation of sulfonated poy(arylene ether sulfone) membranes (data taken from [166])

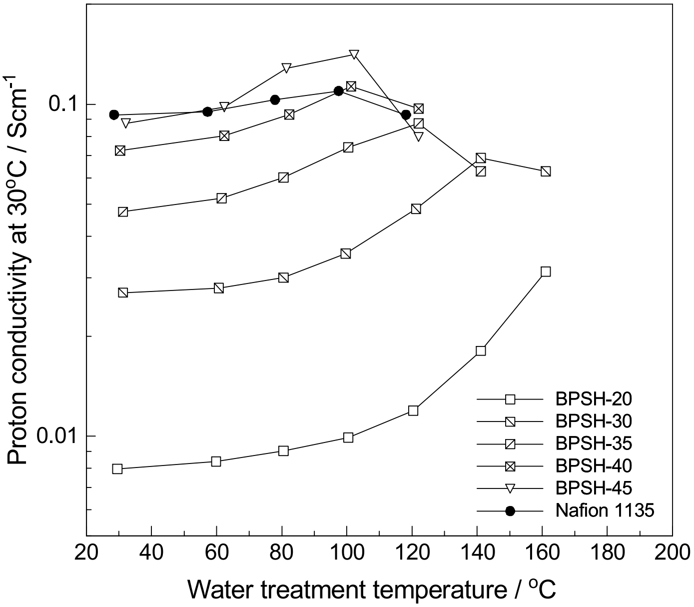


Fig. 32 Proton conductivities of sulfonated poy(arylene ether sulfone) membranes (data taken from [166])

Table 8 Transition temperatures of sulfonated poly(arylene ether sulfone)s and Nafion® (data taken from [166])

Sample	Transition temperature (°C) Regime 1/Regime 2	Transition temperature (°C) Regime 2/Regime 3
BPSH-20	130[a]	n.d.
BPSH-30	100	140
BPSH-35	80	110
BPSH-40	70	100
BPSH-45	50 (53[b])	90
BPSH-50	30	80
BPSH-60	n.d.[c]	60 (59[c])
Nafion® 1135	n.d.	100

[a] Detected by swelling measurements

[b] Detected by dynamic mechanical measurements

[c] n.d. not detected

attributed to the T_g depression in the presence of absorbed water. For the poly(arylene ether sulfone) membranes, the lowering of T_g with the water content was much more pronounced than for Nafion® 1135 [168].

Similar results were reported by the same author while performing acidification treatment under different conditions (variation of time and temperature) [167]. Contrary to the findings for poly(arylene ether sulfone) membranes, the conductivity and water sorption were invariant with treatment temperature.

5.4
Poly(Arylene Thioether Sulfone)s

Poly(phenylene sulfide)s (PPS) are an interesting class of high performance engineering thermoplastics. They possess high melting temperatures, good mechanical properties, as well as good chemical resistances, which is on one hand of certain interest for fuel cell membranes, for example. On the other hand, some of these properties are restricting the processability of poly(phenylene sulfide)s, in particular to membranes, due to their very limited solubility in common organic solvents. Schauer and Brozova reported on the sulfonation of PPS with chlorosulfonic acid in 1,2-dichloroethane [180]. Even samples having an IEC of 1.6 mmol/g were insoluble in organic solvents. Liu et al. [181] reported on the effect of preparation conditions on the properties of poly(phenylene sulfide sulfone), which has been described as an amorphous polymer with a T_g around 217 °C (see ref. 4 and 5 in [181]) and which is now soluble in dipolar aprotic solvents, such as NMP or DMAc. In a paper of the McGrath group, Wiles et al. [182] reported on poly(arylene thio ether sulfone)s based on 4,4′-difluorodiphenylsulfone, sulfonated 4,4′-difluorodiphenylsulfone, and 4,4′-thiobisbenzenethiol (for further references on the synthesis of (sulfonated) poly(arylene thio ether)s the reader is referred to ref [183] and the literature cited in there). High-proton conductivities up to 160 mS/cm at 30 °C in water with an IEC of 1.65 mmol/g were observed. AFM-images revealed the build-up of a continuous hydrophilic matrix when the content of the sulfonated monomer in the polymer backbone exceeds 40 mol %. Since then, severals groups reported on the synthesis of sulfonated poly(arylene tio ether sulfone) and/or sulfonated poly(arylene thio ether ketone)s as potential ion-exchange materials for fuel cell applications [184–190]. In all cases, 4,4′-thiobisbenzenethiol was used as thiol-component, which was reacted with various sulfonated and non-sulfonated dihalogeno aromatics such as difluorobenzophenon, difluorodiphenylsulfone, and others. On treatment with water at elevated temperatures, all these sulfonated poly(sulfide sulfone)s and poly(sulfide ketone)s showed excellent dimensional stability, even at high ion-exchange capacities (up to 3.2 mmol/g). These high IECs are responsible for proton conductivities higher than those observed for Nafion under similar test conditions. Furthermore, a very high oxidative stability was observed. Shen et al. [184] reported on the formation of sulfone groups as a result of the oxidation of the thio ether groups. In order to further improve the mechanical properties and the dimensional stability of these materials, Bai et al. [187] and Lee and Kerres [189] prepared blend membranes with polybenzimidazole as blend partner. The proton conductivities were slightly lowered due to the formation of ion-pairs (SO_3H-imidazole), but the effect on water uptake (reduction) was much more pronounced. As a side-effect, the oxidative stability was also improved. Another approach towards the improvement of mechanical properties and reduction of methanol permeability was described by Zhang et al. [188]. They prepared chemically crosslinked membranes (compared to ionically crosslinked membranes discussed before) by the treatment of sulfonated poly(sulfide sulfone) membrane with polyphosphoric acid at 180 °C for 1.5 h. Since the crosslinking occurs by the intermolecular reaction of sulfonic acid groups within non-sulfonated aromatic rings of neighbor chains, a loss of ion-exchange capacity (10–20%) and, therefore, proton conductivity is unavoidable (up to 50%). Simultaneously, the water uptake and the methanol crossover was reduced by 50% and 50 to 80%, respectively. Recently, Schönberger and Kerres reported on the synthesis of multiblock copolymers, including poly(sulfide sulfone)s, consisting of hydrophilic sulfonated segments and fluorinated hydrophobic segments. These authors reported on the effect of different building blocks (monomers) linking elements on the stability of the resulting polymer. It turned out, that thio ether groups linked to assymetrically substituted rings are less stable than thio ether groups between symmetrically substituted rings. The properties of the latter were similar to those ionomers with sulfone linkages although having a slightly lower oxidative stability.

As the hydrolytic stability of aromatic sulfonic acids depends strongly on the electron densitiy and, therefore, on the substitutes at the aromatic ring, electron-withdrawing groups should protect the sulfonic acid groups from hydrolytic cleavage. The electron-withdrawing groups should further increase the acidic strength of the sulfonic acid group when attached to the same ring. Shen et al. [184] and other researchers already mentioned that the thio ether linkage in poly(arylene thio ether)s is oxidized to sulfoxides or sulfones on treatment with Fenton's reagent, for example. Taking this fact into account, Schuster et al. synthesized highly sulfonated poly(*p*-phenylen sulfide)s and converted these polymers into the corresponding sulfonated poly(*p*-phenylen sulfones) [183, 191]. This synthetic route is a smart way to get sulfonated poly(*p*-phenylene sulfone)s by converting the electron-donating thio ether groups into electron-withdrawing groups, which are not accessable by the direct sulfonation of poly(phenylene sulfone). Secondly, the hydrolytic stability and the acidity of the sulfonic acid groups is very much improved [183]. Although many of the properties for a highly effective fuel cell membrane are improved, it should be mentioned that low IEC materials are insoluble in common organic solvents and that high IEC materials are very brittle.

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