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Liu, Baijun; Guiver, Michael D.

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Solid State Proton Conductors

Properties and Applications in Fuel Cells

Edited by

PHILIPPE KNAUTH

*Laboratoire Chimie Provence, Aix-Marseille University - CNRS,
Marseille, France*

and

MARIA LUISA DI VONA

*Department of Chemical Science and Technology,
University of Rome Tor Vergata, Rome, Italy*



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9

Proton Conductivity of Aromatic Polymers

Baijun Liu and Michael D. Guiver

9.1 Introduction

Known for their high performance, aromatic polymers play an important role in high-technology fields. Aromatic polymers are composed of benzene rings or aromatic heterocyclic rings connected by flexible or rigid linkages, which impart the polymers with excellent thermal and mechanical properties [1]. Through tailoring their chemical structures, these polymers can be endowed with special functionality or properties. During the last few years, aromatic hydrocarbon-based polymers containing acid functionality have attracted much attention because of their potential applications as proton-conductive membranes for use in proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) systems. In comparison with commercial perfluorinated sulfonic acid polymers (e.g., Nafion[®]), some advantages of hydrocarbon PEMs include lower cost, lower fuel cross-over, higher temperature stability, and wide variability of their chemical structure, which makes the materials potentially attractive alternatives [2].

One of the most important proton exchange membrane (PEM) property parameters is proton conductivity. However, achieving high proton conductivity without concurrent deterioration of other physical properties, such as mechanical integrity, dimensional and oxidative stability, and fuel resistance, is a difficult challenge in the field of PEM materials for fuel cells [2–4]. In this chapter, we discuss some promising approaches toward achieving this goal.

9.2 Synthetic Strategies of the Various Acid-Functionalized Aromatic Polymers with Proton Transport Ability

Protons derived from acid groups play a crucial role in PEMs operating in a fuel cell system. One of the core tasks is the methodology to incorporate acid groups (e.g., $-\text{SO}_3\text{H}$, $-\text{PO}(\text{OH})_2$, and $-\text{COOH}$) into polymer chains through chemical reactions or physical interactions. Undoubtedly, the achievement of high proton conductivity requires the PEMs to have a sufficiently high content of acid groups. The first topic discussed concerns the introduction of acid groups and the effect of acid group content on proton conductivity. It is well known that the amount of the acid groups, their location on the polymer chain, their distribution, and even the chemical makeup of the polymer chain impact the properties of the PEMs. With the rapid development of PEMs in the last two decades, numerous acid-functionalized aromatic polymers possessing suitable ion exchange capacity (IEC) have been prepared for intended fuel cell applications using various synthetic strategies [2, 4]. First, several typical acid-functionalized aromatic polymers are depicted.

9.2.1 Sulfonated Poly(arylene ether)s

Poly(arylene ether)-type polymers such as poly(arylene ether ketone)s, poly(arylene ether sulfone)s, poly(arylene ether nitrile)s, and poly(arylene ether)s, with backbones typically composed of aromatic rings connected by ether and other linkages (e.g., ketone and sulfone), are well-known families of high-performance plastics utilized in applications for aerospace, optics, electronics, and other high-technology fields [1]. To attain sufficiently conductive membranes for use in fuel cells, proton-conducting acidic groups must be introduced into the polymers by chemical reaction or doping [4].

Several synthetic methods have been developed for the incorporation of acidic groups [2]. Although differences may arise from a variety of testing conditions used, it is evident that the content of the ionic groups and the location of the acid groups are strongly associated with the proton conductivity. Clearly, molecular design and the application of synthetic approaches are important for preparing PEMs with the desired IEC and proton conductivity values. For poly(arylene ether)-type PEMs, the following synthetic approaches are often adopted.

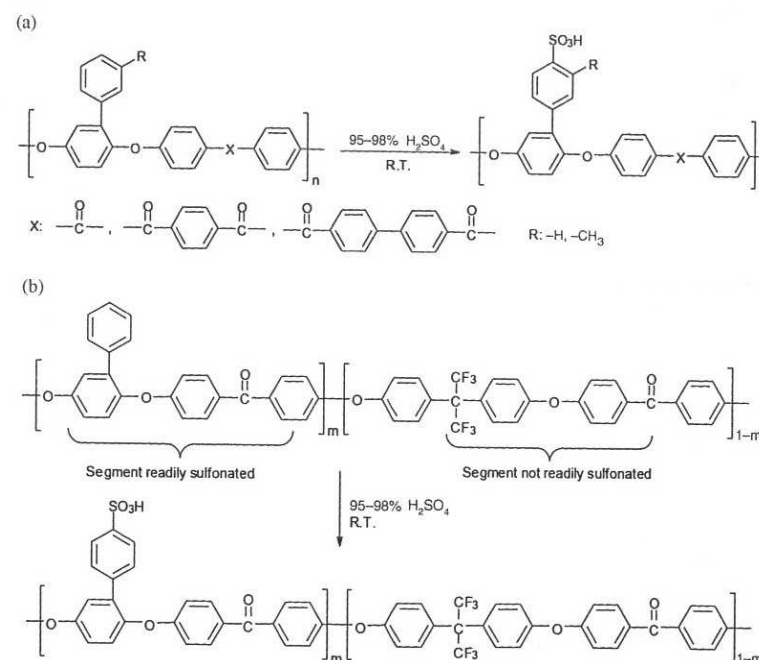
9.2.1.1 Sulfonation of Polymers (Post-Sulfonation)

The introduction of sulfonic acid groups onto substituent-activated sites of benzene rings in small molecular systems is well known. In macromolecular systems containing activated benzene rings, sulfonation reactions also occur under suitable reaction conditions. One advantage of this method is the simple reaction procedure, enabling the process to be readily scaled up. In some circumstances, it may be difficult to achieve precise control of the site of sulfonation and the degree of sulfonation (DS), which may result in a random and less defined distribution of sulfonic acid groups in the polymer chain. If the degree of activation of the polymer benzene rings by substituents is low, vigorous reaction conditions, such as high temperature and strongly acidic sulfonating agent, may be required for sulfonation, which in some cases may lead to the occurrence of side reactions and degradation of the polymer backbone [5].

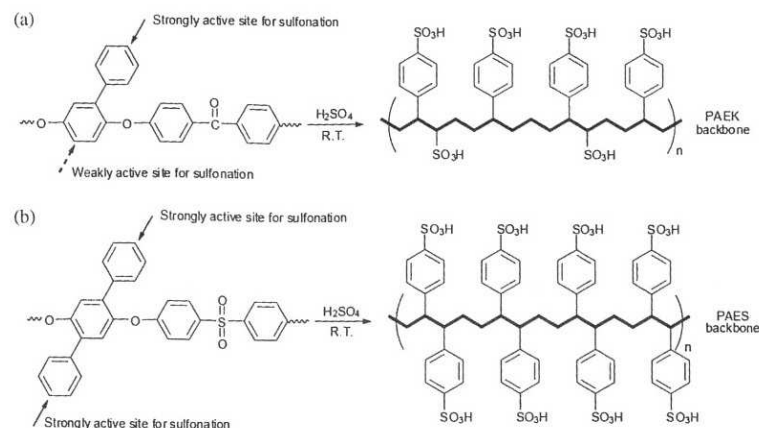
Post-polymerization sulfonation has been used to modify commercially available polymers (e.g., Victrex PEEK) using sulfonation reagents such as concentrated sulfuric

acid, fuming sulfuric acid, chlorosulfonic acid, and sulfur trioxide, resulting in random copolymers containing sulfonated and unsulfonated segments [6]. Generally, any electron-rich benzene rings that are activated toward electrophilic substitution with ether or other groups have the possibility of being sulfonated in macromolecular systems. Thus, through judicious choice of sulfonation reagents and reaction conditions, polymers with suitable IEC values may be obtained. However, the preparation of sulfonated polymers with well-defined chemical structure and adequately high proton conductivity, by using simple sulfonation reactions, is an attractive approach. Importantly, the design and synthesis of the polymer precursor are crucial to meet this requirement.

The post-sulfonation reaction of PEKs with various side substituents, such as phenyl, methylphenyl, trifluoromethylphenyl, and phenoxyphenyl groups, has been investigated, which resulted in sulfonated polymers targeted with single- or double-substituted sites per repeat unit on the pendant phenyl groups [5]. Two series of these sulfonated PEKs based on methylphenylated and phenylated PEKs (Me-SPEKs and Ph-SPEKs) with site-specific substitution have been prepared under mild reaction sulfonation conditions, as shown in Scheme 9.1a. Series of sulfonated poly(ether ketone)s (SPEKs) with ion exchange capacities in the range of 2.23–0.84 mequiv/g could be obtained either by controlling the length of the repeat unit in the homopolymers (Scheme 9.1a), or by adjusting the



Scheme 9.1 Postsulfonation of poly(arylene ether)s. (a) Monosulfonated polymers from homopolymers, and (b) monosulfonated polymers from copolymers. Adapted from [5] B. Liu et al., *Aromatic poly(ether ketone)s with pendant sulfonic acid phenyl groups prepared by a mild sulfonation method for proton exchange membranes*, *Macromolecules*, 40, 1934–1944 (2007).



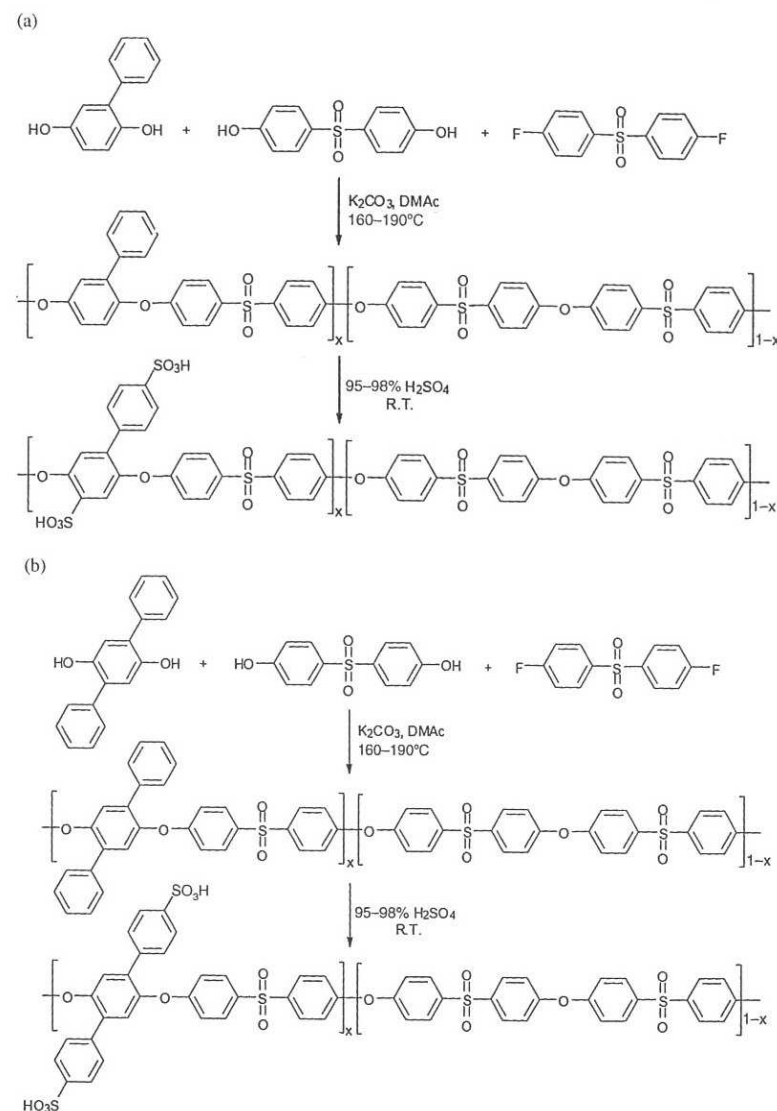
Scheme 9.2 Schematic representations of sulfophenylated polymers based on (a) monophenylated PAEKs, and (b) diphenylated PAEKs. Adapted from [7] B. Liu et al., *Enhanced thermo-oxidative stability of sulfophenylated poly(ether sulfone)s*, *Polymer*, 51, 403–413, Copyright (2010), with permission from Elsevier.

composition of the sulfonatable and nonsulfonatable repeat units in copolymers (Scheme 9.1b). Homopolymer-like Me-SPEKK and Ph-SPEKK with appropriate IEC values (IEC ~ 1.8 mequiv/g) exhibited a high proton conductivity of 0.15 S/cm at 100 °C. In pendant phenyl polymers, the sulfonation reaction occurs on the pendant benzene ring within several hours under mild conditions, but if the reaction time is prolonged, main chain sulfonation also occurs slowly.

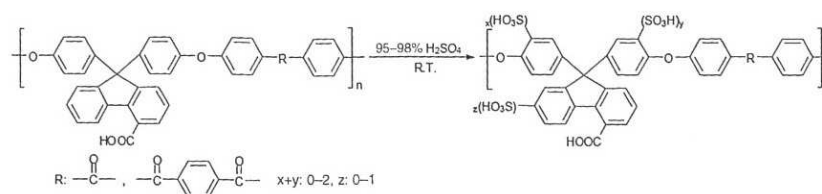
Following this initial work, a series of diphenylated poly(ether sulfone)s (DiPh-PES) were synthesized as precursor materials for the preparation of polymers with two sulfophenylated units per repeat unit (Scheme 9.2). A difference in reaction between the monophenylated poly(ether sulfone)s (Ph-PES) and diphenylated poly(ether sulfone)s could be found. As shown in Scheme 9.3, postsulfonation of Ph-PES in concentrated sulfuric acid led to Ph-SPES bearing sulfonic acid groups on both the pendant phenyl group and the backbone, while the same reaction on DiPh-PES led exclusively to disulfophenylated DiPh-SPES [7]. It was demonstrated by Fenton's oxidative degradation test that the pendant-phenyl-sulfonated (disulfophenylated) DiPh-SPES copolymers possessed obviously better thermal and oxidative stability compared with the corresponding pendant-phenyl-sulfonated/main-chain-sulfonated Ph-SPES copolymers. This clearly indicates a stability advantage for sulfonation on pendant phenyl versus sulfonation on the polymer main chain. DiPh-SPES-50 had a proton conductivity of 0.13 S/cm at 100 °C.

In comparison with the aforementioned sulfophenylated polymers, those containing multiple sulfophenylated units have been reported, which may facilitate the formation of phase separation in the membranes. From the molecular design perspective, starting polymers containing readily sulfonated multiphenyl moieties have to be synthesized.

Several types of fluorenyl-containing poly(arylene ether)s have been prepared for the purpose of making sulfonated PEMs [8]. We investigated the sulfonation of carboxylated



Scheme 9.3 Synthesis of the sulfonated PAES. (a) Sulfonic acid groups on both the pendant phenyl rings and backbones, and (b) exclusively sulfophenylated substitution. Adapted from [7] B. Liu et al., *Enhanced thermo-oxidative stability of sulfophenylated poly(ether sulfone)s*, *Polymer*, 51, 403–413, Copyright (2010), with permission from Elsevier.



Scheme 9.4 Sulfonation of carboxylated fluorenyl-containing polymers (PFEKK-COOH and PFEKK-SO₃H). Adapted from Reference [9].

fluorenyl-containing polymers (PFEKK-COOH), as shown in Scheme 9.4 [9]. Concentrated H_2SO_4 was utilized as both the sulfonation reagent and solvent for this reaction. It is of interest to observe that there are three specific sulfonatable sites per repeat unit, which is quite different from the structural characterization reported for the post-sulfonation of fluorenyl-containing PES without $-\text{COOH}$ groups, in a $\text{ClSO}_3\text{H}-\text{CH}_2\text{Cl}_2$ system [8]. The reaction kinetics of PFEKK-COOH in H_2SO_4 at room temperature clearly showed that the PEMs with certain IEC values could be obtained by simply controlling reaction time.

As shown in Scheme 9.5, Ueda *et al.* reported that up to eight sulfonic acids could be introduced into the four 2-phenylphenoxy pendants of poly(ether sulfone)s using chlorosulfonic acid [10]. For another series of poly(ether sulfone)s with similar chemical structure, simply by changing the sulfonation reagent from chlorosulfonic acid to concentrated sulfuric acid, all the benzene rings connected to the phenylene core could be sulfonated, giving ten $-\text{SO}_3\text{H}$ groups per repeat unit [11, 12]. Through adjusting the monomer feed ratio of the starting polymers, IEC values in the range from 1.77 to 2.40 mequiv/g were obtained. The proton conductivity under different relative humidities of these two series of membranes and Nafion 117 was measured at 80 °C, as shown in Figure 9.1.

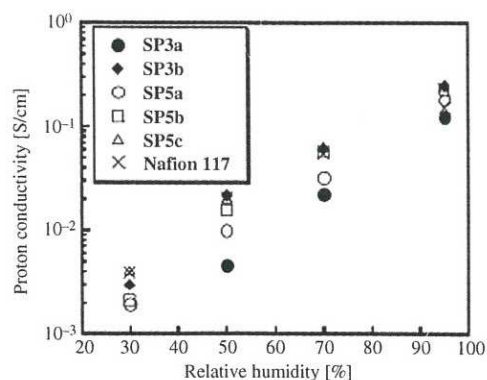
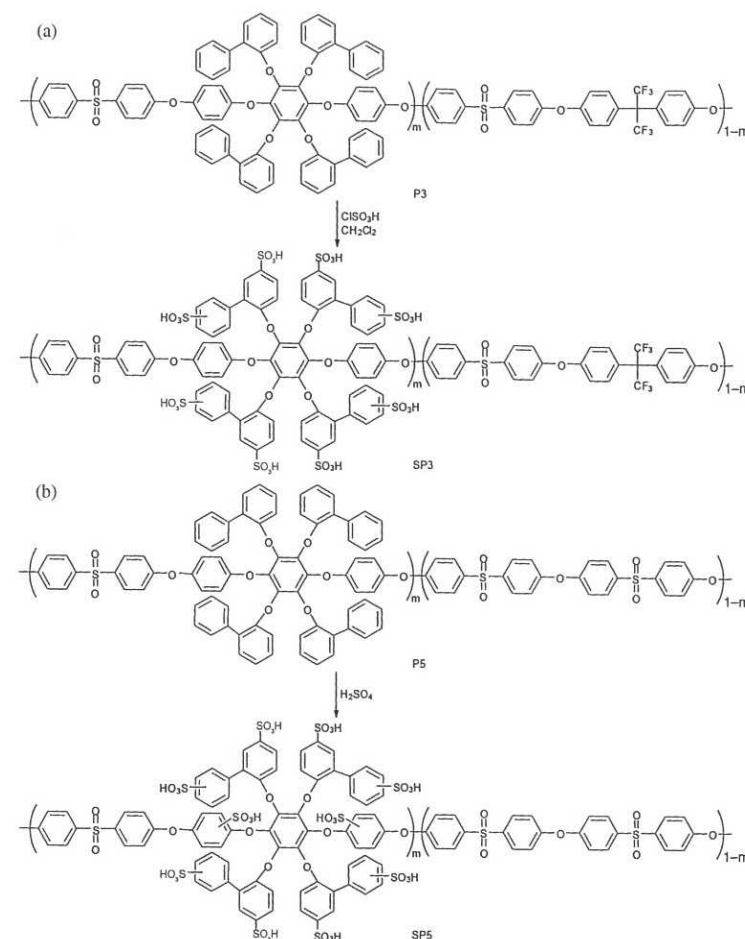


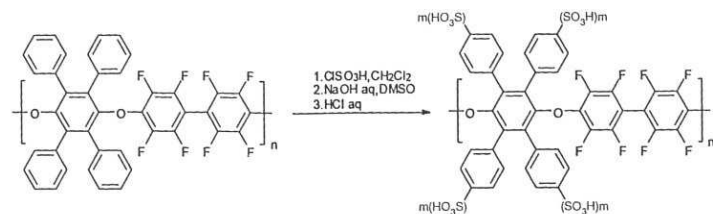
Figure 9.1 Proton conductivity of multisulfonated poly(ether sulfone)s as a function of relative humidity [12]. Reprinted with permission from Polymer, Sulfonated aromatic hydrocarbon polymers as proton exchange membranes for fuel cells by T. Higashihara, K. Matsumoto, M. Ueda, 50, 23, 5341–5357 Copyright (2009) Elsevier Ltd.



Scheme 9.5 Synthesis of multisulfonated poly(ether sulfone)s. (a) Polymers bearing eight acid groups, and (b) polymers bearing ten acid groups. Adapted from [12] T. Higashihara, K. Matsumoto and M. Ueda, Sulfonated aromatic hydrocarbon polymers as proton exchange membranes for fuel cells, *Polymer*, 50, 5341–5357 (2009).

Some membranes were reported to have higher proton conductivity than that of Nafion 117 at 95% relative humidity (RH), which was explained by the formation of well-connected proton-conducting paths, and supported by atomic force microscopy (AFM) tapping phase images of these densely sulfonated PEMs.

Hay's group developed several series of multisulfophenylated polymers by the post-sulfonation of the multiphenylated starting polymers, and some structures are given in Scheme 9.6 [13, 14]. Several of the PEMs had good proton conductivity and cell



Scheme 9.6 Synthesis of the multisulfophenylated poly(arylene ether)s. Adapted from References [13,14].

performance, which might be associated with the well-defined phase-separated microstructure induced by the densely sulfonated moieties.

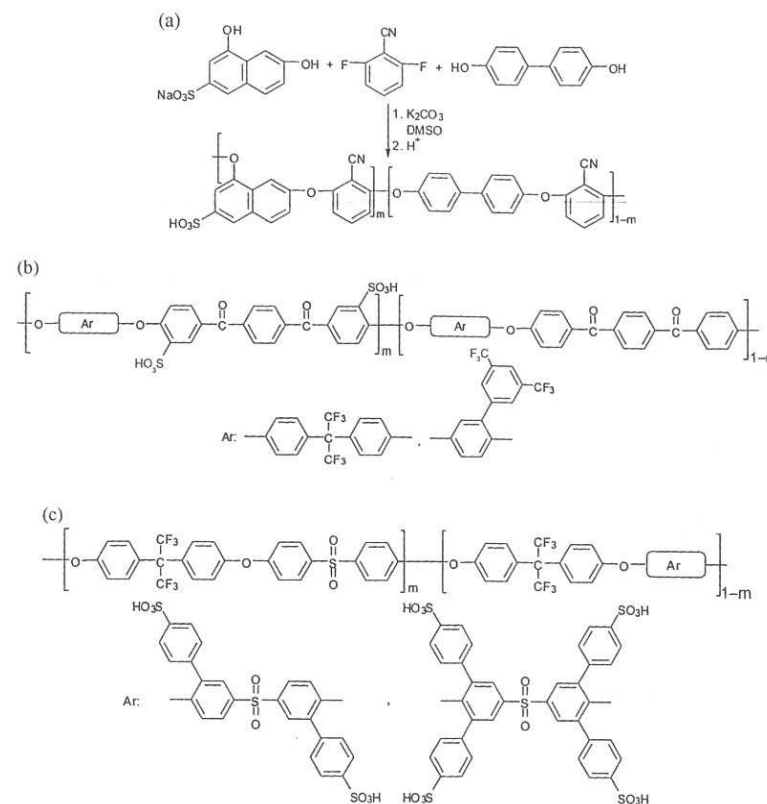
9.2.1.2 Incorporation of Acid Groups through the Polymerization of Sulfonated Monomers

Despite the limited number of available sulfonated monomers and the preparative challenges of some sulfonated monomers, the direct copolymerization approach of combining sulfonated and nonsulfonated monomers has the potential for achieving a better control of the sulfonation content (SC) and provides more defined chain structures in comparison with the copolymers obtained by the post-sulfonation approach [2, 4]. It is worth noting that some polymers derived from certain sulfonated monomers lead to $-\text{SO}_3\text{H}$ groups situated on electron-deficient aromatic rings, which are different from those obtained by the direct post-sulfonation approach, where the sulfonic acid groups are generally bonded to electron-rich aromatic rings.

Up to now, hundreds of sulfonated polymers have been developed that were derived from combinations of various sulfonated and nonsulfonated monomers [2, 4]. The excellent controllability over the IEC values and chemical structure and tailoring the sequence of the sulfonated and unsulfonated monomers allows good property optimization.

As shown in Scheme 9.7a, Guiver *et al.* reported nitrile-containing poly(arylene ether)s derived from three commercially available monomers. Interestingly, one of the structures of polynitrile was observed to have unusually low-dimensional swelling and attractive proton conductivity [15]. Proton conductivity values were similar to that of Nafion 117, particularly for the SC 0.6, which had the best compromise combining mechanical strength, water uptake, and proton conductivity. The good overall properties are believed to result from the rigid and contorted chemical structure and strong interaction between the molecular chains caused by the nitrile groups.

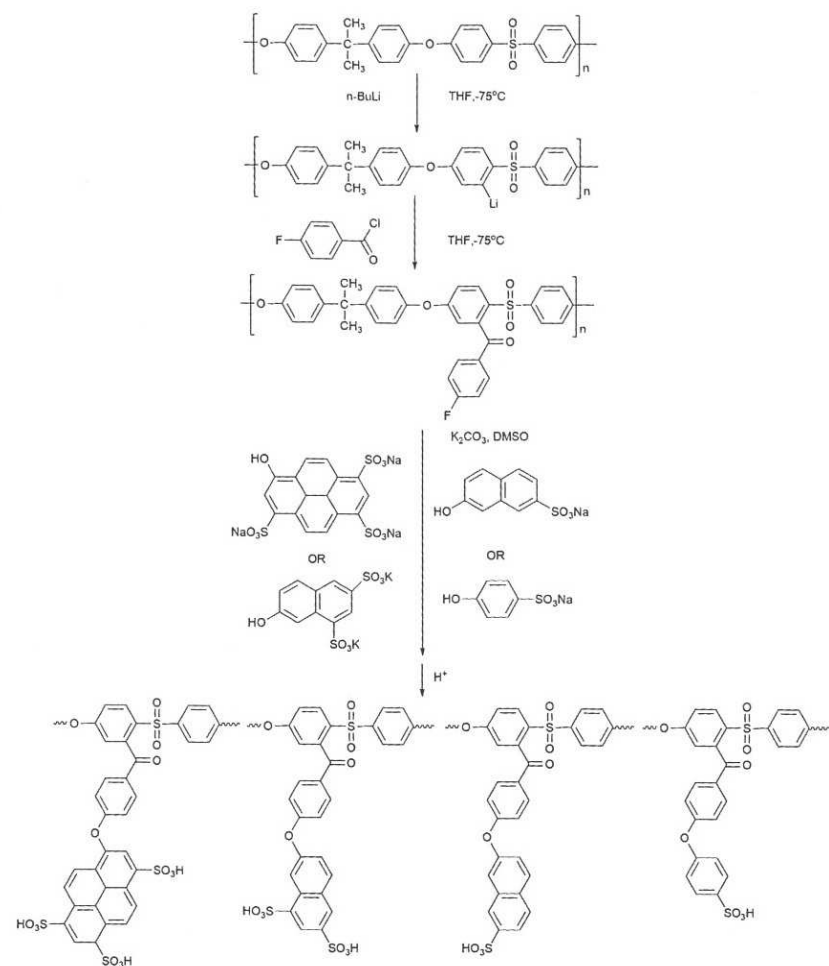
Sulfonated poly(aryl ether ether ketone)s shown in Scheme 9.7b, where the SC and IEC were controlled by the monomer feed ratios, had low water uptake and dimensional swelling, thought to be due to the presence of fluorine-containing moieties and rigid phenyl-ketone-phenyl-ketone-phenyl linkages. The proton conductivity values of several polymers were comparable to that of Nafion at high relative humidity [16]. Most recently, Guiver and Lee reported a series of new polymers having two or four pendant sulfonic acid groups, which exhibited a combination of high proton conductivities, low water uptake, and low methanol permeabilities [17].



Scheme 9.7 Representative chemical structures of sulfonated poly(arylene ether)s obtained by the copolymerization of the sulfonated monomers. (a) Poly(aryl ether nitrile)s, (b) fluorine-containing sulfonated poly(aryl ether ether ketone)s, and (c) poly(arylene ether sulfone)s bearing pendant $-\text{SO}_3\text{H}$ groups. Adapted from References [15–17].

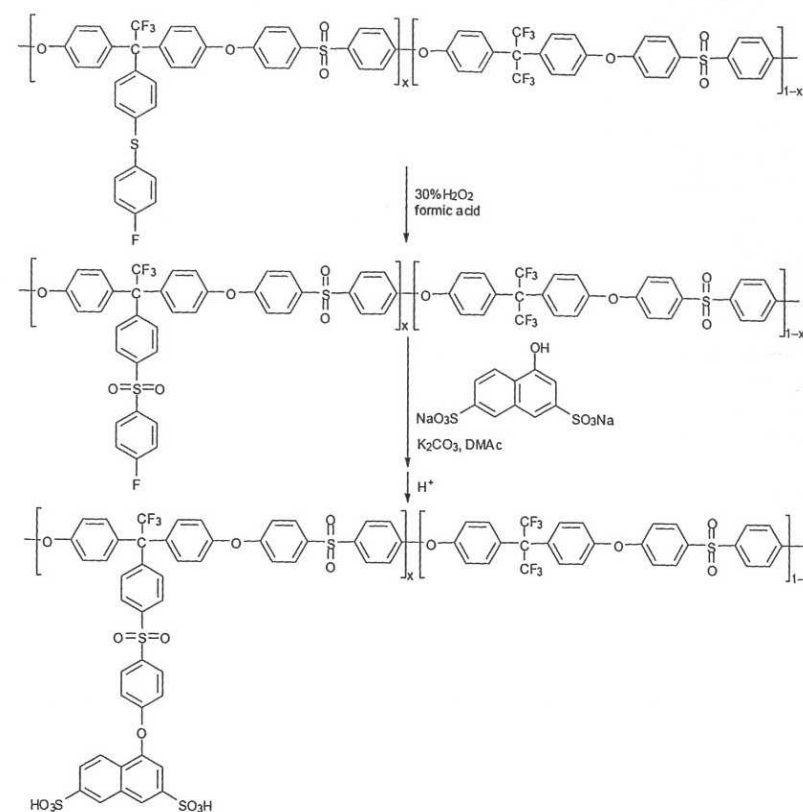
9.2.1.3 Introducing Acid Groups via Grafting Reactions

It is of interest to incorporate $-\text{SO}_3\text{H}$ groups through alternative synthetic strategies, to access polymers with longer side chains. Here, two types of approaches are described as examples. Jannasch reported the preparation of proton-conducting ionomers by attaching pendant sulfonated aromatic side chains to polysulfone with activated fluorine atoms (Scheme 9.8) [18, 19]. First, lithiated polysulfone [20, 21] was reacted with 4-fluorobenzoyl chloride to introduce 4-fluorobenzoyl side chains to the polymer main chain. The activated fluorine atoms were then reacted with various sulfonated phenolates via a nucleophilic substitution reaction. Four types of aromatic side chains, including those terminated by disulfonaphthoxy or trisulfopyrenoxy, led to densely sulfonated side groups that may be beneficial for the formation of proton-conducting channels.



Scheme 9.8 Synthetic route to polysulfones with acid side chains via lithiation-graft reactions. Adapted from References [18,19].

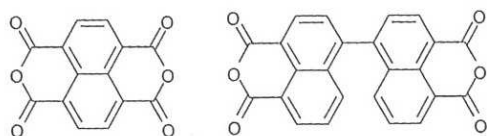
In a different approach, Guiver *et al.* reported polyethersulfone graft copolymers containing a masked grafting site (Scheme 9.9) [22]. Oxidation of the 4-fluorophenylsulfide site to sulfone activates the para fluorine for a further grafting via conventional aromatic nucleophilic substitution to introduce sulfonic acid groups. Different IEC values were obtained by controlling the feed ratio of the graft monomer.



Scheme 9.9 Synthesis of sulfophenylated poly(ether sulfone)s via graft reactions. Adapted from Reference [22].

9.2.2 Sulfonated Polyimides

Sulfonated polyimides (SPIs) have received widespread interest as PEMs, and extensive studies concerning thermal and hydrolytic stability, morphology, and performance related to fuel cells have been conducted [2, 23]. Mercier *et al.* reported the synthesis of a series of SPIs from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), and the results indicated that NTDA-based six-membered-ring polyimides (PIs) were more stable than five-membered-ring PIs under fuel cell conditions [24]. McGrath reported the synthesis of a novel sulfonated diamine containing flexible sulfone and ether linkages, in an attempt to improve hydrolytic stability and membrane ductility [25]. In a recent review by Mercier [23], this important family of sulfonated aromatic polymers was well represented. Therefore, in this chapter, only several typical results are discussed.



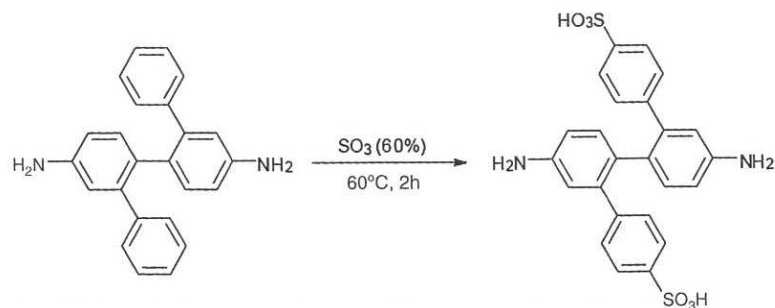
Scheme 9.10 Naphthalenic dianhydrides for the SPIs. Adapted from Reference [23].

9.2.2.1 SPIs from Sulfonated Diamines

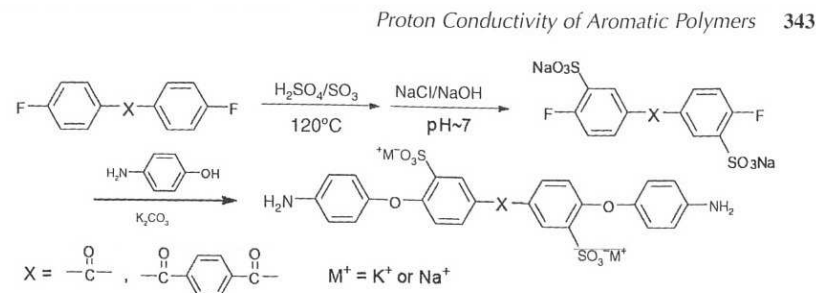
Unlike polyarylether-type polymers (e.g., polyetherketones and polyethersulfones), which can be functionalized either by post-polymerization sulfonation or by direct copolymerization of sulfonated monomers, PIs are sensitive to the hydrolysis of PIs under acidic conditions, and the low solubility of the polyimide precursors limits the post-polymerization sulfonation approach. Except for a few SPIs prepared by the post-sulfonation approach, almost all of the reported SPIs have been synthesized by direct copolymerization of sulfonated monomers [3, 23, 26]. Thus, the preparation of the sulfonated monomers, for example sulfonated diamines or dianhydrides, is especially important. Up to now, most of the sulfonated polyimides for PEMs have been synthesized by the polycondensation of the sulfonated and non-sulfonated diamines and NTDA dianhydride (Scheme 9.10). Apart from several commercially available sulfonated diamines, sulfonated diamine monomers are normally obtained either by sulfonation of the diamine monomers (Scheme 9.11) or by the condensation of sulfonated compounds during the process of diamine synthesis (Scheme 9.12). Okamoto *et al.* classified the above-mentioned sulfonated diamines into two groups: those having a sulfonic group directly bonded to the phenyl ring on which the amino group is present ("Type 1"), and those having the sulfonic group on a bridged phenyl ring ("Type 2") [27].

Many SPIs derived from these sulfonated diamine monomers have been prepared for PEMs. For example, based on a commercially available diamine, 4,4'-diamino-2,2'-biphenyldisulfonic acid, Miyatake *et al.* prepared sulfonated polyimides containing fluorenyl groups that showed good thermal and oxidative stability as well as a high proton conductivity of 1.67 S/cm at 120 °C and 100% RH (Scheme 9.13 and Figure 9.2) [28].

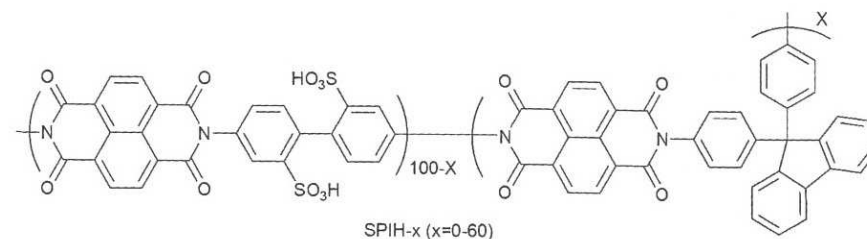
Recently, SPIs containing side chain sulfonic acids have been under increasing consideration for their possibility to induce microphase separation, leading to improved hydrolytic



Scheme 9.11 Synthesis of the sulfonated diamines by direct sulfonation. Adapted from Reference [23].



Scheme 9.12 Synthesis of the sulfonated diamines by condensation of sulfonated compounds. Adapted from Reference [26].



Scheme 9.13 Sulfonated polyimides containing fluorenyl groups. Adapted from Reference [28].

and oxidative stability. As shown in Scheme 9.14, Okamoto reported SPIs derived from 2,2'-(4-sulfophenyl)benzidine, which had improved thermal and hydrolytic stability [29]. The PEMs showed reasonably good proton conductivities, which declined more than Nafion with reduced humidity levels (Figure 9.3). A PEM with an IEC of 1.77 mequiv/g had proton conductivities of 0.12 and 0.26 S/cm at 60 °C and 120 °C, respectively, in water.

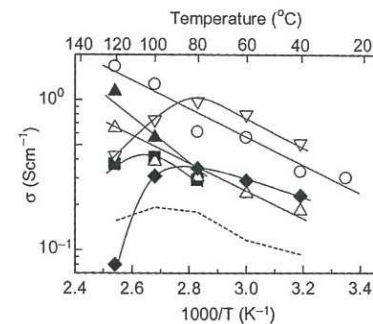
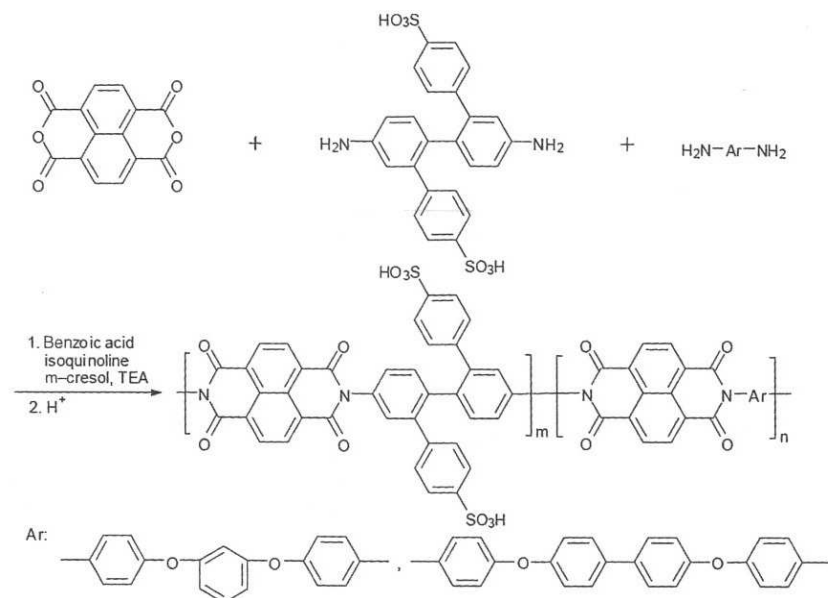


Figure 9.2 Temperature dependence of the proton conductivity of the fluorenyl-containing SPIs and Nafion 112 (dashed line) at 100% RH [28]. Reprinted with permission from *Macromolecules, Proton conductive polyimide electrolytes containing fluorenyl groups; synthesis, properties and branching effect* by K. Miyatake *et al.*, 37, 13, 4956–4960 Copyright (2004) American Chemical Society.



Scheme 9.14 Side-chain-acid SPIs derived from 2,2'-(4-sulfophenyl)benzidine. Adapted from Reference [29].

9.2.2.2 SPIs from Sulfonated Dianhydrides

While SPI PEMs have been primarily prepared from sulfonated diamine monomers, only a few sulfonated dianhydride-based SPIs have been reported as PEM materials for fuel cells. Zhang *et al.* recently reported a novel locally and densely sulfonated dianhydride with four sulfonic acid groups by direct sulfonation of a tetraphenoxypylene-type dianhydride, from which sulfonated copolyimides were prepared (Scheme 9.15) [30]. A copolymer membrane with an IEC of 2.69 mequiv/g had a proton conductivity of 0.126 S/cm at 20 °C and 0.292 S/cm at 100 °C (Figure 9.4). The mechanical properties of the copolymer membranes were almost unchanged after accelerated water stability testing at 140 °C for 100 h, indicating their excellent hydrolytic stability.

In summary, sulfonated aromatic polyimides are a class of well-investigated PEMs that show good proton conductivity and attractive overall performance. The diversity of chemical structures facilitates the design and preparation of SPI PEMs possessing good properties. For example, Watanabe and Miyatake reported SPIs containing aliphatic segments having a stability of greater than 5000 h when operating under fuel cell conditions [31]. However, for SPI PEMs, uncertainties remain about hydrolytic stability in acidic conditions and the loss of mechanical properties under a humidified environment.

9.2.3 Other Aromatic Polymers as PEMs

Besides sulfonated poly(arylene ether)s and polyimides, many other acid-functionalized high-temperature polymers, such as polyphenylenes [32, 33], polybenzimidazoles [34, 35],

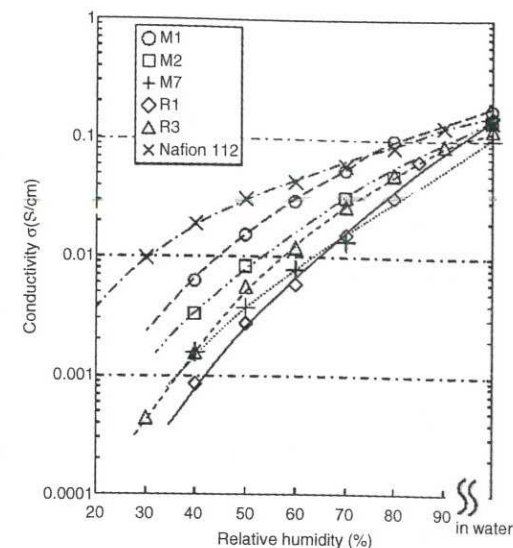


Figure 9.3 Relative humidity dependence of proton conductivity for side-chain-acid SPIs at 60 °C [29]. Reprinted with permission from Polymer, Synthesis and properties of novel sulfonated polyimides bearing sulfophenyl pendant groups for polymer electrolyte fuel cell application by Z. Hu, Y. Yin, H. Kita *et al.*, 48, 7, 1962–1971 Copyright (2007) Elsevier Ltd.

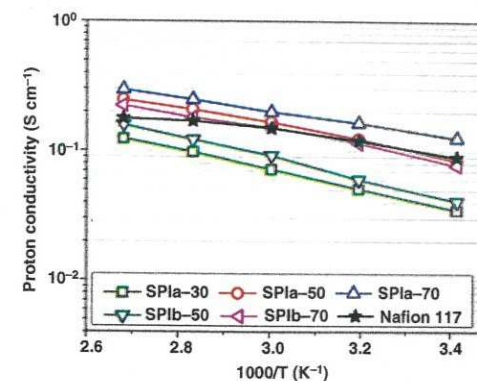
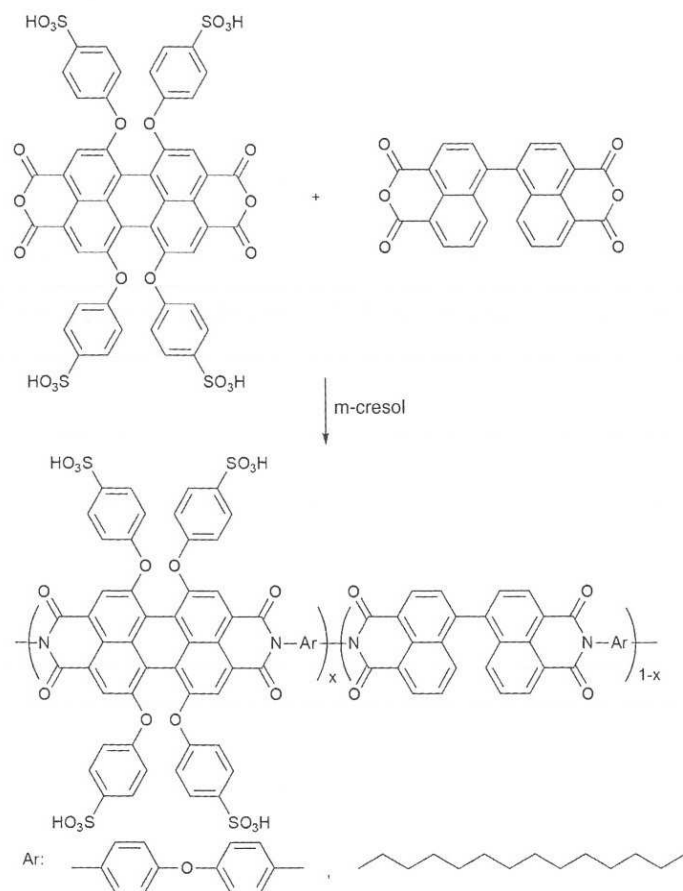


Figure 9.4 Temperature dependence of the proton conductivity of dianhydride-based SPIs and Nafion 117 [30]. Reprinted with permission from Journal of Power Sources, Ionomers based on multisulfonated perylene dianhydride: Synthesis and properties of water resistant sulfonated polyimides by Feng Zhnag *et al.*, 195, 8, 2159–2165 Copyright (2010) Elsevier Ltd.



Scheme 9.15 Side-chain-acid SPIs derived from a sulfonated dianhydride. Adapted from Reference [30].

polyphosphazenes [36], and poly(phenylquinoxaline)s [37], have been prepared for the purpose of fuel cells. Here, we briefly introduce acid-functionalized polybenzimidazoles and phosphonated polymers, which have utility for high-temperature fuel cell applications. The advantages of high-temperature fuel cells include increased electrochemical reaction kinetics at the electrodes, reduced risk of catalyst poisoning, reduced amount of catalyst needed, reduced cathode flooding, and a simpler water management system [38].

9.2.3.1 Benzimidazole-Containing Polymers (Scheme 9.16)

Early work by Wainright showed that polybenzimidazole (m-PBI) doped with ~ 5 moles phosphoric acid per repeat unit (PA/PRU) had a proton conductivity of 0.025 S/cm at 150 °C [39]. Later, it was found that m-PBI with a doping level of between 2 and 8 moles

PA/PRU has a conductivity typically in the range of 10^{-1} to 10^{-4} S/cm at elevated temperatures (> 120 °C) in a nonhumidified environment [40]. Generally, it is believed that higher acid-doping levels lead to increased proton conductivity. Li reported an m-PBI/PA complex with 16 moles PA/PRU and a conductivity of 0.13 S/cm at 160 °C, which is comparable to Nafion under 100% RH at 80 °C [41]. However, high doping levels can result in a loss of mechanical integrity that prevents fabrication into membrane electrode assemblies (MEA)s.

Although polybenzimidazoles doped by strong acids have promising performance at high temperature, there are still some challenges including low ionic conductivity at low temperature; phosphoric acid retention during operations, start-up, and shut-down; and membrane durability at higher doping levels. Recently, the attachment of sulfonic groups onto SPI chains or PBI/sulfonated polymer blend systems was studied, since they show great potential for use as PEMs in high-temperature fuel cells [42, 43].

Rozière *et al.* [44] reported sulfonated m-PBIs with various degrees of sulfonation by grafting sulfonated aryl groups onto polybenzimidazole, and the structure is shown in Scheme 9.16b. Their proton conductivities, measured at room temperature, improved from 10^{-4} S/cm to 10^{-2} S/cm for the SPBIs with a high benzylsulfonic acid content. Bae *et al.* [45] prepared sulfonated SPIs bearing different lengths of flexible side chains. The butylsulfonated-PBI exhibited higher conductivity. Importantly, acceptable conductivities up to 160 °C could be maintained (Scheme 9.16). Through the substitution of the hydrogen atom of the N–H groups in the benzimidazole ring, Gieselman *et al.* synthesized PBI containing aliphatic or aromatic sulfonic pendant groups [46]. In addition, PBI containing acid groups could be synthesized via the polymerization of sulfonated monomer [47].

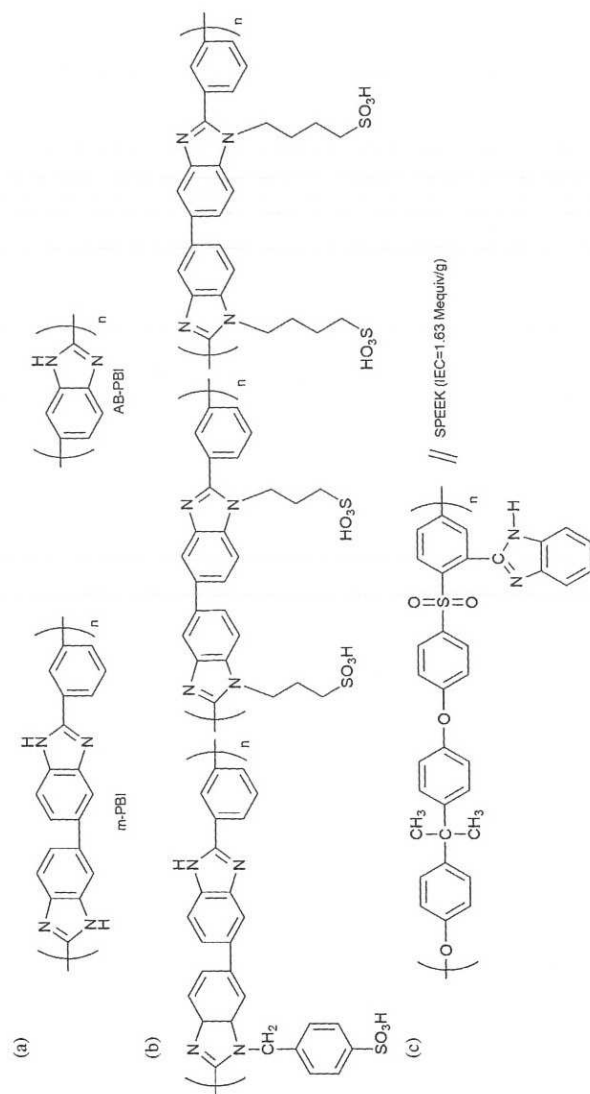
Recently, novel acid–base blend membranes based on sulfonated poly(ether ether ketone) (SPEEK) and polysulfone-bearing benzimidazole side groups have been synthesized by Manthiram, as shown in Scheme 9.16c. Blend membranes exhibit higher proton conductivity and better performance in PEMFC at 90 °C and 100 °C compared to individual SPEEK or Nafion membranes. It was claimed that this may be a promising strategy to develop PEMs that can operate at elevated temperatures and reduced relative humidity [48].

9.2.3.2 Phosphonated Polymers

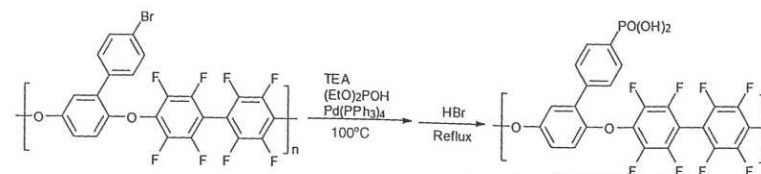
Due to their high and oxidative stability at elevated temperatures, the preparation of aromatic polymers bearing proton-conducting phosphonic acid groups is of growing interest [49–51].

Although phosphonic acid-based PEMs may have considerable potential in higher temperature fuel cells, few phosphonated polymers have been prepared. This is primarily due to the relatively lower acidity of phosphonic acids in comparison with sulfonic acids, such that a high degree of phosphonation is required to achieve adequately high proton conductivity.

A fluorinated poly(arylene ether) with a high degree of phosphonation, derived from a brominated precursor (Scheme 9.17), was reported to possess excellent mechanical properties, thermal and oxidative stability, and low methanol permeability [52]. The phosphonated PEM had a conductivity of 2.6 mS/cm in water at room temperature, and 6.0 mS/cm at 95% RH at 80 °C, which illustrates the considerably lower conductivity compared with the sulfonic acid analog [53]: 68 mS/cm at 30 °C and 135 mS/cm at 80 °C, which is more than one order of magnitude lower.



Scheme 9.16 Representative chemical structure of acid-functionalized PBIs. (a) Typical polybenzimidazoles used for phosphoric acid doped complexes, (b) sulfonated polybenzimidazoles, and (c) blends of polymers containing benzimidazole groups and sulfonated polymers. Adapted from References [38, 44–48].



Scheme 9.17 Synthesis of a phosphonated poly(arylene ether). Adapted from Reference [52].

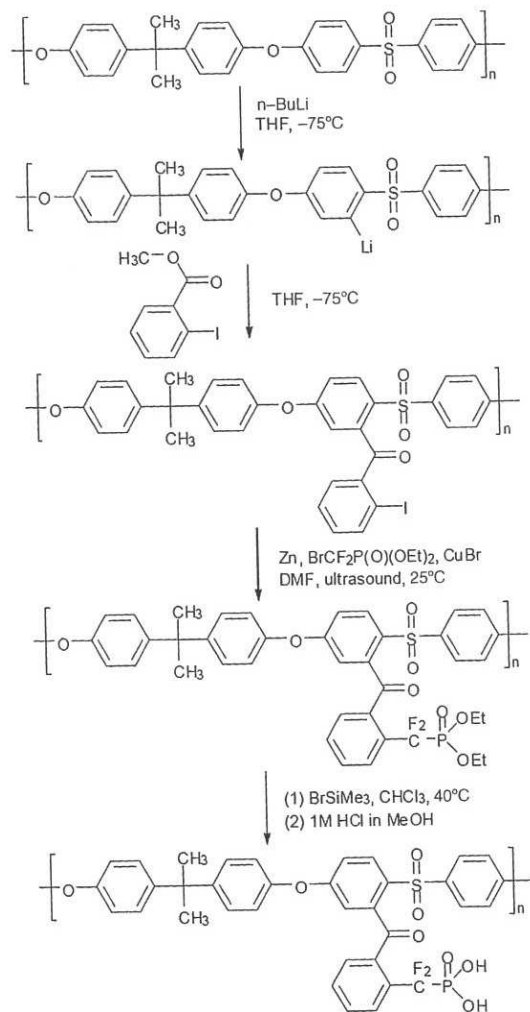
Lafitte and Jannasch reported modified polysulfones with higher acidity phosphonic acid $-\text{CF}_2-\text{PO}_3\text{H}_2$ pendants via a multistep synthetic procedure utilizing a lithiated polysulfone intermediate (Scheme 9.18). Polymers with a degree of phosphonation of up to 0.5 were synthesized and studied. Membranes based on ionomers having 0.90 mmol of phosphonic acid units/g of dry polymer demonstrated proton conductivities up to 5 mS/cm at 100 °C [54].

9.3 Approaches to Enhance Proton Conductivity

It is understood that for a series of the polymers having the same structural backbone, but different contents of sulfonic acid or other proton-conducting groups, the proton conductivity scales with the content of proton conductors (i.e., IEC values). While it is relatively simple to prepare PEMs with high IEC values (e.g., >2.0 mequiv/g), most cannot maintain adequate mechanical properties in a humidified or wet environment, because the hydrophilic acidic groups absorb excessive amounts of water that swell or dissolve the PEM. Excessive dimensional changes in PEMs that occur at different temperatures and humidities render them impractical for fabricating into MEAs, since a dimensional mismatch between the catalyst-ionomer layer and the PEM leads to failure when operating in the fuel cell [55]. Addressing the performance trade-off between conductivity, on one hand, and water uptake and dimensional swelling, on the other hand, is currently an intense area of research. As well, strategies to maintain PEM proton conductivities at elevated temperatures and reduced relative humidity levels that target the automotive fuel cell sector are another important area. Here, synthetic approaches that improve the proton conductivity and overall PEM and cell performance for hydrocarbon-based polymers are discussed.

9.3.1 Nanophase-Separated Microstructures Containing Proton-Conducting Channels

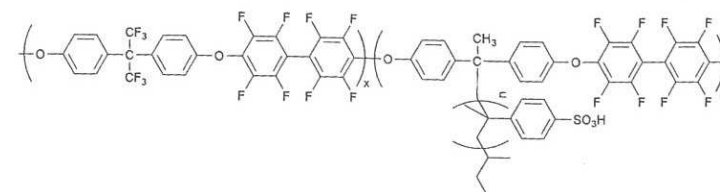
Sulfonated hydrocarbon PEMs generally have lower proton transport ability than perfluorinated PEMs such as Nafion® for several reasons. One of the reasons is that sulfonated aromatic polymer membranes tend to have an ambiguous or ill-defined hydrophobic or hydrophilic nanostructure [56]. The design of PEMs with distinctly phase-separated nanostructure and connected proton-conducting channels is one approach that can improve proton conductivity at relatively lower IEC values, and has the potential to allow better water retention and conductivity at elevated temperatures. From the viewpoint of polymer architecture, nanophase-separated ordered morphology can be induced most commonly



Scheme 9.18 Synthesis of a phosphonated polysulfone. Adapted from Reference [54].

either through block copolymers or by graft (or comb-type) structures, and Holdcroft *et al.* made an interesting comparison of PEM properties between the two types of systems [57].

A new class of comb-shaped polymers was prepared (Scheme 9.19) comprising a rigid and fluorinated hydrophobic backbone and sulfonated α -methyl polystyrene hydrophilic side chains [58]. As shown in the TEM images in Figure 9.5, the rigid hydrophobic polymer backbone and the flexible sulfonated hydrophilic side chains self-assemble into phase-separated nanometer-sized structures, and one of the membranes even showed clear



Scheme 9.19 Structure of comb-shaped sulfonated polymers. Adapted from Reference [58].

worm-like connected channels. Excellent proton conductivity values of these PEMs were obtained for relatively low IEC, as shown in Figure 9.6.

Most recently, Kim [59] compared three sulfonated aromatic polymers with different sequence lengths in order to better understand the relationship between molecular structure, morphology, and the properties of proton exchange membranes as a function of relative humidity (Scheme 9.20). Tapping-mode scanning force microscopy (SFM) was used to compare the morphological arrangements of the sulfonated aromatic PEMs as a function of RH (Figure 9.7). Alternating (homo-polymer-like) polymers were found to have large hydrophobic and hydrophilic domains, although the continuity between hydrophilic domains is poor. This lack of connectivity may help to explain the relatively low water diffusivity and conductivity at reduced RH. The random copolymer exhibited a disordered morphology with some connectivity between the hydrophilic regions, but with no well-defined ionic pathways for proton or water transport. Some change in the phase contrast can be seen, as the hydrophilic and hydrophobic domains undergo a small amount of further phase separation upon increasing RH. The multiblock copolymer showed a well-defined structure with continuous hydrophilic and hydrophobic pathways, which may be responsible for fast proton transport, even at low humidity, as well as the faster water transport than

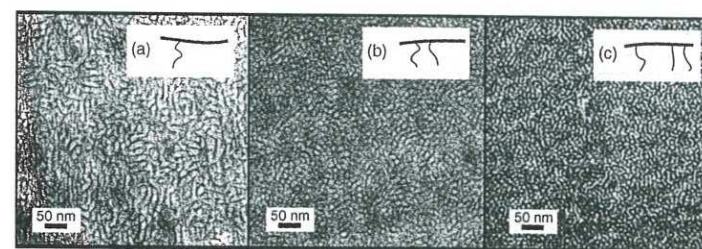


Figure 9.5 TEM images of the comb-shaped sulfonated polymers: (a) polymer 1 (IEC = 0.87 mequiv/g), (b) polymer 2 (IEC = 1.40 mequiv/g), and (c) polymer 3 (IEC = 1.75 mequiv/g) [58]. Reprinted with permission from *Advanced Functional Materials*, Highly fluorinated comb-shaped copolymers as proton exchange membranes (PEMs): improving PEM properties through rational design by T. Norsten, M. Guiver, J. Murphy *et al.*, 16, 1814–1822 Copyright (2006) Wiley-VCH.

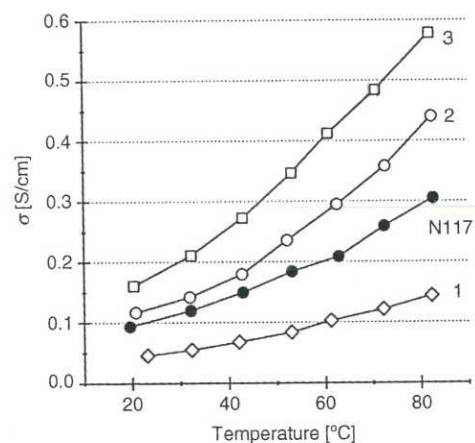
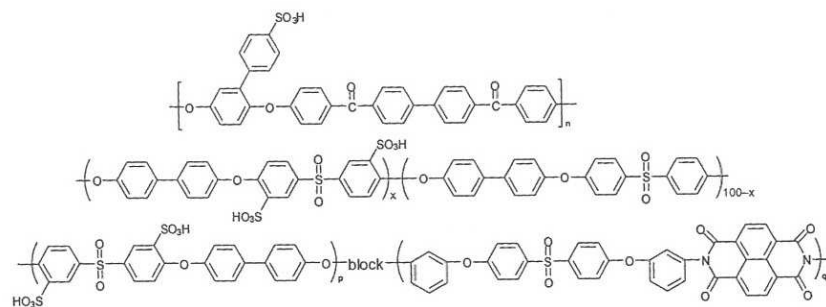


Figure 9.6 Temperature dependence of proton conductivity for comb-shaped sulfonated polymers and Nafion 117. For polymers 1, 2, and 3, the IEC values are 0.87, 1.40, and 1.75 mequiv/g, respectively [58]. Reprinted with permission from *Advanced Functional Materials, Highly fluorinated comb-shaped copolymers as proton exchange membranes (PEMs): improving PEM properties through rational design* by T. Norsten, M. Guiver J. Murphy et al., 16, 1814–1822 Copyright (2006) Wiley-VCH.

that of the alternating and random polymers. These morphological features help to explain that improved proton conductivity can be obtained with multiblock copolymers at low RH. For all PEMs, the proton conductivity increased with RH, but the conductivity of the multiblock copolymer was significantly higher than that of the random and alternating systems at low RH. The relative slopes of the log (conductivity) versus RH in a plot



Scheme 9.20 Structure of sulfonated aromatic PEMs (Ph-PEEKDK: alternating polymer; BPSH-35: random copolymer; BPSH-15-PI-15: multiblock copolymer). Adapted from [59] M. Einsla et al., *Toward improved conductivity of sulfonated aromatic proton exchange membranes at low relative humidity*, *Chem. Mater.*, 20, 5636–5642 (2008).

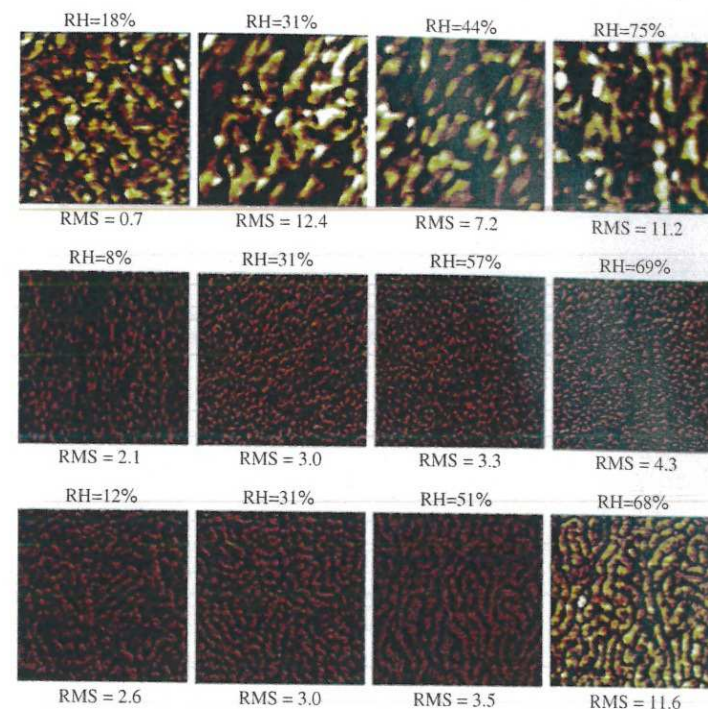
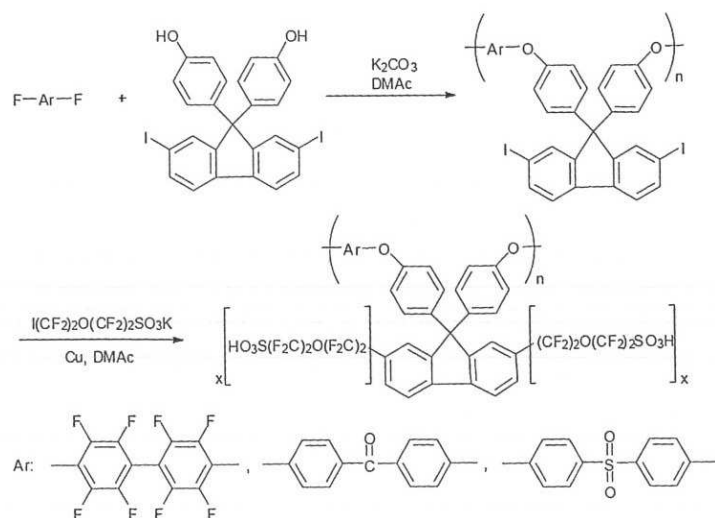


Figure 9.7 SFM images of alternating (top), random (center), and multiblock (bottom) PEMs as a function of RH. Image size is 1 μm . Reprinted with permission from *Chemistry of Materials, Toward Improved Conductivity of Sulfonated Aromatic Proton Exchange Membranes at Low Relative Humidity* by M. L. Einsla et al., 20, 17, 5636–5642 Copyright (2008) American Chemical Society.

illustrated the effect of humidity on PEM conductivity. The multiblock copolymer had the lowest slope, meaning that its conductivity was less dependent on RH.

9.3.2 Replacement of $-\text{Ph}-\text{SO}_3\text{H}$ by $-\text{CF}_2-\text{SO}_3\text{H}$

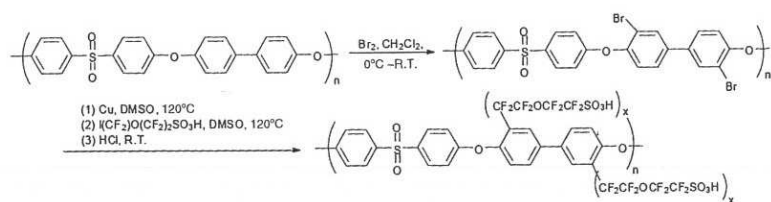
One of the reasons for the lower proton conductivity of sulfonated aromatic PEMs is attributed to their weaker acidity in comparison with perfluorosulfonic acid PEMs; the pK_a value for $\text{Ph}-\text{SO}_3\text{H}$ is -2.5 , whereas that for $\text{CF}_3-\text{SO}_3\text{H}$ is -13 . Therefore, the effective proton concentration and proton mobility are comparatively much lower in aromatic PEMs. Moreover, the weak acidity combined with the more rigid chemical structure of aromatic ionomers (compared with perfluorosulfonic acids) may result in poor hydrophilic and hydrophobic phase separation, further contributing to their lower proton conductivity. Thus, one approach to improve conductivity in aromatic PEMs is by the incorporation of perfluoroalkyl sulfonic acid side chains onto aromatic polymers, which have higher thermal stability than perfluoroalkyl ionomer backbones [60, 61].



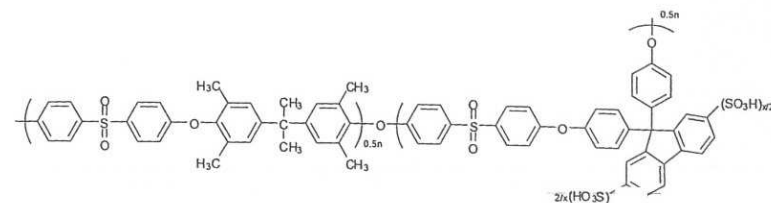
Scheme 9.21 Synthesis of poly(arylene ether)s containing superacid groups. Adapted from Reference [60].

Miyatake *et al.* synthesized a series of poly(arylene ether)s containing perfluorosulfonic acid pendants through a nucleophilic aromatic polycondensation of an iodine-substituted fluorenyl bisphenol with activated difluoro-monomers, followed by an Ullmann coupling reaction of the resulting iodo-polymers with potassium tetrafluoro-2-(tetrafluoro-2-iodoethoxy)ethanesulfonate, as shown in Scheme 9.21 [60]. It was reported that a degree of perfluorosulfonation up to 92% could be obtained, which corresponds to an IEC value of 1.52 mequiv/g. The flexible membranes exhibited obvious hydrophilic and hydrophobic phase separation with small interconnected hydrophilic clusters (2–3 nm). Importantly, these aromatic PEMs containing superacid groups showed much higher proton conductivities than those of conventional sulfonated aromatic polymers with similar polymer backbones.

Using a similar reaction, Yoshimura [61] reported poly(ether sulfone)s incorporating $-\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_3\text{H}$ as side chains (PES-PSA) by dihalogen coupling of a bromine-containing PES-Br with an iodo-perfluorinated sulfonic acid using copper metal, followed by treatment with aqueous HCl, as shown in Scheme 9.22. The proton conductivity of PES-PSA



Scheme 9.22 Synthesis of poly(arylene ether)s with perfluoroalkyl sulfonic acid pendants (PES-PSA). Adapted from Reference [61].



Scheme 9.23 Chemical structure of methyl-substituted poly(arylene ether sulfone)s containing fluorenyl groups. Adapted from Reference [63].

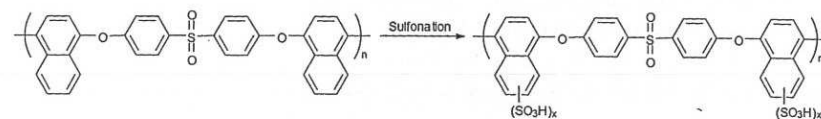
with an ion exchange capacity of 1.58 mmol/g was 0.12 S/cm at 80 °C and 90% RH. The proton conductivities of PES-PSA were higher than those of SPES PEMs at any IEC level and under any humid conditions, although the IEC dependence on the water uptake behavior of PES-PSA was similar to that of SPES. The high conductivity values obtained were explained by the higher acidity of the perfluoroalkyl sulfonic acid of PES-PSA compared with arylsulfonic acid. An MEA for PEMFC was fabricated from PES-PSA with an IEC of 1.34 mequiv/g, and the maximum power output at 80 °C was 805 mW/cm².

9.3.3 Synthesis of High-IEC PEMs

As discussed earlier, there is a well-known trade-off between high IEC (and proton conductivity) and water uptake and dimensional stability. Since these properties are highly dependent on molecular structures, it is hard to determine the range of IEC values that give useful properties for PEMs. Some high-IEC sulfonated aromatic polymers exhibit unusually good dimensional stability in water. This may offer a way to prepare high-proton-conductivity PEMs [62].

Miyatake reported a poly(arylene ether sulfone) that was water-insoluble, even at a high IEC value of 3.26 mequiv/g, as shown in Scheme 9.23 [63]. The isopropylidene tetramethylbiphenylene moieties were helpful in improving the hydrolytic, oxidative, and dimensional stability of the PEM, which had a proton conductivity of 5.6 mS/cm at 80 °C and very low humidity (20% RH). The conductivity was comparable to or higher than that of Nafion 112 at 80–120 °C and 20–93% RH. The fluorenyl PEM also had better ohmic performance than Nafion in H₂ and O₂ fuel cells at a temperature of 90 °C, which was attributed to possibly having good water retention capacity.

Recently, Ueda reported sulfonated binaphthyl-containing poly(ether sulfone)s having low water solubility at high-IEC levels (Scheme 9.24) [64]. In order to achieve a high IEC value of 3.19 mequiv/g, a two-stage sulfonation technique was employed, involving trimethylsilyl chlorosulfonate at the first stage, followed by sulfuric acid. As shown in Scheme 9.24, the sulfonated samples are designated BNSH-X, where X shows the degree of



Scheme 9.24 Synthesis of the sulfonated poly(1,10-dinaphthyl ether phenyl sulfone)s. Adapted from Reference [64].

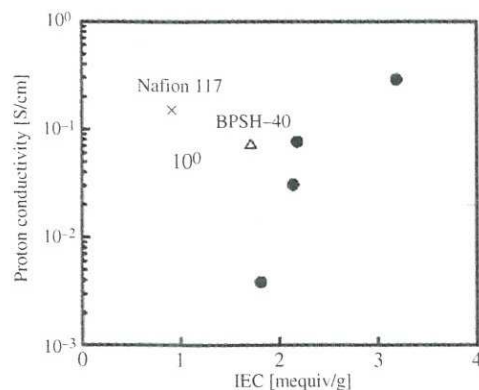


Figure 9.8 IEC dependence of proton conductivity in 95%RH at 80°C [12]. Reprinted with permission from Polymer, Sulfonated aromatic hydrocarbon polymers as proton exchange membranes for fuel cells by T. Higashihara, K. Mtsmoto, M. Ueda, 50, 23, 5341–5357 Copyright (2009) Elsevier Ltd.

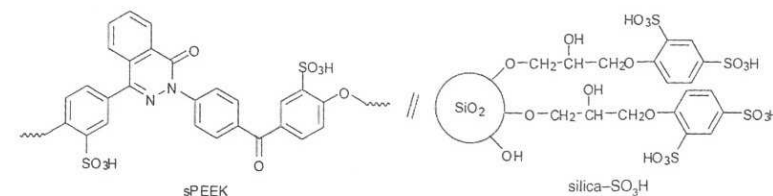
sulfonation (%) per naphthalene unit. It is noteworthy that the highest IEC membrane, BNSH-100, remained insoluble in water and maintained its mechanical integrity at 80°C and 30–95% RH. This was attributed to its rigid and bulky binaphthyl structure. A comparison of proton conductivity for BNSH-X, BPSH-40, and Nafion is shown in Figure 9.8. The proton conductivity of the BNSH-100 membrane was higher than that of Nafion 117. A commonly reported PEM, poly(arylene ether sulfone) BPSH-40, is included for comparative purposes [12, 64].

9.3.4 Composite Membranes

The preparation of composite or hybrid PEMs by the addition of certain “fillers” into polymer electrolytes to enhance the proton conductivity, improve water retention, or reduce fuel cross-over is a topic of current interest.

Nanocomposite PEMs were prepared from sulfonated poly(phthalazinone ether ketone) (sPPEK) and sulfonated silica nanoparticles (silica-SO₃H), and their structure is shown in Scheme 9.25 [65]. The strong -SO₃H/-SO₃H interaction between sPPEK chains and silica-SO₃H particles was explained as the reason for the observed increase in both the thermal stability and methanol resistance of the PEMs. The NM-SA-7.5 membrane (7.5 g of silica-SO₃H/100 g of sPPEK) showed a 3.6-fold increase in proton conductivity over that of the unfilled sPPEK membrane, demonstrating that the addition of certain fillers could enhance proton conductivity. As illustrated in Figure 9.9, two principal mechanisms, vehicle and Grotthuss (hopping), were suggested to occur. Later, the same group reported another kind of nanocomposite membrane using a similar preparative method [66]. The formation of microphase separation within the membranes was observed by TEM, and the proton conductivity and selectivity were higher than the unfilled PEM.

Another approach to enhance the proton conductivity of aromatic polymer membranes is by incorporating acid-functionalized polysilsesquioxane (POSS-SO₃H), IEC~5.71 mequiv/g, as shown in Scheme 9.26 [67]. The hybrid membranes were prepared



Scheme 9.25 Structures of polymer electrolyte sPPEK and sulfonated silica nanoparticles silica-SO₃H. Adapted from [66] Y. Su et al., Increases in the proton conductivity and selectivity of proton exchange membranes for direct methanol fuel cells by formation of nanocomposites having proton conducting channels, J. Power Sources, 194, 206–213, (2009).

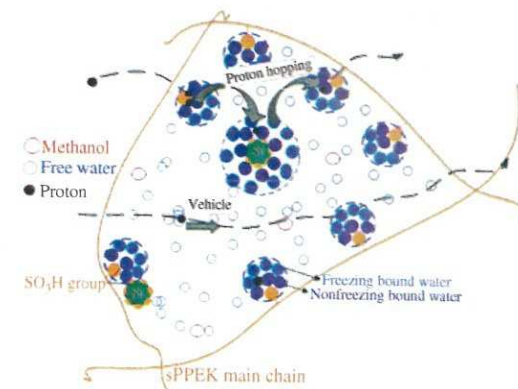
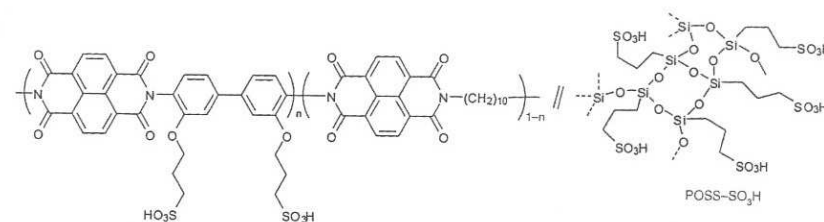


Figure 9.9 Illustration on the state of water and the proton-transport mechanism in the sulfonated-silica nanocomposite membranes [66]. Reprinted with permission from Journal of Power Sources, Increases in the proton conductivity and selectivity of proton exchange membranes for direct methanol fuel cells by formation of nanocomposites having proton conducting channels by Y.-H. Su et al., 194, 1, 206–213 Copyright (2009) Elsevier Ltd.



Scheme 9.26 Chemical structures of polymer electrolytes (matrix) and sulfopropylated polysilsesquioxane (POSS-SO₃H). Adapted from [67] K. Miyatake et al., Enhanced proton conduction in polymer electrolyte membranes with acid-functionalized polysilsesquioxane, Angew. Chem. Int. Ed., 46, 6646–6649 (2007).

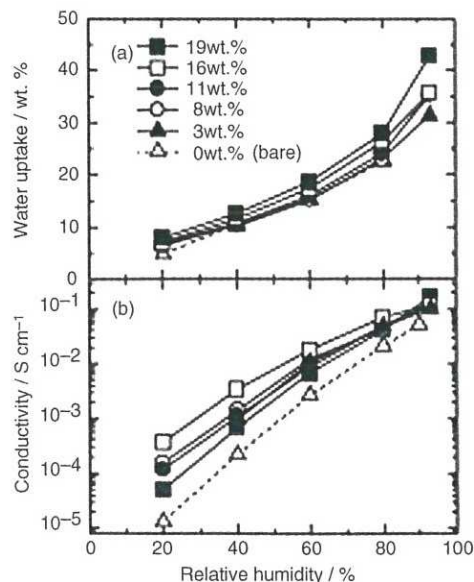


Figure 9.10 Humidity dependence of (a) water uptake, and (b) proton conductivity of SPI/SiOPS nanocomposite membranes at 80°C [67]. Reprinted with permission from *Angewandte Chemie Int. Ed.*, Enhanced proton conduction in polymer electrolyte membranes with acid-functionalized polysilsesquioxane by H. Miyatake, T. Tombe et al., 46, 6646–6649 Copyright (2007) Wiley-VCH.

by sol–gel processing and had higher proton conductivity over a wide humidity range of 20–90% RH compared with unmodified sulfonated polymer membrane. At 20% RH, the hybrid SPI membrane containing 16 wt.% POSS–SO₃H showed much higher proton conductivity (up to 30 times) than that of the original membranes (Figure 9.10). In particular, the conductivity at low humidity was significantly improved and was believed to be due to the increased IEC and the improved water retention capability.

9.4 Balancing Proton Conductivity, Dimensional Stability, and Other Properties

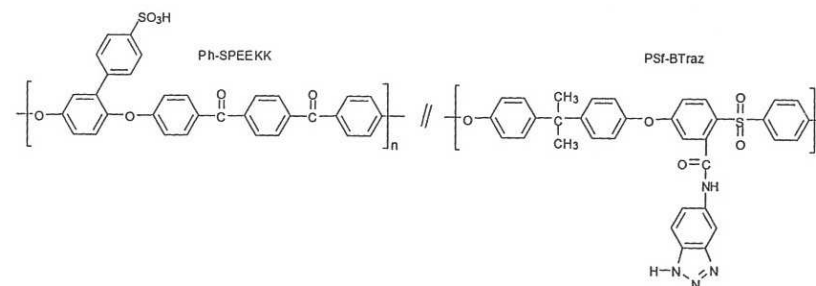
Several approaches to enhance proton conductivity are discussed in the preceding sections, but PEMs used in fuel cells are required to have a combination of other properties, such as appropriate water uptake, good dimensional stability under variable temperature and humidity conditions, mechanical integrity, good oxidative and hydrolytic stability, and low fuel permeability, and be suitable for MEA fabrication. Therefore, high proton conductivity alone is insufficient to judge the properties of PEMs, and it is important that other properties be considered [2].

Generally, fully aromatic polymers without functional groups possess excellent thermal and mechanical properties, and could be used in harsh environments. The incorporation of acid groups, for example –SO₃H and –PO(OH)₂, usually compromise the thermal and oxidative stability and the mechanical properties. The operating conditions within fuel cells make PEM water management crucial [68]. A sufficient amount of bound water in most PEMs is necessary to achieve high proton-conductive capacity, but an excessive amount invariably leads to a loss of mechanical properties and dimensional stability. Maintaining dimensional stability under humidification for highly proton-conductive membranes is a technical challenge and several approaches to achieve this have included covalent cross-linking, acid–base blends, inorganic–organic composites, and dipolar interactions through polar groups.

As shown in Scheme 9.27, Manthiram reported acid–base blend membranes consisting of acidic sulfophenylated poly(ether ether ketone ketone) (Ph-SPEEKK) and various amounts of basic polysulfone tethered with 5-amino-benzotriazole (PSf-BTraz) [69]. The blend membranes had higher proton conductivity and lower liquid uptake and dimensional swelling compared with Ph-SPEEKK and sulfonated poly(ether ether ketone) (SPEEK) membranes. Acid–base interactions are believed to facilitate proton transfer through both the vehicle and Grotthuss mechanisms, and the increased proton conductivity could be associated with the wider hydrophilic channels caused by the insertion of the heterocyclic groups into the ionic channel. All the blend membranes were found to have a much reduced liquid uptake and dimensional swelling compared with their plain counter-part, and these differences were even more evident at high methanol concentrations (5–10 M). The blend membranes had good DMFC performance at high methanol concentrations.

Recently, acid–base blend membranes composed of sulfonated poly(aryl ether ketone) (6FSPEEK) and aminated poly(aryl ether ketone) containing a naphthyl group (AmPEEKK-NA) (Figure 9.11) were reported [70]. The PEMs exhibited improved thermal, oxidative, and dimensional stability, while maintaining acceptable proton conductivity. In particular, the blend membranes possessed excellent tensile properties in both the dry and wet states, which were associated with the strong acid–base interactions.

Another well-investigated approach for stabilizing the dimensional swelling of highly conductive PEMs is by the construction of polymer networks by covalent cross-linking. As



Scheme 9.27 Chemical structures of sulfophenylated poly(ether ether ketone ketone) (Ph-SPEEKK) and polysulfone tethered with 5-amino-benzotriazole (PSf-BTraz). Adapted from Reference [69].

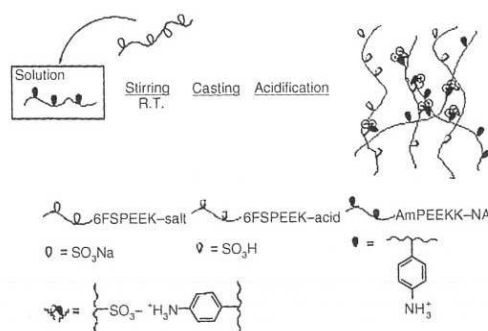
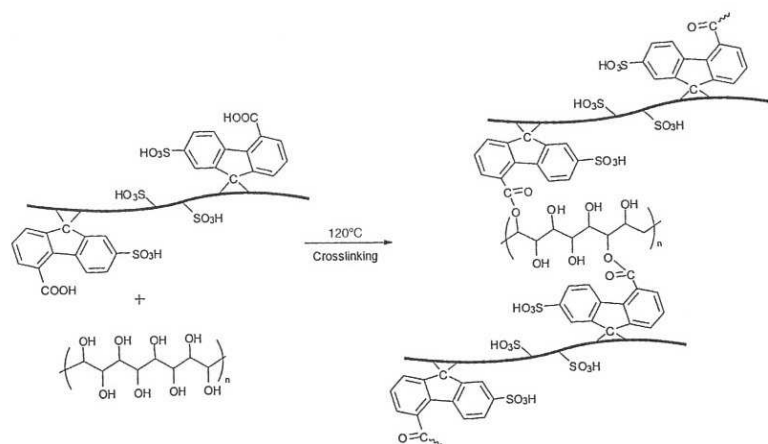


Figure 9.11 Scheme for the preparation of acid-base blend poly(arylene ether ketone) membranes [70]. Reprinted with permission from J. Power Sources, Novel acid-base molecule-enhanced blends/copolymers for fuel cell applications by M. Guo et al., 189, 2, 894–901, Copyright (2009) Elsevier.

an example, poly(aryl ether ether ketone) (PFEEKK–COOH) with carboxylic acid cross-link sites was used to form a network by reaction with poly(vinyl alcohol) (PVA), as shown in Scheme 9.28 [9]. The proton conductivity of the cross-linked SPFEEKK–COOH-1.6/PVA PEM was 0.15 S/cm at 65 °C, while it maintained acceptable dimensional stability in water. It should be pointed out that the ester linkages may not have adequate stability in a fuel cell environment, and more robust cross-links are needed.

More stable covalent cross-link bridges have recently been developed. For example, cross-linked poly(phenylene sulfide sulfone nitrile) PEMs were cross-linked using a



Scheme 9.28 Plausible schematic representation of sulfonated poly(aryl ether ether ketone)s cross-linked by ester linkages. Adapted from [9] B. Liu et al., Poly(aryl ether ketone)s with carboxylic acid groups: synthesis, sulfonation and crosslinking, J. Mater. Chem., 18, 4675–4682 (2008).

carboxylic acid site to give a stable arylketone bridge [71]. The cross-linked PEM had a proton conductivity of 0.22 S/cm at 90 °C while maintaining acceptable dimensional stability. The proton-conducting sulfonic acid sites were originally shown to be cross-linkable through glycerol and other alcohols [72], but the linkage is not believed to be sufficiently robust. More recently, sulfonic acid sites were thermally treated to provide much more stable arylsulfone cross-linked PEMs [73–75]. These cross-linked PEMs exhibited a good balance of proton conductivity and dimensional stability.

Di Vona and Knauth reported several series of hydroxysilylated SPEEK or SPSPU, from which covalently cross-linked systems could be fabricated into blend or composite PEMs [76–78]. The water uptake, transport, and mechanical properties of the blend materials were investigated, and it was shown that the introduction of silylated components enhanced the mechanical strength and the dimensional stability of the membranes, while maintaining acceptable proton conductivity.

Other strategies to enhance the overall properties of PEMs involve inorganic–organic hybrid systems. For example, Kaliaguine reported a cross-linked sulfonated poly(ether ether ketone) by using diamino-organosilicon as a cross-linker for the purpose of improving mechanical and hydrolytic properties [79]. Mendes reported sulfonated poly(ether ether ketone)–zirconium oxide PEMs whereby the incorporation of zirconium oxide resulted in a decrease in the reactant permeability coefficients and an increase in the water and methanol selectivity [80]. Moeller reported sulfonated poly(ether ether ketone)–silica–phosphotungstic acid membranes, and found the hybrid membranes had improved proton conductivity and higher power densities than Nafion 112 in DMFCs [81].

9.5 Electrochemical Performance of Aromatic Polymers

The ultimate destiny of PEMs lies in their utility as a fuel cell component that exhibits good electrochemical performance. Although numerous aromatic PEMs with a wide variety of polymer architecture and structural features have been prepared so far, relatively few of them have been fabricated into MEAs for evaluation of their power output in fuel cells. The majority of the scientific literature is concerned with the polymer synthesis, characterization, and fabrication of PEMs [2]. High proton conductivity, obtained either through optimization of structural architecture and morphology or through polymer structure, is often regarded as the most important parameter when PEMs are evaluated for fuel cell applications. However, due consideration must be given to a combination of other important basic properties that include low fuel cross-over; good thermal, oxidative, and dimensional stability; and mechanical properties. Because the optimal conditions for MEAs prepared from different PEMs are different, it is hard to make a direct performance comparison between different membranes as far as fuel cell performance is concerned. Another compounding factor is the propensity of applying “standard” MEA fabrication procedures to novel hydrocarbon-based PEMs, procedures that were developed over many years for Nafion-based MEAs. In many instances, there are challenging issues of poor adhesion of Nafion ionomer–catalyst mixtures to the hydrocarbon-based PEMs due to their very different chemical compositions, as well as dimensional mismatch between the components when swelling occurs during the humid operating conditions in the cell. For significant

progress in the durability and performance of hydrocarbon-based PEM fuel cells, these issues need to be addressed, which could be through a number of different approaches including modified MEA fabrication techniques, the use of different ionomers, and the surface modification of PEMs. Here, two examples of fuel cell performance based on some of the above-mentioned polymers are presented.

9.5.1 PEMFC Performance

In the previous section, some results on different PEM morphologies between block and random polymers were introduced, as reported by Kim *et al.* [59]. It is of interest to understand how the different morphologies impact fuel cell performance. As shown in Figure 9.12, the polarization curves show the relationship between cell performance and morphology (conductivity) at various RH values. At 70% RH, the random and multiblock copolymers had similar performance, but the alternating PEM had lower cell performance.

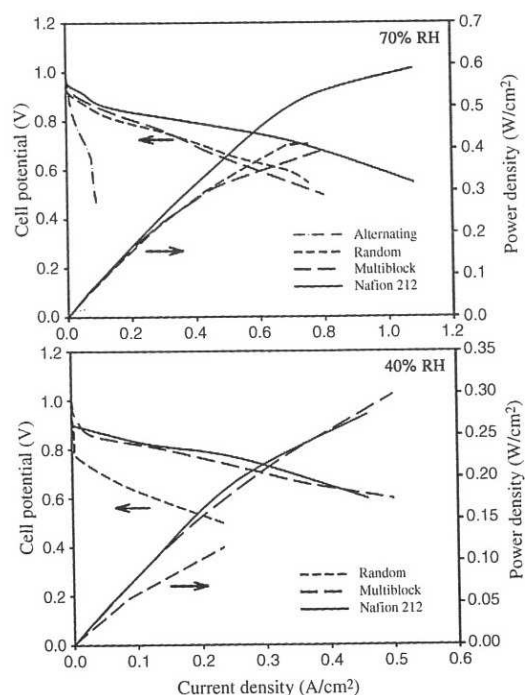


Figure 9.12 Hydrogen–air fuel cell performance of alternating, random, and multiblock PEMs at 100 °C with gas inlet humidification at 70% (top) and 40% (bottom); Nafion performance is shown for comparison [59]. Reprinted with permission from *Chemistry of Materials, Toward improved conductivity of sulfonated aromatic proton exchange membranes at low relative humidity* by M. L. Einsla *et al.*, 20, 17, 5636–5642 Copyright (2008) American Chemical Society.

Interestingly, at low relative humidity of 40%, the performance of the random copolymer suffered significantly, whereas the multiblock copolymer achieved similar performance to that of Nafion. The performance at low RH was believed to be due to the multiblock copolymer's unique morphology, giving it excellent proton transport properties. The power density curves from test membranes are also shown in Figure 9.12, and the same trends as the voltage–current curves were observed. These results provide supporting evidence that optimized morphology improves fuel cell performance at low RH, but further studies are needed to develop this area.

9.5.2 DMFC Performance

Unlike PEMFC performance, the DMFC performance of a number of aromatic polymer electrolytes has been shown to be higher than Nafion [82, 83]. One of the main reasons is that the more rigid aromatic polymer chains generally give lower methanol cross-over. As mentioned in the above section, acid–base Ph-SPEEKK/PSf-BTraz blend PEMs had lower methanol cross-over, liquid uptake, and swelling compared with the individual unblended polymers [68]. In this section, the DMFC performance of this PEM will be discussed.

Figure 9.13a shows a comparison of the polarization curves and power densities for Nafion-115, Ph-SPEEKK, and Ph-SPEEKK–PSf-BTraz blend (with 5 wt.% PSf-BTraz) membranes at 80 °C with 1 M methanol concentration. The power density at 0.4 V of the blend membrane (176 mW/cm²) was considerably higher than the plain Ph-SPEEKK (126 mW/cm²) and Nafion-115 (128 mW/cm²). Figure 9.13b shows the maximum power densities of the blend membrane with 5 wt.% PSf-BTraz content compared with the Nafion-115 membrane, as a function of methanol concentration at 65 °C. The blend membrane had better performance in comparison with the Nafion-115 membrane at all methanol concentrations, due to its lower methanol permeability combined with comparable proton conductivity. With an increase in the methanol concentration, the difference in the maximum power density values between the blend membranes and Nafion-115 widened considerably. At 5 M methanol, the 5 wt.% PSf-BTraz blend membrane had the highest power density of 154 mW/cm², which was 1.4 times higher than that of Nafion-115. It was suggested that the blend membrane approach may be useful for DMFCs operated at high methanol concentrations.

9.6 Summary

Although numerous acid-functionalized aromatic polymers have been prepared and characterized for *ex situ* PEM properties, a relatively smaller proportion of them have been taken to the next step: evaluation of *in situ* fuel cell properties. For PEMFC, it is observed that only selected PEM properties are often improved and their overall performance in a fuel cell matches or is still inferior to Nafion. Part of the problem lies in the use of routine fabrication techniques that were established for Nafion-type PEMFC, which do not necessarily translate well for hydrocarbon-based PEMs. Currently, particular interest is being focused on performance at elevated temperatures and reduced relative humidity conditions, in light of the need for suitable PEMs that meet the demanding US Department of Energy (DOE) specifications for fuel cells in the automotive sector. Nevertheless, there are promising

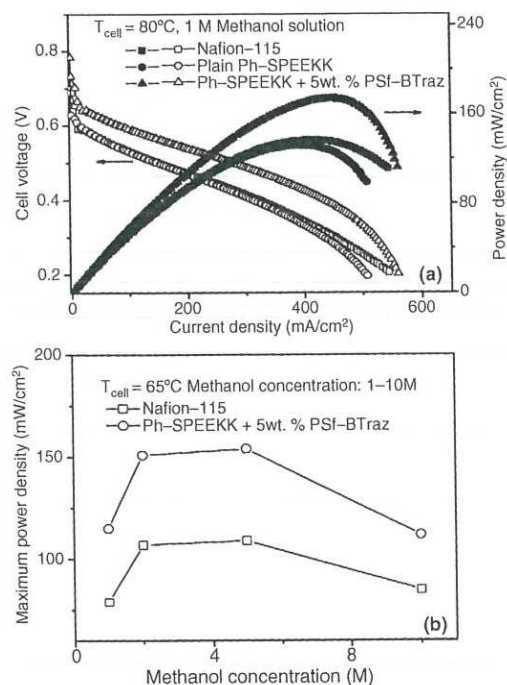


Figure 9.13 Comparison of the (a) DMFC performances and power densities at 80°C with 1 M methanol solution, and (b) maximum power density as a function of methanol concentration at 65°C of the Ph-SPEKK-PSf-BTraz blend membranes having 5 wt.% PSf-BTraz with those of Nafion-115 and plain Ph-SPEKK membranes. Reprinted with permission from *Electrochemistry Communications, High performance direct methanol fuel cells based on acid-base blend membranes containing benzotriazole* by Wen Li, A. Manthiram, et al., 12, 4, 607–610 Copyright (2010) Elsevier Ltd.

advances made in the molecular design of PEMs, for example multiblock copolymers that exhibit performance similar to that of Nafion at reduced humidity levels. Further optimization of polymer architecture, structure, and composition is needed to develop PEMs that can exhibit excellent long-term performance under PEMFC operating conditions. Thus, a clear understanding of the mechanisms of proton transport under different humidity and temperature conditions, and how it relates to polymer structure and architecture, is needed. For DMFC, hydrocarbon-based PEMs, particularly aromatic polymers, have an intrinsic advantage over Nafion in having a more rigid backbone that leads to lower methanol cross-over. In addition, the DMFC is, by its nature, a humidified system (at least at the anode), so some of the issues with dehydration are avoided. One of the keys to good PEM performance is achieving high proton conductivity while controlling the liquid uptake in the membrane, which has been done successfully in a number of instances. Consequently, several PEMs have shown excellent DMFC performance compared with Nafion.

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References

1. Liu, B., Wang, G., Hu, W. et al. (2002) Poly(aryl ether ketone)s with 3-methylphenyl and 3-(trifluoromethyl)phenyl side groups. *Journal of Polymer Science Part A: Polymer Chemistry*, **40**, 3392–3398.
2. Hickner, M., Ghassemi, H., Kim, Y. et al. (2004) Alternative polymer systems for proton exchange membranes (PEMs). *Chemical Reviews*, **104**, 4587–4612.
3. Gubler, L. and Scherer, G. (2008) A proton-conducting polymer membrane as solid electrolyte – function and required properties. *Advances in Polymer Science*, **215**, 1–14.
4. Liu, B., Kim, D., Guiver, M. et al. (2008) Sulfonated poly(aryl ether)-type polymers as proton exchange membranes: synthesis and performance, in *Membranes for Energy Conversion*, Membrane Technology series (eds K.V. Peinemann and S.P. Nunes), Wiley – VCH, Weinheim.
5. Liu, B., Robertson, G., Kim, D. et al. (2007) Aromatic poly(ether ketone)s with pendant sulfonic acid phenyl groups prepared by a mild sulfonation method for proton exchange membranes. *Macromolecules*, **40**, 1934–1944.
6. Bishop, M., Karasz, F., Russo, P. and Langley, K. (1985) Solubility and properties of a poly(aryl ether ketone) in strong acids. *Macromolecules*, **18**, 86–93.
7. Liu, B., Robertson, G., Kim, D. et al. (2010) Enhanced thermo-oxidative stability of sulfophenylated poly(ether sulfone)s. *Polymer*, **51**, 403–413.
8. Chikashige, Y., Chikyu, Y., Miyatake, K. and Watanabe, M. (2005) Poly(arylene ether) ionomers containing sulfofluorenyl groups for fuel cell applications. *Macromolecules*, **38**, 7121–7126.
9. Liu, B., Hu, W., Robertson, G. and Guiver, M. (2008) Poly(aryl ether ketone)s with carboxylic acid groups: synthesis, sulfonation and crosslinking. *Journal of Materials Chemistry*, **18**, 4675–4682.
10. Matsumoto, K., Higashihara, T. and Ueda, M. (2009) Locally and densely sulfonated poly(ether sulfone)s as proton exchange membrane. *Macromolecules*, **42**, 1161–1166.
11. Matsumoto, K., Higashihara, T. and Ueda, M. (2009) Locally sulfonated poly(ether sulfone)s with highly sulfonated units as proton exchange membrane. *Journal of Polymer Science Part A: Polymer Chemistry*, **47**, 3444–3453.
12. Higashihara, T., Matsumoto, K. and Ueda, M. (2009) Sulfonated aromatic hydrocarbon polymers as proton exchange membranes for fuel cells. *Polymer*, **50**, 5341–5357.
13. Miyatake, K. and Hay, A. (2001) Synthesis and properties of poly(arylene ether)s bearing sulfonic acid groups on pendant phenyl rings. *Journal of Polymer Science Part A: Polymer Chemistry*, **39**, 3211–3217.
14. Tian, S., Meng, Y. and Hay, A. (2009) Membranes from poly(aryl ether)-based ionomers containing randomly distributed nanoclusters of 6 or 12 sulfonic acid groups. *Macromolecules*, **42**, 1153–1160.

15. Gao, Y., Robertson, G., Guiver, M. *et al.* (2006) Low-swelling proton-conducting copoly(aryl ether nitrile)s containing naphthalene structure with sulfonic acid groups meta to the ether linkage. *Polymer*, **47**, 808–816.
16. Liu, B., Robertson, G., Guiver, M. *et al.* (2006) Sulfonated poly(aryl ether ether ketone)s containing fluorinated moieties as proton exchange membrane materials. *Journal of Polymer Science Part B: Polymer Physics*, **44**, 2299–2310.
17. Li, N., Shin, D.W., Hwang, D.S. *et al.* (2010) Polymer electrolyte membranes derived from new sulfone monomers with pendant sulfonic acid groups. *Macromolecules*, **43**, 9810–9820.
18. Lafitte, B., Puchner, M. and Jannasch, P. (2005) Proton conducting polysulfone ionomers carrying sulfoaryloxybenzoyl side chains. *Macromolecular Rapid Communications*, **26**, 1464–1468.
19. Lafitte, B. and Jannasch, P. (2007) Proton-conducting aromatic polymers carrying hypersulfonated side chains for fuel cell applications. *Advanced Functional Materials*, **17**, 2823–2834.
20. Guiver, M.D., ApSimon, J.W. and Kutowy, O. (1988) The modification of polysulfone by metalation. *Journal of Polymer Science, Polymer Letters Edition*, **26**, 123–127.
21. Guiver, M.D., Robertson, G.P., Yoshikawa, M. and Tam, C.M. (1997) Functionalized polysulfones: methods for chemical modification and membrane applications. *ACS Symposium Series*, **744**, 137–161.
22. Li, Z., Ding, J., Robertson, G. and Guiver, M. (2006) A novel bisphenol monomer with grafting capability and the resulting poly(arylene ether sulfone)s. *Macromolecules*, **39**, 6990–6996.
23. Marestin, C., Gebel, G., Diat, O. and Mercier, R. (2008) Sulfonated polyimides. *Advances in Polymer Science*, **216**, 185–258.
24. Genies, C., Mercier, R., Sillion, B. *et al.* (2001) Soluble sulfonated naphthalenic polyimides as materials for proton exchange membranes. *Polymer*, **42**, 359–373.
25. Einsla, B.R., Hong, Y.T., Kim, Y.S. *et al.* (2004) Sulfonated naphthalene dianhydride based polyimide copolymers for proton exchange membrane fuel cells. I. Monomer and copolymer synthesis. *Journal of Polymer Science Part A: Polymer Chemistry*, **42**, 862–874.
26. Liu, C., Li, L., Liu, Z. *et al.* (2011) Sulfonated naphthalenic polyimides containing ether and ketone linkages as polymer electrolyte membranes. *Journal of Membrane Science*, **366**, 73–81.
27. Watari, T., Fang, J., Tanaka, K. *et al.* (2004) Synthesis, water stability and proton conductivity of novel sulfonated polyimides from 4,4'-bis(4-aminophenoxy)biphenyl-3,3'-disulfonic acid. *Journal of Membrane Science*, **230**, 111–120.
28. Miyatake, K., Zhou, H. and Watanabe, M. (2004) Proton conductive polyimide electrolytes containing fluorenyl groups: synthesis, properties, and branching effect. *Macromolecules*, **37**, 4956–4960.
29. Hu, Z., Yin, Y., Kita, H. *et al.* (2007) Synthesis and properties of novel sulfonated polyimides bearing sulfophenyl pendant groups for polymer electrolyte fuel cell application. *Polymer*, **48**, 1962–1971.
30. Zhang, F., Li, N., Zhang, S. and Li, S. (2010) Ionomers based on multisulfonated perylene dianhydride: synthesis and properties of water resistant sulfonated polyimides. *Journal of Power Sources*, **195**, 2159–2165.
31. Miyatake, K. and Watanabe, M. (2008) Polyimide ionomer membranes for PEFCs and DMFCs, in *Membranes for Energy Conversion*, Membrane Technology Series (eds K.V. Peinemann and S.P. Nunes), Wiley–VCH, Weinheim.
32. Kobayashi, T., Rikukawa, M., Sanui, K. and Ogata, N. (1998) Proton-conducting polymers derived from poly(ether-etherketone) and poly(4-phenoxybenzoyl-1,4-phenylene). *Solid State Ionics*, **106**, 219–225.
33. Ghassemi, H. and McGrath, J. (2004) Synthesis and properties of new sulfonated poly(p-phenylene) derivatives for proton exchange membranes. *Polymer*, **45**, 5847–5854.
34. Gieselmann, M. and Reynolds, J. (1992) Water-soluble polybenzimidazole-based polyelectrolytes. *Macromolecules*, **25**, 4832–4834.
35. Asensio, J., Borros, S. and Gomez-Romero, P. (2002) Proton-conducting polymers based on benzimidazoles and sulfonated benzimidazoles. *Journal of Polymer Science Part A: Polymer Chemistry*, **40**, 3703–3710.
36. Wycisk, R. and Pintauro, P. (1996) Sulfonated polyphosphazene ion-exchange membranes. *Journal of Membrane Science*, **119**, 155–160.
37. Kopitzke, R., Linkous, C., Anderson, H. and Nelson, G. (2000) Conductivity and water uptake of aromatic-based proton exchange membrane electrolytes. *Journal of the Electrochemical Society*, **147**, 1677–1681.
38. Mader, J., Xiao, L., Schmidt, T. and Benicewicz, B. (2008) polybenzimidazole/acid complexes as high-temperature membranes. *Advances in Polymer Science*, **216**, 63–124.
39. Wainright, J., Wang, J., Weng, D. *et al.* (1995) Acid-doped polybenzimidazoles: a new polymer electrolyte. *Journal of the Electrochemical Society*, **142**, 121–123.
40. Schuster, M. and Meyer, W. (2003) Anhydrous proton-conducting polymers. *Annual Review of Materials Research*, **33**, 233–261.
41. Li, Q., Hjuler, H. and Bjerrum, N. (2001) Phosphoric acid doped polybenzimidazole membranes: physicochemical characterization and fuel cell applications. *Journal of Applied Electrochemistry*, **31**, 773–779.
42. Li, Q., He, R., Jensen, J. and Bjerrum, N. (2003) Approaches and recent development of polymer electrolyte membranes for fuel cells operating above 100°C. *Chemistry of Materials*, **15**, 4896–4915.
43. Mader, J.A. and Benicewicz, B.C. (2010) Sulfonated polybenzimidazoles for high temperature PEM fuel cells. *Macromolecules*, **43**, 6706–6715.
44. Glipa, X., Haddad, M., Jones, D. and Roziere, J. (1997) Synthesis and characterisation of sulfonated polybenzimidazole: a highly conducting proton exchange polymer. *Solid State Ionics*, **97**, 323–331.
45. Bae, J., Honma, I., Murata, M. *et al.* (2002) Properties of selected sulfonated polymers as proton-conducting electrolytes for polymer electrolyte fuel cells. *Solid State Ionics*, **147**, 189–194.
46. Gieselmann, M. and Reynolds, J.R. (1992) Water-soluble polybenzimidazole-based polyelectrolytes. *Macromolecules*, **25**, 4832–4834.
47. Jouanneau, J., Mercier, R., Gonon, L. and Gebel, G. (2007) Synthesis of sulfonated polybenzimidazoles from functionalized monomers: preparation of ionic conducting membranes. *Macromolecules*, **40**, 983–990.
48. Fu, Y., Manthiram, A. and Guiver, M.D. (2006) Blend membranes based on sulfonated poly(ether ether ketone) and polysulfone bearing benzimidazole side groups for proton exchange membrane fuel cells. *Electrochemistry Communications*, **8**, 1386–1390.
49. Lafitte, B. and Jannasch, P. (2007) Chapter 3, on the prospects for phosphonated polymers as proton-exchange fuel cell membranes. *Advances in Fuel Cells*, **1**, 119–185.
50. Rusanov, A., Kostoglodov, P., Abadie, M. *et al.* (2008) Proton-conducting polymers and membranes carrying phosphonic acid groups. *Advances in Polymer Science*, **216**, 125–155.
51. Parcerro, E., Herrera, R. and Nunes, S.P. (2006) Phosphonated and sulfonated polyphenylsulfone membranes for fuel cell application. *Journal of Membrane Science*, **285**, 206–213.
52. Liu, B., Robertson, G., Guiver, M. *et al.* (2006) Fluorinated poly(aryl ether) containing a 4-bromophenyl pendant group and its phosphonated derivative. *Macromolecular Rapid Communications*, **27**, 1411–1417.
53. Kim, D.S., Robertson, G.P., Kim, Y.S. and Guiver, M.D. (2009) Copoly(arylene ether)s containing pendant sulfonic acid groups as proton exchange membranes. *Macromolecules*, **42**, 957–963.

54. Lafitte, B. and Jannasch, P. (2007) Polysulfone ionomers functionalized with benzoyl(difluoromethylenephosphonic acid) side chains for proton-conducting fuel-cell membranes. *Journal of Polymer Science Part A: Polymer Chemistry*, **45**, 269–283.
55. Kim, Y.S. and Pivovar, B.S. (2010) The membrane-electrode interface in PEFCs IV. The origin and implications of interfacial resistance. *Journal of the Electrochemical Society*, **157**, B1616–B1623.
56. Kreuer, K. (2001) On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells. *Journal of Membrane Science*, **185**, 29–39.
57. Tsang, E.M.W., Zhang, Z., Shi, Z. *et al.* (2007) Considerations of macromolecular structure in the design of proton conducting polymer membranes: graft versus diblock polyelectrolytes. *Journal of the American Chemical Society*, **129**, 15106–15107.
58. Norsten, T., Guiver, M., Murphy, J. *et al.* (2006) Highly fluorinated comb-shaped copolymers as proton exchange membranes (PEMs): improving PEM properties through rational design. *Advanced Functional Materials*, **16**, 1814–1822.
59. Einsla, M., Kim, Y., Hawley, M. *et al.* (2008) Toward improved conductivity of sulfonated aromatic proton exchange membranes at low relative humidity. *Chemistry of Materials*, **20**, 5636–5642.
60. Mikami, T., Miyatake, K. and Watanabe, M. (2010) Poly(arylene ether)s containing superacid groups as proton exchange membranes. *Applied Materials and Interfaces*, **2**, 1714–1721.
61. Yoshimura, K. and Iwasaki, K. (2009) Aromatic polymer with pendant perfluoroalkyl sulfonic acid for fuel cell applications. *Macromolecules*, **42**, 9302–9306.
62. Schuster, M., de Araujo, C.C., Atanasov, V. *et al.* (2009) Highly sulfonated poly(phenylene sulfone): preparation and stability. *Macromolecules*, **42**, 3129–3137.
63. Miyatake, K., Chikashige, Y., Higuchi, E. and Watanabe, M. (2007) Tuned polymer electrolyte membranes based on aromatic polyethers for fuel cell applications. *Journal of the American Chemical Society*, **129**, 3879–3887.
64. Matsumoto, K., Nakagawa, T., Higashihara, T. and Ueda, M. (2009) Sulfonated poly(ether sulfone)s with binaphthyl units as proton exchange membranes for fuel cell application. *Journal of Polymer Science Part A: Polymer Chemistry*, **47**, 5827–5834.
65. Su, Y., Liu, Y., Sun, Y. *et al.* (2007) Proton exchange membranes modified with sulfonated silica nanoparticles for direct methanol fuel cells. *Journal of Membrane Science*, **296**, 21–28.
66. Su, Y., Liu, Y., Wang, D. *et al.* (2009) Increases in the proton conductivity and selectivity of proton exchange membranes for direct methanol fuel cells by formation of nanocomposites having proton conducting channels. *Journal of Power Sources*, **194**, 206–213.
67. Miyatake, K., Tombe, T., Chikashige, Y. *et al.* (2007) Enhanced proton conduction in polymer electrolyte membranes with acid-functionalized polysilsesquioxane. *Angewandte Chemie-International Edition*, **46**, 6646–6649.
68. Eikerling, M., Kornyshev, A. and Spohr, E. (2008) Proton-conducting polymer electrolyte membranes: water and structure in charge. *Advances in Polymer Science*, **215**, 15–54.
69. Li, W., Manthiram, A., Guiver, M. and Liu, B. (2010) High performance direct methanol fuel cells based on acid–base blend membranes containing benzotriazole. *Electrochemistry Communications*, **12**, 607–610.
70. Guo, M., Liu, B., Liu, Z. *et al.* (2009) Novel acid–base molecule-enhanced blends/copolymers for fuel cell applications. *Journal of Power Sources*, **189**, 894–901.
71. Phu, D.S., Lee, C.H., Park, C.H. *et al.* (2009) Synthesis of crosslinked sulfonated poly(phenylene sulfide sulfone nitrile) for direct methanol fuel cell applications. *Macromolecular Rapid Communications*, **30**, 64–68.
72. Mikhailenko, S.D., Wang, K.P., Kaliaguine, S. *et al.* (2004) Proton conducting membranes based on cross-linked sulfonated poly(ether ether ketone) (SPEEK). *Journal of Membrane Science*, **233**, 93–99.
73. Zhang, C., Guo, X., Fang, J. *et al.* (2007) A new and facile approach for the preparation of cross-linked sulfonated poly(sulfide sulfone) membranes for fuel cell application. *Journal of Power Sources*, **170**, 42–45.
74. Fang, J., Zhai, F., Guo, X. *et al.* (2007) A facile approach for the preparation of cross-linked sulfonated polyimide membranes for fuel cell application. *Journal of Materials Chemistry*, **17**, 1102–1108.
75. Di Vona, M.L., Sgreccia, E., Tamilvanan, M. *et al.* (2010) High ionic exchange capacity poly(phenylsulfone) (PPSU) and polyethersulfone (SPES) cross-linked by annealing treatment: thermal stability, hydration level and mechanical properties. *Journal of Membrane Science*, **354**, 134–141.
76. Di Vona, M.L., Sgreccia, E., Licoccia, S. *et al.* (2008) Composite proton-conducting hybrid polymers: water sorption isotherms and mechanical properties of sulfonated PEEK and substituted PPSU blends. *Chemistry of Materials*, **20**, 4327–4334.
77. Di Vona, M.L., Marani, D., D'Ottavi, C. *et al.* (2006) A simple new route to covalent organic/inorganic hybrid proton exchange polymeric membranes. *Chemistry of Materials*, **18**, 69–75.
78. Di Vona, M.L., Marani, D., D'Epifanio, A. *et al.* (2007) Hybrid materials for polymer electrolyte membrane fuel cells: water uptake, mechanical and transport properties. *Journal of Membrane Science*, **304**, 76–81.
79. Kayser, M.J., Reinholdt, M.X. and Kaliaguine, S. (2011) Cross-linked sulfonated poly(ether ether ketone) by using diamino-organosilicon for proton exchange fuel cells. *Journal of Physical Chemistry B*, **115**, 2916–2923.
80. Silva, V.S., Ruffmann, B., Silva, H. *et al.* (2005) Proton electrolyte membrane properties and direct methanol fuel cell performance I. Characterization of hybrid sulfonated poly(ether ether ketone)/zirconium oxide membranes. *Journal of Power Sources*, **140**, 34–40.
81. Colicchio, I., Wen, F., Keul, H. *et al.* (2009) Sulfonated poly(ether ether ketone)-silica membranes doped with phosphotungstic acid: morphology and proton conductivity. *Journal of Membrane Science*, **326**, 45–57.
82. Liu, B., Hu, W., Robertson, G. *et al.* (2010) Sulphonated biphenylated poly(aryl ether ketone)s for fuel cell applications. *Fuel Cells*, **10**, 45–53.
83. Liu, B., Hu, W., Kim, Y. *et al.* (2010) Preparation and DMFC performance of a sulfophenylated poly(arylene ether ketone) polymer electrolyte membrane. *Electrochimica Acta*, **55**, 3817–3823.