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Proton Exchange Membranes for Direct Methanol Fuel Cells[1)]

Dae Sik Kim, Michael D. Guiver, and Yu Seung Kim

10.1
Introduction

Fuel cells are now widely recognized as one solution to increasing power demands, mitigation of air pollutants, and efficient use of fossil fuels. It is increasingly recognized that portable direct methanol fuel cells (DMFC)s will likely be the first fuel cells commercially available to the general public; there has been a recent increase in the number of pre-commercial portable devices powered by DMFCs that have been demonstrated in the press and at conferences.

Extensive efforts have been made to develop alternative polymer electrolyte membranes (PEM)s to overcome the drawbacks of the current widely used per-fluorinated sulfonic acid (PFSA) copolymer membrane (e.g., Nafion) such as performance deterioration at high temperature and high methanol permeability, which leads to lower cell voltage and decreased fuel efficiency in DMFCs. Nafion is a statistical copolymer comprising a highly hydrophobic perfluorinated backbone that contains a number of short, flexible pendant side chains with single strongly hydrophilic sulfonic acid groups. This structure produces nanophase separated membrane morphology and thus they show excellent thermal, mechanical and electrochemical properties. The flexibility of the side chain of Nafion allows for the aggregation of the superacid fluoroalkyl sulfonic sites into channels, which conduct protons well. However, the proton conductivity of Nafion is reduced above $100\,^\circ$C due to morphological relaxations.

Significant research has been conducted on developing lower methanol permeable electrolytes. Various polymer types such as polyarylenes, polyimides, polyphospha-zenes, radiation grafted polystyrenes, polystyrene block copolymers and polyvinyl alcohols (PVA)s have been developed over the last 10 years. Much of the research on polyarylenes has been performed on poly(arylene ether sulfone)s (PES) [1–8], poly (arylene ether ketone)s (PAEKs) [9–11], and other polyphenylene copolymers [12–14]. These polymers are traditional engineering polymers and are known for their good thermal/mechanical properties, oxidative stability and processibility [15]. In their

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1) NRCC publication number 50886.

sulfonated form, they have shown good mechanical properties, proton conductivities and relatively low methanol permeabilities compared with Nafion. The goals of this chapter are (i) to give an overview of non-PFSA alternative hydrocarbon-based PEMs investigated specifically for DMFCs. In order to achieve this goal, we consider that there are two categories of alternative PEMs. One contains aliphatic polymer such as polystyrene sulfonic acid (PS), and PVA. The other one comprises PEMs having aromatic polymer backbones such as PES, PAEK, and poly(arylene ether nitriles); (ii) to present currently reported properties and performance of DMFCs, particularly those using alternative membranes. In order to achieve this goal, we first present the *ex situ* membrane properties required for a successful fuel cell electrolyte, such as high proton conductivity, low methanol permeability, chemical stability, and good mechanical properties. Finally, DMFC performance, the ultimate goal of any novel electrolyte, is presented using reported performance of a number of polymers.

10.2
Synthesis of Polymer Electrolyte Membranes for DMFC

A wide variety of PEMs have been developed for DMFC over the last 10 years and there is continued effort in developing new materials. The discussion presented here is divided into two categories of PEMs: those containing aliphatic polymer backbones and those containing aromatic polymer backbones, such as poly(arylene ether) copolymers.

10.2.1
Synthesis and Properties of PEMs Containing Aliphatic Polymers

The most commonly known and studied PEMs are based on non-aromatic perfluorinated hydrocarbons such as Nafion, Aciplex, Flemion. The current state-of-the-art PEM is Nafion, a DuPont product that was developed in the late 1960s, primarily as a permselective separator in chlor-alkali electrolyzers [16]. Nafion is a free radical initiated copolymer of a crystallizable hydrophobic tetrafluoroethylene (TFE) backbone sequence (~87 mol% at 1100 equivalent weight) with a comonomer, which ultimately has pendant side chains of perfluorinated vinyl ethers terminated by perfluorosulfonic acid groups. The reported chemical structure of Nafion for PEM membranes is shown in Figure 10.1.

Polymers based on styrene, and particularly its fluorinated derivatives, have been used to form PEMs. Styrenic monomers are widely available and easy to modify, and
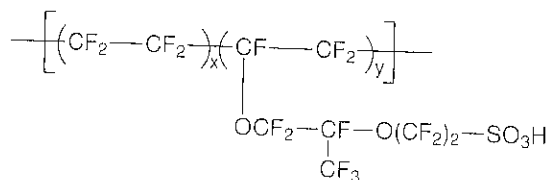
$$-\left[\left(CF_2-CF_2\right)_x\left(CF-CF_2\right)_y\right]-$$
$$OCF_2-CF-O(CF_2)_2-SO_3H$$
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Figure 10.1 Chemical structure of Nafion.

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their polymers are easily synthesized via conventional free radical and other polymerization techniques. One of the primary concerns with this type of polymer is loss of ion exchange capacity (IEC) due to backbone degradation of polystyrene under fuel cell conditions [17, 18], caused by the presence of the labile α-proton. Some literature reports of these materials have shown reasonable lifetimes, up to 2000 h, with little performance degradation in DMFC testing [19, 20]. Several researchers have suggested that sulfonated styrene copolymers could be used for DMFC membranes. Copolymers, such as poly(vinylidene fluoride) grafted styrene sulfonic acid (PVDF-g-PSSA) [21, 22], sulfonated poly(styrene-isobutylene-styrene) [23–25], sulfonated poly([vinylidene difluoride-co-chlorotrifluoro ethylene]-g-styrene [P(VDF-co-CTFE)-g-SPS]) [26] have been synthesized and characterized. The Holdcroft group [27] compared graft and diblock copolymers that were synthesized so as to contain a similar ratio of fluorous to styrene components, and similar chemical compositions, but distinctly different macromolecular structures: P(VDF-co-CTFE)-g-SPS consisted of a hydrophobic fluorous backbone with ionic sulfonated styrenic side chains, P(VDF-co-HFP)-b-SPS possessed a hydrophobic fluorous segment linearly connected to an ionic sulfonated styrenic segment as shown in Figure 10.2. A comparison of the two macromolecular systems showed that the graft copolymers yield membranes which tolerate much higher ionic contents without excessive swelling and dissolution, and which leads to membranes that possess highly concentrated, isotropically connected ionic domains.

Early commercialization of DMFC requires new proton-conducting membranes that can significantly reduce methanol permeability while having suitable proton conductivity. In the past, several attempts have been made to minimize methanol crossover by developing new membranes from non-fluorinated and partially fluorinated hydrocarbon-based polymers.

Specific attempts to reduce the excessive swelling of the membranes have been made to modify membranes, such as using chemical crosslinking structure and higher molecular weight (MW)polymers [28–31].

Poly(vinyl alcohol) (PVA) membranes are used in pervaporation-based dehydration of alcohols because they preferentially permeate water and retain alcohol [32–34]. Taking advantage of its high selectivity, PVA based membranes have been investigated for DMFCs. To introduce the proton exchange site and reduce water swelling, several techniques have been used such as crosslinking [35–37], or blending with

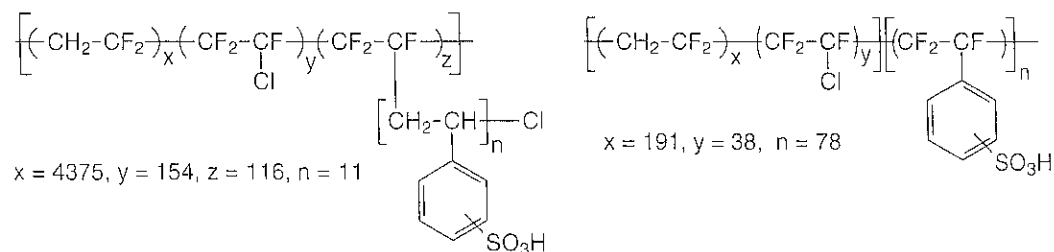x = 4375, y = 154, z = 116, n = 11

x = 191, y = 38, n = 78

Figure 10.2 Chemical structures of (a) P(VDF-co-CTFE)-g-SPS graft and (b) P(VDF-co-HFP)-b-SPS diblock copolymers [27].

inorganic filler [38–42]. PVA itself does not have any negatively charged ions such as carboxylic and sulfonic acid groups. Rhim's group reported that sulfonic acid groups were introduced into the PVA matrix by modifications of the chemical structure of the PVA through esterification with sulfosuccinic acid (SSA) [35], and poly(styrene sulfonic acid-*co*-maleic acid) (PSSA-*co*-MA) [36], and poly(acrylic acid-*co*-maleic acid) (PAA-*co*-MA) [37], which have sulfonic acid and/or carboxylic groups. These materials containing ionic groups were used as a crosslinking agent and as a donor of hydrophilic $-SO_3H$ and/or $-COOH$ groups. Figure 10.3 shows the structure of PVA-based membranes. Kannan reported that a series of semi-interpenetrating network (SIPN) membranes was synthesized by using PVA with crosslinking agent SSA and PSSA-*co*-MA as proton sources, and their physico-chemical and electro-chemical characterizations were reported [43]. Although a power density value of over $100\,mW/cm^2$ was obtained for a SIPN membrane-based membrane electrode assembly (MEA) at $80\,^\circ C$, the PVA-based membranes have some issues with chemical and/or electrochemical stability.

Following this brief review of various types of PEMs containing aliphatic polymers developed for DMFC applications, we now focus attention on the comparative evaluation of these membranes. Numerous studies have investigated the methanol
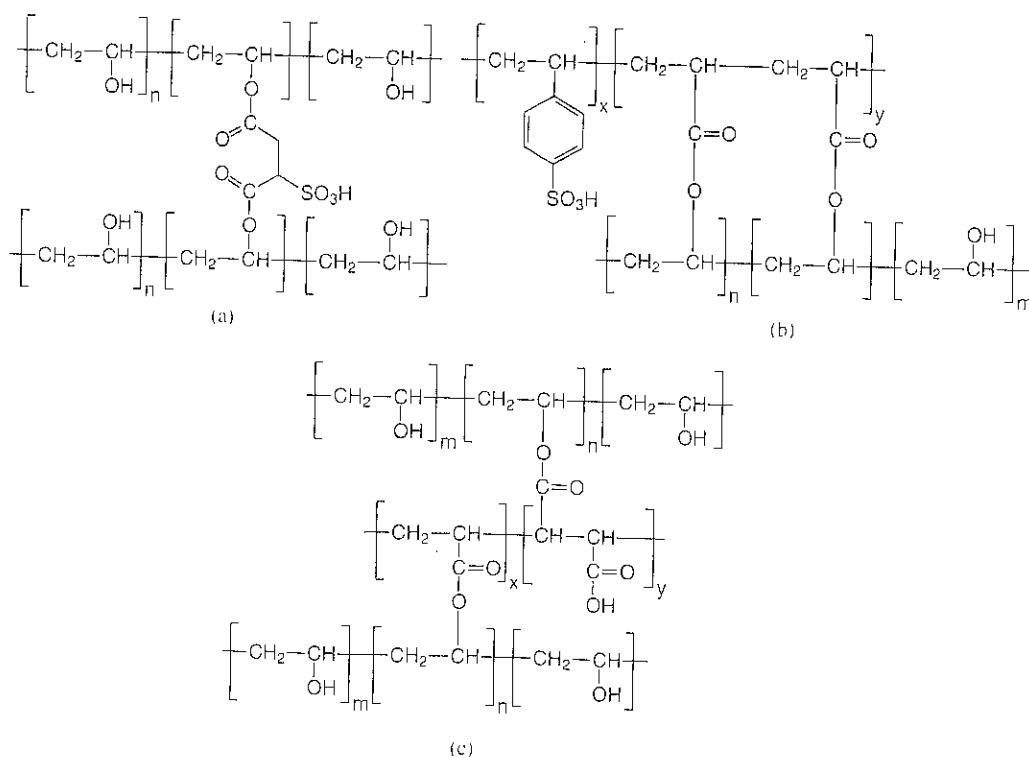

Figure 10.3 Chemical structures of crosslinked PVA with (a) sulfosuccinic acid [35] (b) PSSA-MA [36] and (c) PAA-co-MA [37].

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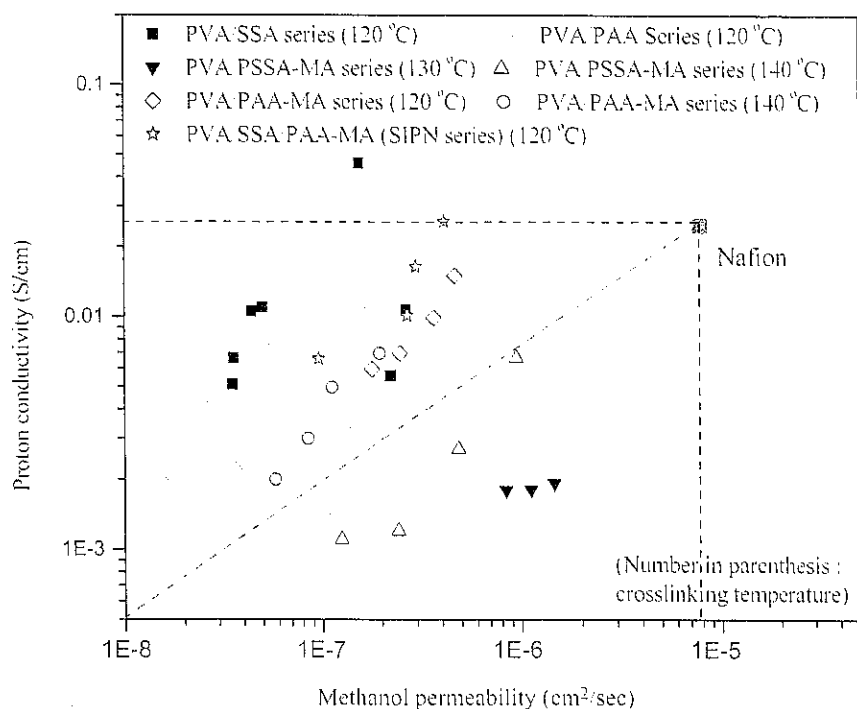es with

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Figure 10.4 Methanol permeability versus proton conductivity for
PEMs based PVA membranes (Refs. [35–38, 43]).

permeability and proton conductivity of alternative PEMs and compared them with
Nafion in an attempt to show improved properties for DMFCs. Figure 10.4 shows the
relationship of proton and methanol permeability for selected PVA membranes at
30 °C. Proton conductivity has a strong trade-off in its relationship with methanol
permeability. The methanol permeabilities of the PVA based membranes are lower
than that of Nafion. However, the proton conductivities are also lower than that of
Nafion, even though the sulfonic acid group was introduced into PVA matrix.

Water uptake of PEMs is an important evaluation parameter for both membrane-
electrode compatibility and mechanical properties of the membrane. Water uptake
versus conductivity has rarely been plotted in the multitude of literature references
although water uptake values are often tabulated along with conductivity data.
Generally, plots of IEC versus conductivity are presented; however, these do not
allow direct comparison of membranes having different compositions. The rela-
tionship between water uptake and proton conductivity can be described by two
different methods. One uses a relative value; the other uses an upper bound
relationship. Figure 10.5a shows the relative conductivity of various PEMs based
on PVA as a function of relative water uptake. In this study, the conductivity and water
uptake of selected membranes have been normalized to the values reported of
Nafion. Hence, Nafion is defined as having a relative conductivity and water uptake
of 1. Figure 10.5b shows the relationship between proton conductivity and water
uptake reported in the temperature range of 20–30 °C [35–39, 43]. The data shown in
Figure 10.5b demonstrate a strong empirical upper-bound relationship. The upper
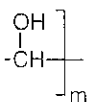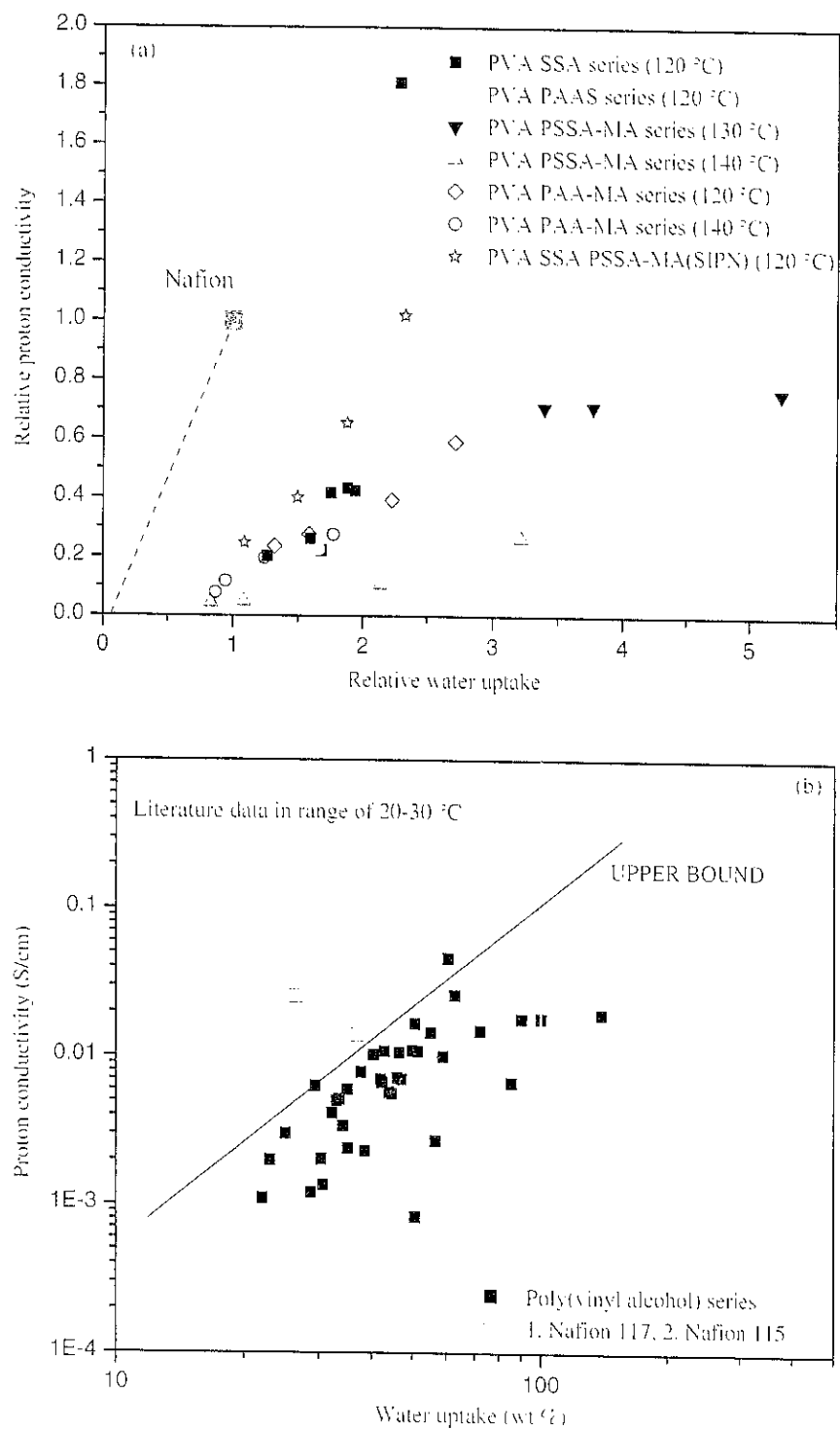
Figure 10.5 (a) Relative proton conductivity versus relative water uptake (b) upper bound relationship for PEMs based PVA membranes (Refs. [35–38, 43]).

bound in this case is an experimental 'state-of-the-art' limit for this type of polymer system of conductivity expressed as a function of water uptake. McGrath's group also showed a similar upper bound relationship for PEM materials [44]. As shown in Figure 10.5a and b, most of the PEMs membranes based on PVA have up to two times higher water uptake and lower proton conductivity, in spite of the introduction of ionic groups in the crosslinking agent. Although there is no clear guideline for the maximum allowable water uptake, PEMs with higher water uptake and lower proton conductivity values typically lead to difficulties in the preparation, durability and performance of MEAs.

10.2.2
Synthesis of Sulfonated Poly(aryl ether) Copolymers

Poly(arylene ether)s such as poly(arylene ether sulfone) (PES), poly(arylene ether ether ketone) (PEEK), and their derivatives are considered as more promising materials on which to base high performance PEMs because of their better oxidative and hydrolytic stability in the fuel cell environment and because many polymer structural variants are possible. At least two methodologies have been used to introduce proton exchange sites, usually sulfonic acid or carboxylic acid, into poly (arylene ether)s. Both post-sulfonation of existing polymers and direct copolymerization of sulfonated monomers are widely used [45], and are discussed below.

10.2.2.1 Post-Sulfonation of Polymers

The sulfonation reaction is an electrophilic aromatic substitution reaction that normally occurs on the site of benzene rings that have a high electron density; therefore, its efficacy depends upon the substituents present on the aromatic ring. Electron-donating substituents favor sulfonation, whereas electron-withdrawing substituents retard or prevent sulfonation. Concentrated sulfuric acid, fuming sulfuric acid, chlorosulfonic acid and trimethylsilylchlorosulfonic acid have been commonly employed as sulfonating agents.

Post-sulfonation is attractive because of the availability of inexpensive commercial high MW thermoplastic starting materials as well as relatively simple reaction procedures, enabling the process to be readily scaled up. However, experimental difficulties are sometimes encountered in achieving precise control over the site of sulfonation and the degree of sulfonation (DS), resulting in a random or less-defined distribution of sulfonic acid groups along the polymer chain. The latter may lead to excessive dimensional swelling in the presence of water, resulting in lower durability of MEAs. Furthermore, consideration must be given to reaction conditions that do not result in polymer chain degradation, which compromise mechanical properties.

The sulfonation reaction of commercial Victrex has been thoroughly studied by several groups [10, 46–48]. Poly(ether ether ketone) (PEEK) shows little solubility in organic solvents due to crystallinity. By introducing sulfonic acid groups to the main chain, the crystallinity decreases and solubility increases. The sulfonation of PEEK has been reported to be a second-order reaction, which takes place at the aromatic ring flanked by two ether links, due to the higher electron density of the ring [10].
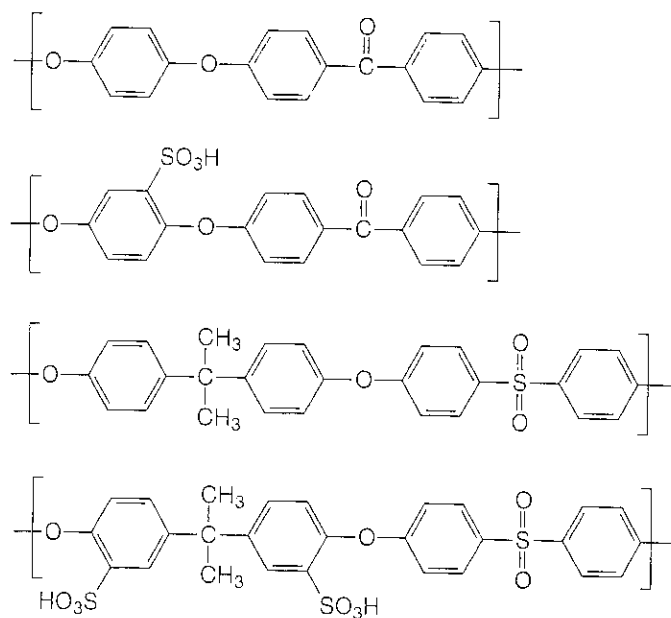
Figure 10.6 General chemical structures for unsulfonated and sulfonated poly(arylene ether sulfone or ketone) copolymers.

Sulfonated PESs as well as PEEK have been investigated intensively using different sulfonating agents such as chlorosulfonic acid, and a sulfur trioxide-triethyl phosphate complex. General chemical structures for the unsulfonated and sulfonated analogs are shown in Figure 10.6.

Guiver's group reported a novel class of PEM materials based on poly(phthalazinone)s (PPs). Poly(phthalazinones) including poly(phthalazinone ether sulfone) (PPES), poly(phthalazinone ether ketone) (PPEK) and poly(phthalazinone ether sulfone ketone) (PPESK) are new high performance polymers in the early stages of commercialization. Among other advantages, this class of polymers is distinguished by excellent chemical and oxidative resistance, mechanical strength, high thermal stability and very high glass transition temperatures (295, 263 and 278 C, respectively) [49]. The structures of PPESK and PPEK are shown in Figure 10.7. Membrane obtained from highly sulfonated PPs showed proton conductivity above 10^{-2} S/cm at room temperature and elevated temperature [49–51].

A series of PAEKs with structurally different phenyl pendant groups was sulfonated with regular reagent concentrated sulfuric acid (95–98%) at room temperature [52]. In comparison to the sulfonation of PEEK, the phenylated and 4-methyphenylated PEEKs have a considerable advantage in having a much faster sulfonation reaction rate (Figure 10.8). For these two PAEKs, the sulfonation reaction proceeded rapidly in concentrated sulfuric acid at room temperature, with polymers having DS of 1.0 being obtained within several hours. It is also relevant to note that sulfonation was site-specific; only one substitution site on the pendant benzene ring per repeat unit occurred for short reaction times, essentially resulting in homopolymer-like structures. Extended reaction times resulted in additional site-specific ring sulfonation,
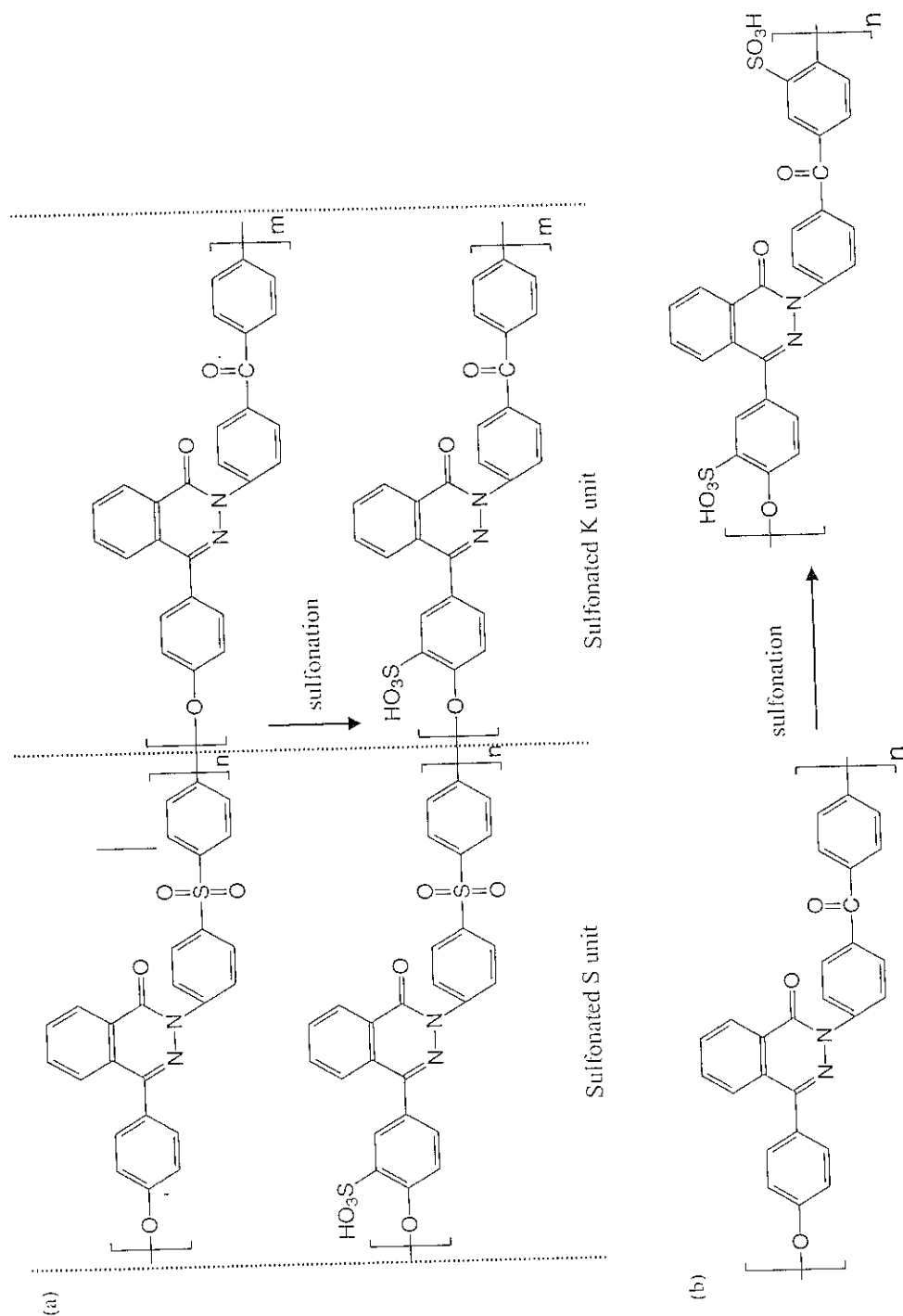
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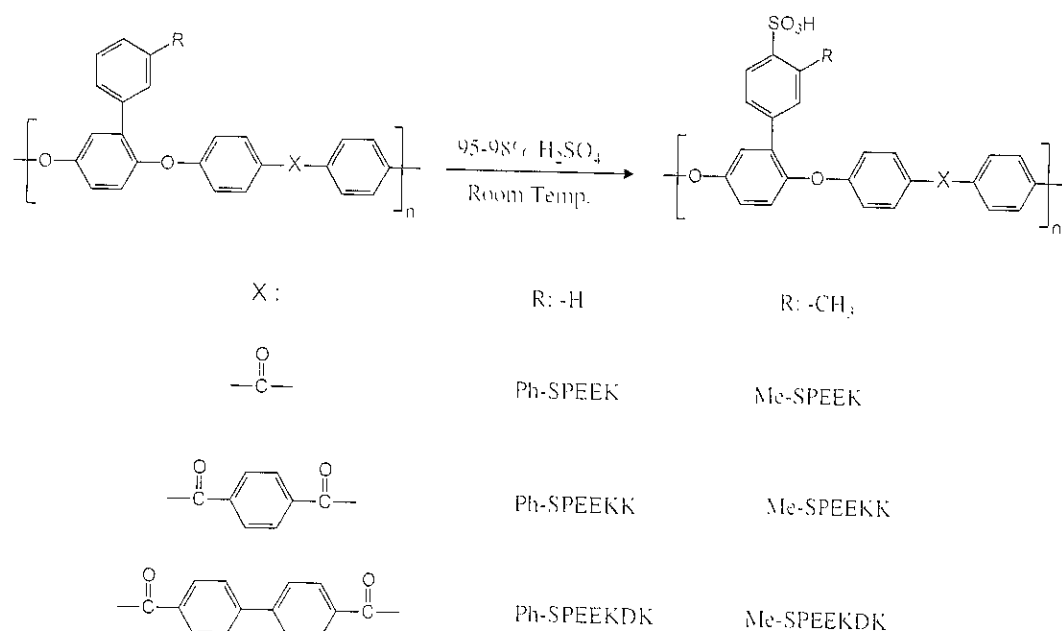**Figure 10.7** Sulfonation reaction of (a) SPPESK, (b) SPPEK.

Figure 10.8 Sulfonation reactions of SPAEK polymers.

leading to homopolymer-like structures with a DS of 2.0 [53]. Recently, sulfonated poly(arylene ether)s containing phenyl pendant groups were prepared using chlorosulfonic acid [53b, c] (Figure 10.9a–c). The copolymers fluorinated sulfonated poly(arylene ether) (Figure 10.9a) and sulfonated poly(arylene ether nitrile)s (Figure 10.9b), each having a DS of 1.0 had high proton conductivities of 135.4 and 140.1 mS/cm at 80 C, and acceptable volume-based water uptake of 44.5–51.9 vol% at 80 C, respectively, compared with Nafion [53b]. The group of Watanabe reported PES-based ionomers containing sulfofluorenyl groups having proton conductivity of 0.3 S/cm at 80 C and 93% relative humidity(RH) (Figure 10.9d) [53d].

10.2.2.2 Direct Copolymerization of Sulfonated Monomers

In comparison with the post-sulfonation of a pre-formed polymer, the direct copolymerization of a sulfonated monomer is an alternative approach with some distinct advantages with respect to the controllability of sulfonic acid content (SC) and site of sulfonation. To some degree, the incorporation of sulfonated or functional monomers allows a closer control of molecular design of the resulting copolymer [54].

Typically cited drawbacks of post-modification include the lack of control over the degree and site of functionalization, which is a common problem in macromolecular chemistry. It is of interest to investigate the effect of introducing sulfonic acids, for example, onto the deactivated sites of the repeat units, since one might expect enhanced stability and higher acidity from sulfonic acid groups that are attached to electron-deficient aromatic rings rather than those bonded to electron-rich aromatic rings as in the case of post-modification [55]. The possibilities of controlling and/or increasing MW to enhance durability are not feasible in the case of post-reaction on an existing commercial product.
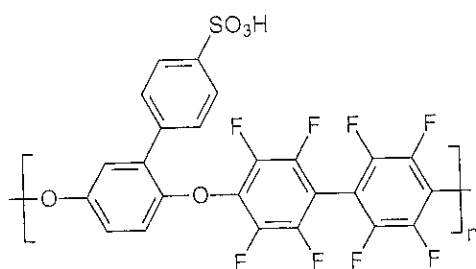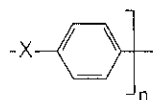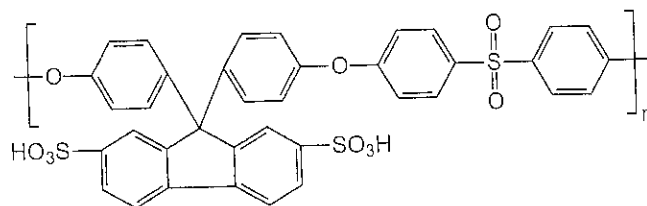
(a) Fluorinated sulfonated poly(arylene ether)s
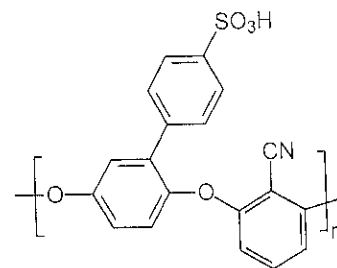
(b) Sulfonated poly(arylene ether nitrile)s
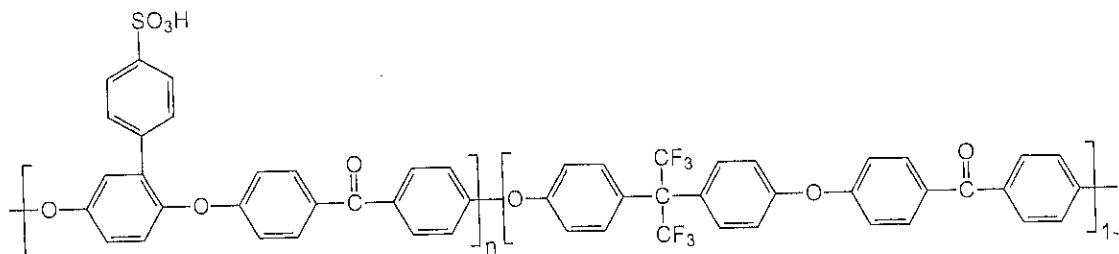
(c) sulfonated poly(arylene ether ketone)s

(d) sulfonated poly(arylene ether sulfone)s

**Figure 10.9** Structure of various sulfonated poly(arylene ether) copolymers.

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Since the first report of a sulfonated dihalo monomer by Robeson and Matzner [56], Ueda *et al.* [57], and Wang *et al.* [58] reported the sulfonation of 4,4-dichlorodiphenyl sulfone, and 4,4-difluorodiphenyl ketone, prepared via an electrophilic reaction using fuming sulfuric acid. Sulfonated 1,4-bis(4-fluorobenzoyl)benzene (1,4-BFBB) was reported by several groups [59, 60]. Powerful sulfonation conditions of fuming sulfuric acid at a relatively high temperature (100 °C) were necessary to sulfonate these monomers.

Guiver's group also synthesized directly copolymerized sulfonated PEKs and PESs using several sulfonated bisphenol monomers available commercially [61–65]. Since it is not easy to control the substitution sites of the small-MW compounds in the sulfonation process and to purify the sulfonated monomers, only a few sulfonated monomers have been developed so far (Figure 10.10). A variety of sulfonated copolymers based on these sulfonated monomers have been prepared via typical aromatic nucleophilic substitution polycondensation, which is the same type of

(a) Sulfonated dihalogenated monomers
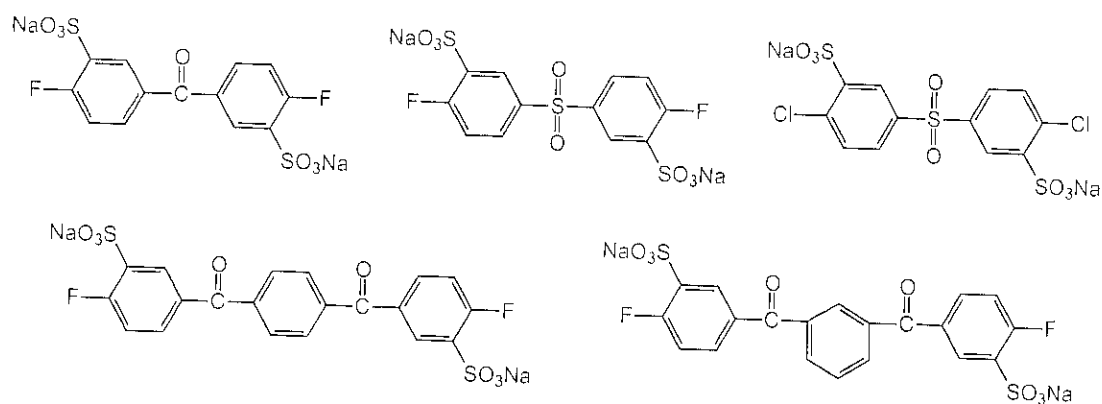
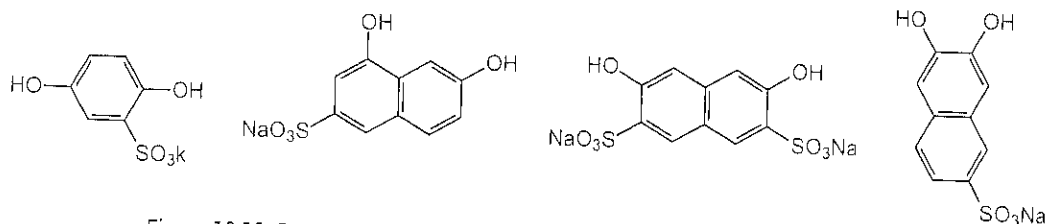(b) Sulfonated bisphenol monomers (available commercially)

Figure 10.10 Reported sulfonated monomers.

reaction used for the polymerization of non-sulfonated poly(aryl ether)-type polymers. It is important to note that the polymerization of sulfonated monomers requires the salt formation of both the phenoxides and the sulfonates, which in some cases may reduce the solubility of the monomer and growing polymer chain, thereby limiting MW.

Poly(arylene ether sulfone)s Directly copolymerized sulfonated polymers were produced under similar reaction conditions employed for many years for the synthesis of unsulfonated poly(arylene ether)s, using a weak base such as potassium carbonate. Only moderately higher reaction temperatures and longer times were needed to obtain high MW copolymers, due to the sterically decreased activity of the sulfonated dihalide monomer [66]. McGrath's group reported a sulfonated polyethersulfone copolymer series having different biphenol and/or polar functional groups, and some of their structures are shown in Figure 10.11. It was shown that the bisphenol structure and SC influenced the properties of the sulfonated copolymers, including the solubility, IEC, and water uptake [5, 67–69]. Four bisphenols including (a) hydroquinone, (b) 4,4'-biphenol, (c) hexafluoroisopropylidene bisphenol (bisphenol 6F), (d) bisphenol A in Figure 10.11, were used for the synthesis of poly(arylene ether)s containing ion conducting units. The copolymers based on bisphenol 6F were especially promising in initial fuel cell tests. It is believed that their fluorine content promotes adhesion and electrochemical compatibility with Nafion-based electrodes and reduces swelling.
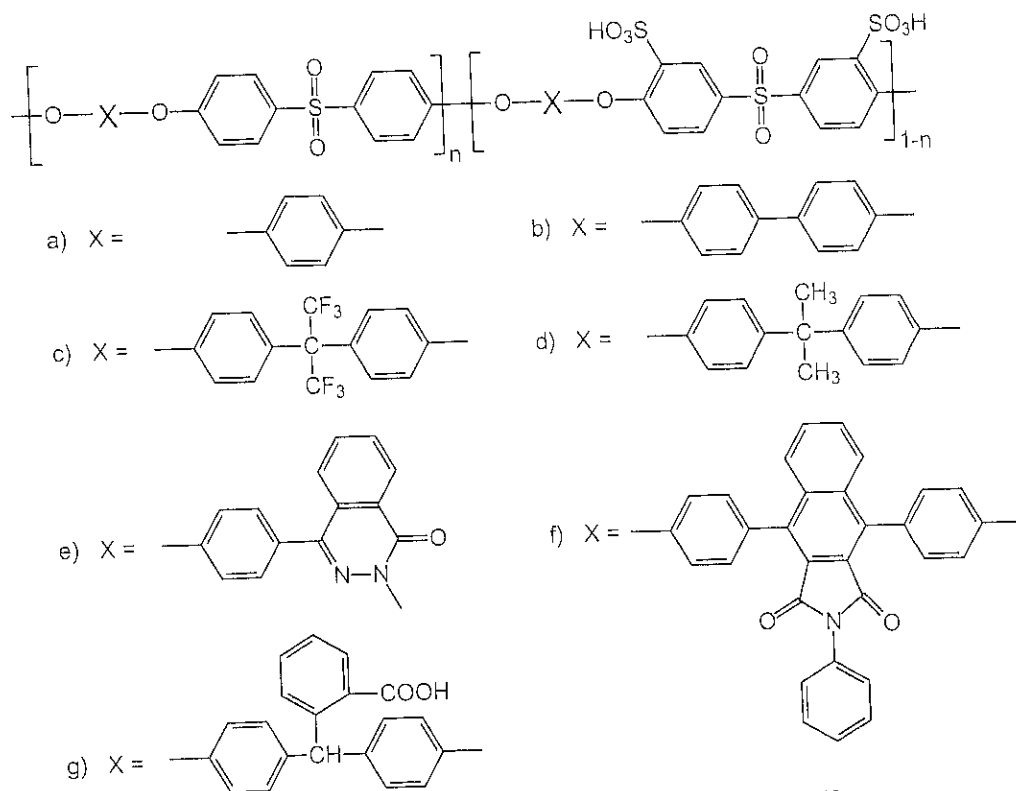
Figure 10.11 Typical copolymers derived from sulfonated 4,4'-dichlorodiphenylsulfone.

Several research groups reported sulfonated PES copolymers containing different biphenols such as (e) phthalazinone, (f) imidoaryl biphenol, and (g) phenolphthalein, as shown in Figure 10.11 [70–72]. Phenolphthalein is a biphenol with a lactone group between two phenolic groups, and it has been used to synthesize aromatic polyesters, PAEKs or sulfones [72]. Phthalazinone has a N—H group that behaves as a phenolic OH group so that the monomer reacts like a bisphenol in nucleophilic aromatic substitution reactions.

McGrath's group and Dang's group also reported poly(arylene sulfide sulfone) disulfonated copolymers using 4,4-thiobisbenzenethiol monomer (Figure 10.12a) and series of poly(aryl ether)-type block copolymers (Figure 10.12b and c) [73–77]. Block copolymer architecture containing hydrophobic/hydrophilic segments is believed to enhance phase-separated morphology, which is expected to improve the PEM properties for FC applications. A typical method to prepare block copolymers is by synthesis of hydrophobic and hydrophilic oligomers with reactive end-groups, followed by their copolymerization. Sulfonated-fluorinated multiblock copolymers were synthesized by copolymerization of activated fluorine-terminated hydrophobic oligomer and hydroxyl-terminated hydrophilic oligomer as shown in Figure 10.12.

Poly(arylene ether ketone)s   Poly(arylene ether ketone)PAEK copolymers are produced by nucleophilic aromatic substitution, in a similar manner to the sulfone analogs. The polymerization is typically conducted in high-boiling polar aprotic
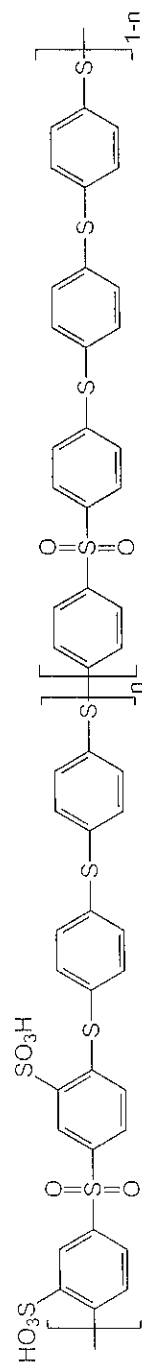
(a) Structure of poly(arylene sulfide sulfone) copolymers
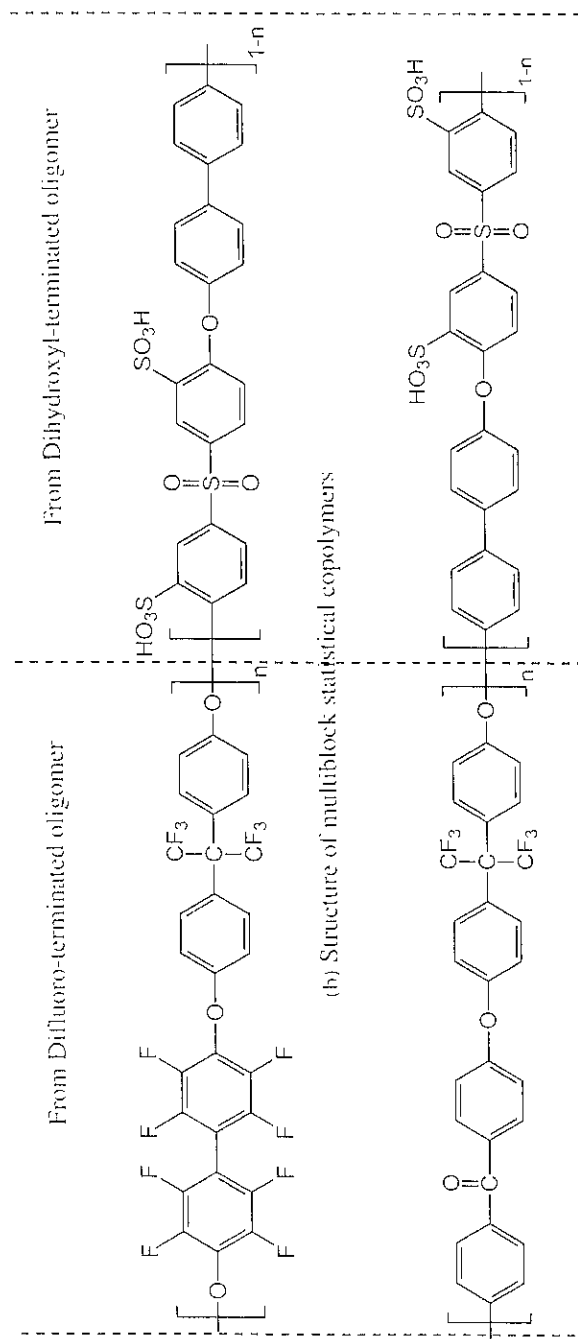
(b) Structure of multiblock statistical copolymers

From Dihydroxyl-terminated oligomer

From Difluoro-terminated oligomer
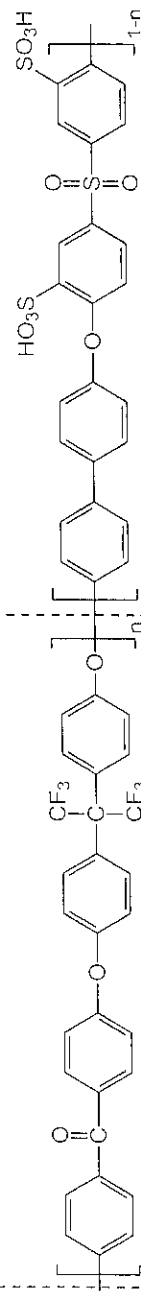
(c) Structure of 6FK-BPSH multiblock copolymers

Figure 10.12 Structure of sulfonated polymer.

solvents, in the presence of excess K_2CO_3 at elevated temperature. SC, and ultimately IEC, is adjusted by the feed molar ratios of sulfonated to non-sulfonated monomers. To obtain the membranes in the proton form, the copolymers (usually after casting films) in salt form (sodium or potassium cations) are immersed in acid (e.g., dilute sulfuric acid or hydrochloric acid) for ion exchange, often under boiling conditions. To do that, the membranes are immersed in dilute sulfuric acid at 100 °C for 2 h followed by similar water treatment at 100 °C for 2 h [55].

The preparation of many directly copolymerized sulfonated PAEKs is possible by employing a sulfonated dihalide ketone monomer, as first reported by Wang *et al.* [58]. Using 3,3'-disulfonated 4,4'-difluorodiphenyl ketone (DFBP) (Figure 10.13), Wang *et al.* produced high MW copolymers from phenolphthalein and non-sulfonated 4,4'-difluorodiphenyl ketone comonomers [78] (Figure 10.13a). The choice of bisphenol-type monomers for the polymerization of PAEKs is large. Guiver's group also reported sulfonated poly(arylene ether ketones) derived from DFBP and

Figure 10.12 Structure of sulfonated polymer.

(c) Structure of 6FK-BPSH multiblock copolymers

(a) Phenolphthalein

(b) 4-(4-Hydroxyphenyl)-1(2H)--phthalazinone (DHPZ)

(c) 2.6-Dihydroxynaphthalene (NA)

(d) Hexafluoro bisphenol A (6F)
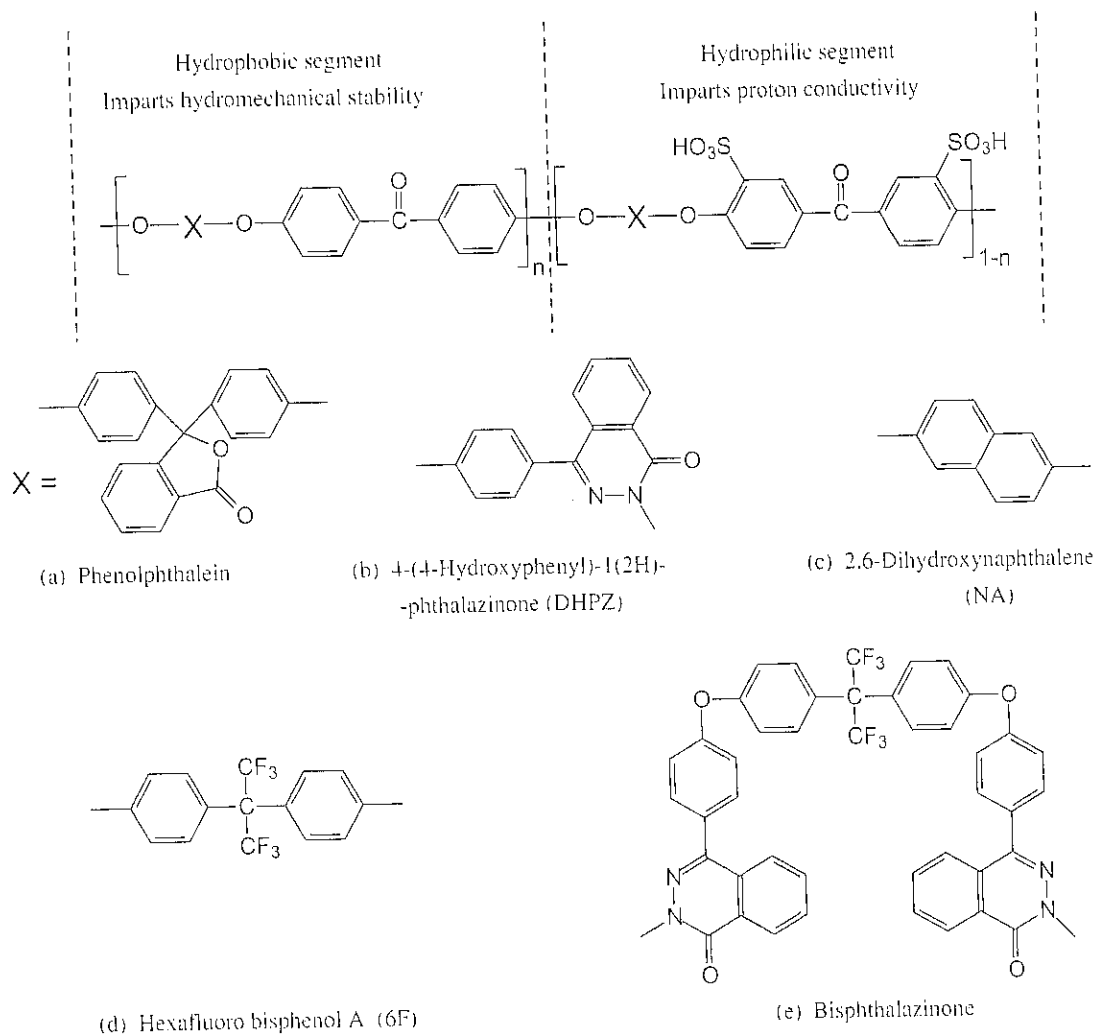
(e) Bisphthalazinone

Figure 10.13 Typical copolymers derived from sulfonated 4,4'-difluorodiphenyl ketone.

sulfonated DFBP using various non-sulfonated comonomers such as (b) 4-(4-hydroxyphenyl)-1(*2H*)-phthalazinone (DHPZ), (c) 2,6-dihydroxynaphthalene (NA), and (d) bisphenol 6F as shown in Figure 10.13 [70, 79, 80]. The rigid planar aromatic NA group was incorporated into the polymers' backbone in order to improve the hot water stability of sulfonated PAEKs having a high SC. Introducing dissymmetric monomers such as NA into the backbone disrupts the polymer chain packing, having implications for free volume, decreasing the melting temperature (T_m) and crystallinity of PAEK, while improving organic solvent solubility [80].

Meng's group reported a new approach to the preparation of ionomers from poly (phthalazinone ether ketone)s that were synthesized by a N—C coupling reaction [11] (Figure 10.13e). These polymers are claimed to exhibit improved oxidative resistance by the Fenton's test when compared with other sulfonated polymers.

From the molecular design viewpoint, the incorporation of long and regular ether-ether-ketone-ketone (EEKK) moieties should increase the relative length of non-sulfonated hydrophobic segments, thereby giving greater separation to the hydrophilic segments, which could lead to possible improvements in the mechanical properties, and methanol and hot water dimensional stability. A series of sulfonated aromatic polymers comprising rigid PEEKK backbones (associated with hot-water stability and low methanol permeability) and bulky pendant fluorenyl group (associated with free volume, and thereby water uptake and proton conductivity) were prepared by polymerization of sulfonated monomer. As shown in Figure 10.14, SPEEKK copolymers derived from sulfonated and non-sulfonated 1,4-BFBB both containing bulky fluorenyl groups and hydrophobic (a) 4,4′-(9-fluorenylidene) diphenol (FDP), (b) bisphenol 6F, (c) ditrifluoromethylphenyl (6F-PH) and (d) 3,3′,5,5′-tetramethyl diphenyl-4,4′-diol (TMDPD) groups have been reported [60, 81, 82].

SPEEKK copolymers derived from 1,3-bis(4-fluorobenzoyl) benzene (1,3-BFBB) were also reported to increase the statistical length of non-sulfonated segments in order to improve the mechanical strength of the membranes, as shown in Figure 10.15 [63, 83]. Tensile strength measurement indicated that these SPAEEKKs membranes are tough and strong at ambient conditions [83].
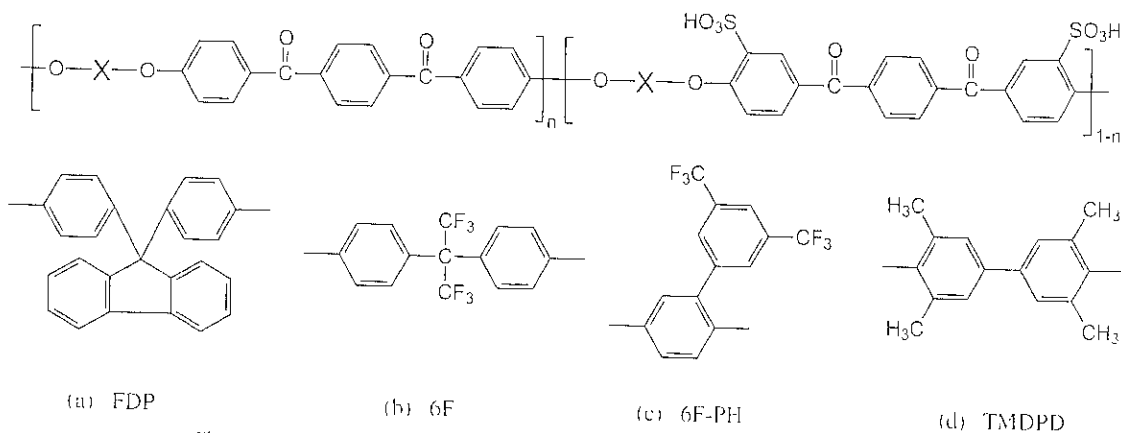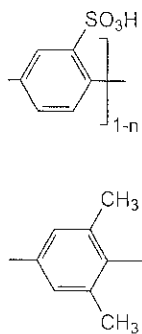

(a) FDP   (b) 6F   (c) 6F-PH   (d) TMDPD

Figure 10.14 Typical copolymers derived from sulfonated 1,4-bis(4-fluorobenzoyl)benzene.

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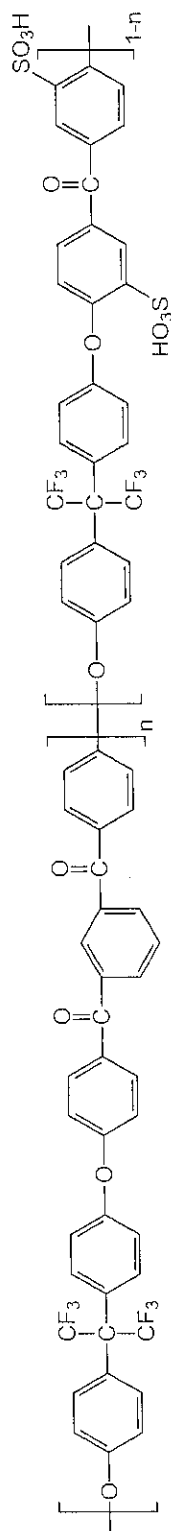
(a) Structure of sulfonated poly(aryl ether ketone) copolymers

(b) Structure of sulfonated polyarylene ether ether ketone ketone) copolymers

$$Ar =$$ or

Figure 10.15 Structures of SPEEKK derived from 1,3-bis(4-fluorobenzoyl) benzene.

Poly(arylene ether nitrile)s   Poly(arylene ether nitrile)s are a class of high performance thermoplastic polymers prepared by polycondensation of bisphenols and dihalobenzonitrile or dinitrobenzonitriles in dipolar aprotic solvent 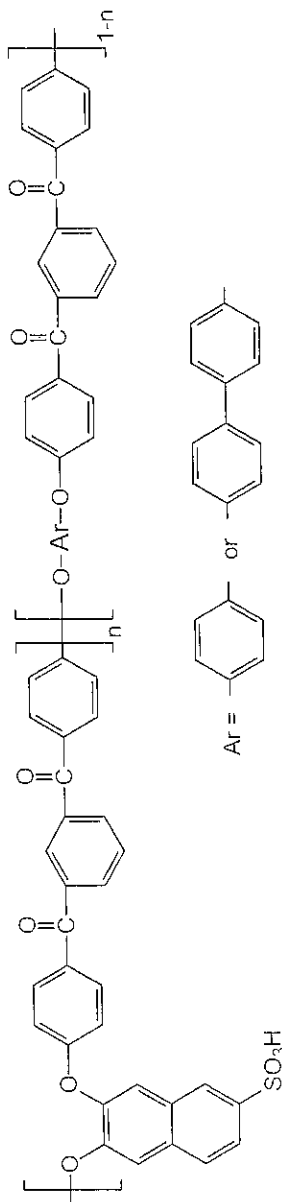[61]. A combination of their good mechanical properties, high chemical and thermal resistance, and strongly polar pendant nitrile groups, make poly(arylene ether nitrile)s good candidates for matrices in advanced composites for the aerospace industry. It is also found that the introduction of nitrile groups into proton conductive sulfonated thermoplastics decreased their moisture absorption [84]. In addition, it is also believed that the presence of nitriles have the potential to promote adhesion of the polymers to heteropolyacids incorporated into composite membranes or to electrodes in the preparation of MEAs.

Poly(arylene ether nitrile)s containing sulfonic acid groups from 2,6-difluorobenzonitrile (2,6-DFBN), potassium 2,5-dihydroxybenzenesulfonate (SHQ), and additional non-sulfonated comonomers 4,4′-biphenol or hydroquinone were reported [62] (Figure 10.16a). The resulting copolymers exhibit lower water uptake than sulfonated PAEKs and PESs of similar equivalent weight and IEC values, and with proton conductivities close to, or higher than that of Nafion 117, reaching 10^{-1} S/cm. However, for this series of poly(arylene ether nitrile)s having comparable conductivities to Nafion, the water swelling still exceeded that of Nafion, particularly in hot water. Guiver's group also reported that a more rigid and hydrophobic naphthalene-based bisphenol containing sulfonic acid groups bonded meta- to the ether linkage was used instead of the more flexible and hydrophilic hydroquinone to prepare an additional series of poly(arylene ether nitrile)s. This is the first example of using this inexpensive commercially available monomer 2,8-dihydroxynaphthalene-6-sulfonate sodium salt (2,8-DHNS-6) as a monomer in a polycondensation reaction [61] (Figure 10.16b). It was incorporated in anticipation of improving in-water dimensional stability and the mechanical properties of the films. The sulfonic acid groups, which are not in a deactivated position, could potentially improve the proton conductivity and hydrolytic stability of the polymer chain. The DMFC performance of this copoly(arylene ether nitrile) derived from 2,8-DHNS-6 was reported [85]. Comparative PEMFC and DMFC performance was reported for poly(arylene ether ether nitrile) copolymers containing sulfonic acid group bonded in structurally different ways (HQ-SPAEEN: Figure 10.16a, m-SPAEEN: Figure 10.16. (b), p-SPAEEN: Figure 10.16c), which are non-fluorinated and have nitrile groups in both the hydrophilic and hydrophobic repeat units [86].

Sulfonated poly(phthalazinone ether ketone nitrile) copolymers (SPPEKN) were prepared by copolymerization of disodium 3,3′-disulfonate-4,4′-difluorobenzophenone (SDFB-Na), 2,6-difluorobenzonitrile (2,6-DFBN), and DHPZ and potassium carbonate at 160 C in N-methyl-2-pyrrolidinone (NMP) [87] (Figure 10.16d). McGrath's group also reported a sulfonated poly(arylene ether) copolymer containing aromatic nitriles [84] (Figure 10.16e).

The presence of highly polar nitrile groups in sulfonated poly(arylene ether)-type copolymer has the apparent effect of reducing water uptake and dimensional swelling through increases in inter-chain molecular forces.
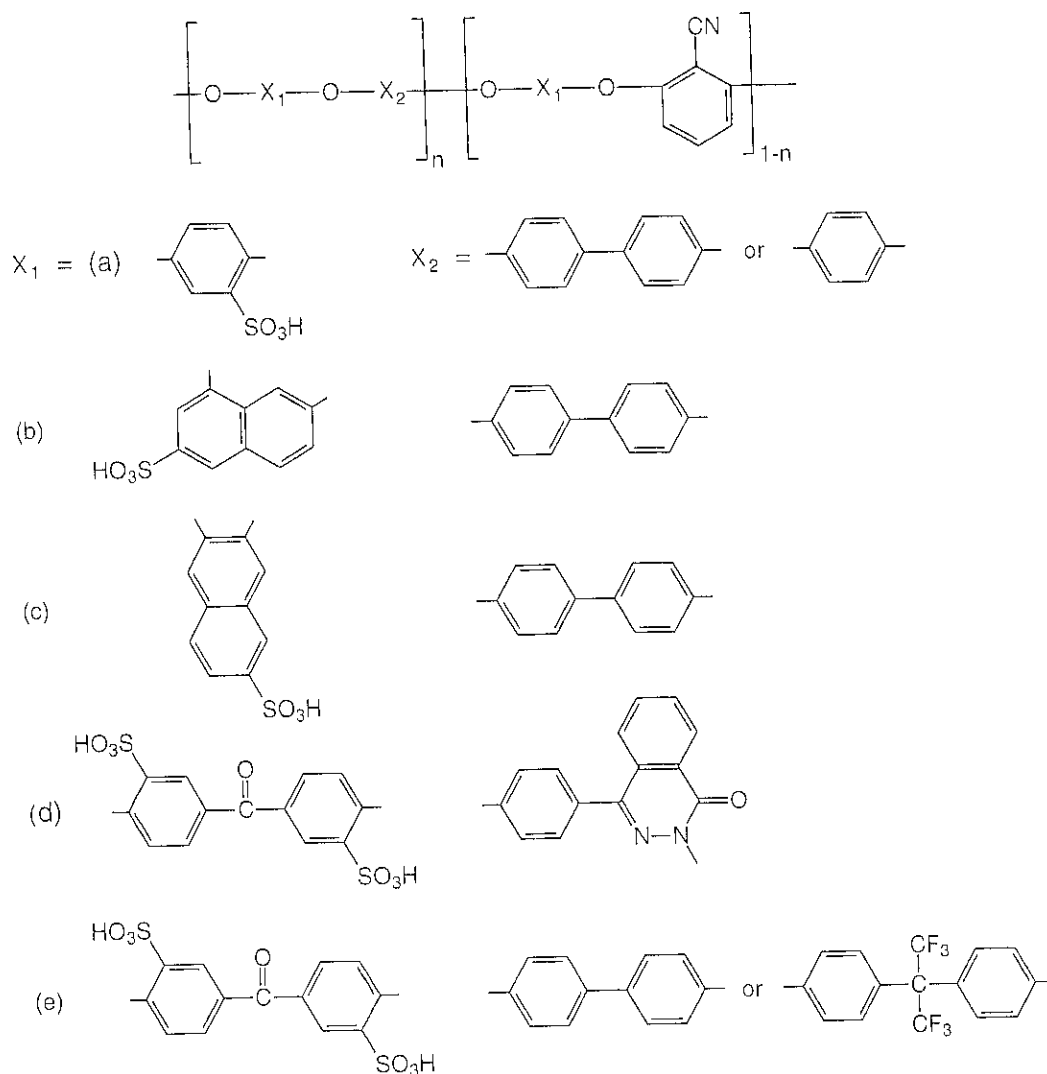
Figure 10.16 Typical copolymers containing nitrile groups.

10.2.2.3 Other Synthetic Strategies: Introducing Sulfonic Acid Groups

In the previous section, we briefly reviewed sulfonated polymers prepared by direct polymerization of sulfonated monomer or by post-sulfonation. The majority of this work is based on poly(arylene ether)s that contain the sulfonic acid groups located along the polymer backbone. The sulfonated aromatic polymers can be divided into two types according to the position of the sulfonic acid groups attached, main-chain-type and side-chain-type, in which the sulfonic acid groups are attached to the polymer backbone and side chains, respectively. In general, main-chain-type polymers show suitable conductivities only at high IECs, resulting in excessive water uptake above a critical temperature (percolation threshold), or a dramatic loss of mechanical properties that makes them unsuitable for practical PEM applications. Kreuer et al. [88] reported that these sulfonated polymers are unable to form defined hydrophilic domains, as the rigid polyaromatic backbone prevents continuous

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ionic clustering from occurring. This discussion covers other synthetic strategies for alternative PEM materials. One promising way to lower the water uptake and enhance properties in terms of PEM performance is to design materials having distinctly separate hydrophilic sulfonic acid group regions from the hydrophobic polymer main chain, by placement of the sulfonic acid groups on side chains grafted onto the polymer main chain [89]. For side-chain-type sulfonated polymers, short pendant side chains provide spacing between the polymer main chain and the sulfonic acid groups, which may facilitate the formation of nanophase separation of hydrophilic and hydrophobic domains, thereby leading to possible improvements in hydrolytic stability and water uptake. A variety of side-chain-type sulfonated polymers have been prepared by the chemical grafting method or by post-sulfonation on activated pendants of the corresponding parent polymers. Ding *et al.* reported the properties of graft polymers comprising graft chains of a macromonomer poly (sodium styrenesulfonate) and a polystyrene backbone [90]. If flexible pendant side chains linking the polymer main chain and the sulfonic acid groups exist in the polymer structure, nanophase separation between hydrophilic and hydrophobic domains may be improved [91].

The group of Jannasch reported [92] convenient methods for preparing polysulfones containing sulfonated side-chains, as shown in Figure 10.17. A side-group-sulfonic acid polysulfone was prepared via lithiation, followed by reaction of the resulting lithiated polysulfone intermediate with sulfobenzoic acid cyclic anhydride (Figure 10.17a). A polysulfone with pendant sulfonated aromatic side chains was also reported (Figure 10.17b), having proton conductivities of 11 to 32 mS/cm at 120 °C [91]. Lithiated polysulfone was first reacted with 4-fluorobenzoyl chloride to introduce 4-fluorobenzoyl side chains to the polymer main chain. The resulting activated fluoro groups were then reacted with 4-sulfophenolate or 7-sulfo-2-naphtholate via a nucleophilic substitution reaction.

Einsla *et al.* reported that sulfonated PES copolymers with pendant sulfonic acid groups were prepared using barium pentafluorobenzenesulfonate and 4-nitrobenzenesulfonyl chloride; the PEMs showed lower proton conductivity of 1 to 8 mS/cm [89]. Guiver's group reported a new class of comb-shaped polymers comprising a rigid, partially fluorinated hydrophobic backbone and monodisperse α-methyl polystyrene hydrophilic side chains prepared by anionic polymerization (Figure 10.18a) [93].

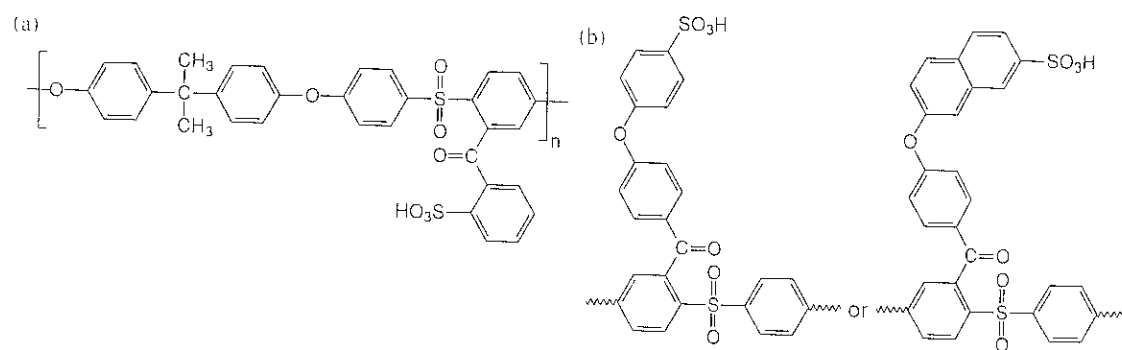Figure 10.17 Polysulfones containing sulfonated side-groups.

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8a) [93].

Acetyl sulfate
(CH$_2$Cl)$_2$, 50 °C

R ≡ H → SO$_3$H

(a) Highly fluorinated comb-shaped copolymer (Comb-22)

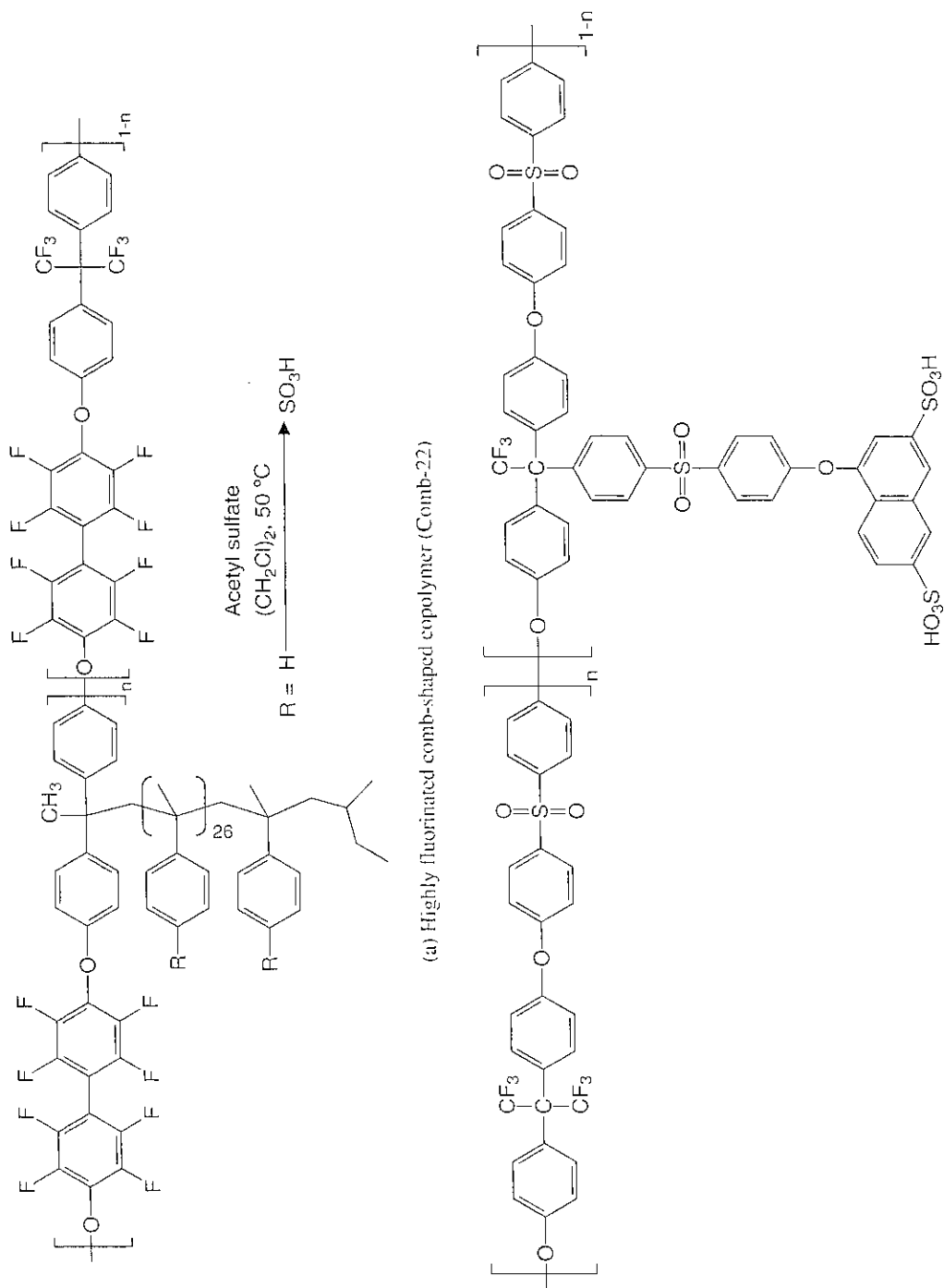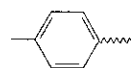(b) Sulfonated polyether sulfones with grafting sulfonated groups

Figure 10.18 Comb-or pendant-type copolymer.

A new bisphenol monomer containing a masked grafting site, 1,1-bis(4-hydroxyphenyl)-1-(4-(4-fluorophenyl)thio)phenyl-2,2,2-trifluoroethane (3FBPT), (Figure 10.18b) was also reported [94]. Copolymers containing 4-fluorophenyl sulfide pendant groups were obtained via conventional aromatic nucleophilic substitution polycondensation using this monomer. Simple oxidation from the sulfide to sulfone activates the *para* fluorine on the polymer pendant group for nucleophilic attack by phenolates and other species in order to introduce arylsulfonic acid.

The group of Jiang [95, 96] also reported a new sulfonated copolymer derived from sulfonated monomers such as sodium-3-(4-(2,6-difluorobenzoyl) phenyl) propane-1-sulfonate (DFPPS) and sodium 4-(4-(2,6- difluorobenzoyl) phenoxy) benzenesufonate (SDFBS) (Figure 10.19). It was reported that all PSA-SPAE membranes exhibited reasonable flexibility and tensile strength in the range of 41–78 MPa. PSA-SPAE copolymers bearing sulfonic acid groups on flexible side chains showed considerably reduced dimensional swelling and improved proton conductivities.

More recently, Kim and Guiver reported [97] comb-shaped PESs as PEMs (Figure 10.20). A sulfonated side-chain grafting unit containing two or four sulfonic
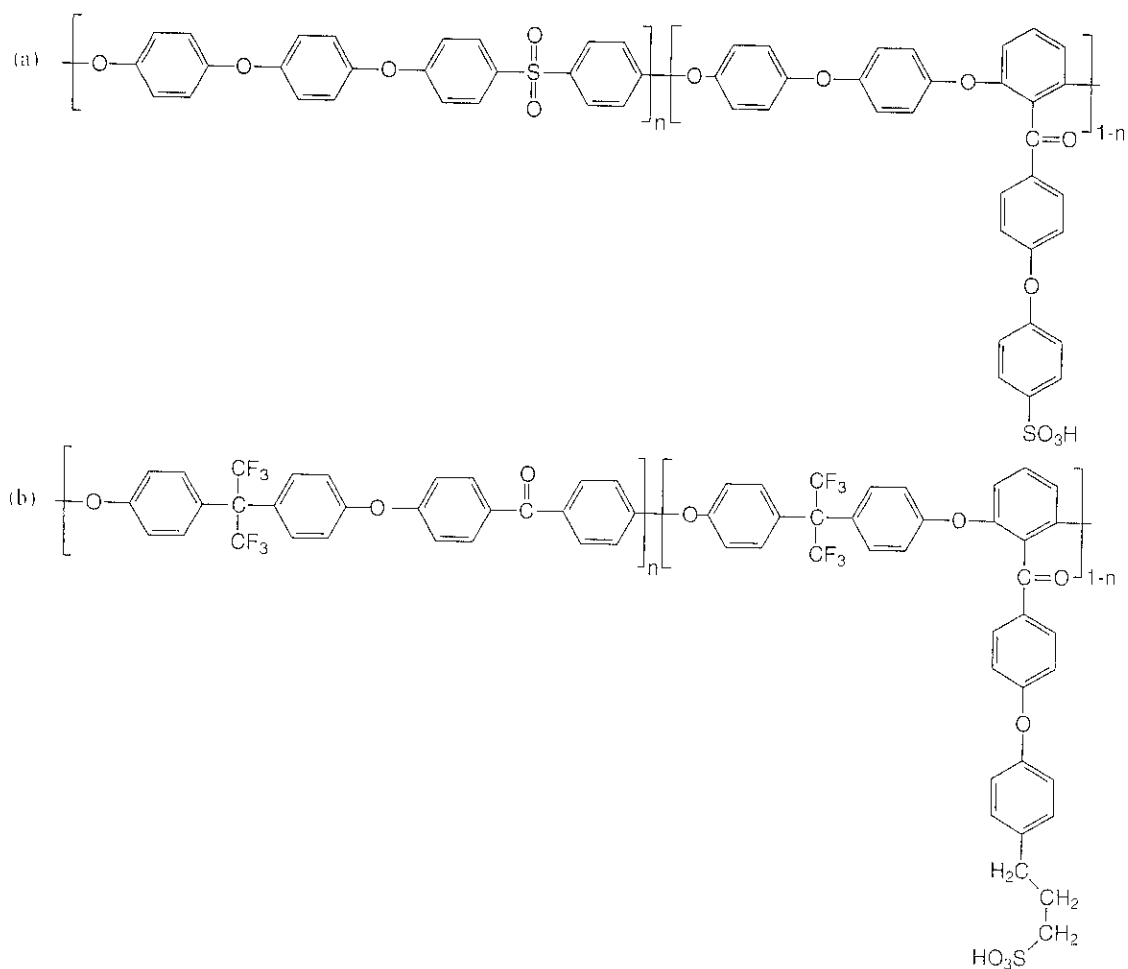

Figure 10.19 Sulfonated poly(arylene ether)s with pendant sulfonated groups.

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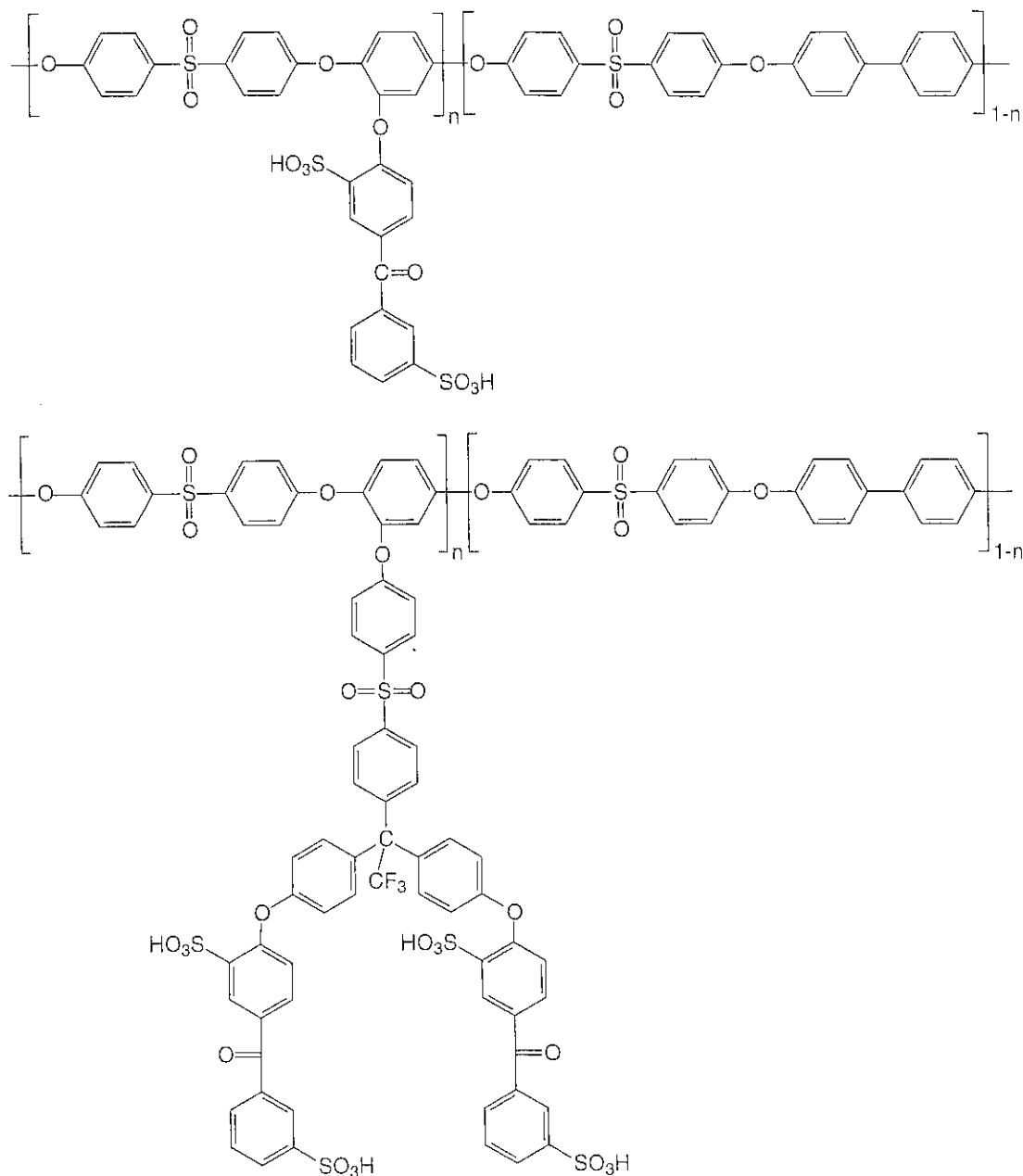ESs as PEMs
or four sulfonic

Figure 10.20 Sulfonated poly(arylene ether sulfone)s with pendant sulfonated groups.

acid groups was synthesized using sulfonated 4-fluorobenzophenone (FBP) and
3FBPT. Poly(arylene ether sulfone) containing methoxy group was synthesized.
After deprotecting the methoxy group to hydroxyl group, the sulfonated side chains
were grafted onto the —OH functionalized copolymer to make the comb-shaped
sulfonated PES copolymers. The comb-shaped copolymers with two or four sulfonic
acid groups show high proton conductivities in the range of 34 to 147 mS/cm and
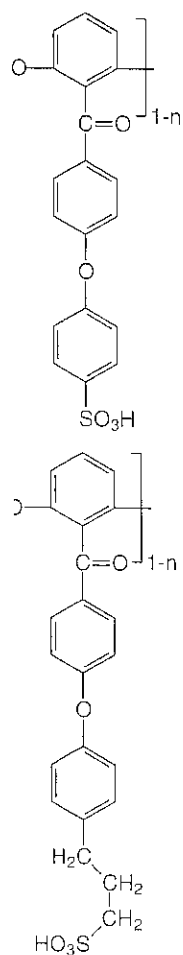
63 to 125 mS/cm, respectively. The methanol permeabilities of these copolymers were in the range of 8.2×10^{-7} to 5.6×10^{-8} cm^2/s.

10.2.2.4 Properties of Sulfonated Poly(arylene ether) Copolymers

Common themes critical to all high performance PEMs include (i) high protonic conductivity; (ii) low permeability to fuel and oxidant; (iii) low water transport through diffusion and electro-osmosis; (iv) oxidative and hydrolytic stability; (v) good mechanical properties in both the dry and hydrated states; (vi) cost; and (vii) capability for fabrication into MEAs [66]. To date, much research has been limited to the polymer synthesis and characterization of stand-alone membranes, while far fewer MEA studies of hydrocarbon-based sulfonated copolymers have been conducted because of issues with dimensional swelling, high methanol permeability and oxidative and hydrolytic stability under fuel cell operating conditions [66, 67, 98–100]. Nearly all existing membrane materials for PEM fuel cells rely on absorbed water and its interaction with acid groups to enable it to conduct protons. Due to the large fraction of absorbed water in the membrane, both mechanical properties and water transport become key issues.

The difficulties in preparing high performance MEAs as a result of membrane-electrode incompatibility is one of the primary reasons that improved membrane properties have not always led to improved DMFC performance. The group of Pivovar [101] attributed membrane-electrode interfacial resistance to differential swelling between the membrane and electrodes, leading to electrode delamination. Water uptake of PEMs is important for both membrane-electrode compatibility and mechanical properties of the membranes.

Generally, polymer composition or IEC is plotted versus conductivity; however, these plots do not allow a direct comparison between different membrane materials. Membrane water uptake is known to have a profound effect on proton conductivity and methanol permeability, and provides a better comparative basis for materials. Although literature data have been compiled for proton conductivity data versus methanol permeability, proton conductivity versus water uptake has rarely been plotted in the multitude of literature references. The group of McGrath suggest that an upper bound relationship may exist, expressed by a linear log-log plot of water content versus proton conductivity of the membrane [44]. Figure 10.21 shows the proton conductivities of various PEMs as a function of water uptake (wt%) at 80 °C. The water uptake values in Figure 10.21 have been reported on a mass basis, because density data for the polymers were not available in many cases. The changes in length scale (reflected in volume measurements) are expected to be the most appropriate comparison basis because electrochemical properties such as proton conductivity and permeability occur over length scales under operating conditions independent of mass [69]. Figure 10.22a shows the proton conductivity as function of volume-based water uptake (vol%) using the previous reported data having density data. Figure 10.22b shows the relative water uptake as function of relative conductivity. In this study the conductivity and water uptake (vol%) of alternative membranes have been normalized to the values reported for Nafion, which is defined as having a relative conductivity and water uptake of 1. The data points of the copolymer
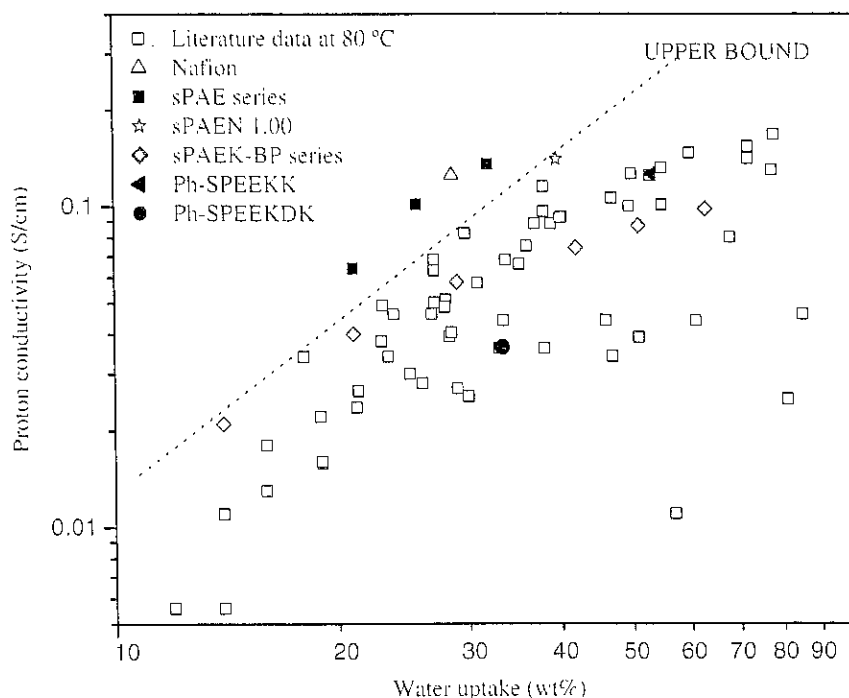
Figure 10.21 Proton conductivity and water uptake (wt.%) at 80 °C (Refs. [52, 53a, 60, 64, 65, 79, 80, 85, 93, 96, 97, 102–106].

membranes (sPAE series and sPAEN 1.0 as illustrated in Figure 10.9a and b) are located above the upper bound line in the area of potential high performance (i.e., high proton conductivity coupled with low water uptake) in the trade-off plot for the relationship between PEM proton conductivity versus water uptake (weight based or volume based) shown in Figures 10.21 and 10.22a. It is often the case that hydrocarbon membranes having the same water uptake as Nafion have lower conductivity, or membranes with similar conductivity have higher water uptake based on weight or volume. Figure 10.23 shows the proton conductivity of sulfonated poly(vinyl alcohol) membrane series and sulfonated poly(arylene ether) copolymer series as a function of water uptake (vol%). The sulfonated poly(arylene ether) copolymer series shows superior properties of proton conductivity and water uptake. Higher water uptakes often lead to difficulties preparing robust and high performance MEAs or decreased durability during cycling between different levels of hydration.

10.2.3
Single Cell Performances

The performance of PEMs is typically evaluated by comparison with Nafion membrane under identical test conditions. This is largely because there is no standard testing protocol for PEMs. Although these studies allow membrane performance comparisons under the same test conditions, one must keep in mind that the test conditions employed may not be equivalent for each membrane. The performance of
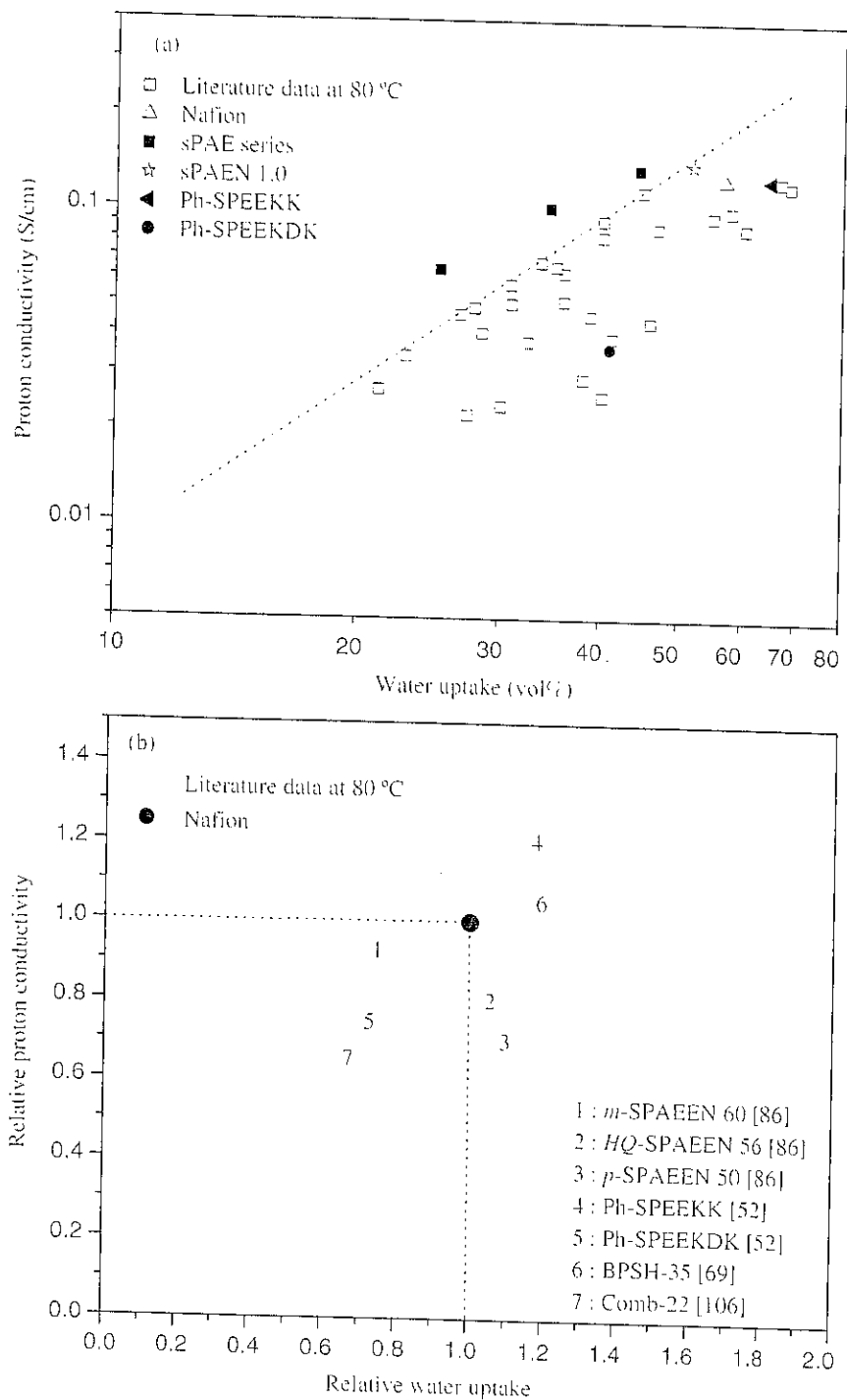
Figure 10.22 (a) Proton conductivity and water uptake (vol.%) at 80 C (b) relative proton conductivity and relative volume water uptake (vol.%) (Refs. [52, 53a, 65, 85, 86, 97, 102, 105, 106].
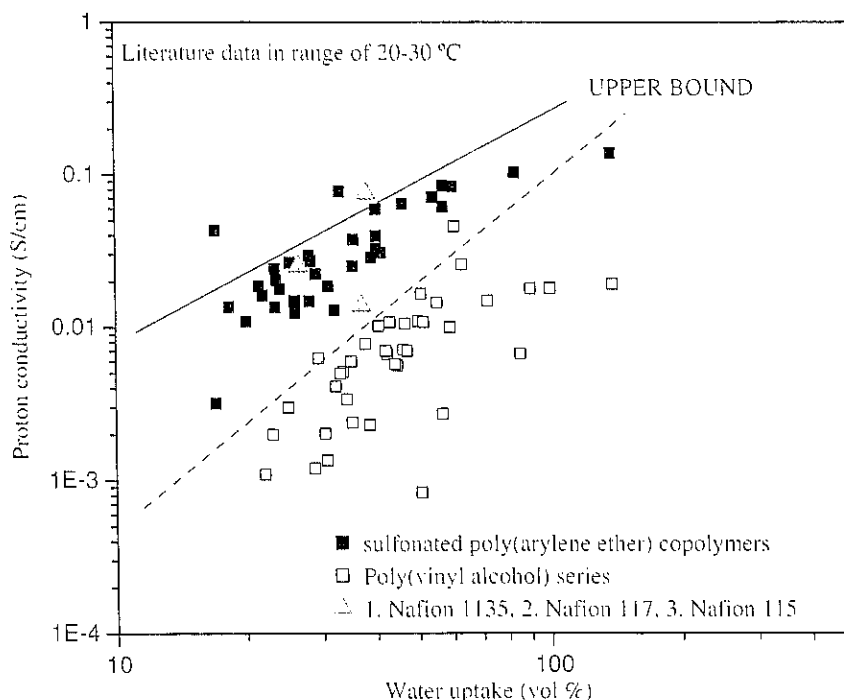
Figure 10.23 Proton conductivity and water uptake (vol.%) at 20–30 °C.

PEM materials is highly variable between various research groups due to the MEA fabrication techniques and fuel cell test conditions. Therefore, in this section, we discuss the performance of MEAs that are measured under the same conditions. To do that, we selected PEMs such as sulfonated PAEKs, PESs, poly(arylene ether nitrile)s, and comb-type copolymers.

Most hydrocarbon-based PEM research has been limited to reporting the polymer synthesis and the characterization of stand-alone membranes. There are relatively fewer MEA studies conducted for fuel cell applications because of the issues with dimensional swelling, high methanol permeability and oxidative and hydrolytic stability under fuel cell operating conditions [86]. Membranes with excessive water uptake tend to be (i) less effective in proton conduction and (ii) mechanically fragile and subject to dimensional changes under dehydration/hydration cycling. Therefore, several hydrocarbon PEMs were selected for further MEA study based on superior *ex situ* membrane properties presented in Figure 10.22b. The seven PEMs were selected based on a favorable combination of proton conductivity and water uptake (vol.%). The structures of sulfonated poly(arylene ether nitrile) copolymers (*m*-SPAEEN-60, *HQ*-SPAEEN-56, and *p*-SPAEEN-50) are shown in Figure 10.16. The structures of Ph-SPEEKK, Ph-SPEEKDK are shown in Figure 10.8. The BPSH-35 and Comb 22 are shown in Figures 10.11b and 10.18, respectively. The properties of these seven membranes are listed in Table 10.1. The changes in length scale (reflected in volume measurements) are expected to directly impact observed properties, because electrochemical properties such as proton conductivity and permeability occur over length scales under operating conditions independent of mass [69]. The

Table 10.1 Properties of the membranes.

Copolymer	Density (g/cm^3)^a	IEC$_w$ (meq./g)^b	IEC$_v$ (meq./cm^3)^c		Water uptake		Proton Conductivity (mS/cm)	
			dry	wet	wt%^{d}	vol%^{e}	30 C	80 C
1. m-SPAEEN-60	1.18	1.91	2.26	1.70	28	33	78	115
2. HQ-SPAEEN-56	1.29	1.90	2.45	1.80	28	36	60	100
3. p-SPAEEN-50	1.55	1.60	1.75	1.20	30	46	65	88
4. Ph-SPEEKK	1.22	1.80	2.20	1.57	33	40	38	151
5. Ph-SPEEKDK	1.23	1.60	1.97	1.49	25	32	23	88
6. BPSH-35	1.33	1.87	2.49	1.63	40	53	78	126
7. Comb 22	1.35	1.20	1.62	1.38	13	18	43	82
Nafion 1135	1.98	0.91	1.78	1.29	19	38	76	125

^{a}Based on dry state.
^{b}Based on weigh of dry membrane.
^{c}Based on volume of dry and/or wet membranes (IEC$_v$ (wet) = IEC$_v$(dry)/(1 + 0.01 WU)).
^{d}WU (mass %) = (W$_{wet}$ − W$_{dry}$)/W$_{dry}$ × 100.
^{e}WU (vol%) = (W$_{wet}$ − W$_{dry}$)/δ_w)/(W$_{dry}$/δ_m) × 100. (W$_{wet}$ and W$_{dry}$ are the weights of the wet and dry membranes, respectively; δ_w is the density of water (1 g/cm^3), and δ_m is the membrane density in the dry state; water uptake measured at room temp.

water uptake directly affects the sulfonic acid concentrations within the polymer matrix under hydrated conditions, which is gauged by comparing wet volume-based IEC (IEC$_V$ (wet)) values with IEC$_W$ values. As listed in Table 10.1, it was found that the introduction of nitrile groups into sulfonated copolymers reduced water uptake and dimensional swelling when compared with polymers that did not contain nitrile, at similar IEC values [84, 87]. We suggest that a plausible factor for the low water uptake of copolymers containing nitrile groups is the presence of strong nitrile dipole interchain interactions occurring in certain polymer structural configurations that combine to limit swelling in water [85, 86]. In addition, nitrile-sulfonic acid group interactions also appear to be important, as nitrile groups have been found to associate with sulfonic acid groups through bridging water molecules in specific spectroscopic studies [107]. The introduction of highly polar nitrile has been suggested to improve mechanical strength of the polymers and promote their adhesion to various substrates.

We compare the voltage-current characteristics (i.e., H$_2$/air and DMFC polarization curves) of MEAs using the seven copolymers, and Nafion 212 and 1135. Figure 10.24 shows the H$_2$/air performance of the selected membranes, since it is useful to compare the performance of similar materials in both the DMFC and the hydrogen system. For comparison, we tested relatively thin membranes in order to reduce cell ohmic resistance. MEAs using nitrile copolymers showed lower performance in comparison with the Nafion 212 MEA, but higher performance compared with the MEA using sulfonated polysulfone BPSH-35. However, it should be noted that with the exception of the comb 22 PEM, the thickness of all hydrocarbon
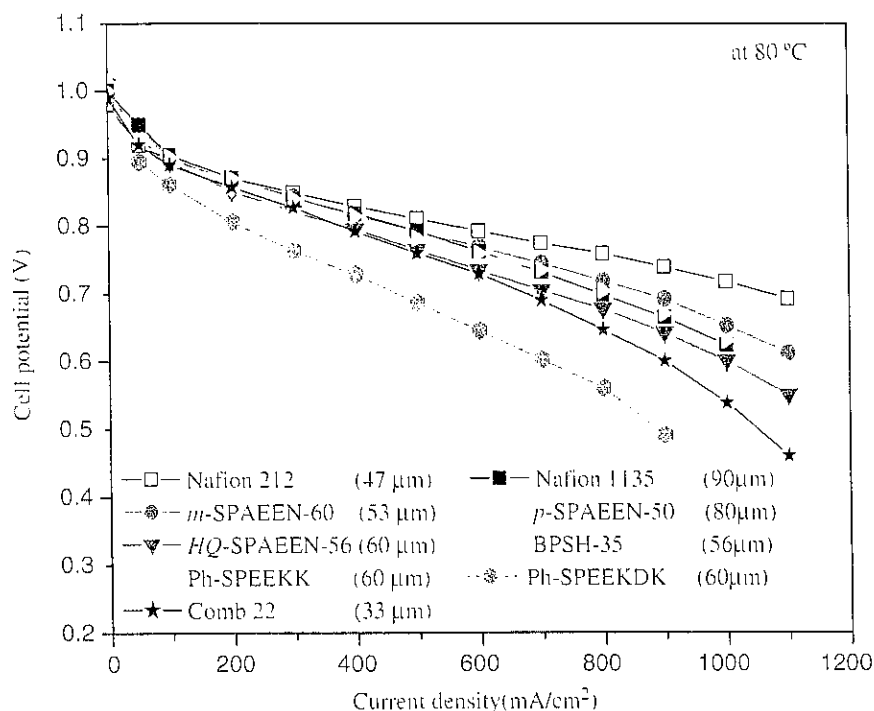
Proton onductivity (mS/cm)	
°C	80 C
8	115
0	100
5	88
8	151
3	88
8	126
3	82
6	125

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Figure 10.24 H$_2$/air fuel cell performance of selected PEM (value in parenthesis denote membrane thickness).

PEMs including *m*-SPAEEN-60 membrane (53 μm) were greater than that of Nafion 212 (47 μm). The slightly lower performance of the cell using *p*-SPAEEN compared with the cell using BPSH-35 may be due to the increased resistance of the thicker membrane. Among the cells incorporating nitrile copolymers, the MEA using *m*-SPAEEN-60 showed the best performance. Although the thickness of Nafion 1135 (90 μm) was higher than that of *m*-SPAEEN-60, the performance of *m*-SPAEEN-60 is higher than that of Nafion 1135. Qualitatively good correlation between cell resistance and polarization characteristics indicates that interfacial incompatibility between membrane and electrode and resulting performance loss is minor, which we expect from relatively low water uptake of the tested membranes.

Methanol crossover and cell resistance play a major role in determining DMFC performance. Methanol crossover in the MEA was estimated by measuring the limiting methanol crossover current [108–110]. The total cell resistance is composed of the sum of membrane resistance, electronic resistances of the fuel cell components (flow field, current collectors, and gas diffusion layers), the resistance of the electrodes and interfacial resistances associated with the interfaces between electronic components and between the electrode and the membranes. Therefore, cell resistance from these cumulative factors is always higher than the associated free-standing membrane resistance. Figure 10.25 shows the high frequency resistance (HFR) and methanol crossover limiting current of single cells using the hydrocarbon copolymers and Nafion at 80 °C under DMFC operating conditions (0.5 M MeOH). A membrane with ideal properties should have very low HFR (ohmic losses) and low methanol crossover
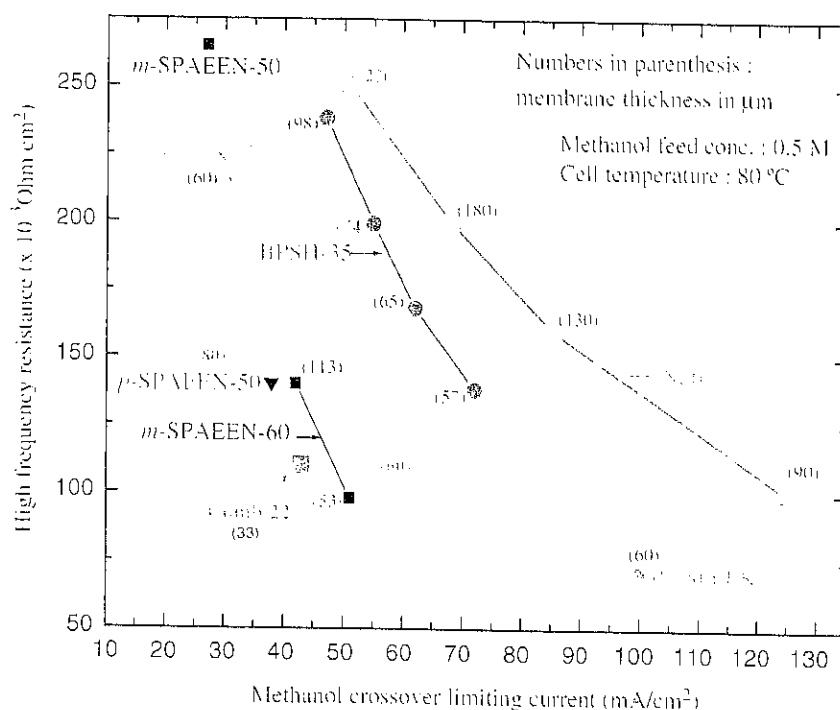
Figure 10.25 HFR vs. methanol crossover limiting current of selected PEMs and Nafion as a function of membrane thickness measured in DMFC mode at 80 C.

(low crossover losses). Of the selected polymers shown, Nafion shows the poorest DMFC performance, having the lowest selectivity resulting from a combination of the higher membrane thickness (resulting in higher HFR) that is required to compensate for high methanol crossover. The selectivity for the PEMs of various thicknesses is listed in Table 10.2. Compared with the selectivities of Nafion, the selected copolymers show significantly improved selectivities, having much lower methanol crossover limiting current at comparable high frequency resistance. From these results, one would expect improved DMFC performance using selected copolymers compared with Nafion.

Although polarization curves are the most popular method for evaluating DMFC performance, making reasonable and relevant performance comparisons across different types of membranes is difficult because cell properties depend on membrane thickness. While DMFC cells using hydrocarbon membranes show the same thickness effect, the optimum thickness of each specific membrane polymer family should be different, due to differences in the conductivity and methanol permeability of the membrane. Apart from the effect of membrane thickness, there are several other factors that make accurate comparative performance evaluation difficult using single polarization curves: (i) methanol crossover (fuel use) is not fully interpreted by polarization curves, and (ii) optimum operating conditions may be very different for different systems [85]. In order to lessen the uncertainty caused by methanol crossover and to provide a meaningful comparison, we selected membranes for the fuel cell tests as having an appropriate thickness for which methanol crossover

Table 10.2 Electrochemical properties of membrane and Nafion at 80 °C (0.5 M MeOH).

Copolymer	Thickness (μm)	HFR (mΩ cm^2)	MeOH limiting current (mA/cm^2)	Selectivity (α)
1. *m*-SPAEEN-60	53	97	52	198
	113	140	42	170
2. *HQ*-SPAEEN-56	60	101	54	183
3. *p*-SPAEEN-50	80	140	38	188
4. Ph-SPEEKK	60	71	100	141
5. Ph-SPEEKDK	60	215	30	155
6. BPSH-35	65	168	62	96
	74	199	55	91
	98	238	47	89
7. Comb 22	33	110	43	211
Nafion 112	50	70	152	94
Nafion 1135	90	100	125	80
Nafion 1110	250	250	51	78

MEA selectivity (α): $\alpha(\text{HFR}^{-1}\ \text{MeOH current}^{-1}) = \frac{1}{HFR \cdot \xi_{lim}}$, ($\xi_{lim}$ limiting methanol crossover current of membrane).

limiting currents were similar (35~55 mA/cm^2) across different polymer systems, as shown in Figure 10.25.

Figures 10.26 and 10.27 show the cell performance of the MEAs using selected copolymers having similar methanol crossover limiting current at methanol feed
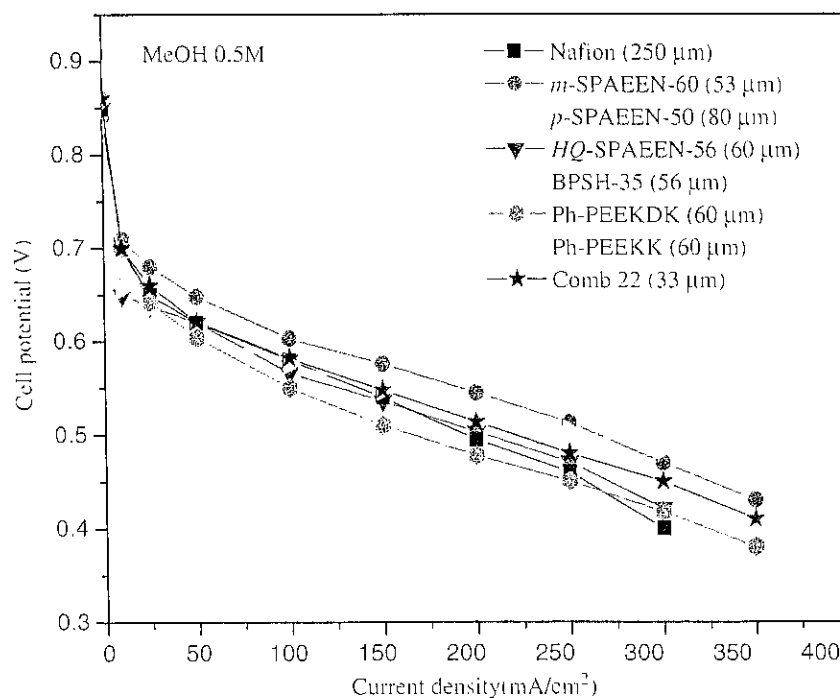

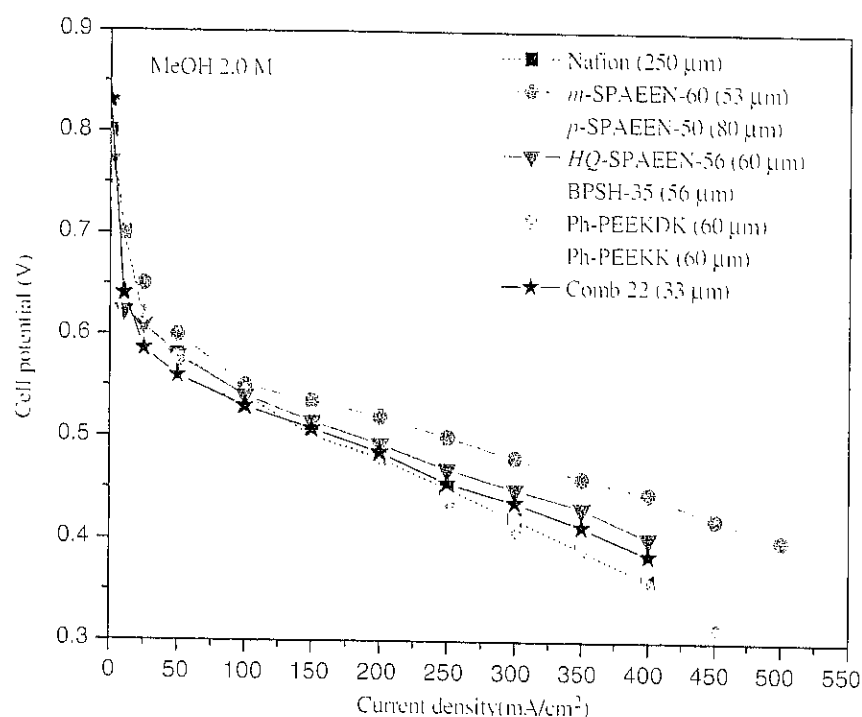Figure 10.26 DMFC performance of selected PEM materials at 0.5 M (Cell temperature: 80 °C).

Figure 10.27 DMFC performance of selected PEM materials at 2.0 M (Cell temperature: 80 °C).

concentrations of 0.5 and 2.0 M. The performance of the MEAs using SPAEEN copolymers and BPSH-35 were superior to that of the Nafion MEA (0.5 M MeOH) (Figure 10.26). The performance of BPSH-35 was superior to the p- and HQ-SPAEEN at 0.5 M methanol concentration, while the performance of p-, and HQ-SPAEEN was superior to the BPSH-35 at the higher 2.0 M methanol concentration.

Among the selected membranes and Nafion, the m-SPAEEN-60 shows the best performance. For example, the current density of the MEA using m-SPAEEN-60 at 0.5 V and 0.5 M methanol was 265 mA/cm^2, whereas the current densities of the MEAs using BPSH-35 and Nafion were 230 and 195 mA/cm^2 (Figure 10.26). At 2.0 M methanol, open circuit potential and mass transport limitations for all MEAs decreased, but the performance trend remained remarkably similar to that at 0.5 M methanol. The current density of the MEA using m-SPAEEN-60 at 0.5 V and 2.0 M methanol was 245 mA/cm^2, whereas the power densities of the MEAs using BPSH-35 and Nafion were 195 and 170 mA/cm^2, respectively. The maximum power density of the MEA using m-SPAEEN-60 was shown in 1.0 M methanol. The maximum power density at 550 mA/cm^2 and 1.0 M methanol was 220 mW/cm^2.

It was reported that the sulfonated hydrocarbon polymer membranes showed better performance than Nafion [67, 100]. However, interfacial incompatibility between hydrocarbon membrane and Nafion PFSA-based electrodes can limit long-term performance. In order to investigate the interfacial stability of the MEA, the DMFC performance for before and after life test for various hydrocarbon-based cells was measured, as shown in Figure 10.28. These results indicate that the interfacial compatibilities of m-SPAEEN-60 and Ph-SPEEKK are likely good using
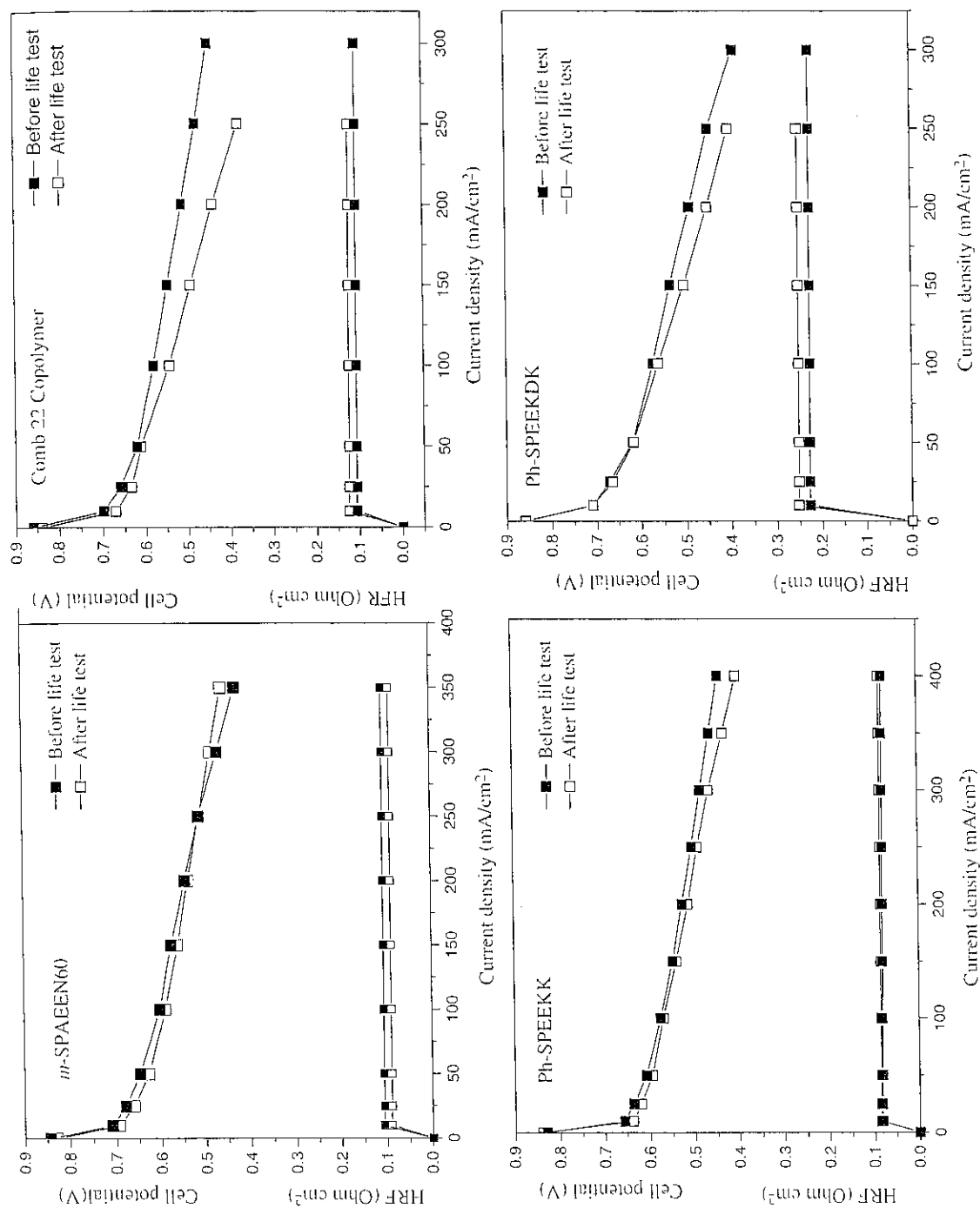
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Figure 10.28 DMFC performance of copolymers before and after life test (120 h) at 0.5 M methanol feed concentration (cell temperature: 80 °C).

Nafion-bonded electrodes, since there was no increase in HFR observed over the experimental time period. In fact, a slight decrease in HFR was observed, which can be attributed to morphological reorganization resulting in an increase in proton conductivity of the membrane [111]. It is known that nitrile groups in polymers promote adhesion of polymer to substrates, possibly through polar interactions with other functional groups. This may be a reason for good adhesion to the catalyst-electrode layer [112].

Although the current density of Comb 22 copolymer showed some loss after the life test, it is not considered to be symptomatic of a hydrocarbon membrane-electrode interfacial problem. The reason is that the performance degradation is too fast and there is linear increase behavior for HFR (Figure 10.28). The most plausible explanation is that the poly(α-methyl styrene) side chain is susceptible to chemical degradation under fuel cell conditions, which caused a loss of the proton-conducting sulfonic acid sites, thereby resulting in decreasing membrane performance. However, the structural architecture of graft and comb-shaped polymers serves to illustrate their potential to improve fuel cell performance.

10.3
Conclusions

In this chapter, we focused on a review of the synthesis and performance of predominately hydrocarbon-based copolymers containing sulfonic acid groups for DMFC application, largely based on the authors' research work. A number of mechanically stable alternative hydrocarbon PEMs with high selectivity has been developed. Many research groups have observed that certain structural design strategies for PEM materials can lead to improved microstructure and performance, by achieving good proton conductivity while maintaining good mechanical properties through controlling water uptake. Our perspective in the design of PEM materials has led us to conclude that two effective strategies for making PEMs with high proton conductivity and lower methanol permeability are (i) introduction of nitrile groups into sulfonated polymers that limit membrane swelling due to nitrile-nitrile dipole interaction; (ii) morphological structures in comb- and/or pendant-type copolymers that are capable of providing materials with high proton conductivity, high mechanical strength and good dimensional stability upon swelling. These materials showed good performance under DMFC conditions.

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