Alternative Polymer Systems for Proton Exchange Membranes (PEMs)

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1. Introduction

Fuel cells have the potential to become an important energy conversion technology. Research efforts directed toward the widespread commercialization of fuel cells have accelerated in light of ongoing efforts to develop a hydrogen-based energy economy to reduce dependence on foreign oil and decrease pollution. Proton exchange membrane (also termed "polymer electrolyte membrane") (PEM) fuel cells employing a solid polymer electrolyte to separate the fuel from the oxidant were first deployed in the Gemini space program in the early 1960s using cells that were extremely expensive and had short lifetimes due to the oxidative degradation of their sulfonated polystyrene−divinylbenzene copolymer membranes. These cells were considered too costly and short-lived for real-world applications. The commercialization of Nafion by DuPont in the late 1960s helped to demonstrate the potential interest in ter-

restrial applications for fuel cells, although its major focus was in chloroalkali processes.

PEM fuel cells are being developed for three main applications: automotive, stationary, and portable power. Each of these applications has its unique operating conditions and material requirements. Common themes critical to all high performance proton exchange membranes include (1) high protonic conductivity, (2) low electronic conductivity, (3) low permeability to fuel and oxidant, (4) low water transport through diffusion and electro-osmosis, (5) oxidative and hydrolytic stability, (6) good mechanical properties in both the dry and hydrated states, (7) cost, and (8) capability for fabrication into membrane electrode assemblies (MEAs). Nearly all existing membrane materials for PEM fuel cells rely on absorbed water and its interaction with acid groups to produce protonic conductivity. Due to the large fraction of absorbed water in the membrane, both mechanical properties and water transport become key issues. Devising systems that can conduct protons with little or no water is perhaps the greatest challenge for new membrane materials. Specifically, for automotive applications the U.S. Department of Energy has currently established a guideline of 120 °C and 50% relative humidity as target operating conditions, and a goal of 0.1 S/cm for the protonic conductivity of the membrane.

New membranes that have significantly reduced methanol permeability and water transport (through diffusion and electro-osmotic drag) are required for portable power oriented direct methanol fuel cells (DMFCs), where a liquid methanol fuel highly diluted in water is used at generally <90 °C as the source of protons. Unreacted methanol at the anode can diffuse through the membrane and react at the cathode, lowering the voltage efficiency of the cell and reducing the system's fuel efficiency. The methanol is usually delivered to the anode as a dilute, for example, 1 M (or less), solution (3.2 wt %), and relatively thick Nafion 117 (1100 EW, 7 mil ∼ 178 μm thick) is used to reduce methanol crossover. The dilute methanol feed increases the system's complexity and reduces the energy density of the fuel, while the thick Nafion membrane increases the resistive losses of the cell, especially when compared to the thinner membranes that are used in hydrogen/air systems. The presence of excessive amounts of water at the cathode through diffusion and electro-osmosis

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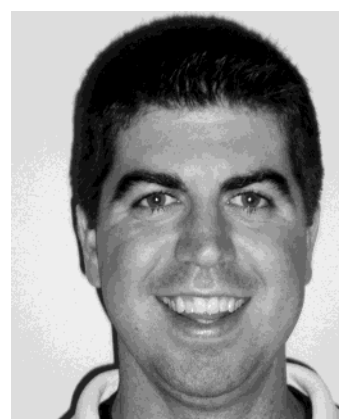
Yu Seung Kim received his Ph.D. at the Korea Advanced Institute of Science and Technology under Prof. Sung Chul Kim (1999). Subsequently, he joined Dr. James. E. McGrath's research group at the Virginia Polytechnic Institute and State University (1999–2003), where he began studying polymer electrolyte membranes. His research was focused on the structure–morphology–property relationships of fuel cell membranes. He is currently working at the Los Alamos National Laboratory; his current research includes developing new membranes and electrodes for H_2/air and direct methanol fuel cells.

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Brian Einsla was born in Wilkes-Barre, PA, in 1978. He earned his Bachelor of Science degree in 2000 in Chemistry at Virginia Polytechnic Institute and State University. He is currently a fourth-year Ph.D. candidate in the Macromolecular Science and Engineering program at VPI&SU. His research interests have centered around sulfonated heterocyclic copolymers for fuel cell applications, including polyimides, polybenzoxazoles, and polybenzimidazoles.

results in water management problems both in the catalyst layer and for the system.

New membrane materials for PEM fuel cells must be fabricated into a well-bonded, robust membrane electrode assembly (MEA) as depicted in Figure 1. In addition to the material requirements of the proton exchange membrane itself as outlined above, the ease of membrane electrode assembly fabrication and the resulting properties of the MEA are also critical. Current work in the area of fabricating MEAs from novel polymeric membranes has focused on the electrode–membrane interface and the problems of having dissimilar ion conducting copolymers in the membrane and as components of the electrode.[1] Novel membranes must also be adaptable and have the necessary physical strength and ductility in the dry and wet states to survive the stress of electrode attachment. Ion conducting copolymers that are compatible for use in the catalyst layer, in concert with novel polymer membranes, are also an emerging area of research.

Advances in fuel cell technology over the last four decades have come primarily from improved electrocatalysts, membrane electrode assembly fabrication strategies, and cell/stack/system engineering. Apart from Nafion, new ion conducting polymeric materials have played only a minor role in significantly increasing cell performance. However, new materials

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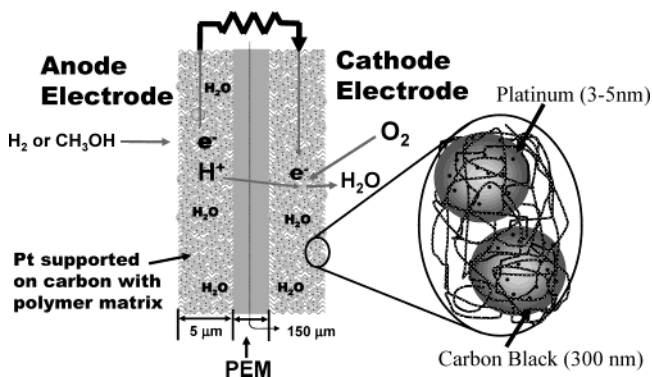

Figure 1. Basic membrane electrode assembly.

are now required to afford successful technology commercialization.

This review will outline the materials requirements for advanced alternative proton exchange membranes for fuel cells, assess recent progress in this area, and provide directions for the development of next-generation materials. The focus will be on the synthesis of polymeric materials that have attached ion conducting groups. State-of-the-art Nafion and its commercially available perfluorosulfonic acid relatives will initially be discussed. Other chain-growth co-

polymers based on styrenic, vinylic, or acrylic monomers will then be reviewed. Next, the large body of recent literature centered on polymeric materials based on step or condensation polymers (poly(ether ether ketone)s, poly(sulfone)s, poly(imide)s, and others) and various strategies for incorporating ionic groups into these materials will be evaluated. Finally, polymeric materials with other acid groups aside from sulfonic acid as the ion conducting moiety will be reviewed and various methodologies for advanced membranes will be presented. This review will highlight the synthetic aspects of ion conducting polymers and the polymer chemical structure considerations for producing useful PEMs. Extensive reviews of polymer-based proton conductors have recently been published.[2,3,4] Only a brief review of important organic−inorganic composite membranes will be included,[3b] even though it is predicted that this strategy will be central to future higher temperature systems.

Most of the synthetic methods currently utilized to form ion containing materials result in random or statistical placement of sulfonic acid units along the backbone copolymer chain. It is postulated that the distribution of sulfonic acid groups along the chain, as well as the acid strength and the connecting moiety to the polymer backbone, will have a considerable effect on the resulting morphology and membrane properties. Some block or segmented copolymer systems have been synthesized, but the subtle differences between random and block systems and the advantages/disadvantages of each are not yet well established in the literature for PEMs. This review will also highlight novel strategies for the controlled placement of ionic groups on a polymer or statistical copolymer backbone.

Some definitions are needed to establish a common framework for comparing different polymeric systems. The foremost of these is protonic conductivity. Scientists at Los Alamos National Laboratory (LANL) have devised a facile method for determining the conductivity of proton exchange membranes using electrochemical impedance spectroscopy and a simple cell that allows equilibration in a variety of environments.[5] This method measures protonic conductivity *in the plane* of the membrane as opposed to *through the plane* (as in a fuel cell), and thus it works well as an initial screening test. Through-plane conductivity measurements[6] are often more difficult experimentally than in-plane measurements because the measured membrane resistances are small in this geometry and interfacial resistances may play a more significant role.

Water uptake is also important in determining the ultimate performance of proton exchange membrane materials. In essentially all current polymeric materials, water is needed as the mobile phase to facilitate proton conductivity. However, absorbed water also affects the mechanical properties of the membrane by acting as a plasticizer, lowering the T_g and modulus of the membrane. Careful control of water uptake is critical for reducing adverse effects of swelling and degradation of the mechanical properties of the membrane in humid environments, as well as inducing stresses between the membrane and

the electrodes. Water uptake is usually reported as a mass fraction, mass percent, or λ value, where λ equals the number of water molecules absorbed per acid site.

Both conductivity and water uptake rely heavily on the concentration of ion conducting units (most commonly sulfonic acid) in the polymer membrane. The ion content is characterized by the molar equivalents of ion conductor per mass of dry membrane and is expressed as equivalent weight (EW) with units of grams of polymer per equivalent or ion exchange capacity (IEC) with units of milliequivalents per gram (mequiv/g or mmol/g) of polymer (EW = 1000/ IEC). Varying the ion content of the membrane can control both its water uptake and conductivity. While it is desirable to maximize the conductivity of the membrane by increasing its ion content (decreasing equivalent weight), other physical properties must be considered. Too many ionic groups will cause the membrane to swell excessively with water, which compromises mechanical integrity and durability.

Meaningful standardized methods for characterizing proton exchange membranes for fuel cells are becoming more established within the fuel cell community and are helping to enhance the identification of promising candidate materials. At the most basic level, the ion exchange capacity, water uptake, and protonic conductivity of the membrane under specific environmental conditions should be measured in comparison to the standard Nafion materials and other systems. Standard important polymer science and engineering parameters such as molecular weight, detailed chemical compositions, morphology, topology, and mechanical behavior are no doubt critical but have only rarely been addressed.

2. Nafion and Other Poly(perfluorosulfonic acid) Membranes

The current state-of-the-art proton exchange membrane is Nafion, a DuPont product that was developed in the late 1960s primarily as a permselective separator in chlor-alkali electrolyzers.[7,8] Nafion's poly(perfluorosulfonic acid) structure imparts exceptional oxidative and chemical stability, which is also important in fuel cell applications.

Nearly all of the commercially available membranes are based on Nafion. Nafion also has the largest body of literature devoted to its study because of its demonstrated industrial importance and availability. Nafion composite systems also have already become significant in both industrial and academic research. In composite structures, Nafion can be impregnated into an inert Teflon-like matrix (i.e. W. L. Gore membranes[9]), or inorganic additives can be added to a supporting Nafion matrix for improved physical or electrochemical properties (i.e. Ionomem[10]). Some critical aspects of Nafion's molecular structure and physical properties will be briefly highlighted to provide a baseline for comparison with the other alternative materials discussed in this review.

Nafion is a free radical initiated copolymer of a crystallizable hydrophobic tetrafluoroethylene (TFE) backbone sequence (~87 mol % at 1100 equivalent
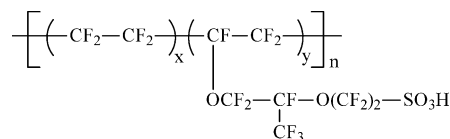

Figure 2. Chemical structure of Nafion. *x* and *y* represent molar compositions and do not imply a sequence length.

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 2.

In theory, ion content can be varied by changing the ratio of the two components (*x* and *y* in Figure 2). Nafion has been commercially available in 900, 1100, 1200, and other equivalent weights. However, Nafion 1100 EW in thicknesses of 2, 5, 7, and 10 mil (1 mil equals 25.4 μm) (Nafion 112, 115, 117, and 1110) seems to be the only grades of Nafion that are currently widely available. This equivalent weight provides high protonic conductivity and moderate swelling in water, which seems to suit most current applications and research efforts. Modest retention of a semicrystalline morphology at this composition is no doubt important for mechanical strength. The thinner membranes are generally applied to hydrogen/ air applications to minimize Ohmic losses, while thicker membranes are employed for direct methanol fuel cells (DMFCs) to reduce methanol crossover.

Unsaturated perfluoroalkyl sulfonyl fluoride and their derivatives are believed to be the starting comonomers for preparing perfluorosulfonic membranes. Nafion is prepared via the copolymerization of variable amounts of the unsaturated perfluoroalkyl sulfonyl fluoride with tetrafluoroethylene.[11,12] Unfortunately, there have been no detailed literature reports of Nafion's synthesis and processing, but it is generally thought that the copolymer is then extruded in the melt processable sulfonyl fluoride precursor to form a membrane, which is later converted from the sulfonyl fluoride form by base hydrolysis to the salt or sulfonic acid functionality. It seems unlikely that the sulfonyl fluoride containing precursor unit in the copolymer would self-propagate under free radical conditions. Thus, the length of the comonomer sequence (*y*) is likely only one unit. Total molecular weight, though obviously important, has not been reported.

Like many other fluoropolymers, Nafion is quite resistant to chemical attack, but the presence of its strong perfluorosulfonic acid groups imparts many of its desirable properties as a proton exchange membrane. Fine dispersions (sometimes incorrectly called solutions) can be generated with alcohol/water treatments.[13] Such dispersions are often critical for the generation of the catalyst electrode structure and the MEAs. Films prepared by simply drying these dispersions are often called "recast" Nafion, and it is often not realized that its morphology and physical behavior are much different from those of the extruded, more crystalline form.

Other perfluorosulfonate cation exchange membranes with similar structures have also been devel-

oped by the Asahi Chemical Company (Aciplex) and the Asahi Glass Company (Flemion).[14] The Dow Chemical Company also developed a material with a shorter side chain than those of Nafion and the other perfluorosulfonates, which is no longer available.[15] The length of the perfluorosulfonic acid side chain and the values for the equivalent weight may be varied to some extent.

All of these polyperfluorosulfonic acid membranes are expensive and suffer from the same shortcomings as Nafion, namely low conductivity at low water contents, relatively low mechanical strength at higher temperature, and moderate glass transition temperatures.

3. PEMs Containing Styrene and Its Derivatives

As discussed above, the most commonly known and studied PEMs are based on nonaromatic perfluorinated hydrocarbons such as Nafion, Aciplex, Flemion, and what are termed the Dow membranes. However, their chemical synthesis is challenging due to the safety concerns of tetrafluoroethylene and the cost/availability of the perfluoroether comonomers. These issues have relegated detailed synthetic research on polyperfluorosulfonic acid materials to the industrial sector or to a few specialized academic labs.

One alternative to the tetrafluoroethylene-based backbones of the previously discussed materials is the use of styrene and particularly its fluorinated derivatives to form PEMs. As extensively reported in the literature, styrenic monomers are widely available and easy to modify, and their polymers are easily synthesized via conventional free radical and other polymerization techniques.

Presently, two commercial (or semicommercial) PEMs are based on styrene or styrene-like monomers: BAM from Ballard, and Dais Analytic's sulfonated styrene−ethylene−butylene−styrene (SEBS) membrane. Ballard Advanced Materials Corporation introduced a styrenic membrane based on a novel family of sulfonated copolymers incorporating α,β,β-trifluorostyrene and substituted α,β,β-trifluorostyrene comonomers. These are registered as BAM membranes, and their general formula is given in Figure 3.
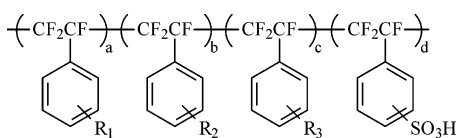
R₁, R₂, R₃ = alkyls, halogens, OR, CF=CF₂, CN, NO₂, OH

Figure 3. Chemical structure of BAM PEMs.[16]

The unsulfonated random copolymers are reportedly synthesized at 50 °C over a period of 48 h using emulsion polymerization with dodecylamine hydrochloride surfactant in water as the reaction system and potassium persulfate as the initiator.[16] The copolymer is then dissolved in an appropriate solvent such as dichloroethane or chloroform and sulfonated using reagents such as chlorosulfonic acid or a sulfur trioxide complex. It has been reported that this generation of BAM membranes exhibited some su-
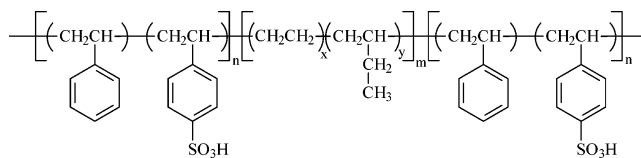
Figure 4. Chemical structure of sulfonated SEBS block copolymer.[21]

perior performance to perfluorinated membranes, such as Nafion 117, at current densities greater than 0.6 A cm⁻².[17] The backbone fluorination was no doubt intended to mitigate hydroperoxide formation, which causes short lifetimes for nonfluorinated partially aliphatic analogues.

There have been few synthetic reports employing these monomers beyond the Ballard work, most likely as a result of presumed high cost and monomer availability. However, the performance and stability demonstrated by these materials in fuel cells may spur further developments in this area. The above-reported copolymers are believed to be random systems both in the chemical composition of the copolymer backbone and with regard to sulfonic acid attachment. Novel methods have been developed for the controlled polymerization of styrene-based monomers to form block copolymers. If one could create block systems with trifluorostyrene monomers, new morphologies and PEM properties with adequate stability in fuel cell systems might be possible, but the mechanical behavior would need to be demonstrated.

Dais Analytic's PEMs (and related materials) are based on well-known commercial block copolymers of the styrene−ethylene/butylene−styrene family, Kraton G1650 being one such system. In one method of forming sulfonated PEMs, the unsulfonated polymer is dissolved in a dichloroethane/cyclohexane solvent mixture. The sulfur trioxide/triethyl phosphate sulfonating complex in solution is then added and allowed to react at temperatures between −5 and 0 °C.[18] The result is a PEM that may be solvent cast (from lower alcohols such as *n*-propanol) to afford an elastomeric hydrogel with conductivities of 0.07−0.1 S/cm when fully hydrated.[19,20,21] The chemical structure of this type of copolymer is shown in Figure 4. The sulfonated styrene moieties are isolated in blocks, as directed by the anionic polymerization and hydrogenated starting material, but there is not much information on the extent of sulfonation of the styrenic moieties in the blocks. For the process described above, the unsulfonated block copolymer could have a number average molecular weight of about 50 000 g/mol with a styrene content of 20−35 wt % of the triblock copolymer. TEM suggests that the cast films possess cylindrical sulfonated polystyrene domains. The films swell in water, with the extent of swelling being dependent on the sulfonation level.[22]

Dais membranes are reported to be much less expensive to produce than Nafion; they are also reported to exhibit a rich array of microphase-separated morphologies because of the ability to tailor the block length and composition of the unsulfonated starting polymer.[23] The main drawback of employing hydrocarbon-based materials is their much
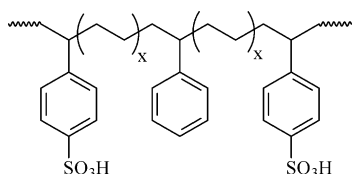
Figure 5. Chemical structure of partially sulfonated styrene−ethylene interpolymer.[21]

poorer oxidative stability compared to perfluorinated or partially perfluorinated membranes due to their partially aliphatic character.[24] For this reason, Dais membranes are aimed at portable fuel cell power sources of 1 kW or less, for which operating temperatures are less than 60 °C.

As an extension of the previous work, copolymers based on partially sulfonated ethylene−styrene pseudorandom "interpolymers" have also been employed instead of the block copolymers (Figure 5).[21,25] Due to the unique nature of the polymerization catalyst, styrene residues are separated by at least one ethylene residue and the acid groups are distributed randomly along the chain. This material provides an economical and unique counterpoint to the sulfonated SEBS PEMs, where the sulfonic acid groups are bunched together in the styrene blocks. Controlling the styrene content in each material provides a route to control the level of sulfonation and resultant ion exchange capacity of the PEM.

Synthetic methods have been developed to incorporate styrene as a graft on to a polymer backbone. Graft polymers, in which ion containing polymer grafts are attached to a hydrophobic backbone, could be suitable structures for studying structure−property relationships in ion conducting membranes, if the length of the graft and the number density of graft chains can be controlled. In principle, the length of the graft would determine the size of ionic domains, whereas the number density of graft chains would determine the number of ionic domains per unit volume. Collectively, the size and number density of ionic aggregates/clusters are expected to control the degree of connectivity between ionic domains.

Recently, several researchers have shown that it is possible to synthesize graft copolymers possessing ionic grafts bound to hydrophobic backbones using macromonomers formed by stable free radical polymerization (SFRP) techniques.[26] The detailed synthesis and characterization of this class of copolymer that comprises a styrenic main chain and sodium styrenesulfonate graft chains (PS-*g-mac*PSSNa) was reported by Holdcroft et al.[27] PS-*g-mac*PSSNa was prepared by (1) pseudoliving, tempo-mediated free radical polymerization of sodium styrenesulfonate (SSNa) and (2) termination with divinylbenzene (DVB). The macromonomer, *mac*PSSNa, serves as both the comonomer and emulsifier in the emulsion copolymerization with styrene. During polymerization, the DVB terminus is located in the core of micellar particles and is incorporated into growing polystyrene (PS) as graft chains. The synthetic scheme is shown in Figure 6. By adjusting the *mac*PSSNa/styrene feed ratio, a series of polymers (PS-*g-mac*PSSNa) with uniform graft chain length
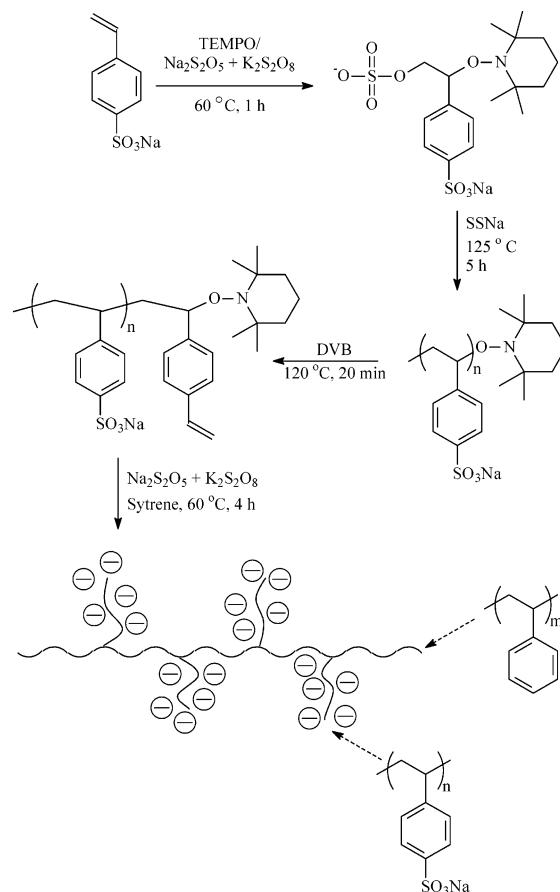

Figure 6. Synthetic scheme of polystyrene-*graft*-polystyrenesulfonic acid copolymers.[26,27]

and variable ion content were obtained. For comparison, random copolymers of SSNa and styrene (PS-*r*-SSNa) were prepared by conventional emulsion copolymerization. The two classes of polymer, graft and random, exhibit very different properties of mechanical strength, water uptake, proton conductivity, and thermal behavior as a result of their inherently different morphologies.

Using the same methodology as described above, Holdcroft et al. have also incorporated sodium styrenesulfonate macromonomers as grafts to poly(acrylonitrile) backbone chains.[28] The poly(acrylonitrile) backbone is more hydrophilic than the poly(styrene) backbone of the previous study. This allowed the authors to examine the effect that the backbone had on ionic domain morphology, water uptake, conductivity, and oxygen permeability and solubility. Holdcroft's synthetic methodology for elucidating important PEM properties is excellent, and therefore, this group was able to draw rational conclusions when developing structure−property relationships of ion conducting polymers. These particular materials are probably not suitable PEMs themselves due to the well-known susceptibility of the poly(styrene) backbone or poly(styrene sulfonate) grafts to oxidative degradation in a fuel cell environment.

Poly(styrene sulfonic acid) grafts have also been attached to poly(ethylene-*co*-tetrafluoroethylene) (ETFE)[28,29] and poly(vinylidene fluoride) (PVDF)[30] as shown in Figure 7. These materials were synthesized
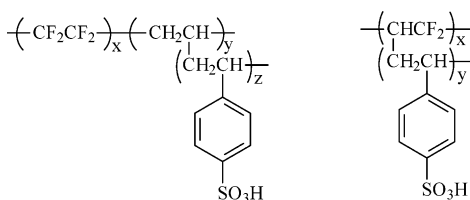
Figure 7. ETFE-*g*-PSSA and PVDF-*g*-PSSA.[28]

Figure 8. Several possible poly(arylene ether) chemical structures.

by irradiating ETFE or PVDF preformed membranes with γ radiation and then immersing the irradiated membranes in styrene (usually diluted with toluene) to affect polymerization of poly(styrene) grafts from the backbone. The extent of grafting was reported to be controlled by styrene concentration, choice of diluent, grafting temperature, and grafting time. Once the extent of grafting was characterized by gravimetric means, the membranes were then sulfonated using chlorosulfonic acid.

Gupta et al.[31,32] and Buchi et al.[33] have investigated the radiation grafting (using a γ radiation source) of tetrafluoroethylene-*co*-hexafluoropropylene (FEP) using styrene and divinylbenzene as monomers in the formation of grafts which are then sulfonated with chlorosulfonic acid. Divinylbenzene was used to create cross-links between grafts and possibly control water swelling of the membranes. Buchi et al. reported that FEP-grafted polystyrene sulfonic acid (FEP-*g*-SSA) systems have physical and electrochemical properties superior to those of Nafion 117 but an inferior fuel cell performance attributed to the gas permeability of the membrane. The excessive gas permeability was proposed to more readily allow HO• attack on the polystyrene grafts and lead to a loss of ion exchange capacity after operating in a fuel cell environment, but no proof was offered. In a study using similar styrene grafted membranes, nearly 10 wt % of the grafts were lost after 100 h of fuel cell operation.[34] PEMs may tolerate some degree of backbone degradation during long-term fuel cell operation, but degradation involving a loss of ion exchange capacity (and thus a loss in conductivity) would be obviously undesirable in all situations.

4. Poly(arylene ether)s

Wholly aromatic polymers are thought to be one of the more promising routes to high performance PEMs because of their availability, processability, wide variety of chemical compositions, and anticipated stability in the fuel cell environment. Specifically, poly(arylene ether) materials such as poly(arylene ether ether ketone) (PEEK), poly(arylene ether sulfone), and their derivatives are the focus of many investigations, and the synthesis of these materials has been widely reported.[35] This family of copolymers is attractive for use in PEMs because of their well-known oxidative and hydrolytic stability under harsh conditions and because many different chemical structures, including partially fluorinated materials, are possible, as shown in Figure 8. Introduction of active proton exchange sites to poly(arylene ether)s has been accomplished by both a polymer postmodification approach and direct co-
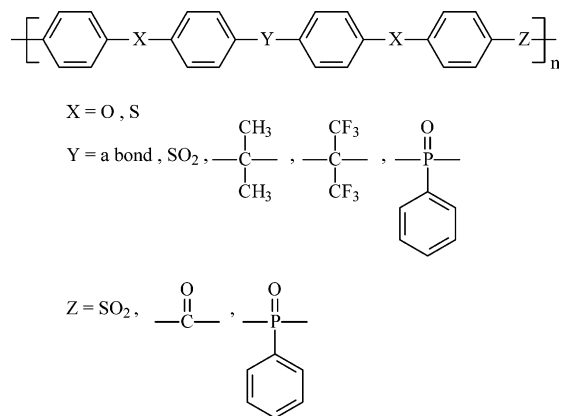
polymerization of sulfonated monomers. Both schemes are discussed below.

4.1. Postsulfonation of Existing Polymers

The most common way to modify aromatic polymers for application as a PEM is to employ electrophilic aromatic sulfonation. Aromatic polymers are easily sulfonated using concentrated sulfuric acid, fuming sulfuric acid, chlorosulfonic acid, or sulfur trioxide (or complexes thereof). Postmodification reactions are usually restricted due to their lack of precise control over the degree and location of functionalization, the possibility of side reactions, or degradation of the polymer backbone. Regardless, this area of PEM synthesis has received much attention and may be the source of emerging products such as sulfonated Victrex poly(ether ether ketone).[3a,36]

Sulfonated poly(arylene ether sulfone)s synthesized by attaching sulfonic acid groups in polymer modification reactions have been investigated intensively since the pioneering work of Noshay and Robeson, who developed a mild sulfonation procedure for the commercially available bisphenol A-based poly(ether sulfone).[37] Different sulfonating agents have been employed for this polymer modification, such as chlorosulfonic acid[3a,4] and a sulfur trioxide–triethyl phosphate complex. Sulfonation is an electrophilic substitution reaction; therefore, its application depends on the substituents present on the aromatic ring. Electron-donating substituents will favor reaction, whereas electron-withdrawing substituents will not. Additionally, the sulfonic acid group is usually restricted to the activated position on the aromatic ring. For the case of the bisphenol A-based systems, no more than one sulfonic acid group per repeat unit could be achieved.[38]

A comparative study of sulfonating agents was undertaken by Genova-Dimitrova et al.[39] Their aim was to investigate the characteristics of chlorosulfonic acid ($ClSO_3H$) and derived trimethylsilylchlorosulfonate ((CH_3)$_3SiSO_3Cl$) on the sulfonation of bisphenol A-based poly(sulfone). The authors indicated that the strong sulfonating agent, chlorosulfonic acid, yielded an inhomogeneous reaction that could be solubilized with a small amount of dimethylformamide as a cosolvent. Reactions with the mild trimethylsilylchlorosulfonate sulfonating agent were
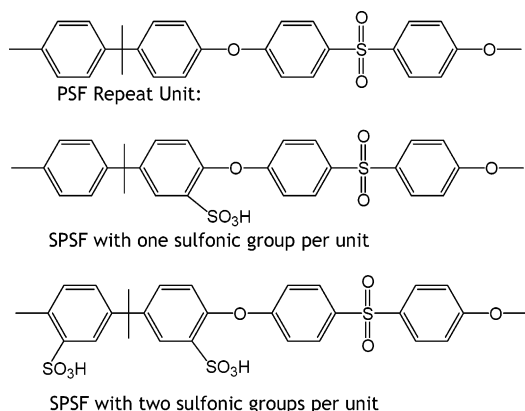
Figure 9. Most likely locations of sulfonic acid attachment in postsulfonated poly(arylene ether sulfone).[39]

homogeneous reactions. Chlorosulfonic acid also induced chain cleavages during some sulfonations, as indicated by viscometric measurements, whereas no polymer degradation or cross-linking was observed with the milder trimethylsilylchlorosulfonate. Proton nuclear magnetic resonance (^{1}H NMR) was used to assemble a detailed picture of the kinetics of the sulfonation reaction with trimethylsilylchlorosulfonate. A marked decrease in reaction rate was observed after a degree of sulfonation of 0.74 (74% of the monomer units sulfonated) and 1.35 (68% of the theoretical yield of a degree of sulfonation of 2), as shown in Figure 9. The authors were not able to present a sound explanation for the rate decrease at these two levels of conversion.

Another drawback of the mild sulfonating reagent is that its sulfonation efficiency was low and during short reaction times (4 h) was limited to a degree of sulfonation of 0.85 even when a 3-fold excess of sulfonating agent was employed. Clearly, tradeoffs exist between strong and mild sulfonating agents, but avoiding polymer degradation and side reactions probably outweighs longer reaction times and somewhat lower sulfonation efficiency. The hydrolytic stability of the isopropylidene unit under fuel cell conditions has not been reported.

Poly(ether ether ketone) (PEEK) is an aromatic, high performance, semicrystalline polymer with extremely good thermal stability, chemical resistance, and electrical and mechanical properties. This polymer shows little solubility in organic solvents due to the crystallinity. One of the first ways to characterize PEEK was by sulfonating the polymer. By adding sulfonic acid groups to the backbone, the crystallinity decreased and solubility increased.[40,41] Commercially available Victrex appears to be one of the more interesting poly(arylene ether)s used for postmodification.

There have been many procedures reported for sulfonating PEEK.[3a,42,43] General chemical structures for the unsulfonated and sulfonated analogues are given in Figure 10. 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.[44] Since the electron density of the other two aromatic rings in the repeat unit is relatively low due to the electron-attracting nature of the neighboring carbonyl group,
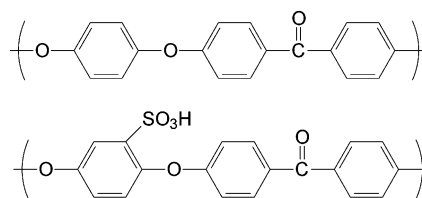

Figure 10. Chemical structures of unsulfonated and sulfonated PEEK.

one sulfonic acid group adds per repeat unit. It has been reported that sulfonation of PEEK with chlorosulfonic acid or fuming sulfuric acid causes a mostly unexplored degradation of the polymer; therefore, concentrated sulfuric acid is typically used.[45] The sulfonation rate of PEEK in sulfuric acid can be controlled by changing the reaction time, temperature, and acid concentration to provide polymers with a sulfonation range of 30−100% without degradation and cross-linking reactions.[46] However, it has been shown that the sulfonation of PEEK in sulfuric acid cannot be used to produce truly random copolymers at sulfonation levels less than 30% because dissolution and sulfonation occur in a heterogeneous environment.[47]

Al-Omran and Rose[48] controlled the location and extent of sulfonation on poly(arylene ether) backbones by copolymerizing 4,4′-dichlorodiphenyl sulfone, durohydroquinone, and hydroquinone to form random copolymers, where only the hydroquinone residue would be expected to be susceptible to sulfonation by sulfuric acid. Although these authors observed sulfonation at positions other than at the desired hydroquinone locations, designing sulfonation sites into a polymer backbone remains an attractive strategy for producing copolymers with known structures. This allows the chemical structure and composition of the material to dictate the extent of sulfonation rather than trying to externally control sensitive and sometimes unpredictable macromolecular sulfonation reactions.

An alternative, but likely expensive, route for derivatizing a commercial polysulfone (Udel) by Kerres et al. was based on a series of steps including metalation, sulfination by SO_2 gas, and oxidation as shown in Figure 11.[49] One of the key steps in this synthesis is the choice of oxidant to convert the lithium sulfinate to sulfonic acid. Cross-linking reactions during oxidation may reduce the ion exchange capacity of the materials, while polymer chain degradation will result in membranes with quite poor mechanical properties. It was determined that hydrogen peroxide was the best oxidant for low IEC materials because of its ability to access all the ionic groups of the polymer in solution. Higher IEC materials were amenable to oxidation by $KMnO_4$ without adverse cross-linking or polymer degradation. This synthetic scheme also allows controlled cross-linking of the materials to manipulate swelling and gas permeability.[50,51] The authors of this study assert the validity of this method for any polymeric species that can be lithiated, and it would be an attractive method for controlled sulfonation if polymer backbone degradation can be avoided.
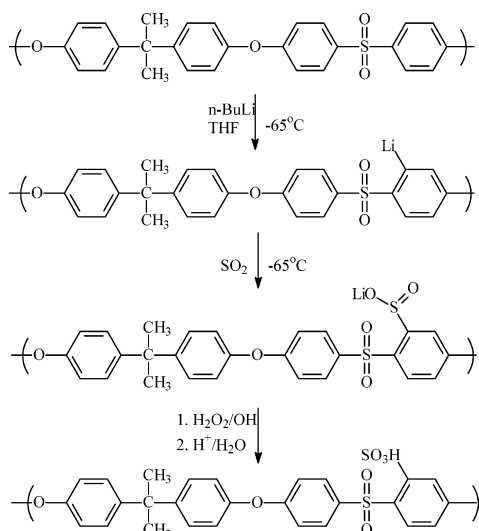
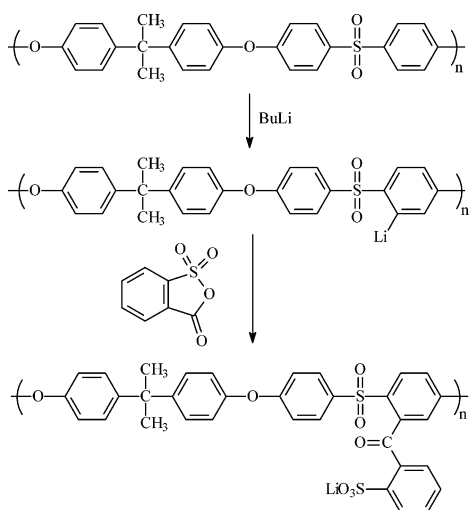**Figure 11.** Metalation route to sulfonated polysulfone.[49]

Figure 12. Chemical structure of sulfophenylated polysulfone.[52]

Similarly, polysulfone has been sulfophenylated by lithiation and anionic reaction with 2-sulfobenzoic acid cyclic anhydride (Figure 12).[52] This provides another method to modify polysulfones by attaching pendant sulfonated phenyl groups via ketone links. It would be interesting to see if the phase separation in these materials was affected by the additional functionality of the ketone or the pendant attachment of the sulfonic acid, as opposed to direct attachment of ionic groups to the aromatic polymer backbone.

4.2. Direct Copolymerization of Sulfonated Monomers To Afford Random (Statistical) Copolymers

There are several major drawbacks of postmodification methods including the lack of control over the degree and location of functionalization, which is usually a problem when dealing with macromolecules. It has been of interest to investigate the effect of sulfonation, for example, on the deactivated sites of the repeat units, since one might expect enhanced stability and higher acidity from two sulfonic acid groups which are attached to an electron-deficient aromatic ring than from one sulfonic acid group
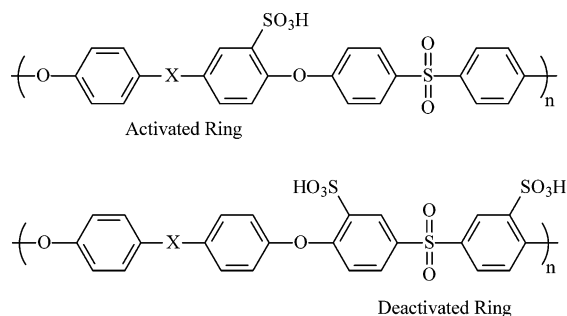

Figure 13. Placement of the sulfonic acid group in postsulfonation (activated ring) versus direct copolymerization (deactivated ring).
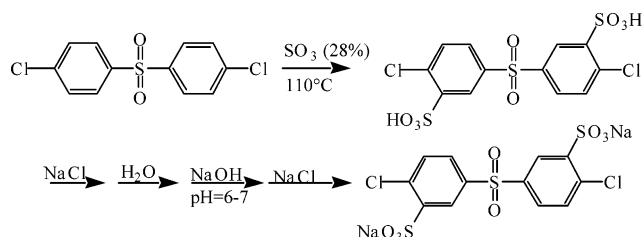

Figure 14. Synthesis of 3,3′-disulfonated 4,4′-dichlorodiphenyl sulfone and its sodium salt.

bonded to an electron-rich aromatic ring.[53] Moreover, the opportunity to control and/or increase molecular weight to enhance durability is not feasible if one chooses to conduct a postreaction on an existing commercial product. The difference between sulfonic acid placement in typical examples of postsulfonation and direct copolymerization is shown in Figure 13.

The first report of the required sulfonated monomer was from Robeson and Matzner,[54] who obtained a composition of matter patent, which primarily was of interest for its flame retarding properties. More recently, Ueda et al.[55] reported the sulfonation of 4,4′-dichlorodiphenyl sulfone and provided general procedures for its purification and characterization. McGrath's group modified the procedure for disulfonation of the monomer, shown in Figure 14. Sulfonated poly(arylene ether sulfone) copolymers were then synthesized via direct copolymerization in any composition desired as shown in Figure 15.[56] The directly copolymerized sulfonated materials were produced under very similar reaction conditions employed for many years for the synthesis of unsulfonated poly(arylene ether)s using the weak base route. Only moderately higher reaction temperatures and longer times were needed to obtain high molecular weight copolymers due to the sterically decreased activity of the sulfonated dihalide monomer. Alternatively, increased reactivity can be realized by employing the more expensive disulfonated difluoro dihalide. The copolymerizations were conducted to afford the potassium salt form of the 3,3′-disulfonated 4,4′-dichlorodiphenyl sulfone to take advantage of the enhanced stability of the sulfonic acid salt. These random copolymers displayed a hydrophilic/hydrophobic phase separated morphology that varied depending on the degree of disulfonation (Figure 15). A tapping mode atomic force microscopy (AFM) phase image comparison of the 40% copolymer with Nafion is shown in Figure 16.
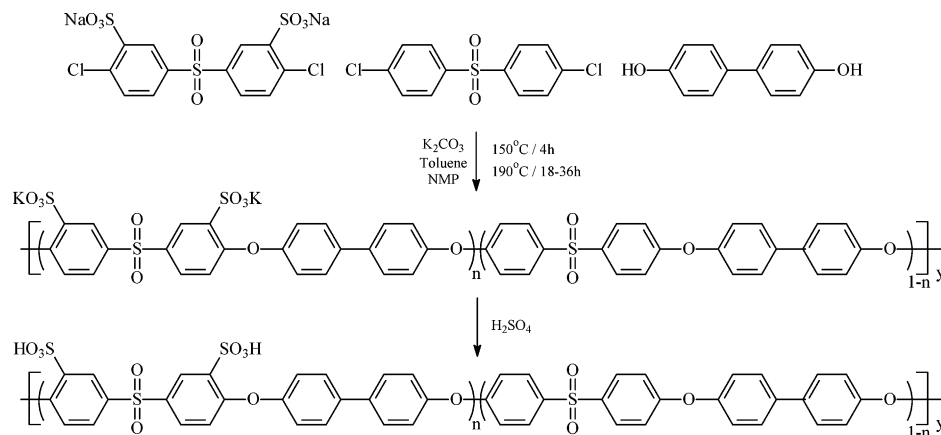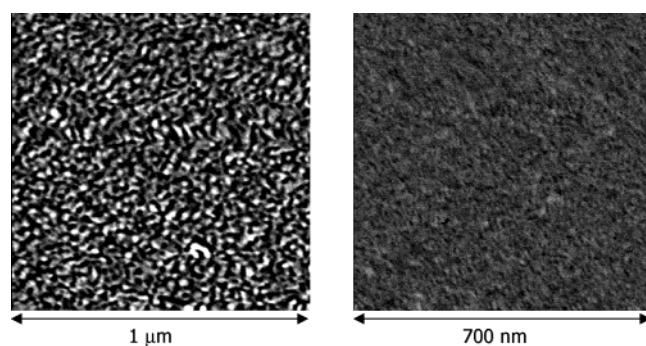
Figure 15. Synthesis of directly copolymerized wholly aromatic sulfonated poly(arylene ether sulfone),[56] BPSH-*xx*, where *xx* is the ratio of sulfonated/unsulfonated activated halide.

Phase Image of BPSH-40 dark regions are sulfonic acid + water(softer portion)

Phase Image of Nafion 117

Figure 16. Atomic force micrographs of BPSH-40 and Nafion 117.

Would like to make membranes **with** as many sulfonic acid groups as possible

Connectivity of hydrophilic phase at high sulfonic acid content yields membranes with very high water swelling and thus low mechanical properties

Must balance ionic conductivity with other physical properties
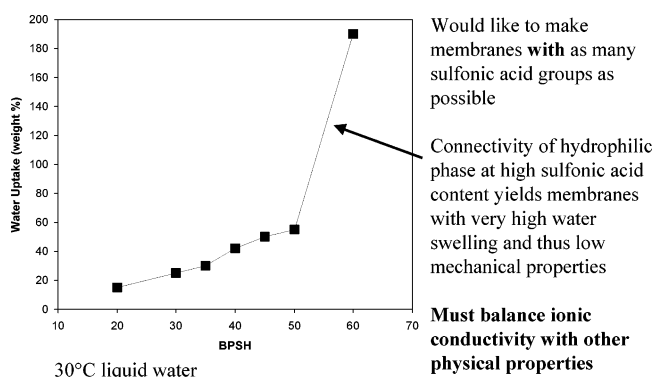
30°C liquid water

Figure 17. Swelling in 30 °C liquid water for the BPSH series of copolymers.

The conductivity and water uptake of this series of copolymers also increased with disulfonation. However, once the degree of disulfonation reached 60 mol %, a semicontinuous hydrophilic phase was observed and the membranes swelled dramatically, forming a hydrogel that would not be useful as a proton exchange membrane, as illustrated in Figure 17. These results indicate that the protonic conductivity must be balanced with the water swelling and mechanical properties of the membrane in these random copolymers. As with the unsulfonated polymers, many variations are possible in the direct synthesis of sulfonated poly(arylene ether sulfone)s

due to the variety of monomers available, as depicted in Figure 18.

The influence of the bisphenol structure on the direct synthesis of sulfonated poly(arylene ether)s has been studied.[57] Four bisphenols including bisphenol A, hexafluoroisopropylidene bisphenol (6F), 4,4′-biphenol, and hydroquinone were used for the synthesis of poly(arylene ether)s containing ion conducting units. Generally, the thin film properties of these copolymers scaled with ion exchange capacity. Sulfonated poly(arylene thioether sulfone) copolymers were prepared by direct copolymerization of sulfonated 4,4-difluorodiphenyl sulfone, unsulfonated 4,4-difluorodiphenyl sulfone, and 4,4-thiobisbenzenethiol.[58] The properties of these copolymers were comparable with those of their poly(ether sulfone) analogue. Copolymers based on hexafluoroisopropylidene bisphenol (6F) have been particularly interesting in initial fuel cell tests.[59] It is thought that their fluorine content promotes adhesion and electrochemical compatibility with Nafion-based electrodes and reduces swelling. Surface fluorine enrichment of the 6F containing materials may also provide enhanced membrane stability. The degree of sulfonation and method of acidification also influenced the dry dynamic mechanical behavior and T_g values, as presented in Figure 19. The modulus-temperature plot provides further evidence of the short-term thermal stability of the acid form membrane. One also notes broadening of the damping peaks, which may reflect different degrees of association or other phenomena.

Directly copolymerized sulfonated poly(arylene ether ketone) PEMs are also possible by employing a sulfonated dihalide ketone monomer (sodium 5,5′-carbonylbis(2-fluorobenzenesulfonate)), as first reported by Wang.[60,61] The sulfonated monomer chemical structure is shown in Figure 20.

As described earlier, the choice of bisphenols for the polymerization of poly(arylene ether ketone)s is large.[62] In particular, the electrochemical properties of the above monomer copolymerized with bisphenol AF were studied. The fundamental PEM characteristics (water uptake and conductivity) were analogous to those of the "BPSH" systems for a given IEC.

Due to the flexibility of incorporating various chemical moieties, sulfonated poly(arylene ether)
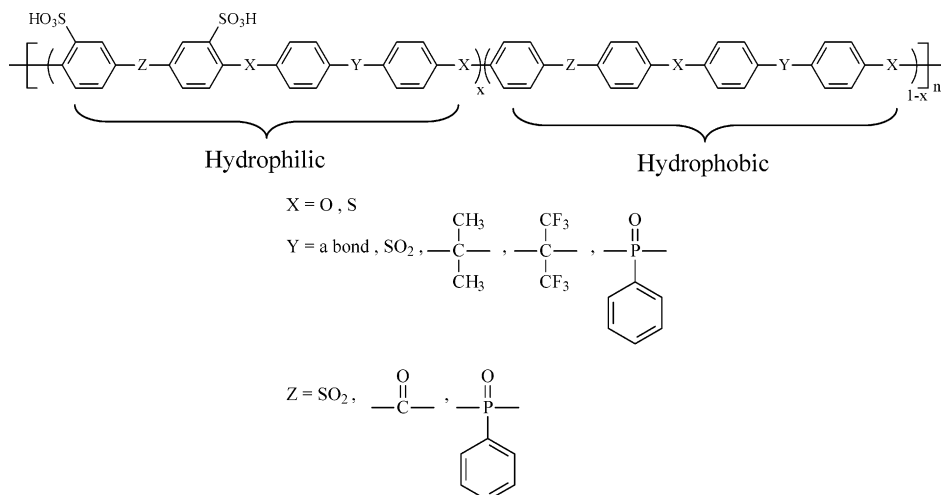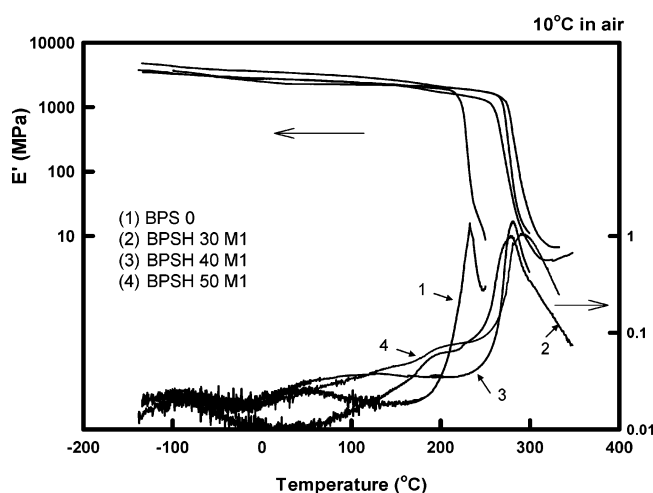
Figure 18. Some possible chemical structures for sulfonated PEMs from poly(arylene ether)s.

Figure 19. Effect of degree of disulfonation and method of acidification on the dynamic mechanical properties of BPSH films.[53] M1 and M2 refer to whether acidification was done at 30 or 100 °C, respectively.

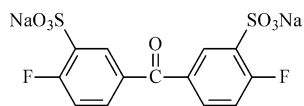| Copolymer	T_g	
	M1	**M2**
BPS-0	223	
BPSH-30	259	270
BPSH-40	268	272
BPSH-50	272	283

Figure 20. Chemical structure of sodium 5,5′-carbonylbis-(2-fluorobenzenesulfonate).

copolymers may serve as ideal hosts for inorganic compounds to form nanocomposite proton exchange membranes.[3b,63] Additional functionality to increase the compatibilization between the organic and inorganic phases can be imparted to the poly(arylene ether) by the copolymerization of 2,6-dichloroben-zonitrile, hexafluoroisopropylidene bisphenol (6F), and 3,3′-disulfonate-4,4′−dichlorodiphenyl sulfone.[64]

These polymers show lower water uptake than the analogous sulfonated poly(arylene ether sulfone) materials, possibly suggesting some interaction between the aromatic nitrile and sulfonic acid. The phosphine oxide functional moiety could also be used as a compatibilizer with other materials. Sulfonated poly(arylene ether phosphine oxide sulfone) terpolymers have been prepared both with sulfonated triphenyl phosphine oxide[65] and with triphenyl phosphine oxide with 3,3′-disulfonate-4,4′−dichlorodiphenyl sulfone[66] as the sulfonic acid bearing monomer. Block copolymers containing phosphine oxide appear to avoid the ether−ether interchange that results when non−phosphine oxide blocks are utilized, and this is being further pursued.[67]

5. PEMs Based on Poly(imide)s

Five-membered ring polyimides are high performance materials and have been investigated for many years. However, when sulfonated phthalic polyimides are used for proton exchange membranes in fuel cells, they quickly degrade, whereas it has been recognized that naphthalenic polyimides are much more stable in fuel cell environments.[2] It is likely that hydrolysis of the phthalic imide structure leads to chain scission (decrease in molecular weight) and causes the membrane to become brittle. Since the six-membered ring of the naphthalenic polyimide is much more stable to hydrolysis, this chemical structure is somewhat better suited for PEM fuel cell applications but its stability is still questionable.

Genies et al.[68] used model compounds along with IR and NMR to examine the nature of hydrolysis associated with the sulfonic acid group (needed for proton conduction) in phthalic and naphthalenic polyimides. Model compounds of the sulfonic acid containing phthalic imide (model A) and the sulfonic acid containing naphthalenic imide (model B) were prepared by a one-step high temperature condensation in *m*-cresol. NMR spectroscopy showed that after aging model A in distilled water at 80 °C for 1 h the structure is modified. After aging for 10 h, ^{13}C NMR shows that the carbon peaks associated with the starting compound disappear. In addition, ^{13}C NMR was used to quantitatively determine the amount of
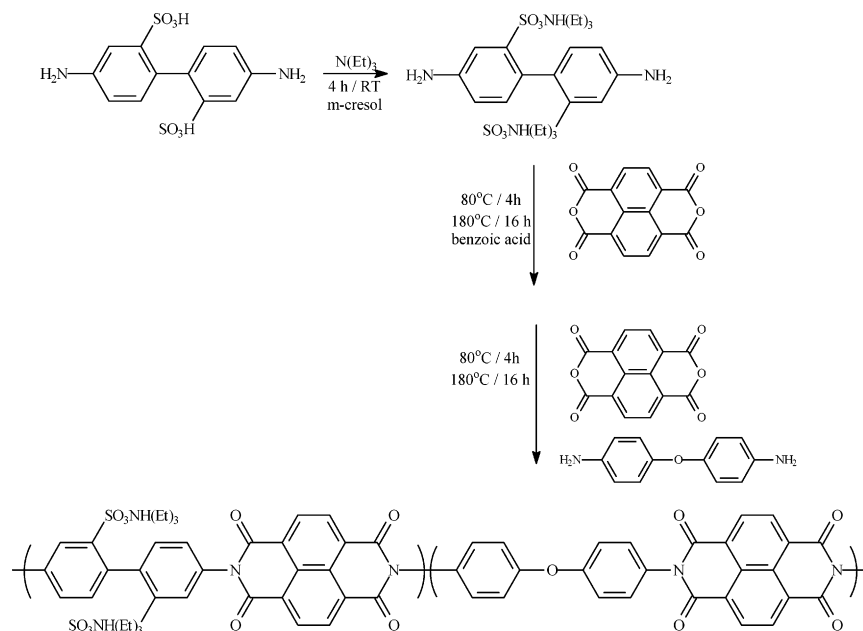
Figure 21. Synthesis of SPI, a sulfonated six-membered ring polyimide based on BDA, ODA, and NDA.[69]

imide, amic acid, and diacid as a function of time during the aging process of model A. From 0 to 2 h of aging, the amic acid is formed preferentially to the diacid. This is interesting because the amic acid should easily hydrolyze to the diacid in water.

In comparison, no structural modification of model B was seen before 120 h of aging (80 °C). However, after 120 h two small doublets appeared in the ^{1}H NMR spectrum and several additional peaks became noticeable in the ^{13}C NMR spectrum. It was determined by NMR and IR spectroscopy that the hydrolysis products were an imide/carboxylic acid and an imide/anhydride. Model B was then aged for 1200 h at 80 °C to quantitatively determine the amount of hydrolysis products as a function of time. The relative intensity of the peaks due to carboxylic acid is constant after some time. The authors suggest that an equilibrium occurs between model B and the products formed during hydrolysis, and therefore, the conversion to hydrolysis products is limited to about 12%. This critical fraction is probably enough to cause some degradation of polymeric materials, but research on six-membered polyimides has remained active.

Genies et al.[69] designed a synthetic method to produce random and block (segmented) sulfonated copolyimides (SPIs). The synthetic procedure for their most studied copolymer is shown in Figure 21. The first step in the synthesis involves preparation of short sequences of 4,4′-diamino-2,2′-biphenyl disulfonic acid (BDA) condensed with 1,4,5,8-tetracarboxylic dianhydride (NDA). An adjusted ratio of these two monomers allows one to create different block lengths of the sulfonated sequence. In the second polymerization step, the degree of sulfonation can be precisely controlled by regulating the molar ratio of BDA and the unsulfonated diamine, which is 4,4′-oxydianiline (ODA) in SPI. Controlling the degree of sulfonation is important because a high degree of sulfonation generally leads to high swelling or even dissolution of the polyimide membrane. It was found

that a block length of three sulfonated repeat units yields the highest proton conductivity.[70]

Preliminary investigations suggested that six-membered ring polyimides had some promise as PEMs; however, their poor solubility limits membrane formation and subsequent use in fuel cells. For example, the SPI membrane shown above is only soluble in chlorophenol. By introducing a slightly different unsulfonated diamine, 2,2′-diamino-3,4′-biphenyl ether, the resulting polymer is made soluble in *m*-cresol.[71] In Figure 21, the unsulfonated diamine added to the reaction in phase 2 was shown to have a large effect on the solubility, and several novel unsulfonated diamines containing ether linkages and/or bulky substituents were shown to improve solubility.[69]

The preparation of sulfonated polyimides with different ion exchange capacities and sulfonated block lengths was also considered. The solubility of the polyimides was greatly improved by introducing phenyl−ether bonds and bulky groups into the polymer backbones. Random sulfonated copolyimides exhibit better solubility than the sequenced ones in organic solvents. Therefore, improved solubility is a result of the unsulfonated diamine and the microstructure of the polymer chain. For a given polymer structure, the water uptake increases as ionic content increases. However, the number of water molecules per ionic group remains constant, which suggests that water is mainly located in the hydrophilic domains. Both the number of water molecules per ionic group and conductivity are systematically lower for random microstructures than for sequenced copolymers.

By introducing bulky unsulfonated diamines into the polymer backbone, greater interchain spacings can be achieved.[72,73] It was proposed that the increased spacing could improve conductivity at low relative humidity. Incorporating the larger comonomers prevents regular close parallel packing of the backbones and results in a more open structure, as
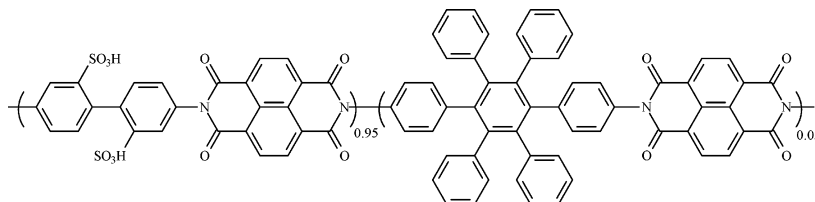
Figure 22. Six-membered ring copolyimide prepared with bulky unsulfonated diamine.

4,4'-diamino-2,2'-biphenyl disulfonic acid

9,9'-Bis(4-aminophenyl)fluorine-2,7-disulfonic acid

4,4'-diaminodiphenylether-2,2'-disulfonic acid

2,2-bis[4-(4-aminophenoxy)phenyl] hexafluoropropane disulfonic acid

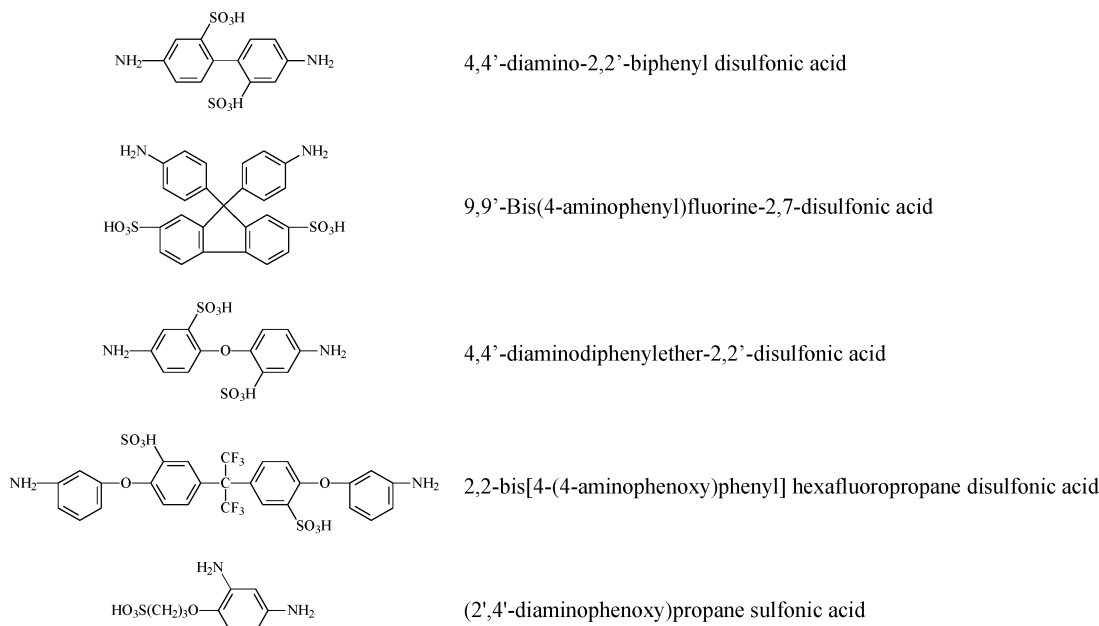(2',4'-diaminophenoxy)propane sulfonic acid

Figure 23. Sulfonated diamines for direct synthesis of sulfonated polyimides.

shown by X−ray diffraction patterns. With greater interchain spacings, more free volume is available for water to occupy. This leads to higher water uptakes and, therefore, higher conductivity, especially at low humidity.

Litt reported that bulky comonomers and sequenced copolymers impart improved water resistance without sacrificing conductivity. However, one sample shown in Figure 22 became brittle after 3 weeks in water above 90 °C. Litt also observed better hydrolytic stability when the unsulfonated diamine with flexible ether linkages was incorporated.[72,73]

Principally, one commercially available sulfonated diamine (4,4′-diamino-2,2′-biphenyl disulfonic acid) has been used to synthesize sulfonated polyimides. In addition to the commercially available diamine, several novel sulfonated diamines incorporating flexible or kinked structures have been prepared in Okamoto's lab.[74−77] The chemical structures and names of all five diamines are shown in Figure 23.

A comparison of the hydrolytic stability of several sulfonated six-membered ring polyimides was previously investigated.[75] Membranes were placed in distilled water at 80 °C until a loss of mechanical properties was observed. Improvements in membrane stability were observed for polymers with lower degrees of sulfonation (lower IEC) and for random copolymers, as opposed to block or sequenced copolymers. Additionally, the flexibility of the sulfonated diamine in the polymer structure was shown to play an important role in stability. By simply changing the sulfonated diamine from the rigid 4,4′-diamino-
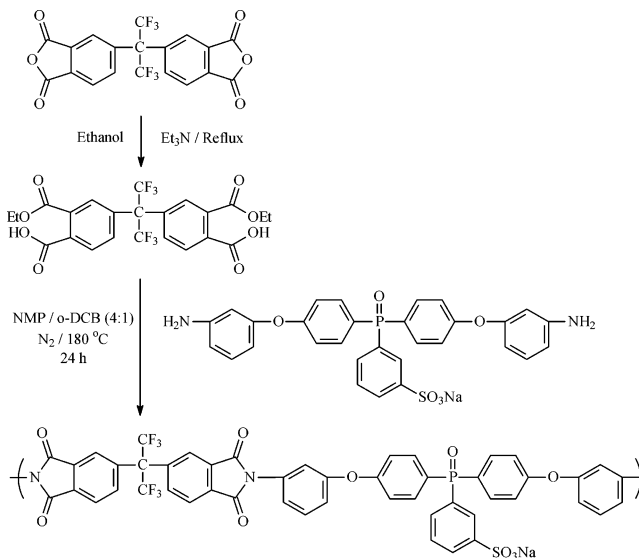

Figure 24. Synthesis of a five-membered ring sulfonated polyimide containing phosphine oxide.[78]

2,2′-biphenyl disulfonic acid (BDA) to the more flexible 4,4′-diaminodiphenyl ether-2,2′-disulfonic acid (ODADS), the stability in water greatly improved. On the other hand, 9,9′-bis(4-aminophenyl)fluorine-2,7-disulfonic acid (BAPFDS), a rigid and bulky sulfonated diamine, showed similar stability to the ODADS series at comparable ion exchange capacities. It is suggested that polyimides derived from BAPFDS should display higher stability due to the highly basic sulfonated diamine.[76] Aromatic diamines with higher basicity are generally more reactive with dian-
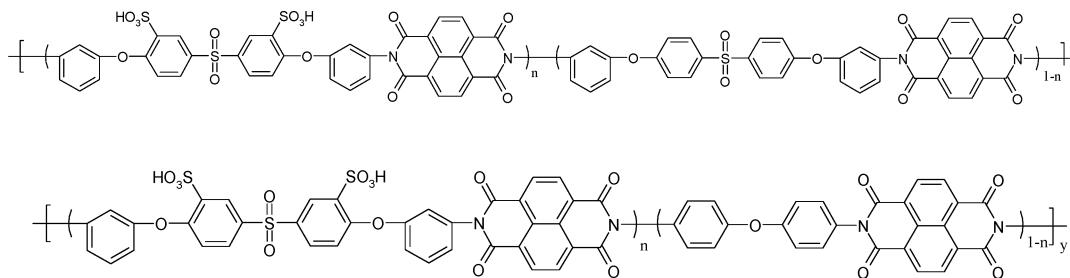
Figure 25. Sulfonated six-membered ring polyimides with novel sulfonated diamines.[79]

hydrides than those with lower basicity. Since hydrolysis is the reverse reaction of polymerization, polyimides derived from more basic diamines should have higher hydrolytic stability. This may be why the more rigid copolymers based on BAPFDS have stabilities similar to the flexible ODADS ones; yet both perform better than BDA-type copolyimides.

Shobha et al.[78] employed a novel sulfonated diamine containing a phosphine oxide moiety in the synthesis of a five−membered ring sulfonated polyimide. The synthesis is shown in Figure 24.

Since this is a five-membered imide, water stability would be expected to be very poor. To improve stability, Einsla et al.[79] synthesized two series of six-membered imides (the first with 4,4′-oxydianiline as the unsulfonated diamine and the second with bis-[4-(3-aminophenoxy)phenyl] sulfone) using 3,3′-disulfonic acid-bis[4-(3-aminophenoxy)phenyl] sulfone as the sulfonated diamine, as shown in Figure 25. These polyimides are soluble in N-methylpyrrolidone (NMP) and have displayed better, but still limited, stability in water. Their electrochemical properties and fuel cell performance are the subject of an upcoming publication.[80] For high temperature fuel cell operations requiring a stability of >5000 h, however, the six-membered polyimides have been disappointing candidates, and they are generally being abandoned for use as PEMs. Nonetheless, most of these polyimides have extremely low methanol permeation and low electro-osmotic drag coefficients and might be useful as room temperature DMFC membranes.[81]

6. High Performance Polymeric Backbones for Use in PEMs

Other high performance polymer backbones have been explored as PEM materials in addition to poly-(arylene ether)s and polyimides. Ductile copolymers with high modulus and glass transition values are desirable PEM candidates. The hydrolytic and oxidative stability of many of these materials remains to be determined. Nevertheless, interesting synthetic methodologies have been employed to investigate these materials, which have been instructive in the search for new PEM candidates.

Poly(phenylquinoxaline) membranes cast from m−cresol were sulfonated by reactions in 50% sulfuric acid solution for 2 h followed by drying at 300 °C for 90 min.[82,83] The attachment site for the sulfonic acid group is believed to be ortho to the ether linkage, as in Figure 26, but even this has yet to be confirmed.

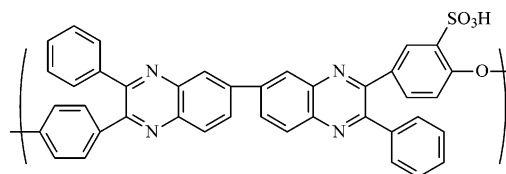The resulting sulfonation levels varied from roughly 50% to well in excess of 100%, but they typically

Figure 26. Chemical structure of sulfonated poly(phenylquinoxaline).[84]

ranged between 70 and 100%. The stability of this material in detailed fuel cell performance studies was shown to be <500 h, and this material was subsequently abandoned in favor of materials that showed increased stability under fuel cell conditions.[17]

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is an attractive material for the preparation of membranes because it possesses excellent membrane-forming properties, as well as good thermal and chemical stability. PPO was sulfonated with chlorosulfonic acid either in a chloroform solution,[85] which is a common technique for PPO sulfonation, or in 1,2−dichloroethane.[86] In both cases, the sulfonated product precipitated after the addition of a certain amount of chlorosulfonic acid and could subsequently be easily isolated. The amount of chlorosulfonic acid needed for the precipitation of SPPO from the 1,2-dichloroethane solution, however, was smaller, and thus the degree of sulfonation of the obtained SPPO was lower (25.4 vs 42.4%) for the sample sulfonated in chloroform. The SPPO has shown good thermal stability and resistance against aqueous solutions of strong acids and bases and oxidation agents.[87] However, one might expect that the benzylic sites would easily oxidize.

Kobayashi et al. reported sulfonation of poly(4-phenoxybenzoyl-1,4-phenylene) (PPBP) with sulfuric acid and compared the data with those of sulfonated PEEK.[88] As reported, the authors employed sulfuric acid for the sulfonation reaction to avoid or at least minimize degradation of the polymer by chlorosulfonic acid or fuming sulfuric acid (Figure 27).

Sulfonated poly(4-substituted benzoyl-1,4-phenylene) homopolymers and copolymers using concentrated sulfuric acid or fuming sulfuric acid have been shown to form sulfonated polymers with variable degrees of sulfonation.[89] To improve film formation of the sulfonated polyphenylenes, multiblock copolymers have been synthesized by reacting a more flexible poly(arylene ether sulfone) with sulfonated polyphenylenes.[90]

1,4-Bis(propylcarbamoyl)-2,3,5,6-tetraphenylbenzene and decafluorobiphenyl were polymerized to form copolymers that could be sulfonated at specific
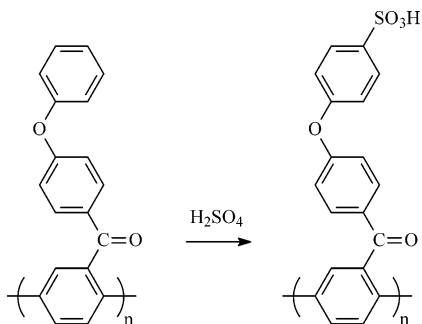
Figure 27. Sulfonation reaction of poly(4-phenoxybenzoyl-1,4-phenylene).[88]

sites by reaction with chlorosulfonic acid in methylene chloride as shown in Figure 28.[91] The reaction of the pendant phenyl rings at the para position with
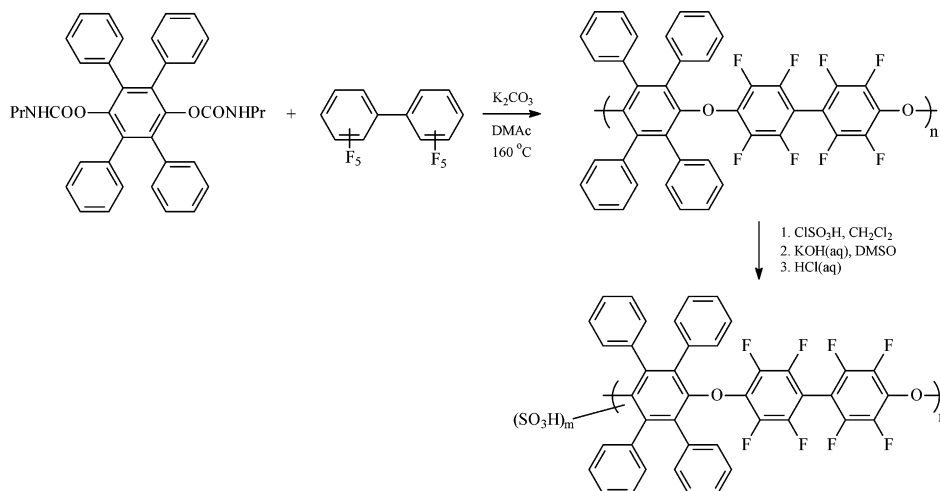
chlorosulfonic acid is quantitative, so the degree of sulfonation can be controlled by the reaction stoichiometry. The above materials were soluble in methanol, which lead to bis(3,5-dimethylphenyl) sulfone being employed as a comonomer, as shown in Figure 29. These copolymers, as well as the synthesis of similar fluoroalkane containing copolymers, highlight the range of materials that can be designed with specific main chain chemical structures to the control resulting properties and sulfonation reactions.[92]

Poly(phthalazinone ether ketone)s (PPEKs) were synthesized by the reaction of the polymer in mixtures of 95−98% concentrated sulfuric acid and 27−33% fuming sulfuric acid in the absence of other solvents.[93] A general reaction scheme is given in Figure 30. The mixed solvent systems of sulfuric acid

Figure 28. Synthesis and sulfonation of polymers containing tetraphenylphenylene ether and perfluorobiphenylene units.[91]
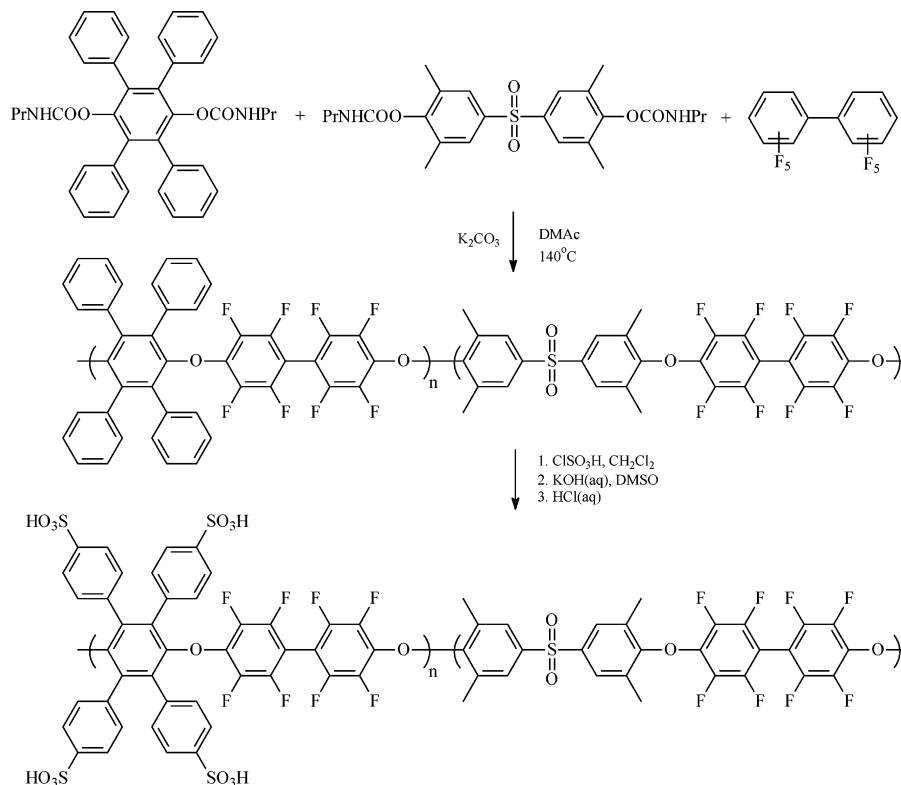

Figure 29. Synthesis of sulfonated copolymers from 1,4-bis(propylcarbamoyl)-2,3,5,6-tetraphenylbenzene, bis(3,5-dimethylphenyl) sulfone, and decafluorobiphenyl.[91]
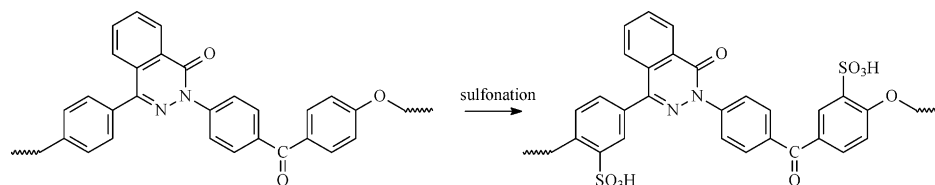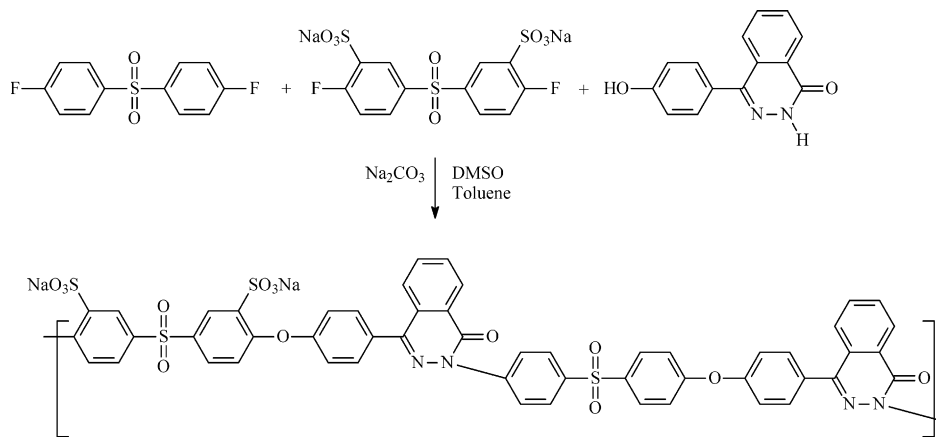
Figure 30. Sulfonation of PPEK.[93]

Figure 31. Synthesis of directly polymerized sulfonated poly(phthalazinone ether sulfone).[94]

and fuming sulfuric acid were utilized to limit degradation of the polymer during sulfonation, which occurred in pure fuming sulfuric acid.

As an alternative to the somewhat undesirable postsulfonation approach, Xiao et al. synthesized sulfonated poly(phthalazinone ether sulfone)s utilizing sulfonated 4,4′-difluorodiphenyl sulfone as the sulfonated monomer, as shown in Figure 31.[94] The authors indicate that the low degree of swelling of these materials may be advantageous in comparison to the case of the directly polymerized sulfonated poly(arylene ether) materials. As they reported, the low swelling is due to hydrogen bonding involving the carbonyl groups of the hydroxyphenyl phthalazinone unit. The proton conductivities of the directly copolymerized materials showed less temperature dependence than those of the corresponding postsulfonated polymers. The hydrolytic stabilities of these copolymers were not reported.

Sulfonation of polybenzimidazole (PBI) can be accomplished by heating the polymer—hydrogen sulfate complex, which can be formed by casting a PBI film from sulfuric acid or immersing a cast PBI film in sulfuric acid and allowing the acid to permeate the membrane, as shown in Figure 32.[95] This material has received much attention, both as a proton exchange membrane candidate and also as a host for phosphoric acid,[3d,96] especially given the success of unmodified PBI/phosphoric acid membranes[97] in high temperature fuel cells, as discussed elsewhere in this review. However, the thermally initiated sulfonation may have induced scission or cross-linking, as evidenced by the sulfonated PBI's insolubility and brittleness.

Sulfonation of polybenzimidazole was also accomplished by proton abstraction with an alkali metal hydride followed by reaction with sodium (4-bromomethyl)benzenesulfonate.[98,99] The degree of sulfonation in this synthesis can be controlled by the
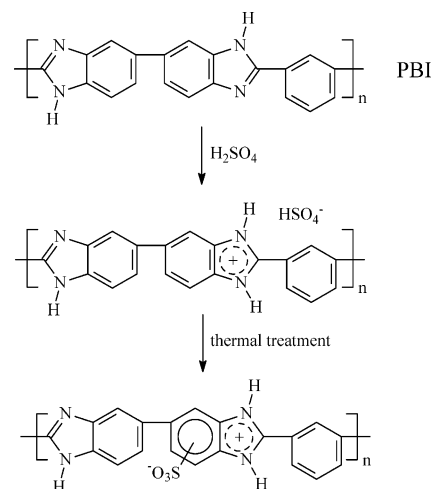

Figure 32. Sulfonation of PBI.[95]

amount of ionized sites with the alkali metal hydride or by controlling the ratio of polybenzimidazole to (4-bromomethyl)benzenesulfonate, as shown in Figure 33. Control of the number and location of ionic groups is critical to a systematic study of the PEM properties and producing consistent material. Complexation phenomena would be expected to be important.

Direct copolymerization of sulfonated monomers has been used to synthesize sulfonated poly(benzimidazoles), poly(benzoxazole)s, and poly(benzothiazole)s. As an example, Kim et al. synthesized poly(benzthiazole)s from 2,5-diamino-1,4-benzenedithiol dihydrochloride and either 2-sulfoterethphthalic acid sodium salt, 5-sulfoisophthalic acid sodium salt, or 2,4-disulfoisophthalic acid potassium salt in polyphosphoric acid (PPA), as shown in Figure 34.[100] Similar sulfonated poly(benzimidazole)[96,101] and sulfonated poly(benzoxazole)[102] structures have also been synthesized. A general synthetic scheme for each is shown in Figure 35. The stability of these polymers in aqueous acidic environments appears
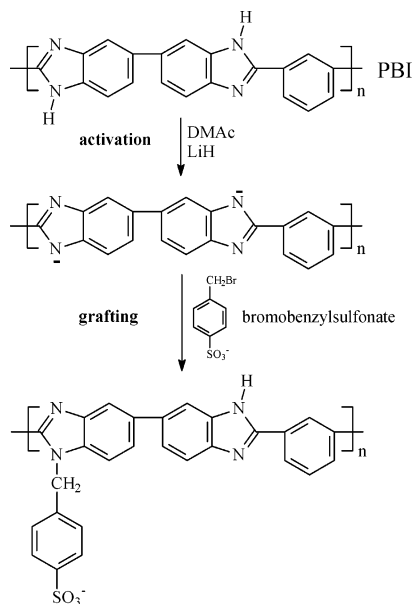
Figure 33. Synthetic scheme for controlled addition of (4-bromomethyl)benzenesulfonate to PBI.[98,99]

limited and will likely hamper their performance as PEMs.[103]

Mulhaupt et al. synthesized novel soluble copolyarylenes via a Ni(0)-catalyzed coupling reaction of aryl chlorides.[104] Molar ratios of dichlorodiphenyl sulfone (*x*) to *m*-dichlorobenzene (*y*) were used to vary the amount of *m*-phenylene in the final copolymer. Then these copolymers were dissolved in chloroform and sulfonated with chlorosulfonic acid. The synthe-

sis and sulfonation are shown in Figure 36. Due to the electron-withdrawing nature of the sulfone group, the copolymers were only susceptible to sulfonation on the *m*-dichlorobenzene residue. The degree of sulfonation could be controlled by the amount of *m*-dichlorobenzene included in the polymerization.

7. Polyphosphazene PEMs

Polyphosphazene-based PEMs are potentially attractive materials for both hydrogen/air and direct methanol fuel cells because of their reported chemical and thermal stability and due to the ease of chemically attaching various side chains for ion exchange sites and polymer cross-linking onto the $-P=N-$ polymer backbone.[105] Polyphosphazenes were explored originally for use as elastomers and later as solvent-free solid polymer electrolytes in lithium batteries, and subsequently for proton exchange membranes.[106]

Polyphosphazenes are of great synthetic and technological interest because of the way in which the side groups can be varied over an exceedingly wide range of structures, and this provides access to species with an almost unprecedented variety of tailored properties. They are also particularly suitable for side-group and surface modification chemistry because of the stability of the phosphorus–nitrogen backbone. The surface chemistry of specific polyphosphazenes has been studied by Allcock et al. with respect to the sulfonation process.[105] The target sulfonation reactions were developed initially with
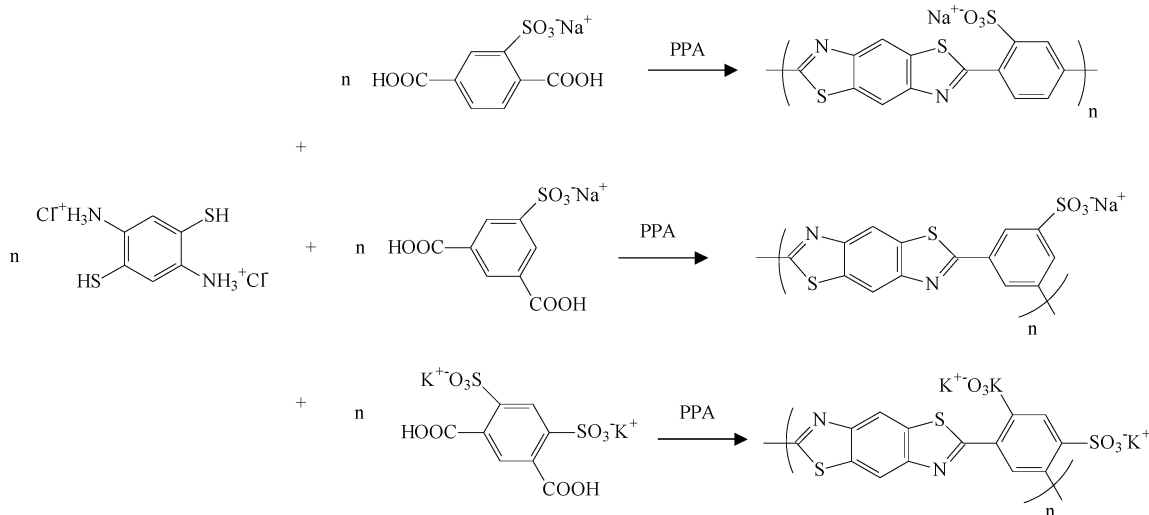

Figure 34. Synthetic scheme for the direct synthesis of sulfonated poly(benzthiazole)s.
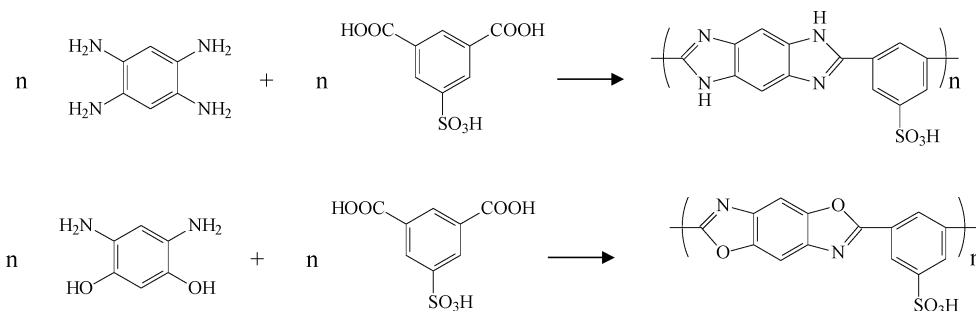

Figure 35. Synthesis of sulfonated poly(benzimidazole) and poly(benzoxazole).
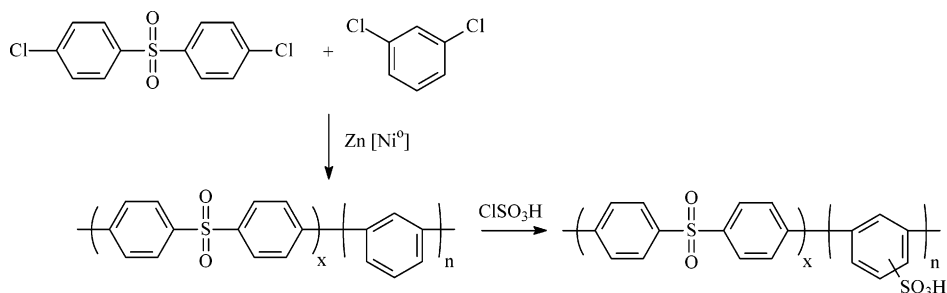
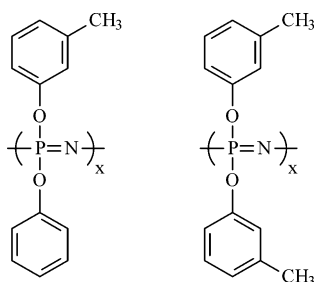**Figure 36.** Synthesis and sulfonation of copolyarylenes.[104]

Figure 37. Poly[(3-methylphenoxy)(phenoxy)phosphazene] and poly[bis(3-methylphenoxy)phosphazene].[111]

Figure 38. Possible sulfonation sites on poly[(3-methylphenoxy)(phenoxy)phosphazene].[109]

small-molecule cyclic trimeric phosphazenes to allow careful molecular characterization using the normal range of small-molecule analysis techniques.[107] Once optimized, the same reactions were carried out with the corresponding polymers. Standard polymer solution and materials characterization methods were applied to the product polymers in order to determine the molecular structures and material characteristics. Finally, the same reactions were applied to the surfaces of films prepared from polyphosphazene. The modified surfaces were examined by several surface analysis techniques.

Allcock's research led to the development of polyphosphazene-based PEMs by his small molecule studies of the sulfonation of cyclic trimeric phosphazenes[107] and the surface chemistry of polyphosphazene macromolecules.[105] In a 1993 report, he described the sulfonation of aminophosphazenes with 1,3−propanesultone.[108] While these specific materials are not necessarily ideal as PEMs, this study demonstrated a novel technique for creating sulfonated polyphosphazene materials that may provide more control over the sulfonated polymer product than wholesale sulfonation of a base polymer by a strong sulfonating agent.

Studies by Pintauro and co-workers have shown that poly[(3-methylphenoxy)(phenoxy)phosphazene] and poly[bis(3-methylphenoxy)phosphazene] (Figure 37) can be sulfonated by adding an SO_3 solution in dichloroethane dropwise to a polymer/dichloroethane solution.[109,110] A high ion exchange capacity (up to 2.0 mequiv/g) material was reported with no detectable polymer degradation.

The sulfonation reaction is controllable, but one report indicates that reaction of the backbone nitrogen occurs before sulfonation on the pendent ring with poly[(3-methylphenoxy)(phenoxy)phosphazene], as shown in Figure 38.[109]

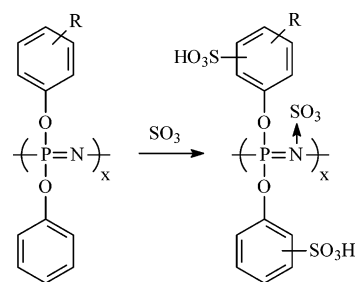Solution-cast membranes (100−200 μm in thickness) from sulfonated polymers with an ion exchange capacity $\leq$ 1.4 mequiv/g exhibited good mechanical properties at room temperature in both the dry and water-swollen states. The reported glass transition temperatures varied from −28 to −10 °C for unsulfonated poly[bis(3-methylphenoxy)phosphazene] and the sulfonated analogue with an IEC of 2.1 mequiv/g, respectively. These low glass transition temperatures may cause membrane failures under fuel cell conditions and have led researchers to explore sulfonation and cross-linking of these polyphosphazene-based materials.

Pintauro et al. reported that proton exchange membranes with sulfonate fixed charge sites were fabricated from poly[bis(3-methylphenoxy)phosphazene].[111] The membrane ion exchange capacity was fixed at 1.4 mequiv/g. Membranes with and without cross-linking were examined, where polymer cross-linking was carried out (after sulfonation) by dissolving benzophenone photoinitiator in the membrane casting solution and then exposing the films to UV light after solvent evaporation. It is clear from this work that cross-linking reduced the water uptake and thus many of the membrane's transport properties. However, the protonic conductivity did not seem to differ between the cross-linked and non-cross-linked specimens even though their water uptakes were different. Once a sufficient level of hydration has been reached, it is possible that further addition of water (increases in λ) will have no effect on the protonic conductivity of the membrane due to the counterbalancing forces of increased hydration (higher λ) and increasing the distance between acidic sites (membrane swelling).

In another report polyphosphazene copolymers were synthesized from bis(2-methylphenoxy)phosphazene, which was sulfonated after polymerization.[112] Polymers such as polyvinylidene fluoride, polyhexafluoropropylene, and polyacrylonitrile were used to produce a blended membrane system. Polymer blends, cross-linking, and other means of re-enforcement are

generally necessary for polyphosphazene PEMs because of the relatively poor mechanical behavior of pure polyphosphazene films—particularly under hydrated conditions. Rational and controlled cross-linking of membranes could enhance the properties of some currently studied PEMs by decreasing the methanol crossover (with some expense to conductivity, but possibly not) and increasing the maximum working temperature of the membrane by increasing the onset of the hydrated T_g.

8. Other Proton Conducting Moieties—Alternatives to Sulfonation

Interest in new solid polymer electrolytes has driven some research groups to investigate other materials containing proton conducting moieties aside from sulfonic acid. Polymers and copolymers from monomers containing phosphonic-based proton conductors have been reported. Phosphonic and/or phosphinic acid containing polymers have not been well studied because of the rather limited synthetic procedures available for their preparation, compared with sulfonic acid derivatives. Miyatake and Hay

reported the first phosphonic acid containing polymers and copolymers from three phosphine containing aromatic difluorides with moderate molecular weight, as shown in Figure 39.[113]

The acid group in this instance is located in the main chain of the copolymer. The majority of acid containing polymers have the sulfonic acid functionality as the proton exchange site. There are a few reports of phosphonic acid containing polymers as membranes for fuel cell applications. They have lower acidity than sulfonic acid; however, their better chemical and thermal stability with respect to the corresponding sulfonic acid-functionalized polymers is believed to offer potential advantages.[114] Poly-(arylene ether)s containing mono- or dibromotetra-phenylphenylene ether and octafluorobiphenyl units may be used as precursors. The brominated polymers were phosphonated with diethyl phosphite by a palladium-catalyzed reaction. Quantitative phosphonation is reported when high concentrations of catalyst were used. The diethylphosphonated polymers were dealkylated by reaction with bromotrimethylsilane in carbon tetrachloride, followed by hydrolysis
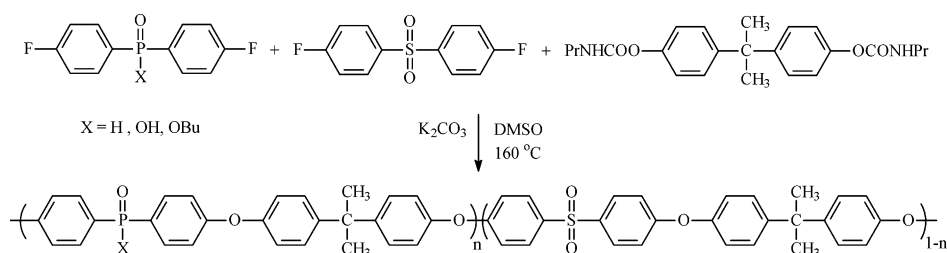
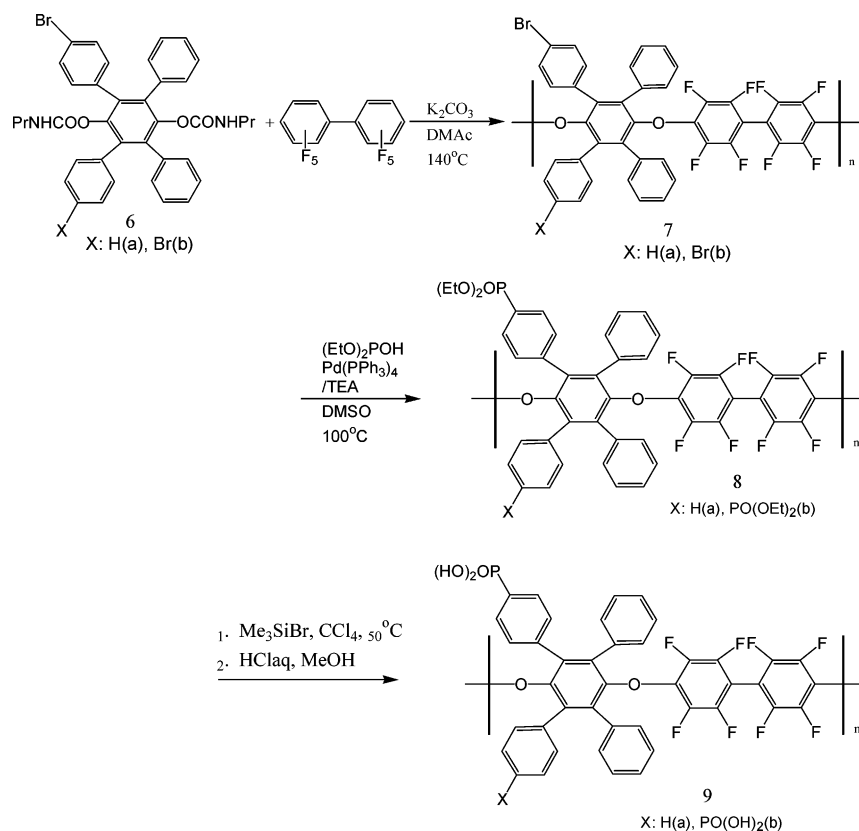**Figure 39.** Synthesis of phosphinic acid (X = OH) containing poly(arylene ether).[113]

Figure 40. Synthesis of poly(arylene ether)s bearing phosphonic acid groups.[114]
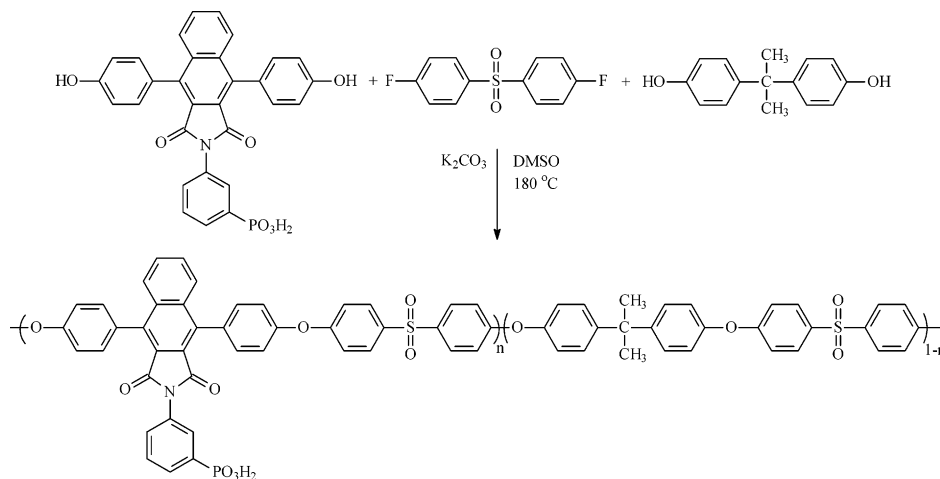
Figure 41. Synthesis of a phosphonic acid containing poly(arylene ether) derived from a phenolphthalein-based bisphenol.[115]

with hydrochloric acid to form polymers with pendent phosphonic acid groups, as shown in Figure 40.

The authors reported that tough, flexible films were obtained by solution casting from dimethyl sulfoxide (DMSO), which would indicate little or no backbone chain degradation occurred during phosphonation and dealkylation.

Another phosphonic acid containing polymer was also reported by Meng et al. and was based on phenolphthalein chemistry.[115] The bisphenol monomer was synthesized from phenolphthalein and *m*-aminophenylphosphonic acid. Poly(arylene ether)s containing phosphonic acid groups were prepared from the bisphenol as shown in Figure 41. This is the first report on the attachment of phenylphosphonic acid groups as side chains to aromatic polyethers. These polyethers had very high glass transition temperatures and high molecular weights. However, their reported conductivities were only $10^{-5}-10^{-6}$ S/cm, which is probably too low for these materials to be considered seriously as PEMs.

Allcock et al. also have investigated the use of phosphonated polyphosphazenes as potential membrane materials for use in direct methanol fuel cells (Figure 42).[116] Membranes were found to have IEC values between 1.17 and 1.43 mequiv/g and proton conductivities between 10^{-2} and 10^{-1} S/cm. Methanol diffusion coefficients for these membranes were found to be at least 12 times lower than that for Nafion 117 and 6 times lower than that for a cross-linked sulfonated polyphosphazene membrane.

The strength of the acid conducting moiety is thought to play a role in the conductivity of proton exchange membranes. This has encouraged researchers to explore the role of strongly acidic functional groups such as sulfonimide moieties in proton exchange membranes.[117] DesMarteau et al. have compared Nafion and a structurally similar bis[(perfluoroalkyl) sulfonyl]imide-based ionomer, as shown in Figure 43.[118] There was not a noticeable increase in proton conductivity produced by incorporation of the sulfonimide moiety in their copolymer, in lieu of the perfluorosulfonic acid moiety of Nafion. In fact, their sulfonimide-based copolymer gave similar results in all respects to Nafion. Allcock et al. have also explored sulfonated poly(phosphazene)s with either
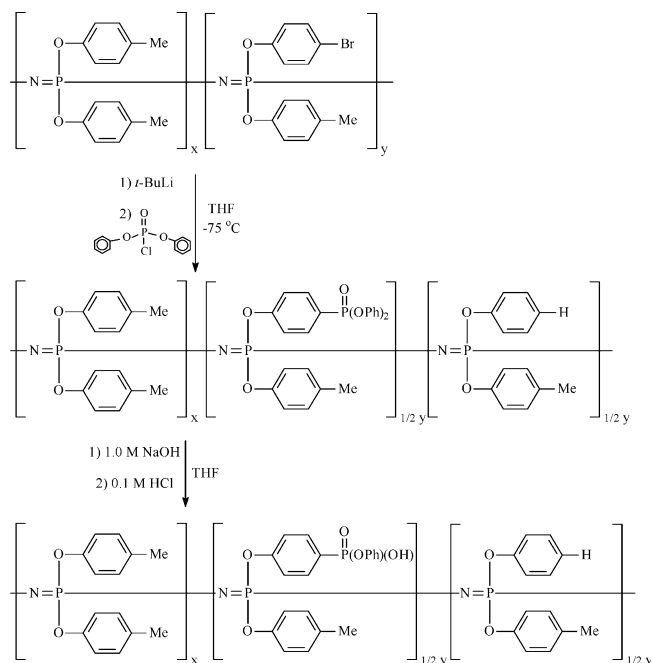
Figure 42. Synthesis of polyphosphazenes bearing phenyl phosphonic acid side groups.[116]
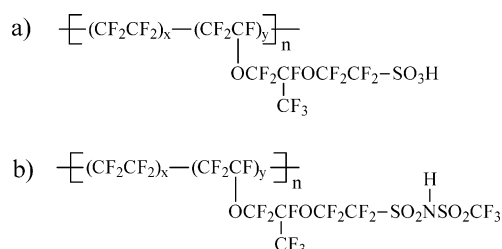
Figure 43. Structure of Nafion and bis[(perfluoroalkyl) sulfonyl]imide.[118]

sulfonic acid[105] or sulfonimide[119] proton conducting substituents.

Cho et al.[120] have recently described the synthesis of a sulfonimide containing monomer and the resulting poly(arylene ether sulfone) copolymers. In this procedure 3,3′-disulfonate-4,4′−dichlorodiphenyl sulfone was refluxed in thionyl chloride, isolated, and then reacted with trifluoromethanesulfonamide in the presence of triethylamine to form the sulfonamide analogue monomer as shown in Figure 44. This
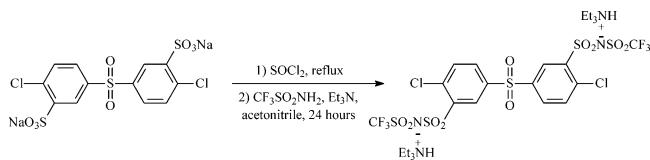
Figure 44. Synthesis of a sulfonimide containing an activiated dichloro monomer.[120]

Figure 45. Imidazole proton conductors—both as free molecules and attached to a polymer backbone.[123]

sulfonimide monomer was then used to form directly polymerized sulfonimide bearing poly(arylene ether sulfone) copolymers in a similar synthesis to that of the sulfonic acid containing copolymer.

All acidic proton conductors discussed so far in this review have relied on the presence of large amounts of water ($\lambda = 10-30$) as a mobile phase for the conduction of protons. Current targets for automotive use 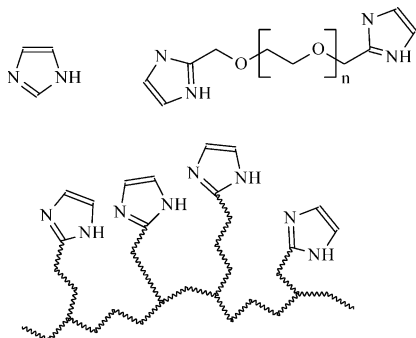of hydrogen/air fuel cells are 120 °C and 50% or lower relative humidity. Under these conditions, the conductivity of the membrane decreases due to low water uptake at 50% relative humidity and thus creates large resistive losses in the cell. To meet the needs of advanced fuel cell systems, membranes will have to function without large amounts of absorbed water. Organic−inorganic composites are one preferred approach.[3b,63]

Imidazole proton conductors have been explored as water replacement solvents[121,122] and have also been attached to polymer backbones[123] to replace the acid/water complex in current PEMs (Figure 45).

9. Important Considerations in the Design of New PEMs

As the preceding sections have illustrated, many families of polymers with differing chemical structures and various strategies for incorporation of sulfonic acid groups have been explored as proton exchange membrane materials. Most reports of new materials have included information on ion content (EW or IEC), protonic conductivity, and water uptake. Despite the large body of research on this topic, there are a few basic polymer properties that are still not well-known for common systems or not measured in most reports. Perhaps the most glaring omission in new ion conducting polymer research is the characterization of molecular weight. Molecular weight is one of the most basic properties of polymeric materials and is most commonly measured by gel permeation chromatography ((GPC) or size exclusion chromatography (SEC)) or MALDI-TOF for quantita-

tive determination of the molecular weight distribution or intrinsic viscosity to obtain a relative measure of the molecular weight. Characterization of molecular weight in ion containing systems is complicated by the presence of ionic groups attached to the polymer backbone where ion−ion interactions affect the characteristic size of the macromolecule in a solvent. This ion effect on chain size is often termed as the polyelectrolyte effect. The ionic groups can also cause the polymer chains to associate with the chromatographic column, giving erroneous results. Adding a small amount of lithium bromide or chloride to the chromatographic mobile phase is helpful in suppressing the polyelectrolyte effect in some GPC and intrinsic viscosity experiments to allow characterization of the ion containing materials.

End group analysis by nuclear magnetic resonance (NMR) can also be used to characterize the effects of molecular weight on the properties of proton exchange membranes. In a study by Wang et al., offsetting stoichiometry and endcapping with NMR sensitive *tert*-butyl phenyl groups (18 protons per chain) was used to create a series of sulfonated poly-(arylene ether sulfone)s with increasing molecular weight (Figure 46).[124] It was determined that molecular weight in the range 20 000−40 000 g/mol (20−40K) did not have a large effect on protonic conductivity, but the mechanical properties and water uptake of the material are nevertheless dependent on the molecular weight of the copolymer, possibly related to chain entanglement issues (see Tables 1 and 2).[81] Refinement of these procedures is continuing in our laboratory.

The dependence of mechanical properties on molecular weight brings up another important area of characterization that is often neglected. Proton exchange membranes with good mechanical properties in both the dry and hydrated states are critical to successful MEA fabrication and long-term durability in a fuel cell device. The membrane must be able to withstand the stresses of both electrode processing and attachment and must also be mechanically robust enough to endure startup and shutdown of the fuel cell with the repeated swelling/drying/heating/cooling of the membrane. Nafion acts reasonably well mechanically up to 80 °C as a rubbery material with low modulus but high elongation to break.

These properties are advantageous for MEA fabrication, but Nafion's rubbery behavior is likely detrimental to its long-term performance in high temperature environments. Because of its low glass transition temperature when hydrated (hydrated T_g),[125] hydrated Nafion undergoes a viscoelastic relaxation causing the membrane to develop pinholes when operated at temperatures near or above 100 °C. A PEM based on a high T_g polymer such as a poly-(arylene ether) can increase the membrane's hydrated T_g and potentially limit mechanical degradation of the membrane at increased temperatures.

Molecular weight and mechanical properties are two common but important properties that are measured for a multitude of polymeric systems, but they have thus far been largely neglected in the characterization of PEMs. Often new PEMs will show
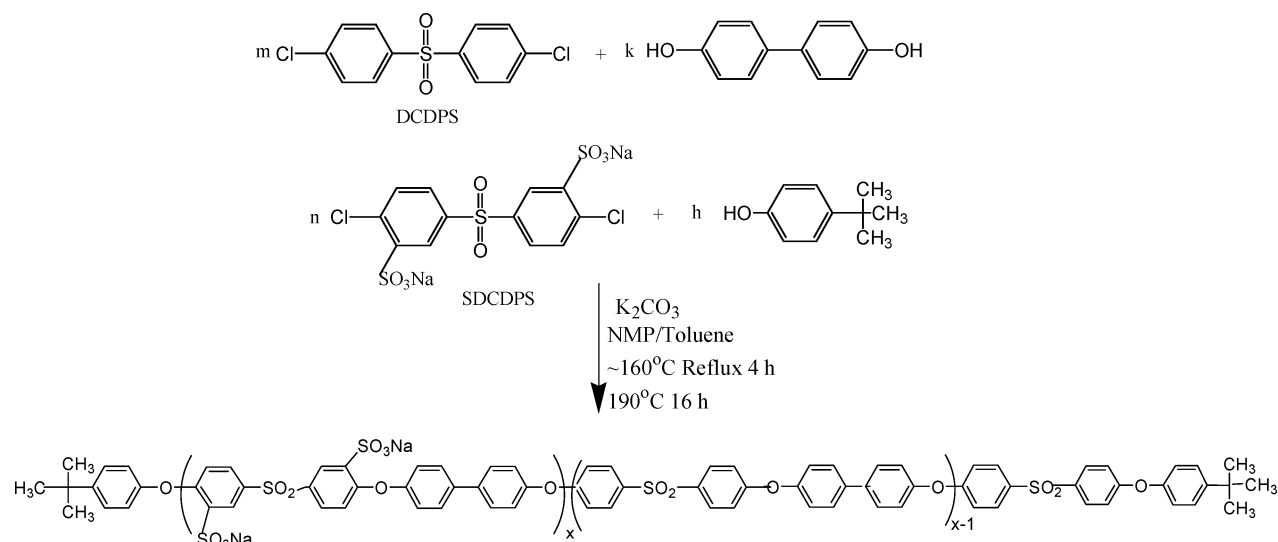
Figure 46. Synthesis of end-capped copolymer (BPS-40): target M_n = 40K g/mol.[124]

Table 1. Characterization of Molecular Weights and Intrinsic Viscosities (no Li salts) for End-Capped BPS-40[a]

calc M_n	monomer ratio by mole[b]	$[\eta]^{NMP}$ at 25 °C (dL/g)	M_n ($\times 10^{-3}$) by NMR
20K	43.13/42.13/2	0.54	23.1
30K	64.69/63.69/2	0.61	32.7
40K	86.26/85.26/2	0.87	40.2

[a] The IV of noncontrolled BPS-40 is 2.5 dL/g, which is much higher than that of BPS-40−40K. The molecular weight of noncontrolled BPS-40 is much more than 40K. Chemical end-cap techniques could be used to characterize the molecular weight of other sulfonated polymers. [b] [(SDCDPS + DCDPS)/biphenol/*tert*-butylphenol]. SDCDPS/(SDCDPS + DCDPS) = 0.4.

Table 2. Characterization of End-Capped BPS-40 and Stoichiometric Copolymers[a]

polymer	IEC (mequiv/g)	SDCDPS (mol %)	water uptake (%)	conductivity (S/cm)
BPS-40−20K	1.60	39.5	51	0.090
BPS-40−30K	1.60	39.8	57	0.092
BPS-40−40K	1.60	39.2	57	0.085
1:1 stoichiometry	1.70	40.1	55	0.100
theory	1.72	40		

[a] Membranes acidified by boiling in 0.5 M H_2SO_4. Controlled copolymers have similar chemical compositions, water uptakes, and conductivities, which are independent of molecular weight.

promising protonic conductivity results, but the mechanical properties are not discussed and remain in question, which can hamper efforts to create MEAs.

10. Conclusions

There is a clear need for the synthesis and more complete characterization of new PEM polymeric materials. Polymers bearing functional moieties for proton conduction might also be designed to serve as a host for inorganic compounds to afford a proton conducting component in a blend, as well as a stand-alone PEM. The two current hurdles for polymeric membranes are the high protonic conductivity at low water contents (e.g. under conditions of 120 °C and 50% relative humidity) and long-term durability under fuel cell conditions. Current sulfonic acid-based materials suffer from low conductivity in the absence of water. New proton conducting moieties and morphologies are required to fulfill the requirements of these higher temperature systems. Lower permeability seems to be a good way to address new DMFC systems.

In addition to new ion conducting strategies, basic polymer characterization measurements must be identified and used to more advantage in the development of new PEMs. Issues of molecular weight, mechanical properties, and chemical/physical degradative mechanisms need to be addressed with much more rigor than they have been in the past.

This review has attempted to review the basic research on alternative polymer membranes with attached ionic groups and has tried to highlight examples of materials with a well-defined chemical structure that have been described in the literature. Nafion and similar polyperfluorosulfonic acid membranes still remain the most studied materials due to their commercial applicability and wide availability. However, for all that is known about the properties of these membranes, little is known about their synthesis, chemical composition, or molecular weight. The search for more in depth understanding of the link between the chemical composition of the polymer and its resulting membrane properties has led researchers to synthesize membranes with new, controlled chemical structures. Sulfonated poly(arylene ether)s such as PEEK and poly(sulfone) have shown excellent chemical and thermal stability in fuel cell applications, but their weaker aryl sulfonic acid groups generally cause lower proton conductivity than perfluorosulfonic acid containing membranes. This can be combated by the addition of more sulfonic acid conductors, but it may lead to undesirably large swelling. The weaker acid groups also impede the performance of poly(arylene ether)-based membranes at low relative humidity. These types of membranes are certainly a viable alternative to Nafion in applications where inlet gases with high relative humidity (above 80%) can be used, but their applica-

bility for low relative humidity applications is more challenging.

Postsulfonation of polymers to form PEMs can lead to undesirable side reactions and may be hard to control on a repeatable basis. Synthesis of sulfonated macromolecules for use in PEMs by the direct reaction of sulfonated comonomers has gained attention as a rigorous method of controlling the chemical structure, acid content, and even molecular weight of these materials. While more challenging synthetically than postsulfonation, the control of the chemical nature of the polymer afforded by direct copolymerization of sulfonated monomers and the repeatability of the reactions allows researchers to gain a more systematic understanding of these materials' properties. Sulfonated poly(arylene ether)s, sulfonated poly(imide)s, and sulfonated poly(styrene) derivatives have been the most prevalent of the directly copolymerized materials.

Using the direct synthesis route, the potential of forming well-defined block copolymers with sulfonated and unsulfonated blocks has been realized in poly(styrene) or poly(acrylonitrile)-based materials using styrene sulfonic acid, in poly(imide)s using sulfonated diamines, and in poly(arylene ether sulfone) utilizing phosphine oxide-based comonomers that avoid ether−ether interchange reactions. The synthesis of block materials presents another level of complexity, but studies involving these materials indicate that the blocky nature of the copolymer chemical structure gives rise to increased proton conductivity without massive increases in water swelling. This is an area that shows promise in the rational design of new materials and should be pursued further as a possible route to high temperature membranes.

Sulfonated poly(arylene ether)s have shown promise for durability in fuel cell systems, while poly(styrene)- and poly(imide)-based systems serve as model systems for studying structure-relationship properties in PEMs because their questionable oxidative or hydrolytic stability limits their potential application in real fuel cell systems. Sulfonated high performance polymer backbones, such as poly(phenylquinoxaline), poly(phthalazinone ether ketone)s, polybenzimidazole, and other aromatic or heteroaromatic systems, have many of the advantages of poly(imides) and poly(arylene ether sulfone)s and may offer another route to advanced PEMs. These high performance backbones would increase the hydrated T_g of PEMs while not being as hydrolytically sensitive as poly(imides). The synthetic schemes for these more exotic macromolecules are not as well-known, but the interest in novel PEMs will surely spur developments in this area.

The inorganic poly(phosphazene) backbone has received attention as a PEM candidate. This is an attractive system for study due to its ease of synthesis and subsequent modification by many functional groups. However, these membranes generally show low glass transition temperatures and somewhat poor mechanical properties, and they require cross-linking to enhance their performance in hydrated environments.

Applications of fuel cell technology can be furthered by the use of advanced materials, including organic−inorganic composites.[3b] Focused programs with clear targets have been developed for fuel cell devices and systems in automotive, stationary, and portable systems. A key component in meeting the goals for each of these systems is the proton exchange membrane. Development efforts have thus far concentrated on the fabrication and design of fuel cell stacks using current materials. New materials must be able to meet the targets for advanced systems, while still remaining somewhat compatible with current hardware and system designs. This can only be accomplished through the directed synthesis of new copolymers with feedback from MEA and fuel cell technology developers.

11. Acknowledgments

12. References

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