

## Feature Article

# Sulfonated aromatic hydrocarbon polymers as proton exchange membranes for fuel cells

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## ABSTRACT

This article reviews recent studies on proton exchange membrane (PEM) materials for polymer electrolyte fuel cells. In particular, it focuses on the development of novel sulfonated aromatic hydrocarbon polymers for PEMs as alternatives to conventional perfluorinated polymers. It is necessary to improve proton conductivity especially under low-humidity conditions at high operating temperatures to breakthrough the current aromatic PEM system. Capable strategies involve the formation of well-connected proton channels by microphase separation between hydrophilic and hydrophobic domains and the increase of the ion exchange capacity of PEMs while keeping water resistance. Herein, we introduce novel molecular designs of sulfonated aromatic hydrocarbon polymers and their performance as PEMs.

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## 1. Introduction

Fuel cells are widely regarded as efficient and clean energy sources as alternatives to limited fossil fuel resources. Among them, polymer electrolyte fuel cells (PEFCs) offer many advantages such as high efficiency, high energy density, quiet operation, and environmental friendliness. Proton exchange membranes (PEMs) especially play an important role in PEFCs, which are responsible for proton transport from the anode to the cathode and the entire fuel cell performance. These membranes should meet several strict requirements as follows; reasonable proton conductivity, high stability and durability in the actual fuel cell environment, outstanding mechanical toughness, high heat endurance, and impermeability to fuel gas or liquid.

Current state-of-the-art PEM materials are perfluorinated polymers, such as Nafion® or Flemion® which have their good physical and chemical stability together with high proton conductivity under a wide range of relative humidity conditions at moderate operation temperatures (see Fig. 1) [1,2]. However, they suffer from such disadvantages as limited operation temperature (0–80 °C), high cost, insufficient durability and high methanol

permeability. To overcome these obstacles, extensive efforts have been made to develop alternative acid-functionalized aromatic hydrocarbon-based polymers [3–5] and a number of sulfonated aromatic polymers such as poly(phenylene)s [6,7], poly(ether ether ketone)s [8,9], poly(ether ether sulfone)s [10,11], poly(arylene ether)s [12,13], and polyimides [14–16] have been investigated as potential PEMs. Nevertheless, there are still unresolved practical application issues of these membranes due to low proton conductivity under low-humidity conditions, although they show high proton conductivity under high humidity conditions.

In general, the ion exchange capacity (IEC) is closely related to the proton conductivity of PEMs because the acid functionalities, such as sulfonic acid groups, contribute to the proton conduction in a membrane. Beyond a certain sulfonation degree, PEMs tend to absorb too much water or are even soluble in water, which negatively affect their mechanical resistance and water resistance [17,18]. Therefore, the improvement of proton conductivity using aromatic polymers with moderately adjusted IEC values has been under intense investigation [19–23]. To achieve high proton conductivity with moderate IEC values, the formation of ion channel structures, which enable effective proton conduction, has been studied. In the course of these studies, an ideal morphology has been pursued by microphase separation of segmented block copolymers in which hydrophilic sulfonated polymer segments form an interconnected three-dimensional network responsible for

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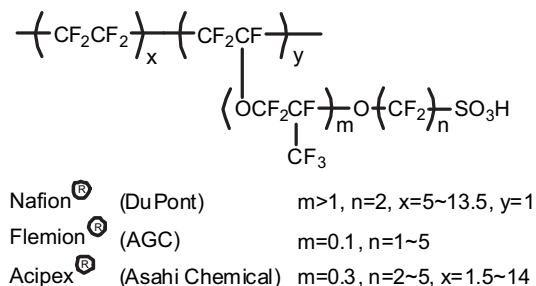


Fig. 1. Chemical structures of perfluorinated polymers.

efficient proton transport, while a complementary network of hydrophobic non-sulfonated segments imparts a reinforcing effect, preventing excessive swelling in water and enhancing the mechanical properties. An image of the ideal morphology for PEMs is shown in Fig. 2.

Actually, a wide variety of block copolymers consisting of hydrophilic and hydrophobic blocks and their phase-separated structures have been reported [24–29]. For example, amphiphilic multiblock copolymers are reported to form hydrophilic/hydrophobic phase-separated structures and their proton conductivity under low-humidity conditions has been improved (Fig. 3a) [24–28,30–33]. The introduction of branched polymers has also been attractive to attain such phase separation, while maintaining water stability (Fig. 3b). The details are discussed later.

As an alternative approach to achieve a similar phase-separated morphology, attention has been paid to locally and densely sulfonated polymers at definite positions within polymer chains or termini, which possess topologically different architectures compared to segmented block copolymers (Fig. 3c). By this approach, the cumbersome multi-step procedure generally needed for the synthesis of block copolymers is simplified, while the proton conducting performance remains intact.

Hay et al. reported poly(arylene ether)s with highly sulfonated units only at the end groups in order to enhance the difference in polarity between hydrophilic and hydrophobic units [20–23]. Their membranes showed a significantly phase-separated morphology. Unfortunately, their structures are limited in terms of number of sulfonated units because the number of terminated groups is only 2 or 3 per molecule. Furthermore, hydrophilic units at the periphery decrease the water resistance of polymers, which limits the increase of IEC values.

The key strategy to improve proton conductivity, especially under low-humidity conditions, is the formation of well-connected proton channels in PEMs. The simplest and most direct strategy to accomplish high proton conductivity seems to involve an increase in the IEC values of PEMs while keeping the membrane insoluble in

water (Fig. 3d). By increasing the number of acid functionalities, proton channels should become wider and well connected. Schuster et al. reported the synthesis of highly sulfonated poly(phenylene sulfone) (IEC = 4.5 meq./g) and very high proton conductivity, exceeding that of Nafion by a factor of 5–7 at high temperatures ( $T=110\text{--}160\text{ }^\circ\text{C}$ ) and low relative humidity (RH = 50–15%) [34]. Unfortunately, this film is totally soluble in water and unsuitable for practical use. In order to maintain stability in water, new specific designs are essential for main-chain structures; for instance, the introduction of rigid rod main chains and hydrophobic units such as fluorenyl, naphthyl units and so on. Of course, providing a sharp contrast of hydrophilic/hydrophobic phase-separated structures is also quite important to form well-connected proton channels, as described above.

In this article, recent progress in the development of aromatic PEMs is reviewed, especially focusing on the synthesis of poly(arylene ether)s, their characterization, and their performance as PEMs.

## 2. Sulfonated multiblock copoly(arylene ether)s

Multiblock copolymers comprised of plural continuous sequences of chemically dissimilar repeating units, are able to spontaneously assemble into a wide variety of nanostructures, such as sphere, cylinder, double gyroid, lamellae and so on. The morphology of such structures generally depends on the block composition and topology. As mentioned in the Introduction, the phase-separated morphology can be exploited for the construction of stable proton channels for PEM application, in which hydrophilic sulfonated polymer segments are responsible for the channels; whereas hydrophobic non-sulfonated segments prevent excessive swelling in water and enhance the mechanical properties.

In 2006, McGrath and coworkers reported the synthesis of multiblock sulfonated and fluorinated poly(arylene ether)s for PEMs [28,35]. The polymers contain perfluorinated poly(arylene ether) as the hydrophobic segment and highly sulfonated poly(arylene ether sulfone) as the hydrophilic segment, with the aim of providing polymeric materials possessing a highly phase-separated morphology. As depicted in Scheme 1, multiblock copoly(arylene ether)s were synthesized by polycondensation of the dialkali metal salt of bisphenol-terminated poly(arylene ether sulfone) and decafluorobiphenyl-terminated poly(arylene ether). The reaction proceeded readily and generated the expected copolymers in high yields. The polymer films had IEC values of 0.95–2.29 meq./g and showed water uptake ranging from 40 to more than 400%. These membranes showed excellent proton conductivity up to  $0.32\text{ S/cm}^{-1}$  in water (IEC = 2.29 meq./g). In particular, very high proton conductivity has still been observed under low humidity (RH ~ 40%) which is superior to Nafion 117. The tapping mode atomic force microscopy (AFM) images of the membranes revealed better-defined phase separation compared to random copolymers having similar chemical structures, which may possibly explain their higher proton conductivity.

The same group also reported the effect of the block length of multiblock copoly(arylene ether)s on the properties [35]. Three polymers, BisAF-BPSH( $x:y$ )K ( $x:y=3:3, 5:5, \text{ and } 8:8$ ), were prepared, where  $x$  and  $y$  represent the block length in g/mol of hydrophobic and hydrophilic units, respectively. Although BisAF-BPSH(8:8)K had the lowest IEC value (1.1 meq./g) and the lowest water uptake (42%) among BisAF-BPSH( $x:y$ )K copolymers, it exhibited the highest proton conductivity, comparable to Nafion 117 under low-humidity conditions. With an increase in block length, the extent of phase separation and the connectivity between the hydrophilic domains increases. This seems to be the driving force for proton transport.

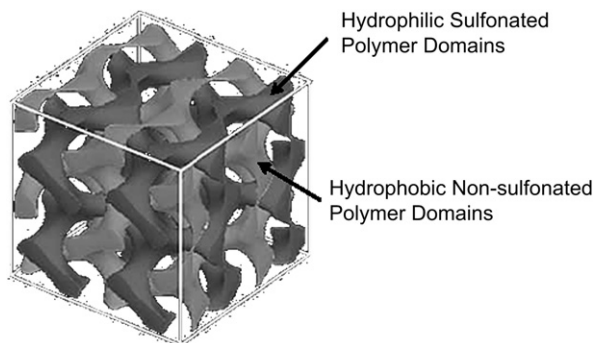


Fig. 2. Ideal morphology of PEMs.

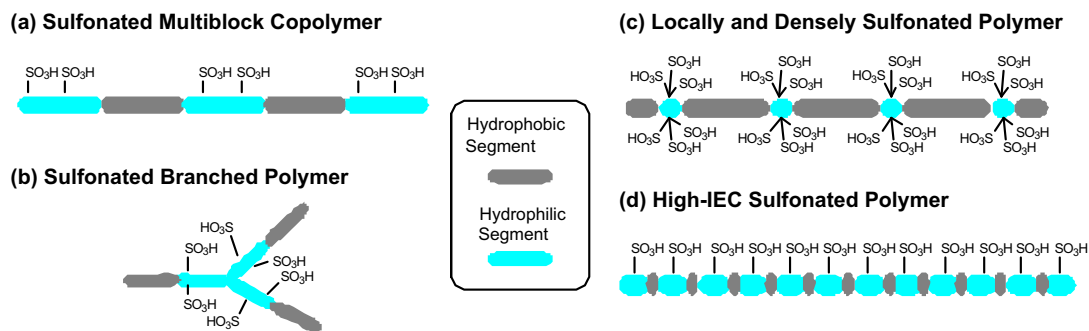


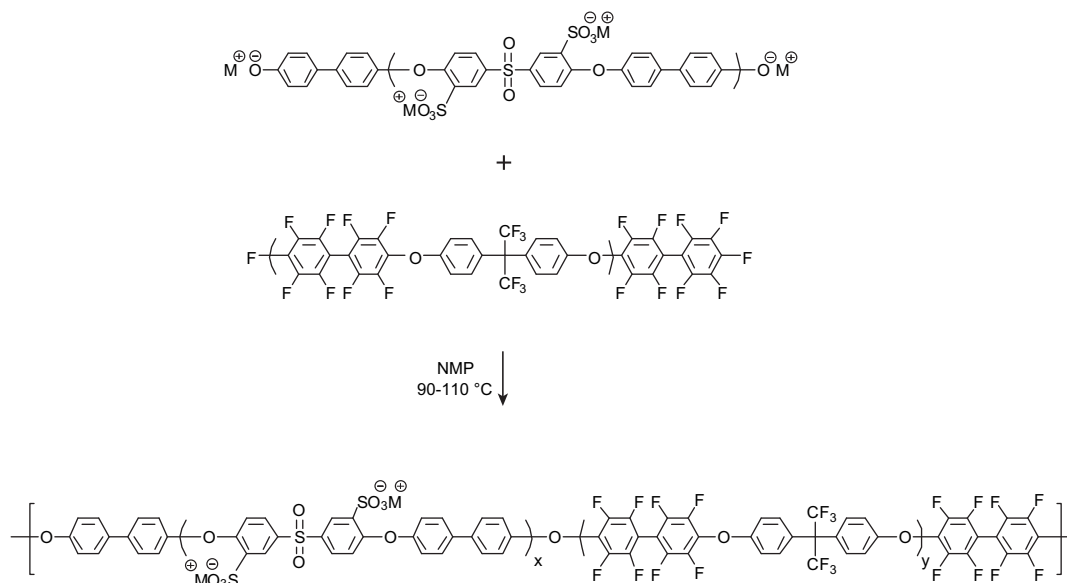
Fig. 3. Illustrations of several polymer architectures for PEMs.

A similar type of multiblock copoly(arylene ether sulfone) (Scheme 2) was also synthesized by the polycondensation of bisphenol-terminated poly(arylene ether sulfone) with highly fluorinated poly(arylene ether sulfone) and evaluated as a PEM [30]. The IEC values of the polymer films ranged between 0.9 and 1.5 meq./g. The polymer films possessing building blocks with the highest molecular weights, 15 K/15 K, showed outstanding proton conductivity, compared to Nafion even at low RH ( $\sim 30\%$ ).

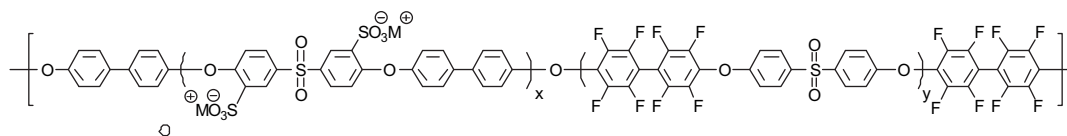
Another strong candidate for the hydrophobic blocks in multiblock copolymer-based PEMs is polyimide because of its high performance properties, such as excellent thermal stability, high mechanical strength, good film-forming ability, low gas permeability, and superior chemical resistance [32]. In order to improve the resistance toward the hydrolysis of imido rings under acidic conditions, the six-membered ring polyimide has been employed. The synthetic procedure is shown in Scheme 3. Amine-terminated sulfonated poly(arylene ether sulfone)s as hydrophilic blocks were prepared via polycondensation of 4,4'-dichlorodiphenyl sulfone, 4,4'-biphenol, and 3-aminophenol (end-capping reagent). On the other hand, naphthalene dianhydride-based polyimides as hydrophobic blocks were prepared via a one-pot imidization of 1,4,5,8-naphthalenetetracarboxylic dianhydride and bis[4-(3-aminophenoxy)phenyl]sulfone. A series of multiblock copolymers was synthesized by an imidization coupling reaction between both blocks in the mixed solvent of *m*-cresol and *N*-methylpyrrolidone (NMP). Transparent and ductile membranes were then prepared.

Their proton conductivity was measured under fully hydrated conditions in water at room temperature. The proton conductivity showed a linear correlation with the IEC and increased up to  $0.161 \text{ S/cm}^{-1}$  at an IEC of 1.9 meq./g. Unfortunately, hydrated films having IEC values larger than 2 meq./g showed poor mechanical strength. The morphologies of the multiblock copolymers were observed by AFM and their measurements revealed well-defined nano-phase separated morphologies. Additionally, a hydrolytic stability test of multiblock copolymer membranes in water at  $80^\circ\text{C}$  for 1000 h confirmed their high stability.

Recently, our group synthesized sulfonic copoly(ether sulfone)s by a chain extender methodology for use as PEMs [25,26]. As mentioned above, McGrath and coworkers reported the synthesis of multiblock sulfonated and fluorinated poly(arylene ether)s using decafluorobiphenyl (DFB) [28,35]. However, in their study, telechelic oligomers were prepared by the polymerization of 4,4'-hexafluoroisopropylidenediphenol or 4,4'-dihydroxydiphenyl sulfone with DFB, which means that DFB is a monomer and not a chain extender. A small amount of chain extender should be sufficient to prepare multiblock copolymers with high molecular weights. The synthetic procedure is depicted in Scheme 4. The multiblock copoly(arylene ether)s (IEC = 1.71–2.08 meq./g) were synthesized by polycondensation of three compounds, that is, hydrophilic dialkali metal salt of bisphenol-terminated poly(arylene ether sulfone), hydrophobic bisphenol-terminated poly(arylene ether sulfone), and the chain extender DFB.



Scheme 1. Synthesis of multiblock copoly(arylene ether)s by polycondensation of perfluorinated poly(arylene ether) and highly sulfonated poly(arylene ether sulfone).



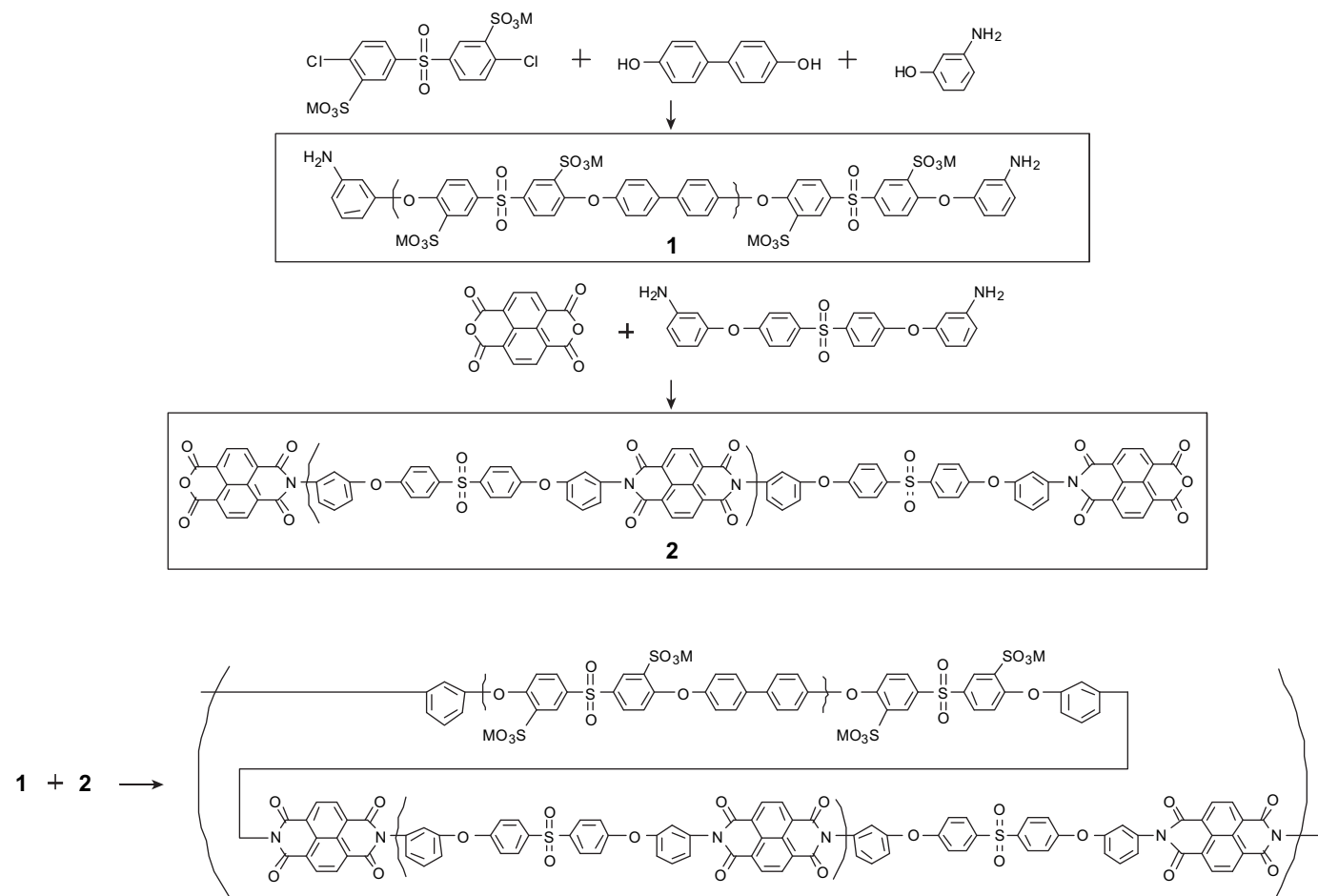
**Scheme 2.** Structure of multiblock copoly(arylene ether sulfone)s.

Due to the mild reaction conditions, no ether–ether interchange reaction was observed at all by  $^{13}\text{C}$  NMR. High molecular weight, tough, flexible, and transparent membranes could be obtained. In addition, all membranes demonstrated excellent oxidative and dimensional stability and good water uptake properties under low RH. The membranes maintained a relatively high proton conductivity of  $6.0 \times 10^{-3} \text{ S/cm}$  under 50% RH at  $80^\circ\text{C}$ . It was also confirmed that the proton conductivity was higher than that of random block copolymers with a similar composition. AFM observations of the multiblock copolymer membrane confirmed the formation of a clear hydrophilic/hydrophobic phase-separated structure, which gave good proton conductivity and dimensional stability simultaneously. It should be mentioned here that the obtained copolymers are not complete alternating multiblock copolymers in which each hydrophilic/hydrophobic segment is connected alternately, but are random multiblock copolymers. However, the aforementioned data indicate that the polymer structure of the obtained multiblock copolymers with the chain extender system is highly controlled.

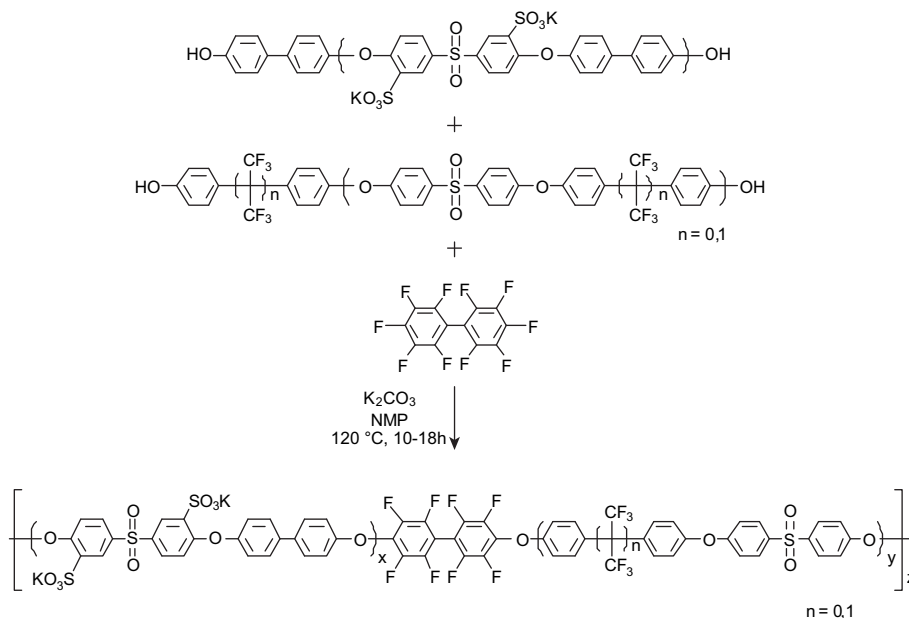
We further prepared several sulfonated multiblock copoly(ether sulfone)s by changing the hydrophilic/hydrophobic block lengths

and investigated the influence of each length on the membrane properties [26]. Polycondensation was carried out on hydrophilic sulfonated bisphenol-terminated poly(arylene ether sulfone) ( $M_n = 6000, 10\,000, 14\,000$ ), hydrophobic bisphenol-terminated poly(arylene ether sulfone) ( $M_n = 6000, 10\,000, 14\,000$ ), and DFB as the chain extender. Multiblock copoly(ether sulfone)s with high molecular weights ( $M_n > 50\,000, M_w > 150\,000$ ) were successfully obtained in all runs under moderate reaction conditions. All polymer membranes showed good oxidative stability for hot Fenton's reagent and good water uptake properties even under low RH. Particularly, the membranes possessing the longest block lengths demonstrated good proton conductivity of  $7.0 \times 10^{-3} \text{ S/cm}$  under 50% RH. From AFM images, the hydrophilic domains of the membranes are larger and better connected to each other, and that induces good proton conduction (Fig. 4a–c). In addition, transmission electron microscope (TEM) observation also confirmed the formation of cross-sectional phase separation of the membranes (Fig. 4d–e).

As mentioned above, our membranes consist of random multiblock copolymers in which hydrophilic and hydrophobic segments are statistically distributed. Thus, it is interesting to compare the properties of random multiblock copolymers and alternating



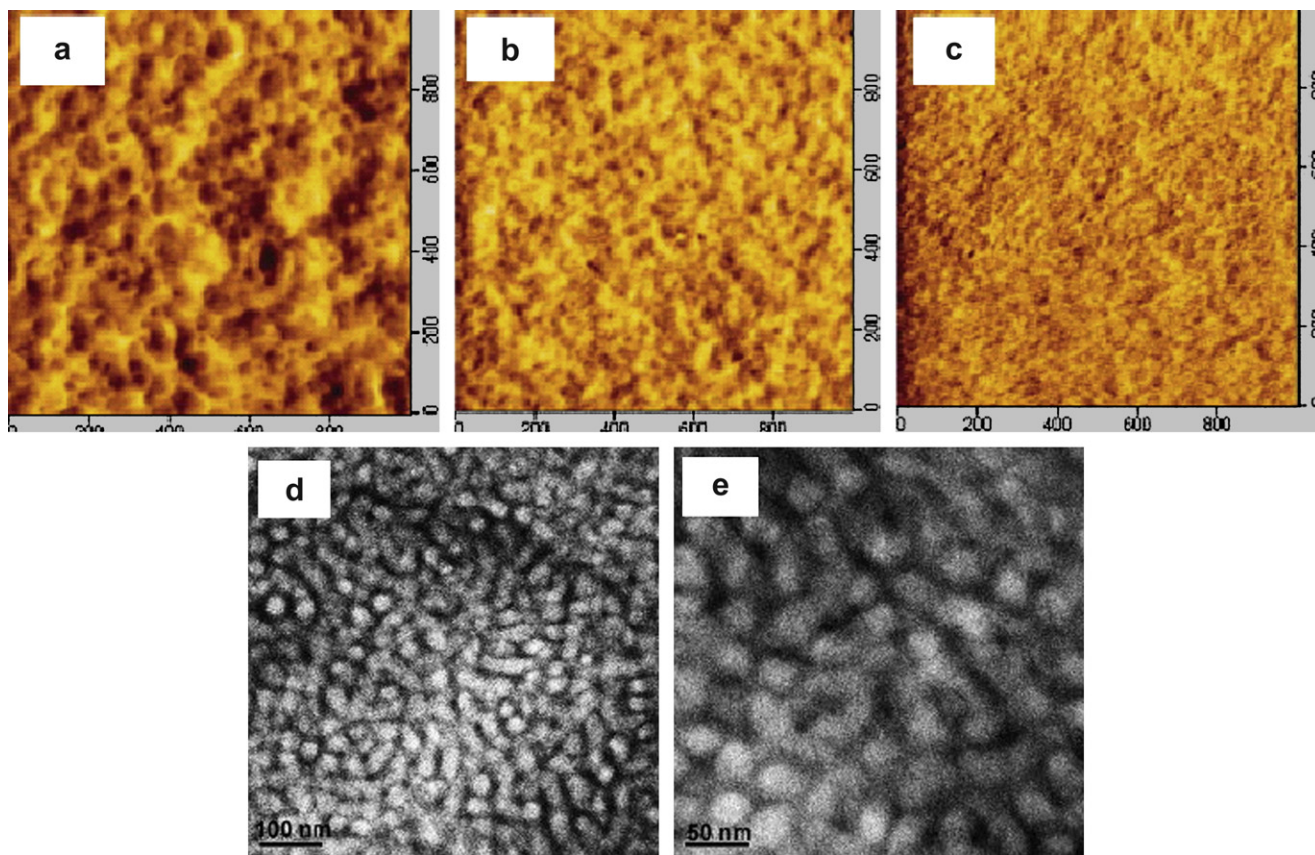
**Scheme 3.** Synthesis of multiblock poly(arylene ether sulfone)-*b*-polyimide.



**Scheme 4.** Synthesis of multiblock poly(arylene ether sulfone) by chain extender method.

multiblock copolymers in which hydrophilic and hydrophobic segments are alternately connected (see Fig. 5), because the latter is expected to produce a highly phase-separated morphology compared to the former. The alternating multiblock copolymers could be successfully synthesized by an end-capping method

(Scheme 5), and were investigated for water uptake and proton conductivity [27]. It should be noted that the synthetic method employed a very small amount of DFB for end capping. The results indicated that alternating multiblock copolymers showed better performance ( $8.6 \times 10^{-3}$  S/cm, 50% RH) than random multiblock



**Fig. 4.** AFM tapping mode phase images of multiblock copoly(ether sulfone)s with hydrophilic/hydrophobic block lengths: (a) 14 K/14 K, (b) 6 K/6 K, and (c) random block copoly(ether sulfone), and cross-sectional TEM images of multiblock copoly(ether sulfone)s with hydrophilic/hydrophobic (14 K/14 K) block lengths: (d) low resolution and (e) high resolution.

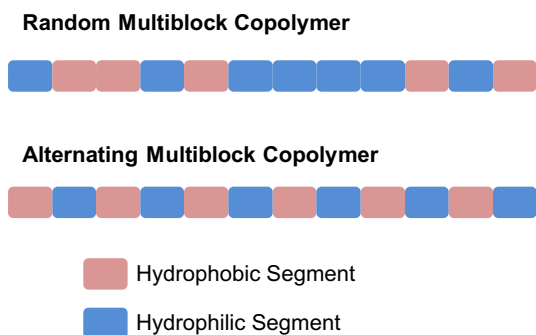


Fig. 5. Images of random multiblock copolymer and alternating multiblock copolymer.

copolymers ( $6.1 \times 10^{-3}$  S/cm, 50% RH) having similar IEC values ( $\sim 2$  meq./g).

### 3. Sulfonated poly(arylene ether)s with branched structures

Branched polymers, such as star-branched polymers, comb-shaped polymers, graft copolymers, dendrimers, and hyper-branched polymers, are well known to exhibit distinctly different properties from linear counterparts of similar compositions. As PEM materials, specific structural designs such as graft copolymers [36–39] and other branched polymers [20–23] have been reported to improve proton conductivity compared to that of conventional polymers.

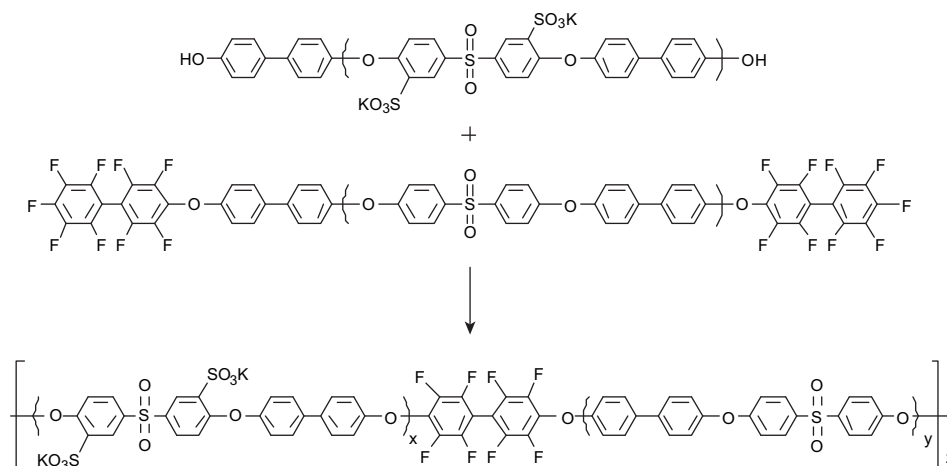
Ding et al. synthesized graft copolymers by copolymerization of styrene with poly(sodium styrene sulfonate) macromonomers [36]. The latter were prepared with controlled molecular weights and low polydispersities by stable free-radical polymerization. Membranes based on long hydrophilic graft chains are able to phase separately to a greater extent than those based on shorter ones. Furthermore, a continuous network of ion domains evolves with increasing IEC values. As a result, a phase-separated network of graft polymers with longer hydrophilic segments enhances proton conductivity in high-ionic-content regime.

Highly fluorinated graft copolymers have been developed as PEMs by Norsten et al. [37]. The molecular design was directed to a Nafion-like structure where a fluorinated hydrophobic backbone had flexible ionic grafted chains in order to create a defined polymer microstructure within the PEMs. In practice, the main chain polymer was composed of a highly fluorinated poly(arylene ether), while the grafted chain segments containing the ionic groups were composed

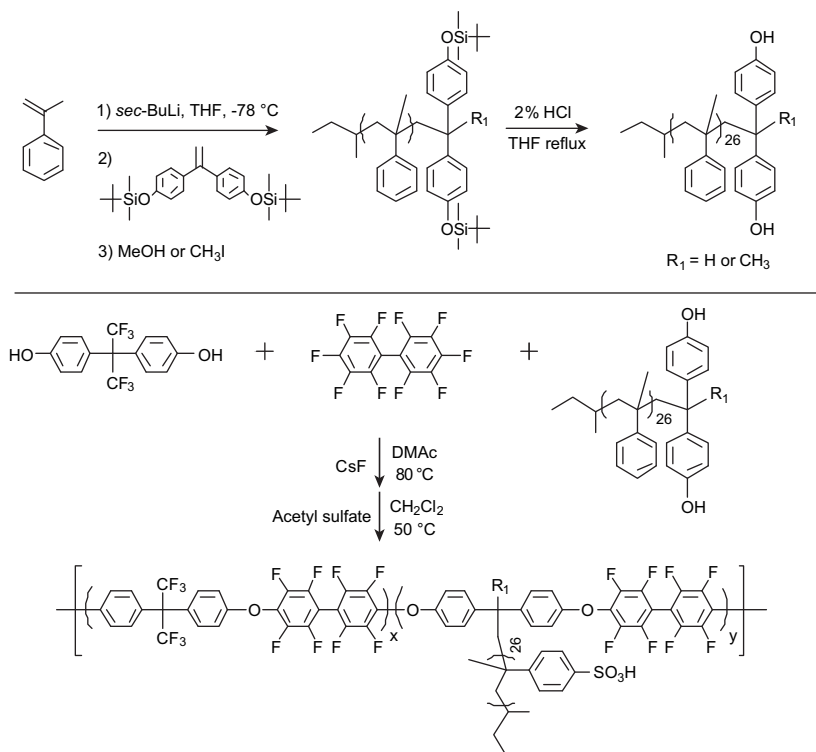
of monodisperse poly( $\alpha$ -methylstyrene sulfonate). Unlike Nafion, however, these grafted chains were relatively longer and contained multiple sulfonic acid groups. The synthetic strategy of graft copolymers is depicted in Scheme 6. First, living anionic polymerization of  $\alpha$ -methylstyrene was performed with *sec*-BuLi as the initiator in THF at  $-78^\circ\text{C}$ , followed by end-capping with 4,4'-di-*tert*-butyldimethylsilyloxy-1,1-diphenylethylene and quenching with methanol or methyl iodide. After deprotection under an acidic condition, a bisphenol grafted with poly( $\alpha$ -methylstyrene) ( $M_n = 2810$ , PDI = 1.09) could be obtained. Second, polycondensation of hexafluorobisphenol A, DFB, and the bisphenol grafted with poly( $\alpha$ -methylstyrene) was carried out in the presence of CsF in *N,N*-dimethylacetamide (DMAc) at  $80^\circ\text{C}$ . Third, the polymer was sulfonated with acetyl sulfate in  $\text{CH}_2\text{Cl}_2$  at  $50^\circ\text{C}$ . High-molecular-weight graft copolymers ( $>60$  K) were obtained. Polymers having IEC = 1.75 meq./g showed high proton conductivity (0.58 S/cm) when measured in water, which was almost twice as high as that of Nafion 117 (0.30 S/cm). TEM images of lead-stained grafted copolymer membranes clearly showed a high contrast between the hydrophobic and hydrophilic domains. Thus, branched architectures provided a positive effect on the microphase separation, which is highly responsible for the connectivity of proton channels.

By using this material, fuel cell performance has been demonstrated in a direct methanol fuel cell (DMFC) and  $\text{H}_2/\text{air}$  in comparison with that of sulfonated polysulfone (BPSH-35) and Nafion [38]. The low water uptake of graft copolymers enabled an increase in proton exchange site concentrations in the hydrated polymer, which was the desirable membrane property for DMFC application. The initial performance of the membrane electrode assemblies (MEAs) using BPSH-35 and graft copolymers was comparable to and higher than that of Nafion MEAs at all methanol concentrations.

Jannasch and coworkers opened the possibility to use phosphonic acid-based graft copolymers as PEMs in fuel cell application instead of sulfonic acid-based counterparts [39]. Polysulfones were successfully grafted with poly(vinylphosphonic acid) using an anionic grafting-from methodology, as shown in Scheme 7. The polysulfone was first lithiated with butyllithium at the ortho positions of sulfone links, then capped with 1,1-diphenylethylene to generate 1,1-diphenylalkyl anions, followed by anionic polymerization of diethyl vinylphosphonate. The resulting membranes were phase-separated because of the inherent immiscibility of the stiff and hydrophobic backbone polymer and the strongly hydrogen-bonded grafted chains. The poly(vinylphosphonic acid) grafted chains thus formed separate phases in the membranes with very high local concentrations of interacting phosphonic acid units,

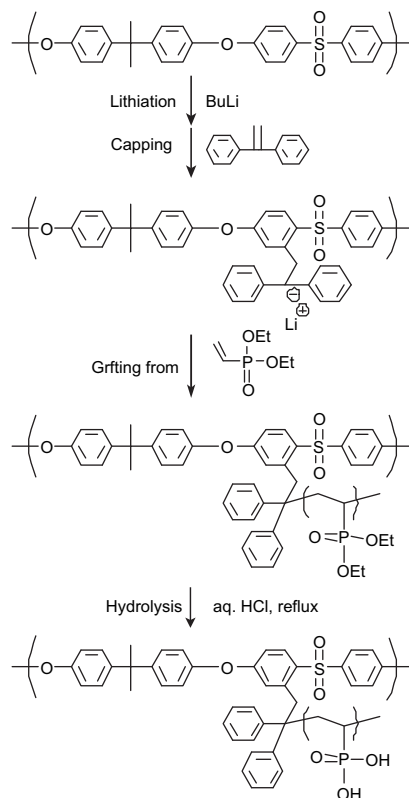


Scheme 5. Synthesis of alternating multiblock copolymer by end-capping method.



**Scheme 6.** Synthesis of macromonomer and sulfonated graft copolymer.

giving rise to large hydrogen-bonded aggregates. These aggregates are essential for efficient proton conductivity in the nominally dry state. At 120 °C, the membrane with the poly(vinylphosphonic acid)



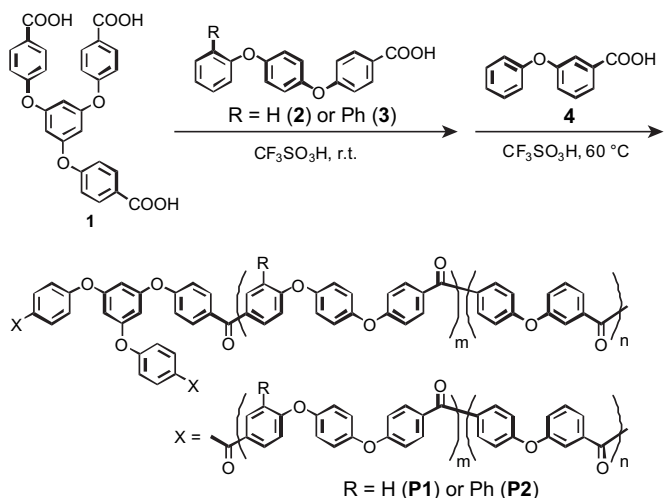
**Scheme 7.** Synthesis of polysulfone grafted with poly(vinylphosphonic acid).

content (57 wt%) reached a conductivity of  $4.6 \times 10^{-3}$  S/cm under nominally dry conditions and 0.093 S/m under 100% RH.

Recently, we designed unique star-shaped block copolymers with AB block copolymers as arms [29]. The AB block copolymers are composed of hydrophilic and hydrophobic segments, where the hydrophilic segments are attached to the core, and the hydrophobic ones are placed at the periphery of the star polymers. Since hydrophilic segments are localized around the core, a large difference in polarity between the hydrophilic and hydrophobic segments, which would induce defined phase-separated structures, is expected. An additional advantage is that hydrophobic segments at the periphery of the star polymers enhance their water insolubility and dimensional stability.

The star-shaped block copolymers were prepared by polycondensation of the tri-functional core, 1,3,5-tri(4-carboxyphenoxy)benzene (**1**) with either of two types of carboxylated phenylene ethers as an AB monomer (**2** or **3**), followed by 3-phenoxybenzoic acid (**4**) using trifluoromethanesulfonic acid as the solvent and activating reagent, as shown in Scheme 8. The polymer solution was conducted at 60 °C and the reaction was continued for 24 h to give star-shaped block copolymers **P1**, which have AB block copolymers composed of poly(ether ether ketone) and poly(ether ketone) segments. Polymers **P2** were also prepared in the same manner using monomer **3** instead of monomer **2**.

Differential scanning calorimetry (DSC) measurements were performed to characterize the polymer structures. Two distinct transition temperatures corresponding to each polymer domain could be observed, indicating the desired block polymer structure. Selective sulfonation onto the inner poly(ether ether ketone) segments is a big issue in preparing amphiphilic block copolymers. Phenyl rings activated by two phenoxy units in poly(ether ether ketone)s and pendant phenyl groups were easily sulfonated by concentrated sulfuric acid under mild conditions, because sulfonation was an electrophilic reaction. On the contrary, poly(ether ketone) segments could not be sulfonated under mild conditions at all

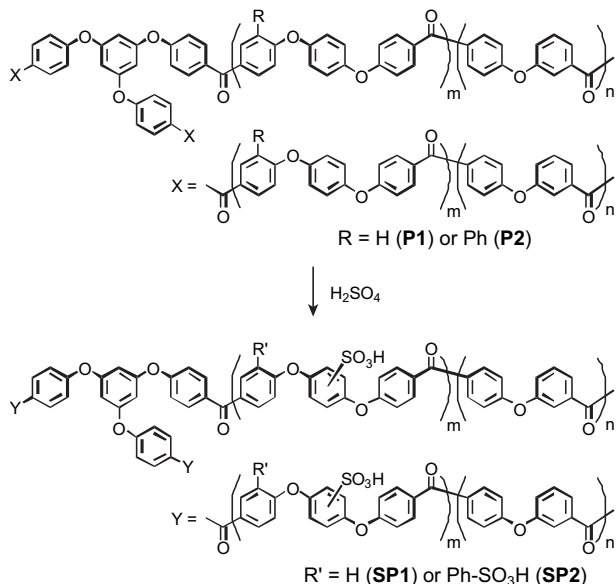


Scheme 8. Synthesis of star-shaped copolymers **P1** and **P2**.

because all of the phenyl rings were deactivated by strong electron-withdrawing carbonyl groups. Therefore, sulfonations of **P1** and **P2** were performed using concentrated sulfuric acid at 45 °C to accomplish selective sulfonation to the poly(ether ether ketone) segments (see Scheme 9).

All sulfonated polymers were readily soluble in polar aprotic solvents and gave tough and flexible membranes by solvent casting. The IEC values ranged from 1.77 to 2.18 meq./g as determined by titration. The thermal and oxidative stabilities of **SP1** and **SP2** were corroborated by thermogravimetry (TG) and exposition with hot Fenton's reagent, respectively. The high oxidative-stability of the polymers may be derived from the surrounding hydrophobic segments.

Water uptake is closely related to membrane properties such as proton conductivity, dimensional stability, and mechanical strength. Generally, water in a membrane acts as a transportation medium of protons for sulfonated polymer systems and enables high proton conduction. Water uptake at 95% RH was in the range of 20–26%, and was decreased by decreasing relative humidity, reaching below 10% at 50% RH for all samples.



Scheme 9. Sulfonation of **P1** and **P2**.

Proton conductivity was measured for the **SP1** and **SP2** membranes at 80 °C in the range of 50–95% RH. The results are shown in Fig. 6, in comparison with those of Nafion 117. At 95% RH, the **SP1** and **SP2** membranes showed comparable or even higher proton conductivity than Nafion 117. Generally, sulfonated aromatic polymers require high IEC values to attain high proton conductivity because of the lower acidity of sulfonic acid groups, the smaller flexibility, and the smaller hydrophilic/hydrophobic difference compared to Nafion. In this case, the **SP1** and **SP2** membranes also require high IEC values over 1.8 meq./g to achieve high proton conductivity, while that of Nafion 117 is only 0.91. Proton conductivity decreased by decreasing the relative humidity for all samples. The humidity dependence of the **SP2** membranes was smaller than that of the **SP1** membranes. Especially, the **SP2b** (IEC = 2.18 meq./g) membrane showed high proton conductivity of 0.014 S/cm even at 50% RH, which was comparable to that of Nafion 117 (0.021 S/cm at 50% RH). Thus, the effectiveness of topological star-branched structures where hydrophilic domains are covered by hydrophobic domains has been attested, maintaining good proton conductivity at low RH.

#### 4. Locally and densely sulfonated polymers

There are many reports on PEMs using amphiphilic segmented block copolymer systems as mentioned above. By introducing hydrophilic and hydrophobic units in a single molecule, well-defined phase-separation, which allows effective proton conduction, is formed in those systems. The key point of the systems is to make a high contrast in polarity between hydrophilic and hydrophobic units. On the other hand, locally and densely sulfonated homopolymers, in which the concentrated sulfonic acid units in a membrane allow for the creation of hydrophilic domains (making the matrix be hydrophobic), have not ever been investigated as another approach to efficient PEMs. Quite recently, Hay and our group independently developed a novel concept of the use of such polymers. These architecturally novel classes of polymers are capable of better microphase separation of the nonpolar and ionic moieties which enhance proton conductivity than that of random copolymers.

Hay and coworkers reported the synthesis of end-functionalized poly(sulfide ketone)s with six sulfonic acid moieties at the  $\alpha,\omega$ -chain ends for PEMs [20]. They designed an end group with a definite number of pendant phenyl rings providing selective sulfonation sites and soluble, non-fluorinated, chemically stable, and wholly aromatic poly(sulfide ketone)s as the main chains. The synthetic outlines are illustrated in Scheme 10.

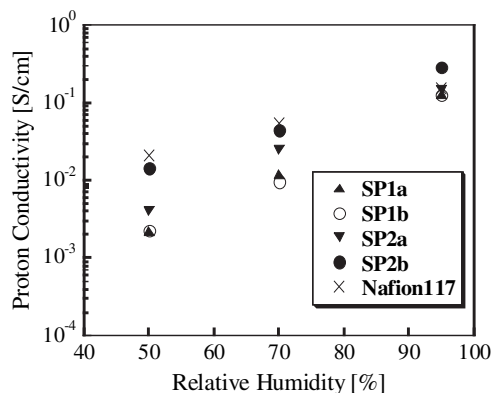


Fig. 6. Relative humidity dependence of proton conductivity of **SP1a** (IEC = 1.77 meq./g), **SP2a** (IEC = 1.98 meq./g), **SP2a** (IEC = 1.80 meq./g), **SP2b** (IEC = 2.18 meq./g), and Nafion 117 at 80 °C.



Aromatic dihalides (**2**) and aromatic dithiols (**3**) bearing at least one ketone group on each phenyl ring were employed as monomers to ensure the stability of the main chain toward sulfonation. At first, end-capped poly(sulfide ketone)s were synthesized by the condensation of aromatic dihalide (**2**) and aromatic dithiol (**3**) in the presence of 1-(4-hydroxyphenyl)-2,3,4,5,6-pentaphenylbenzene (**1**). Subsequent sulfonation was done with sulfonyl chloride followed by hydrolysis with a KOH aqueous solution. The analytical results indicated that selective and quantitative sulfonation occurred exclusively only at the chain end groups in the poly(sulfide ketone)s. Actually, the synthesized polymers achieved relatively high proton conductivity ( $3.7\text{--}6.9 \times 10^{-3}$  S/cm) with a very low IEC (0.47–0.48 meq./g) at 100% RH compared to randomly sulfonated PEMs with the same IEC. However, it is difficult to increase the IEC of poly(sulfide ketone)s and their proton conductivity based on this methodology because the sulfonated groups are located only at two chain ends.

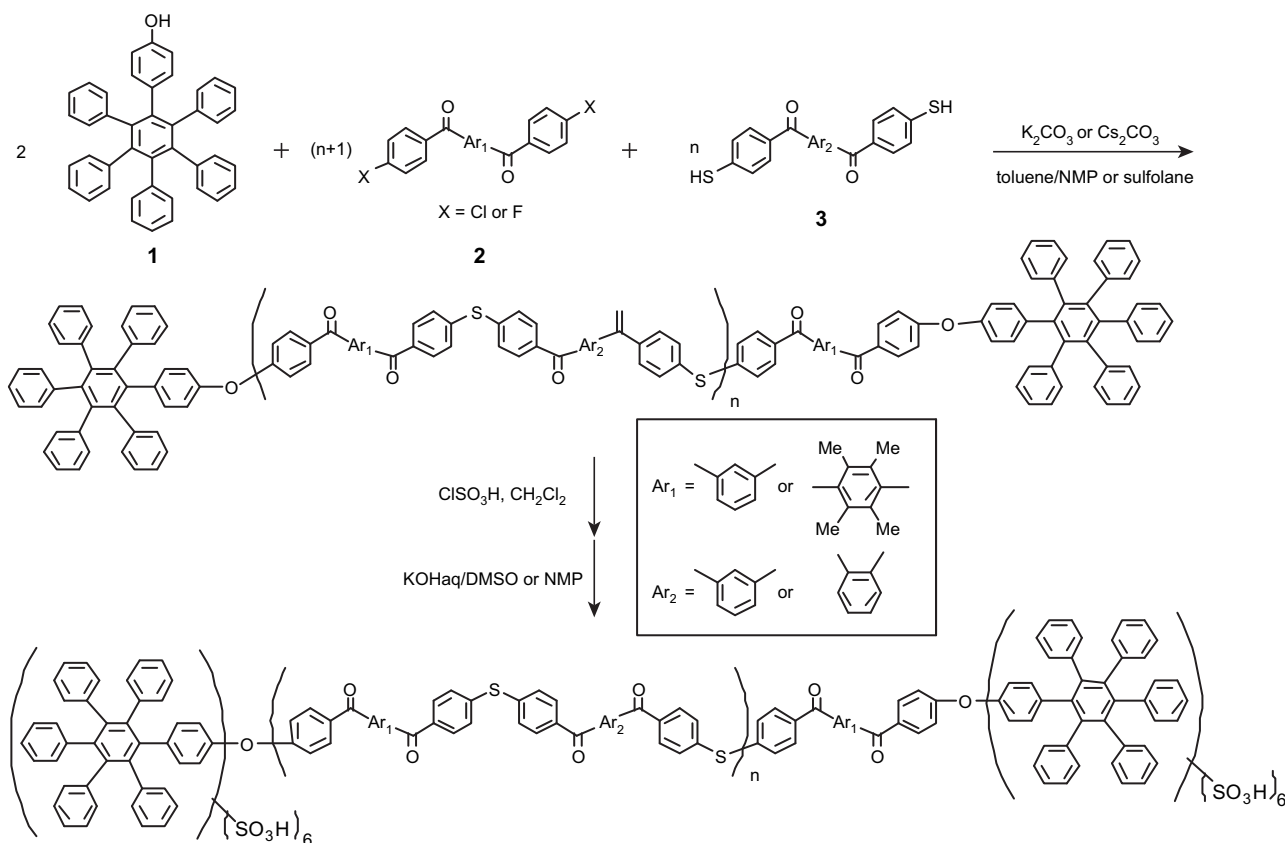
As an extensive work, Hay and coworkers synthesized branched poly(ether ketone)s bearing 6 or 8 sulfonated groups at each of the chain ends by a similar approach in order to increase the IEC (see Fig. 7) [21,22]. Indeed, the IEC could be increased to 1.25 meq./g and the polymer membrane showed better proton conductivity.

The new concept of localizing and concentrating sulfonic acid moieties into a polymer has been successfully demonstrated to some extent; however the structures are still limited in the number of sulfonated units because the number of termini is restricted. Furthermore, hydrophilic units at the periphery increase the water solubility of polymers, which prevents an increase in IEC values. Therefore, very high proton conductivity is not expected from this methodology. For this reason, star-shaped sulfonated block copoly(ether ketone)s with inner hydrophilic segments surrounded by

outer hydrophobic segments was newly developed by us, as already mentioned above [29]. We intended to apply that idea to random copolymer systems by introducing densely sulfonated hydrophilic units because the use of a linear homopolymer system is simple and direct [40,41]. The locally and densely sulfonated units in random copolymers are expected to produce clear phase-separated structures, which can induce effective proton conduction.

As shown in Scheme 11, random copoly(ether sulfone)s (**SP3**) could be synthesized via nucleophilic aromatic substitution polymerization and sulfonated with chlorosulfonic acid. Generally, the introduction of sulfonic acid moieties by chlorosulfonic acid preferentially occurs on electron-rich aromatic rings because sulfonation is an electrophilic reaction. In this case, each phenyl ring of the 2-phenylphenoxy groups was mono-sulfonated; therefore, the number of sulfonic groups per monomer unit was 8. There was no observation of the sulfonation of phenylene units in the hydrophobic part. The feed ratio of bisphenol monomers and 2,2-bis(4-hydroxyphenyl)hexafluoropropane (Bis-AF) was varied to prepare polymers with different IEC values.

In order to further synthesize similar poly(ether sulfone)s with increased sulfonic groups, another approach was employed. The synthetic outline is shown in Scheme 12. By using concentrated sulfuric acid, it was possible to sulfonate a phenylene ether unit next to the multifunctional phenylene core in the main chain in addition to pendant aromatic groups. Therefore, the number of sulfonic groups per monomer unit was increased from 8 to 10. To prevent unwanted sulfonation of the hydrophobic part, we selected random copolymers containing poly(ether sulfone) units in both the hydrophilic and hydrophobic parts, which were not sulfonated by concentrated sulfuric acid due to deactivation with electron-withdrawing sulfone groups. The polymers were prepared via



Scheme 10. Synthesis of end-functionalized poly(sulfide ketone)s with 6 sulfonic acid moieties at  $\alpha,\omega$ -chain ends.

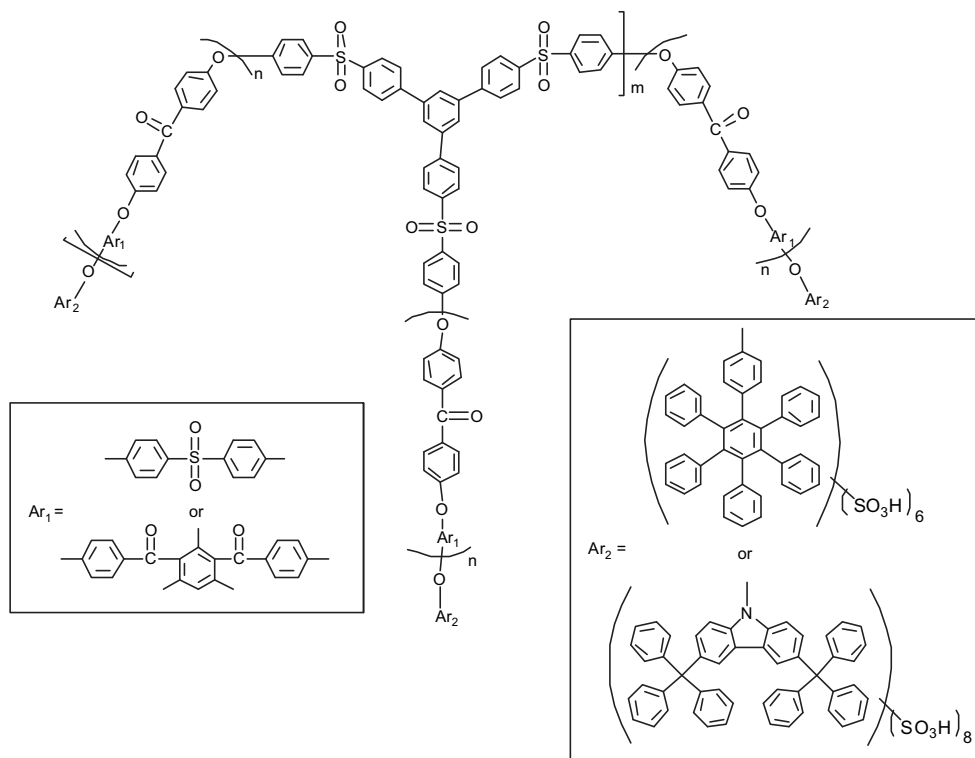
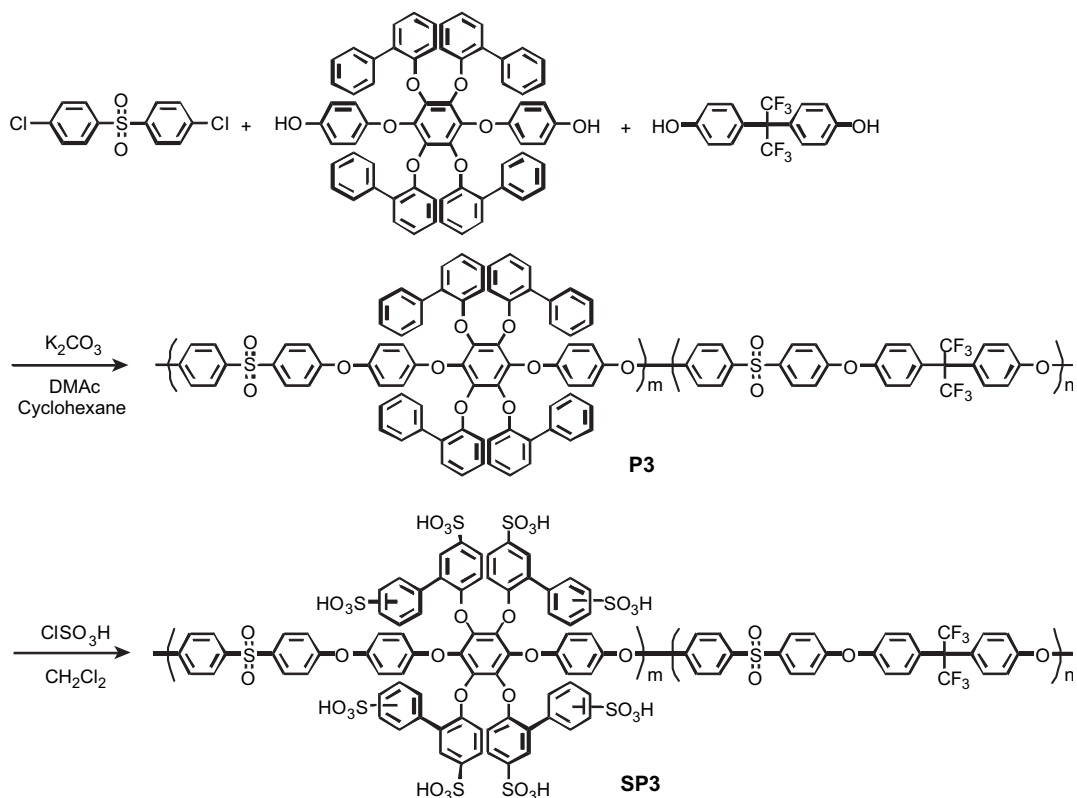


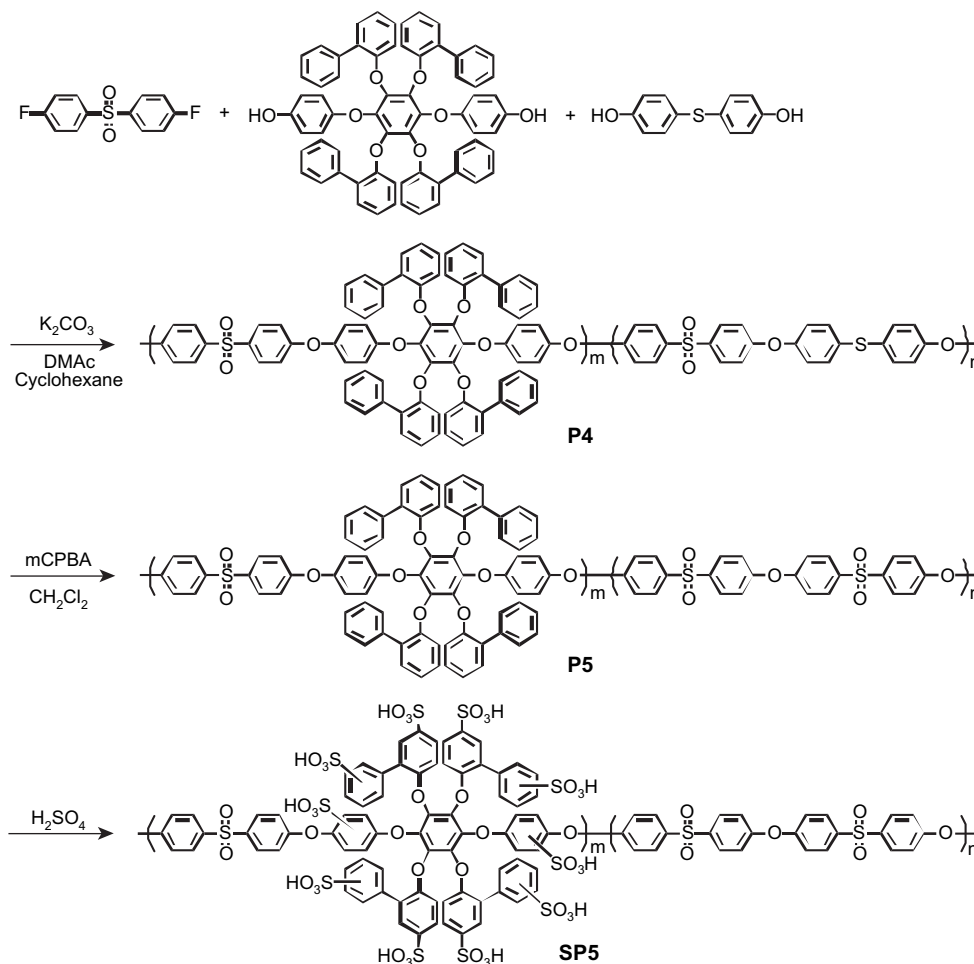
Fig. 7. Structures of branched polymers functionalized with 6 or 8 sulfonic acid moieties at each chain end.

nucleophilic aromatic substitution polymerization, followed by oxidation of sulfide bonds to sulfone bonds using *m*-chloroperoxybenzoic acid as oxidant and sulfonation with concentrated sulfuric acid (Scheme 12).

The thermal stability of **SP3** and **SP5** was evaluated by TG. For all samples, a three-step weight loss was observed from 50 to 200 °C, from 320 to 450 °C, and above 450 °C. The first weight loss is due to the evaporation of hydrated water, and the second and third ones



Scheme 11. Synthesis of poly(ether sulfone) bearing 8 sulfonic acid moieties randomly distributed within the chains.



**Scheme 12.** Synthesis of poly(ether sulfone) bearing 10 sulfonic acid moieties randomly distributed within the chains.

correspond to the decomposition of the sulfonic acid groups and the polymer main chains, respectively. The oxidative stability of the **SP3** and **SP5** membranes was evaluated with hot Fenton's reagent (80 °C) for 1 h as an accelerated test (Table 1). For all samples, no weight loss was observed and their film properties, such as flexibility and transparency, were maintained even after the test. Dimensional changes in both the length and thickness directions of the polymer membranes increased by increasing the IEC values. Moreover, all membranes exhibited isotropic swelling.

The water uptake of the **SP3** and **SP5** membranes was investigated after being immersed in water (Table 1). As expected, the water uptake increased by increasing the IEC values. The rigidity of the poly(ether sulfone) units enabled the preparation of water-insoluble polymers with high IEC values up to 2.4 meq./g, while the **SP3** system with an IEC value of 2.4 meq./g was soluble in water.

**Table 1**  
Properties of **SP3** and **SP5**.

Sample	IEC <sup>a</sup> (mequiv/g)	IEC by titration <sup>b</sup>	Water uptake (%)	$\Delta l$	$\Delta t$	Water residue <sup>c</sup> (%)
<b>SP3a</b>	1.77	1.80	36.5	0.12	0.12	100
<b>SP3b</b>	1.99	2.03	197	0.34	0.38	100
<b>SP5a</b>	1.97	1.96	68.3	0.10	0.11	100
<b>SP5b</b>	2.20	2.21	82.6	0.21	0.24	100
<b>SP5c</b>	2.40	2.38	108	0.35	0.34	100

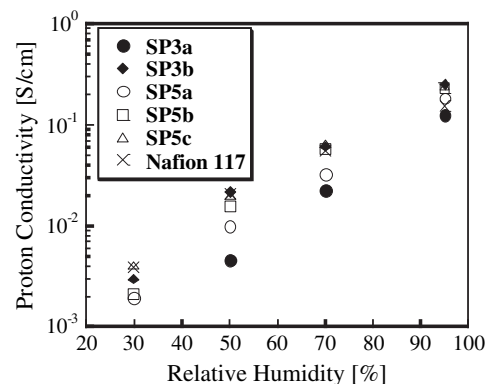
<sup>a</sup> Theoretical IEC value.

<sup>b</sup> Determined by titration with 0.02 M NaOH aq.

<sup>c</sup> After treatment with Fenton's reagent (3% H<sub>2</sub>O<sub>2</sub> aq containing 2 ppm FeSO<sub>4</sub>).

Moreover, the **SP5c** membrane exhibited smaller water uptake (108%) than the **SP3b** membrane (197%). The humidity dependence of the water uptake was measured for the **SP3** and **SP5** membranes at 80 °C. For all samples, the water uptake tended to decrease by decreasing the relative humidity. Among them, **SP3b** and **SP5c** showed higher water uptake over the measured range. They exhibited high water uptake of around 10% even at 30% RH.

The humidity dependence of the proton conductivity of the **SP3** and **SP5** membranes was measured at 80 °C in a range of 30–95% RH. The results are shown in Fig. 8, in comparison with those



**Fig. 8.** Relative humidity dependence of proton conductivity of **SP3**, **SP5**, and Nafion 117 at 80 °C.

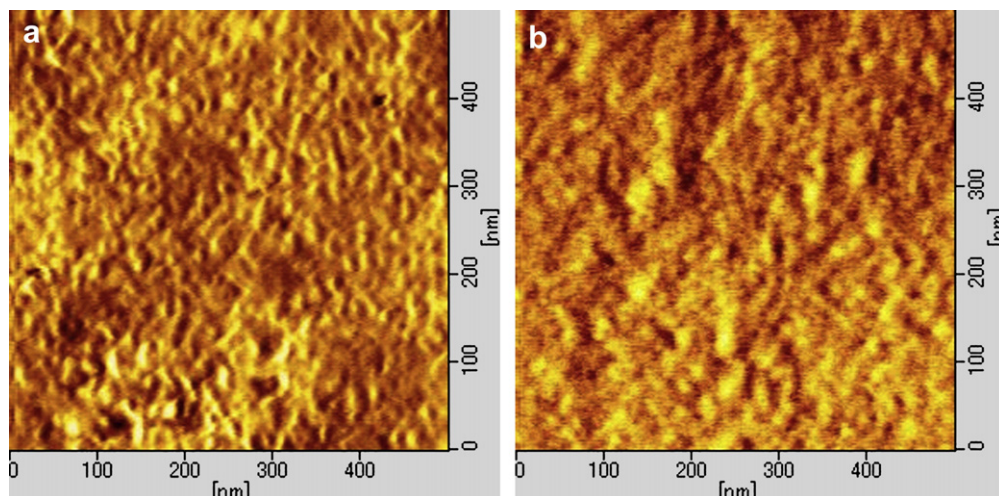
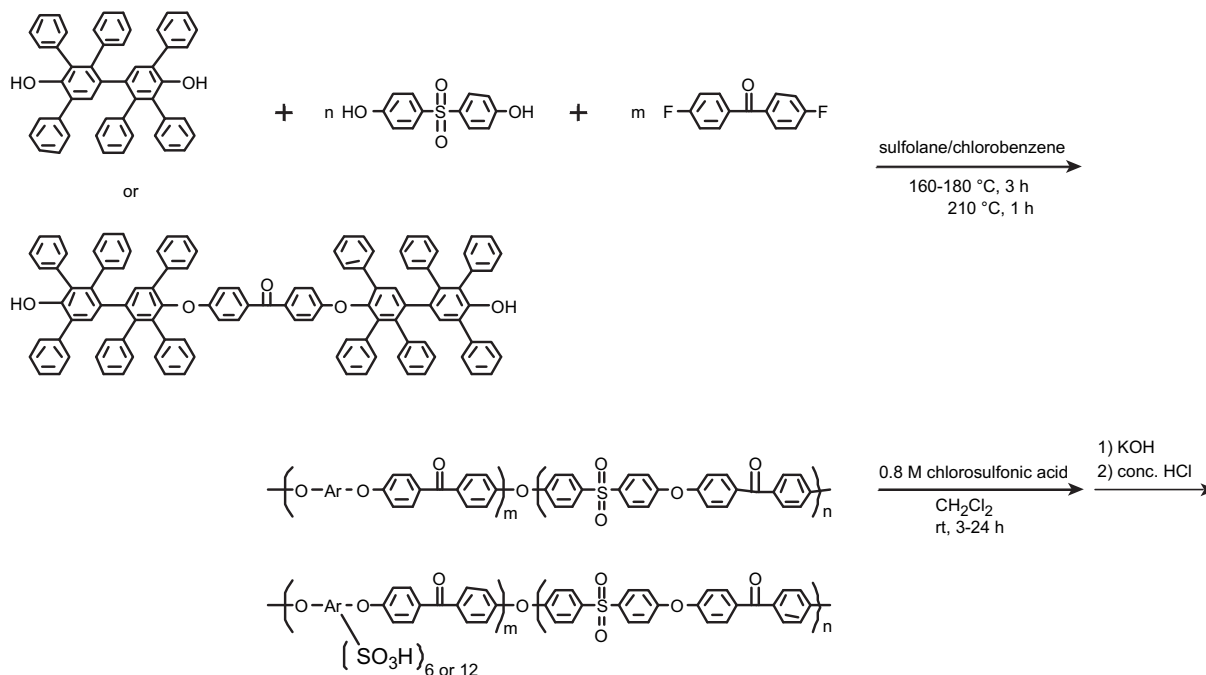


Fig. 9. AFM tapping phase images of (a) **SP3b** (b) **SP5c**.

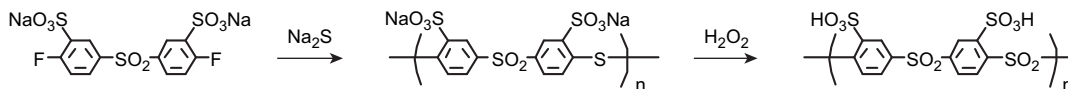
of Nafion 117. All the membranes exhibit comparable or even higher proton conductivity than that of Nafion 117 at 95% RH. However, the difference in proton conductivity among the membranes was more pronounced under low-humidity conditions. The **SP3a** membrane showed the highest humidity dependence. This is due to its relatively low IEC value. The humidity dependence of proton conductivity became smaller by increasing the IEC values. The proton conductivity of the **SP5c** membrane at 30% RH was  $4.0 \times 10^{-3}$  S/cm, two times higher than that of the **SP5a** membrane. Generally, the vehicle mechanism, in which protons are transferred by the migration of hydronium ions ( $\text{H}_3\text{O}^+$ ), is dominant in sulfonated polymer systems under low-humidity conditions. Therefore, the difference in proton conductivity of the **SP5** membranes under low-humidity conditions is explained as follows; the proton paths of the **SP5c** membrane are more connected than those of the **SP5a** and **SP5b** membranes due to its higher IEC value, and enable effective

migration of hydronium ions. Moreover, the proton conductivity of the **SP5c** membrane ( $4.0 \times 10^{-3}$  S/cm) was comparable to that of Nafion 117 ( $3.9 \times 10^{-3}$  S/cm) at low (30%) RH. These results suggest that the **SP5c** membrane has well-connected proton paths, as with Nafion 117.

Tapping mode phase images of the **SP3b** and **SP5c** membranes were recorded under ambient conditions on a scale of  $500 \times 500 \text{ nm}^2$  to clarify their hydrophilic/hydrophobic morphology (Fig. 9). The bright and dark regions are derived from hard segments corresponding to hydrophobic units and soft segments corresponding to hydrophilic units containing water, respectively. Both membranes showed well-defined phase-separated structures and hydrophilic domains, which are assigned to the dark region, and were connected to each other. Compared to the **SP3b** membrane, the hydrophilic domains of the **SP5c** membrane seem to be wider and more connected than those of membrane **SP3b**. The difference in morphology between the **SP3b** and **SP5c** membranes is caused by the difference in



Scheme 13. Synthesis of poly(arylene ether) bearing 6 or 12 sulfonic acid moieties randomly distributed within the chains.



**Scheme 14.** Synthesis of sulfonated poly(phenylene sulfone).

the IEC values. This result agrees well with the results from the proton conductivity of the **SP5c** membrane, especially under low-humidity conditions.

Hay and coworkers have also developed a multiblock copoly-(ether sulfone) in which sulfonic acids were locally and densely introduced within the main chain at definite interval positions [23]. However, simultaneously introduced hydrophobic dendritic units prevented an increase in the IEC values (IEC = 1.35 meq./g), even the existence of 12 and 15 sulfonic acid moieties at each monomer unit and chain end, respectively. In addition, analysis of proton conductivity could not be done because of the brittle films. Quite recently, the same group reported PEMs and their fuel cell performance from poly(arylene ether) containing 6 or 12 randomly distributed sulfonic acid moieties [42]. As depicted in Scheme 13, polycondensation of multi-functionalized biphenol with phenyl groups, bis(4-hydroxyphenyl) sulfone, and 4,4'-difluorobenzophenone was carried out, followed by a reaction with chlorosulfonic acid and hydrolysis in an alkali solution. The larger sulfonated clusters in the polymers resulted in higher proton conductivity and much better cell performance than polymers with smaller sulfonated clusters. The highest power density of a fuel cell using these materials (IEC = 1.16 meq./g) was 0.29 W/cm<sup>2</sup> at an effective work potential of 0.6 V, better than Nafion 117 showing 0.21 W/cm<sup>2</sup> at an effective work potential of 0.5 V. The TEM images of the polymers revealed a phase separation similar to Nafion, which may explain their high proton conductivity and good cell performance.

### 5. Sulfonated aromatic hydrocarbon polymers with high IEC values

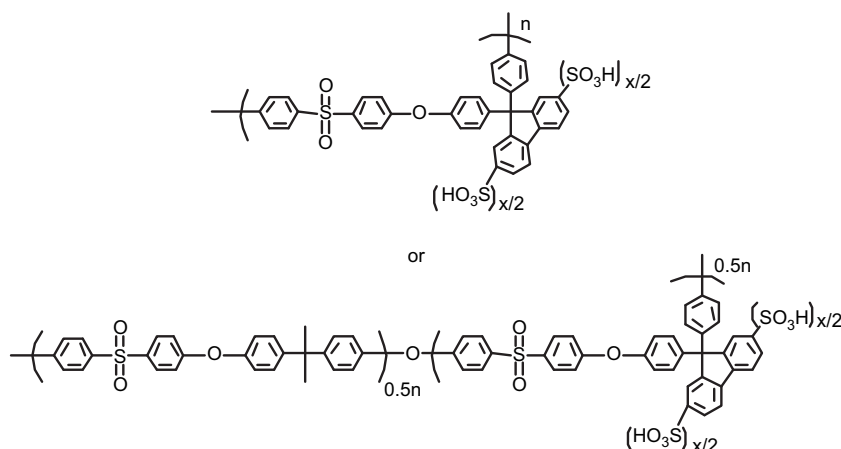
The simplest and most promising approach among all methodologies accessible for the improvement of proton conductivity is to increase the IEC values of PEMs. By increasing the IEC values, the proton channels should become wider and better connected. Schuster et al. reported the synthesis of 100% sulfonated poly(phenylene sulfone) with extremely high IEC values (IEC = 4.5 meq./g) and its application to PEMs [34]. The preparation succeeded in a two-step process involving a polycondensation

reaction of sulfonated difluorodiphenyl sulfone with sodium sulfide, yielding sulfonated poly(phenylene sulfide sulfone), and subsequent oxidation of the targeted poly(phenylene sulfone) (Scheme 14).

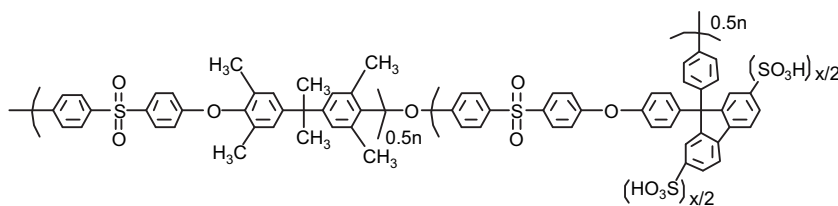
Molecular weights of up to  $M_w \sim 61,000$  g/mol were obtained, corresponding to intrinsic viscosities of up to 0.73 dL/g. The obtained polymers exhibited a very high density (1.75 g/cm<sup>3</sup> in dry state), no glass transition or melting temperature, and very high thermo-oxidative and hydrothermal stability. The latter is attributed to the specific molecular structure comprised of extremely electron-deficient aromatic rings. At high temperatures (110–160 °C) and low relative humidity (RH = 50–15%), the proton conductivity exceeded that of Nafion by a factor of 5–7. However, the polymers were water-soluble and film-forming properties were rather poor (brittle in the dry state), as described in the paper. Therefore, it is highly necessary to form insoluble and dimensionally stable membranes while keeping a high level of IEC values.

Watanabe and coworkers reported the synthesis of novel sulfonated poly(arylene ether) ionomers containing fluorenyl groups which generate a large free volume [43]. The chemical structure of the ionomers is shown in Scheme 15. Careful sulfonation reaction afforded ionomers regioselectively substituted with sulfonic acid groups on the 2,7-positions of pendant fluorenyl groups. The ionomers possessed high molecular weight ( $M_w > 2 \times 10^5$ ,  $M_n > 4 \times 10^4$ ) to give tough and flexible membranes. Under dry conditions, the ionomers were stable up to 250 °C without any thermal transitions or decomposition. Under wet conditions at 140 °C and 100% RH, the ionomers did not show any hydrolytic degradation for 700 h. It was assumed that the pendant fluorenyl groups are effective to improve the hydrolytic stability of the ionomers. The membrane with an IEC value of 1.14 meq./g showed proton conductivity comparable to Nafion 112 and the highest conductivity (0.2 S/cm) was obtained at 140 °C and 100% RH. In addition, the hydrogen and oxygen permeability of the membranes were much lower than that of Nafion 112 under a wide range of conditions (40–120 °C and 0–90% RH).

As an extension of this work, poly(arylene ether sulfone) ionomers containing fluorenyl groups as well as 2 mol% of branching or cross-



**Scheme 15.** Chemical structure of poly(arylene ether sulfone)s containing fluorenyl groups.



**Scheme 16.** Chemical structure of water-insoluble high-IEC poly(arylene ether sulfone).

linking moieties have been developed to increase the IEC values up to 2.63 meq./g while maintaining water-insolubility [44]. These ionomer membranes were dimensionally stable, as confirmed by the swelling degree in water at 50 °C which was lower than that of the linear analogue. The branching and cross-linking should suppress the molecular motion of ionomers to reduce the swelling. The cross-linked ionomer membrane with IEC value of 2.63 meq./g showed very high proton conductivity of 0.2 S/cm at 87% RH and 0.02 S/cm at 57% RH.

Similarly, the cross-linking approach has also been applied to poly(arylene ether)s, as reported by Lee and coworkers [45]. The introduced alkyne moieties were responsible for efficient thermal cross-links, reducing the water uptake and the swelling ratio of the membranes, while high proton conductivity and low methanol permeability were maintained.

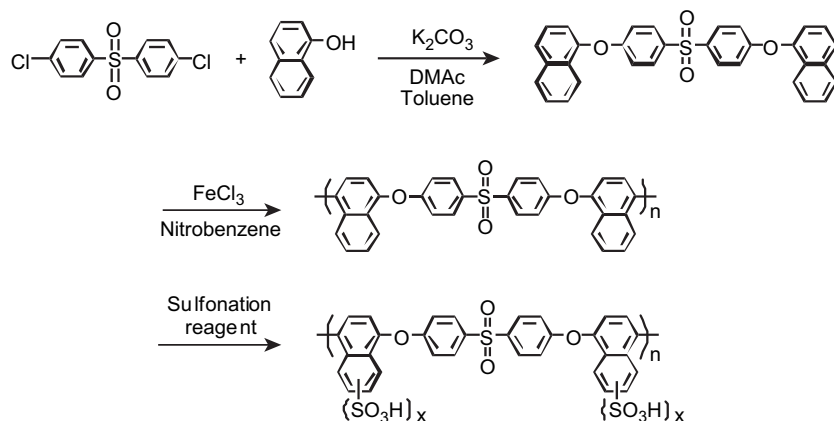
Miyatake et al. have described the optimization of poly(arylene ether sulfone) structures which produce water-insoluble polymers with extremely high IEC values (IEC = 3.26 meq./g) [11]. The chemical structure achieving the highest IEC among the series is illustrated in Scheme 16. A tough, flexible, and transparent membrane was obtained from the methyl-substituted polymer. Isopropylidene tetramethylbiphenylene moieties were found to be more effective than the methyl-substituted fluorenyl groups in giving a high-IEC ionomer membrane with substantial stability in regard to hydrolysis and oxidation. Dimensional stability was significantly improved for the methyl-substituted ionomer membranes compared to that of the non-methylated ones. By increasing the IEC, the proton conductivity remarkably increased at low RH. The membrane (IEC = 3.26 meq./g) showed a proton conductivity of  $5.6 \times 10^{-3}$  S/cm at 80 °C and 20% RH, which is comparable to that of the Nafion membrane. Microscopic analyses revealed that the connectivity of ionic clusters was significantly improved in the membrane and was similar to that of Nafion 112. In addition, the membrane has proved to have a better ohmic performance than Nafion in H<sub>2</sub>/O<sub>2</sub> fuel cells at the high temperature of 90 °C. The advantage of the membrane was possibly due to its good water-holding capacity.

The scope and possibility regarding a high-IEC polymer (IEC > 3 meq./g) for PEMs without dissolution in water by tuning polymer structures prompted us to prepare another series of high-IEC sulfonated poly(ether sulfone)s derived from simpler monomer structures [46]. We focused our attention on a binaphthyl structure, which has high hydrophobicity and a large free volume derived from its twisted structure [47], and is expected to show low water solubility even after sulfonation.

The synthesis of the monomer and non-sulfonated polymer precursor was performed according to the previous report [48]. The monomer, 4,4'-di(1-naphthoxy)diphenyl sulfone, was successfully prepared by a nucleophilic aromatic substitution reaction between 4,4'-dichlorodiphenyl sulfone and 1-naphthol. Then, the polymer, poly(1,1'-dinaphthyl ether phenyl sulfone), was synthesized by oxidative coupling polymerization using FeCl<sub>3</sub> as the oxidant. A high-molecular-weight polymer with 29,000 g/mol in *M<sub>n</sub>* value was easily obtained. A sulfonation reaction of poly(1,1'-dinaphthyl ether phenyl sulfone) was then conducted as the first attempt by our group. The synthetic routes are shown in Scheme 17 and the results are summarized in Table 2.

To achieve the highest IEC value, we employed a two-stage sulfonation technique where treatment with trimethylsilyl chlorosulfonate, which can suppress cross-linking reactions [3], was carried out to prepare a polymer with an IEC value of 1.81 meq./g which was further treated with concentrated sulfuric acid. As a result, an extremely high-IEC (3.19 meq./g) poly(ether sulfone) could be obtained (Run 8) and, surprisingly, it was insoluble in water despite its high IEC value. This IEC value indicates that each naphthalene ring is substituted by one sulfonic acid group (*x* = 1 in Scheme 17). The sulfonated samples are named as BNSH-*X*, where *X* shows the sulfonation degree (%) per naphthalene unit.

The water uptake of the BNSH membranes after being equilibrated at 80 °C and 95% RH was investigated. BPSH-40, which is a typical sulfonated poly(ether ether sulfone) [13], was used for comparison. As a trend, the water uptake of the BNSH membranes increased by increasing their IEC values. Compared to the BPSH-40



**Scheme 17.** Synthesis of sulfonated poly(ether sulfone) containing a binaphthyl structure.

**Table 2**  
Sulfonation reaction of poly(1,1'-dinaphthyl ether phenyl sulfone).<sup>a</sup>

Run	Sample code	Sulfonation reagent <sup>b</sup>	Reaction time [h]	IEC [mequiv/g] <sup>c</sup>	Reaction efficiency [%]	
1		ClSO <sub>3</sub> H	4.2	3	1.07	14
2		ClSO <sub>3</sub> H	9.4	3	Gelation	–
3		Me <sub>3</sub> SiSO <sub>3</sub> Cl	7.8	3	1.21	8.5
4	BNSH-55	Me <sub>3</sub> SiSO <sub>3</sub> Cl	7.8	24	1.81	14
5	BNSH-65	Me <sub>3</sub> SiSO <sub>3</sub> Cl	9.8	24	2.14	13
6	BNSH-67	Me <sub>3</sub> SiSO <sub>3</sub> Cl	12	24	2.18	11
7		Me <sub>3</sub> SiSO <sub>3</sub> Cl	16	24	Gelation	–
8 <sup>d</sup>	BNSH-100	H <sub>2</sub> SO <sub>4</sub>	–	14	3.19	–

<sup>a</sup> Reaction was carried out with 0.5 mmol of polymer in 9 mL of CH<sub>2</sub>Cl<sub>2</sub> at room temperature.

<sup>b</sup> Amount of sulfonation reagent with respect to a repeating unit.

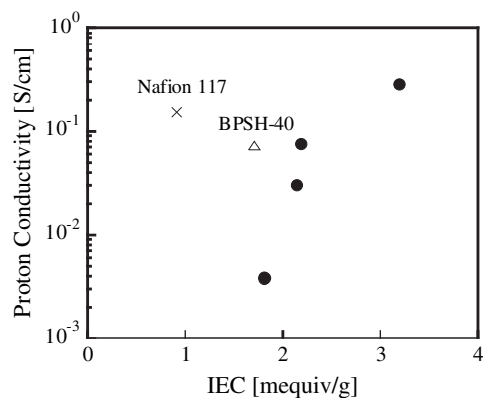
<sup>c</sup> Determined by titration.

<sup>d</sup> Reaction was carried out with 0.03 g of BNSH-55 in concentrated H<sub>2</sub>SO<sub>4</sub> at room temperature.

membrane, the BNSH membranes showed lower water uptake up to an IEC value of 2.18 meq./g. On the other hand, the BNSH-100 membrane showed a high water uptake of 65.2%. It is noteworthy that the BNSH-100 membrane was still insoluble in water despite its high IEC value of 3.19 meq./g. This result indicates that the binaphthyl structure has very high hydrophobicity, which is due to its rigidity and bulkiness, and the hydrophobicity enables the formation of water-insoluble membranes with high IEC values.

The humidity dependence of water uptake was measured for the BNSH membranes at 80 °C. The results are shown in Fig. 10, in comparison with BPSH-40 and Nafion 117. The water uptake for all membranes decreased by decreasing the relative humidity. Among all samples, the BNSH-100 membrane showed the highest water uptake over a range of 30–95% RH. The BNSH-100 membrane exhibited a high water uptake of 11% even at 30% RH.

Next, the relationship between IEC values and proton conductivity (80 °C at 95% RH) for the BNSH membranes was investigated and the results are shown in Fig. 11. As expected, the proton conductivity of the BNSH membranes increased alongside an increase in their IEC values. The proton conductivity of the BNSH-100 membrane showed a higher value than that of Nafion 117, while the BNSH-55, 65, and 67 membranes exhibited lower values than Nafion 117. To clarify the relationship between relative humidity and proton conductivity, the proton conductivity of the BNSH membranes was measured in a range of 30–95% RH at 80 °C (Fig. 12). The BNSH-100 membrane with an IEC value of 3.19 meq./g showed a low dependence of proton conductivity on relative humidity and exhibited excellent proton conductivity over a range of 30–50% RH. Furthermore, the proton conductivity of the BNSH-



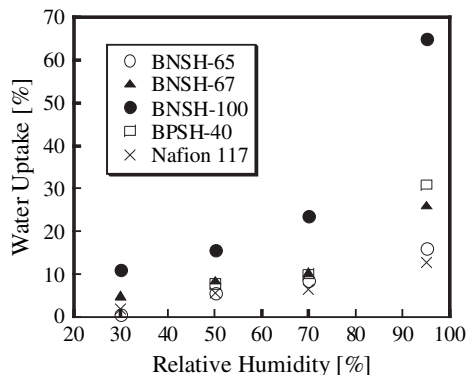
**Fig. 11.** Influence of IEC on proton conductivity in 95% RH at 80 °C.

100 membrane surpassed that of Nafion 117 in the measured range. The excellent proton conduction of the BNSH-100 membrane may be explained by its high IEC value of 3.19 meq./g, which provides outstanding connectivity of proton paths.

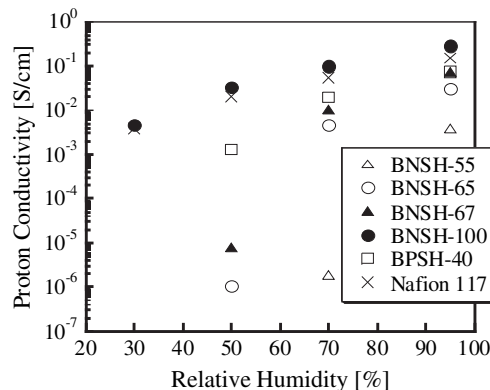
A tapping mode phase image of the BNSH-100 membrane was recorded under ambient conditions on a scale of 500 × 500 nm<sup>2</sup> to clarify its hydrophilic/hydrophobic morphology (Fig. 13). The bright and dark regions are derived from the hard segments corresponding to the hydrophobic units and the soft segments corresponding to the hydrophilic units containing water, respectively. As shown in Fig. 13, a large part of the image of the BNSH-100 membrane is dark because of its high IEC value. Moreover, the dark regions seem to be connected and form hydrophilic proton paths. This observation agrees well with the result from the proton conductivity of BNSH-100. As a result, the approach, which involves a simple increase in the IEC values of polymers, is effective to form proton paths, and the binaphthyl structure is suitable for achieving both a high IEC value and low water solubility due to its high hydrophobicity.

## 6. Summary

In order to develop efficient and practical PEM materials on behalf of currently used perfluorosulfonic acid membranes, the synthesis of new sulfonated aromatic polymers and their performance as PEMs has been widely investigated by several research groups. The aim of this review was to introduce recent progress in polymer synthesis, characterization, and performance as PEMs,



**Fig. 10.** Relative humidity dependence of water uptake of BNSH, BPSH-40, and Nafion 117 membranes at 80 °C.



**Fig. 12.** Relative humidity dependence of proton conductivity of BNSH, BPSH-40, and Nafion 117 membranes at 80 °C.

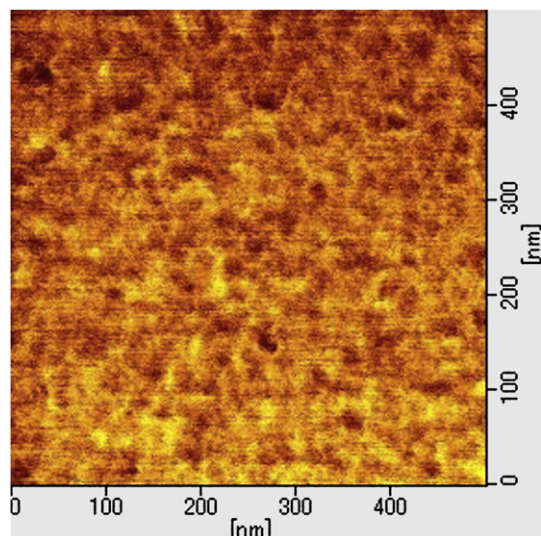


Fig. 13. AFM tapping phase image of BNSH-100.

mostly focusing on proton conductivity. The promising candidates for the breakthrough in PEM application are categorized into the following four materials; (1) sulfonated/non-sulfonated multiblock copolymers which contain hydrophobic and hydrophilic oligomers, (2) branched polymers in which the inner hydrophilic domains are surrounded by outer hydrophobic domains, (3) locally and densely sulfonated polymers with multiple sulfonic acid moieties along the main chains, and (4) high-IEC polymers ( $IEC > 3 \text{ meq./g}$ ) with a highly hydrophobic main chain skeleton. All methods aim at the generation of clear and well-connected proton channels while maintaining the water stability for high proton conduction even at low RH and high operating temperature. By further pursuing new and/or optimal polymer structures following (1)–(4), extraordinarily useful materials possessing well-balanced properties must emerge for fuel cell applications in the near future.

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