Synthesis and Properties of Sulfonated Poly(arylene ether)s Containing Azole Groups

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ABSTRACT: Random and multiblock sulfonated poly(arylene ether sulfone)s (SPEs) containing various azole groups such as oxadiazole and triazole were synthesized and characterized for fuel cell application. Successful preparation of SPE membranes depended on the structure of azole groups, which affected solubility of precursors and the resulting SPEs. Although oxadiazole groups were incorporated into hydrophobic component, they were found to be hydrophilic to give higher proton conductivity. Introduction of oxadiazole groups into random SPE gave comparable proton conductivity to that of Nafion NRE at >60% relative humidity at 80 °C. Block copolymer structure further increased the proton diffusion coefficient without increasing ion exchange capacity. Hydrolytic and oxidative stability of the SPE membranes was affected by both hydrophilic and hydrophobic components. Oxadiazole groups gave negative impact on hydrolytic and mechanical stability to the SPE membranes. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 3863–3873, 2011

KEYWORDS: azoles; block copolymers; ionomers; poly(ether sulfones); sulfonation

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INTRODUCTION Proton exchange membrane fuel cells (PEMFCs) have received great attention as clean energy source for mobile, transportation, and cogeneration system.[1] One of the essential components of the PEMFCs is the electrolyte membrane that controls both performances and durability. Perfluorosulfonic acid (PFSA) polymers such as Nafion have been regarded as state-of-the-art materials due to their excellent proton conductivity, chemical, and physical stability.[2] Nevertheless, the high production cost as well as low glass transition temperature (T_g) of the PFSAs have restricted their wide-spread application as PEMs. Perfluorinated compounds are environmentally unfriendly. Therefore, demands for inexpensive and less-fluorinated PEMs with high T_g have increased especially for the automobile applications.[3,4]

Aromatic polymers are one of the attractive candidates for the purpose. Sulfonated aromatic polymers such as poly(arylene ether)s,[5–14] polyimides,[15–18] polyphenylenes,[19,20] and polybenzimidazoles[21,22] have been extensively investigated. These aromatic ionomers are advantageous in terms of thermal stability and gas impermeability, however, require larger amount of water to achieve similar level of proton conductivity to PFSA membranes. Recent research works have revealed that multiblock architecture,[23–28] highly acidic moieties,[29–31] and sulfonic acid clusters[32–34] are effective in improving proton conductivity at low water content. We discovered that multiblock sulfonated poly(arylene ether)s (SPEs) showed comparable proton conductivity to PFSA membranes even under low humidity and high temperature conditions.[35–37] The key component is highly sulfonated fluorene groups in the hydrophilic blocks. Compared with the hydrophilic components, effect of hydrophobic ones has been less investigated. Xing et al.[8] reported naphthalene moiety is effective to improve hot water stability. We also reported that flat and rigid hydrophobic groups contributed to higher proton conductivity, lower water uptake and gas permeability.[38]

Effect of heterocyclic groups has been explored. The azole groups are known to provide polymer membranes with excellent chemical and thermal stability in engineering polymers.[39–41] Benzimidazole groups, for example, provide basic functionality as well as high thermal and mechanical stability. Several kinds of imidazole with sulfonic acid groups have been reported to enhance proton conductivity and stability.[22,42–45] Polybenzoxazole with sulfonic and phosphonic acid groups[46] and polyphosphazenes with triazole groups have been reported.[47] Recently, H-triazole groups were claimed to improve proton conductivity[48,49] and mechanical strength.[50,51]

In this contribution, we report novel SPEs containing heterocyclic azole groups such oxadiazole and triazole as

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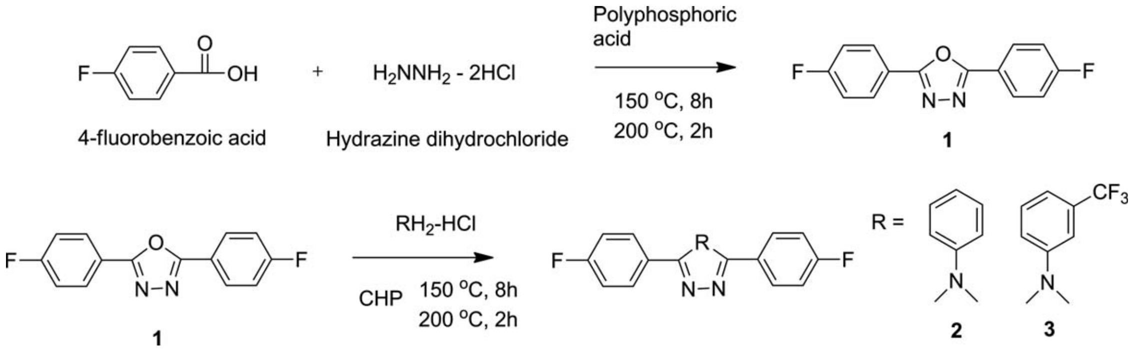


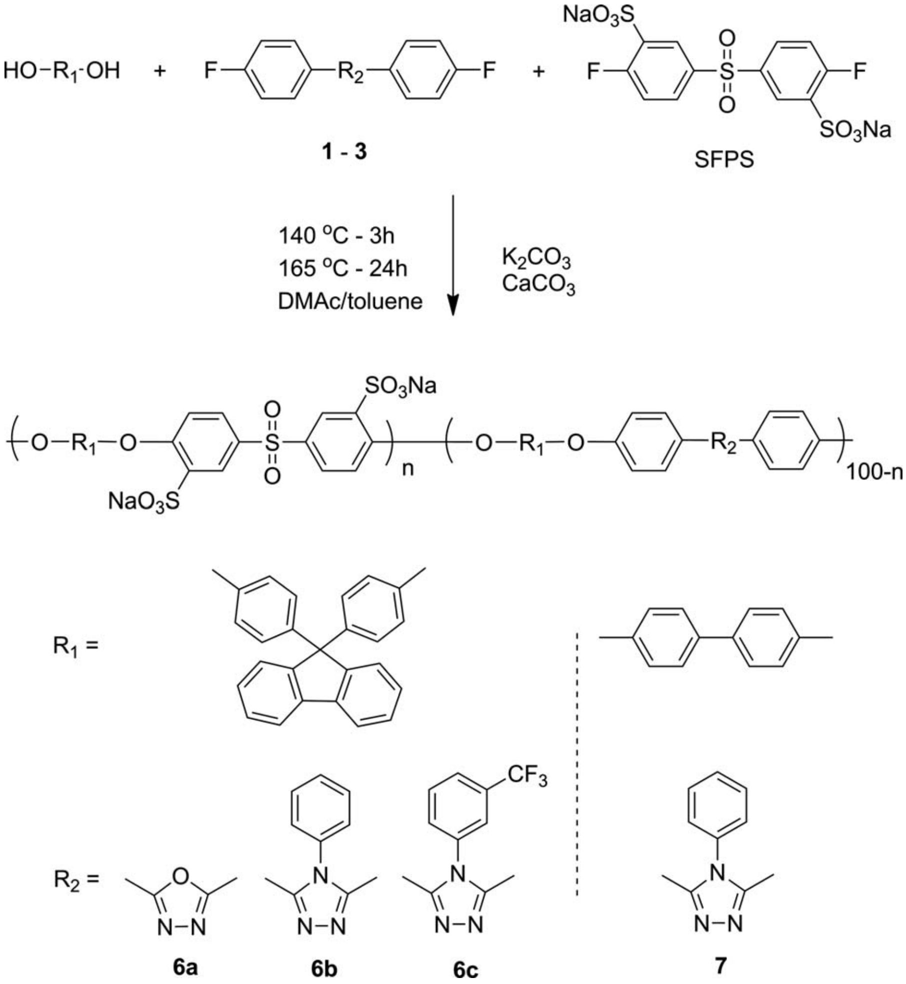
SCHEME 1 Preparation of oxdiazole (**1**) and triazole (**2** and **3**) containing monomers.

hydrophobic moieties. Monomers with 1,3,4-oxadiazole and 1,2,4-triazole were synthesized and SPEs with these azole groups were prepared by post-sulfonation or direct polymerization of sulfonated monomers. We have investigated the effect of hydrophobic components by comparison of **6a–c** (see Scheme 2 for chemical structures). Effect of other hydrophobic components has been evaluated with **6b** and **7**. Random and block copolymer structures have also been compared with **6a** and **10b**. Properties such as solubility, water uptake, proton conductivity, proton diffusion coefficients, mechanical strength, thermal stability, oxidative, and hydrolytic stability were investigated in detail.

EXPERIMENTAL

Materials

4-Fluorobenzoic acid, hydrazine dihydrochloride and 3-aminobenzotrifluoride were purchased from TCI and used as received. 4-Fluorophenyl sulfone (FPS), 9,9′-bis(4-hydroxyphenyl)fluorene (BHF), 4,4′-biphenol (BP), and



SCHEME 2 Synthesis of **6a–c**, and **7** polymers via sulfonated monomers.

decafluorobiphenyl (DFB, TCI., Inc.) were crystallized from toluene. *N*-cyclohexyl-2-pyrrolidone (CHP) was purchased from Sigma–Aldrich and used as received. Aniline was purchased from Kanto Chemical Co. Disodium 3,3′-disulfo-4,4′-difluorophenyl sulfone (SFPS) was synthesized by the method of Robeson et al.[52]

Fuming sulfuric acid (30 wt % SO_3), chlorosulfonic acid, potassium carbonate, calcium carbonate, and toluene were purchased from Kanto Chemical Co. and used as received. *N*,*N*-Dimethyl acetamide (DMAc, organic synthesis grade, 99%), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidinone (NMP) were provided from TCI and dried over 3 Å molecular sieves prior to use.

Measurements

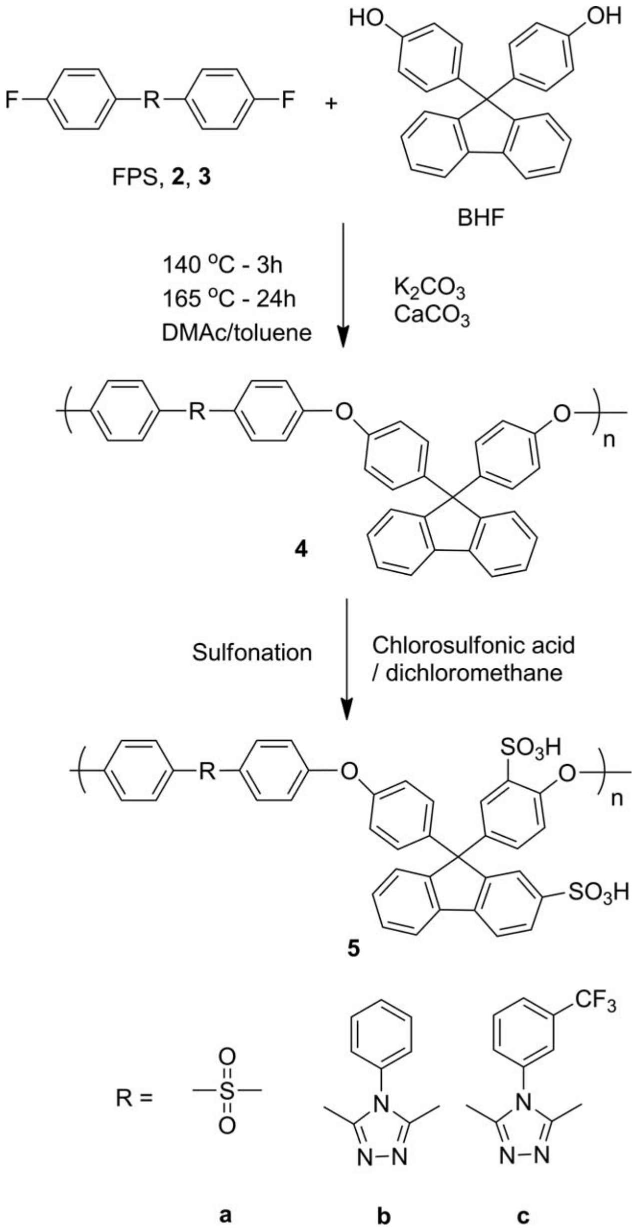
^1H and ^{19}F NMR spectra were obtained on a JEOL JNM-ECA 500 using deuterated dimethyl sulfoxide (DMSO-d_6) or chloroform ($CDCl_3$). Molecular weight was measured with gel permeation chromatography (GPC) with a Jasco 805 UV detector. DMF containing 0.01 M LiBr was used as eluent. One milligram of polymer was dissolved in 1 mL of DMF. Two Shodex KF-805 columns were used for polymers and a Shodex SB-803HQ column was used for oligomers, respectively. Molecular weight was calibrated with standard polystyrene samples. GC/MS analyses were performed using a Shimadzu GC/MS-QP2010 (JAPAN). The gas chromatograph was equipped with a capillary column Ultra ALLOY$^+$-5MS (Frontier Laboratories, Japan).

2,5-Bis(4-fluorophenyl)-1,3,4-oxadiazole (1)

Compound **1** was synthesized according to the method of Hensema et al.[39] Briefly, 4-fluorobenzoic acid (22.4 g, 160 mmol), hydrazine dihydrochloride (8.4 g, 80 mmol), and polyphosphoric acid (100 g) was added in a 200 mL round-bottomed flask. The mixture was heated at 150 °C for 8 h and 200 °C for another 2 h with mechanical stirring and nitrogen purge. The mixture was cooled down to room temperature and poured dropwise over ice to precipitate a white powder. The precipitate was filtered and dried under vacuum at 100 °C overnight. The product was crystallized from the mixture of methanol, chloroform, and water to obtain pure **1** in 74% yield. ^1H NMR ($CDCl_3$): δ (ppm) 8.15 (d, 4H), 7.25 (t, 4H). GC–MS: 258 m/z (>98%)

3,5-Bis(4-fluorophenyl)-4-phenyl-1,2,4-triazole (2) and 3,5-Bis(4-fluorophenyl)-4-(3-(trifluoromethyl)phenyl)-1,2,4-triazole (3)

Compounds **2** and **3** were synthesized by a modified method of Lu et al.[41] A 200 mL round-bottomed flask equipped with nitrogen purge, condenser, and mechanical stirrer was charged with **1** (5.0 g, 19.4 mmol) and 20 mL of CHP. The mixture was heated at 150 °C to dissolve **1**. Then, aniline hydrochloride (27.5 g, 212.9 mmol) for **2** or 3-aminobenzotrifluoride hydrochloride (24.1 g, 149.6 mmol) for **3**, which was readily prepared by treating aniline or 3-aminobenzotrifluoride with hydrochloric acid, was added slowly to the mixture. The mixture was heated at 150 °C for 8 h and at 200 °C for 2 h. It was cooled down to room temperature and poured dropwise into water to precipitate a white powder. The precipitate was filtered and dried under vacuum at 100 °C overnight. The product was crystallized from chloroform/hexane to obtain **2** in 82% yield or **3** in 92% yield.

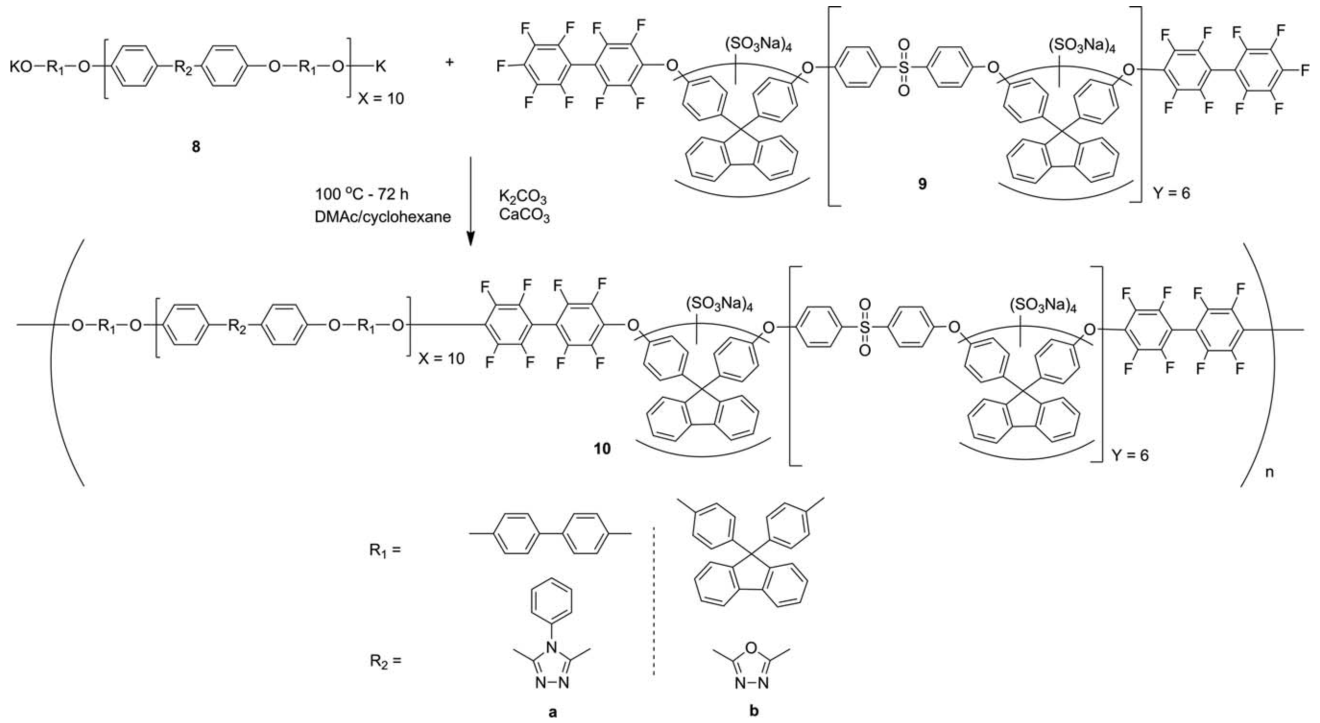


SCHEME 3 Synthesis of **4a–c** and **5a–c** polymers via post-sulfonation.

2 ^1H NMR ($CDCl_3$): δ (ppm) 7.48 (t, 2H), 7.41 (d, 1H), 7.39 (d, 2H), 7.13 (d, 4H), 6.94 (t, 4H). GC–MS: 333 m/z (>99%). **3** ^1H NMR ($CDCl_3$): δ (ppm) 7.77 (d, 1H), 7.61 (t, 1H), 7.38 (d, 4H), 7.35 (s, 1H), 7.32 (d, 1H), 7.04 (s, 4H). GC–MS: 401 m/z (>99%) (Scheme 1).

Synthesis of Sulfonated Poly(arylene ether) Copolymers (5a, 5b, and 5c) via Postsulfonation

FPS (5 mmol) for **4a** (or **2** for **4b**, or **3** for **4c**), BHF (5 mmol), potassium carbonate (8 mmol), and calcium



SCHEME 4 Synthesis of sulfonated multiblock poly(arylene ether) copolymers (**10a** and **10b**) from hydrophobic oligomers (**8a** and **8b**) and sulfonated hydrophilic oligomer (**9**).

carbonate (80 mmol) were charged in a 100 mL round-bottomed flask. To the mixture were added 10 mL of DMAc and 5 mL of toluene with Dean-Stark trap. The reaction was carried out at 140 °C for 3 h before Dean-Stark trap was removed. Then, the temperature was elevated to 165 °C and the reaction was continued for 24 h until the mixture became viscous. After the reaction, additional DMAc was added to the mixture, which was poured into a large excess of 1 M HCl aqueous solution to precipitate the product. The product was filtered, washed with 1 M HCl water and 0.5 M HCl methanol solution several times to remove residual calcium carbonate. It was dried at 80 °C in vacuum oven to remove the residual solvent.

4a, **4b**, and **4c** polymers were sulfonated with an excess of chlorosulfonic acid in dichloromethane solution. The sulfonation reaction was conducted by a flow reactor as reported previously.[53] After the sulfonation, the product was neutralized with NaOH and washed with water several times. Vacuum drying at 80 °C gave sulfonated polymers, **5a**, **5b**, and **5c**, in sodium form.

Synthesis of Sulfonated Poly(arylene ether) Copolymers (6a, 6b, 6c, and 7) from Sulfonated Monomers

A typical polymerization procedure is as follows. A 100 mL round-bottomed flask was charged with SFPS (3 mmol), difluorinated monomers (**1**–**3**), dihydroxy monomers (BHF or BP), potassium carbonate (8 mmol), and calcium carbonate (80 mmol). The feed amounts of each monomer were controlled to adjust ion exchange capacity (IEC) at 2.0 mequiv. g^{-1}. Feed ratios of monomers were calculated by the following equation;

$$\mathrm{IEC} = \frac{2n \times 1000}{100 \times (M_\mathrm{W}\ \text{of dihydroxy monomer}) + (M_\mathrm{W}\ \text{of SFPS}) \times n + (M_\mathrm{W}\ \text{of difluorinated monomer}) \times (100 - n)}$$

where monomers are shown in Scheme 2.

SFPS was dried overnight at 120 °C in vacuum oven before the reaction to remove hydrated water. The reaction was carried out in 10 mL DMAc and 5 mL toluene with Dean-Stark trap. The reaction was maintained at 140 °C for 4 h before Dean-Stark trap was removed. Then, the temperature was elevated to 170 °C to continue the reaction for another 24–96 h, depending on the reactivity of monomers. After the reaction, ca. 20 mL of additional DMAc was added to the mixture, which was poured into a large excess of 1 M HCl water to precipitate the product. The precipitate was filtered, washed with saturated NaCl aqueous solution, deionized water and methanol several times. The crude product was dissolved in DMAc and filtrated with a 0.45 μm membrane filter. The filtrate was evaporated at 80 °C in vacuum oven to remove the solvent to obtain the sulfonated polymers and

TABLE 1 IEC and Molecular Weights of the Sulfonated Polymers **5**, **6**, and **7**

		Molecular Weight (kDa)[b]				
		Before Sulfonation		After Sulfonation		
Polymers	Experimental IEC (mequiv. g^{-1})[a]	M_n	M_w	M_n	M_w	Film[c]
5a	1.9	85	252	97	260	○
5b	2.0	59	142	87	281	○
5c	N/A	96	403	N/A	N/A	×
6a	2.1	N/A	N/A	68	209	○
6b	1.9	N/A	N/A	111	222	○
6c	N/A	N/A	N/A	20	61	×
7	1.7	N/A	N/A	31	93	○

[a] Obtained by back-titration.
[b] Determined by GPC (calibrated with standard polystyrene samples).
[c] O, Self-standing film; X, Brittle film.

their yields were 90% for **6a**, 93% for **6b**, 75% for **6c**, and 81% for **7**, respectively.

Synthesis of Hydrophobic Oligomers (8a and 8b), Sulfonated Hydrophilic Oligomer (9), and Sulfonated Multiblock Poly(arylene ether) Copolymers (10a and 10b)

Hydrophobic oligomers **8a** and **8b** were synthesized in a similar procedure in Scheme 3, except a slight excess of BHF or BP was added to control the chain length of hydrophobic block (X) to be 10. Fluorene-containing oligomer as a precursor for sulfonated hydrophilic oligomer **9** ($Y = 6$) was synthesized in a similar way. Sulfonation reaction of the precursor oligomer was conducted under severer conditions than those in Scheme 3. Details on synthesis and characterization were previously reported.[54]

Block copolymers **10a** and **10b** were synthesized from **8a** or **8b** and **9** as shown in Scheme 4. Oligomer **9** was dried overnight at 120 °C in vacuum oven before the reaction to remove hydrated water. Equimolar amounts (0.08 mmol) of **8a** or **8b** and **9**, potassium carbonate (0.16 mmol), calcium carbonate (1.6 mmol), and 10 mL of DMAc were added in a 100 mL round-bottomed flask. The polymerization reaction was conducted at 100 °C for 48–72 h. Isolation and purification of the resulting block copolymers were conducted similarly to **6a–c** and **7**. Their yields were 74% for **10a** and 84% for **10b**, respectively.

Characterization of Membranes

Solution casting on glass plate gave tough and flexible 50 μm membranes. DMAc was chosen as a standard solvent for the casting. Characterization of the membranes such as titration, water uptake, proton conductivity, oxidative, and hydrolytic stability was performed according to the method previously reported.[36] From the conductivity data, proton diffusion coefficient (D_σ) was calculated using Nernst-Einstein equation,

$$D_\sigma = \frac{RT}{F^2}\frac{\sigma}{c(\mathrm{H}^+)}$$

where R is gas constant, T is the absolute temperature (K), F is Faraday constant, and $c(\mathrm{H}^+)$ is the concentration of proton charge carrier (mol L^{-1}).

Tensile strength was measured by a universal test machine (AGS-J 500N, Shimadzu) attached with a temperature and humidity controllable chamber (Bethel-3A, Toshin Kogyo). Stress versus strain curves were obtained for samples cut into a dumbbell shape [DIN-53504-S3, 35 mm × 6 mm (total) and 12 mm × 2 mm (test area)]. The measurement was conducted at 80 °C and 60% relative humidity (RH) at a stretching speed of 10 mm min^{-1}.

Thermogravimetric analyses (TGA) were carried out using a Mac Science TGA 2000 system under argon atmosphere.

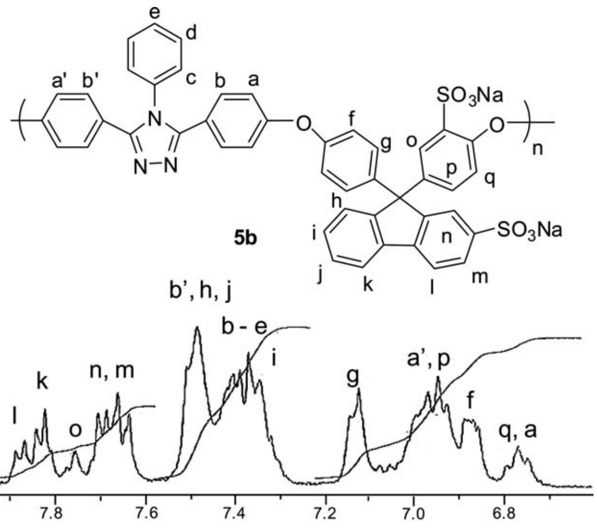


FIGURE 1 ^{1}H NMR spectrum of **5b**.

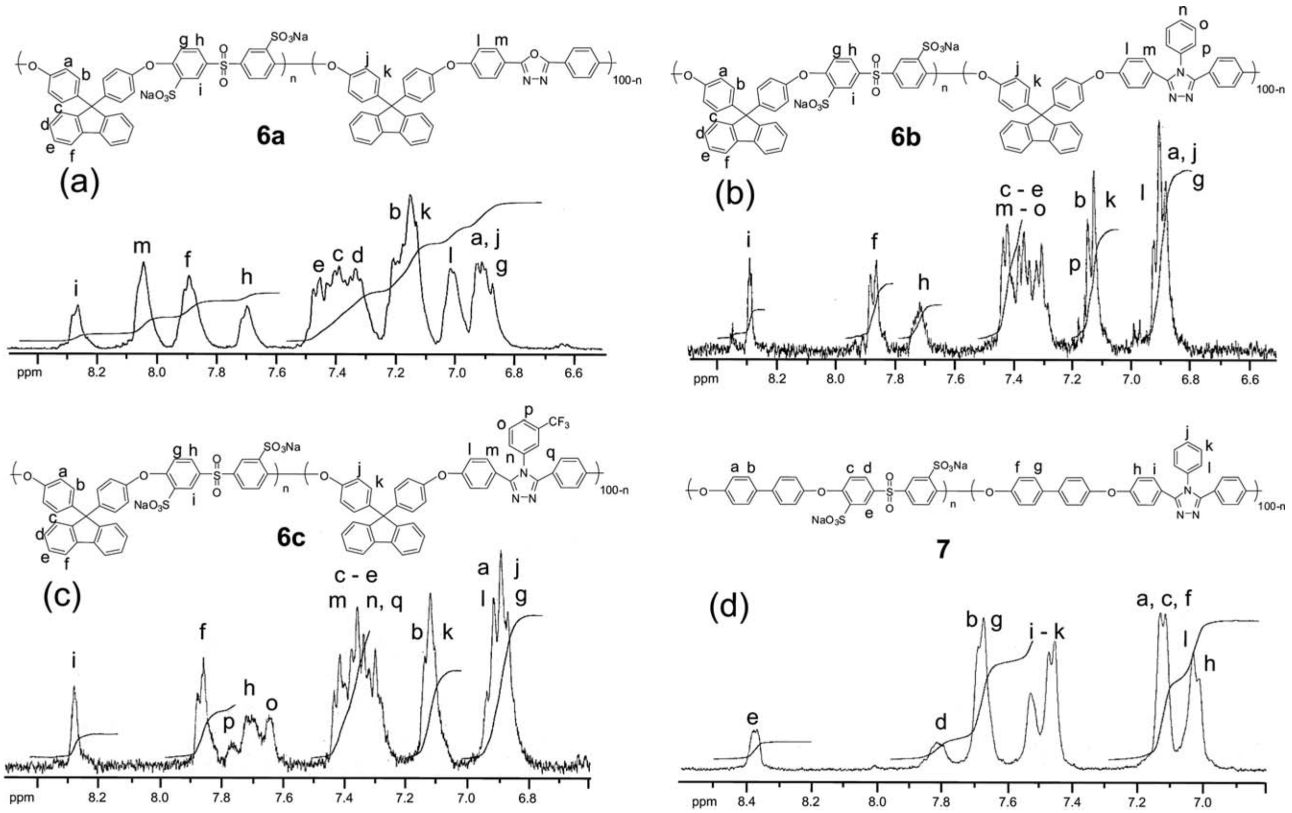


FIGURE 2 ^{1}H NMR spectra of (a) **6a**, (b) **6b**, (c) **6c**, and (d) **7**.

Polymer samples were heated from room temperature to 500 °C at a heating rate of 10 °C min^{-1}. Membranes in proton form were subjected for the analyses.

RESULTS AND DISCUSSION

Synthesis of 4a–c and 5a–c

Copolymers **4a–c** were successfully synthesized by nucleophilic aromatic substitution reaction as shown in Scheme 3. The apparent molecular weight of **4a–c** obtained by GPC was higher than 59 kDa (M_n) and 142 kDa (M_w) indicating successful polymerization. Reaction of **4a–c** with chlorosulfonic acid gave sulfonated polymers **5a–c**. A flow reactor was used for better control of the degree of sulfonation.[53] Target IEC was fixed at 2.0 mequiv. g^{-1} for accurate comparison of the properties with other polymers. The experimental IEC values obtained by back titration were close to the targeted values as shown in Table 1. **5a** and **5b** showed higher apparent molecular weights than those of the precursors **4a** and **4b**, as sulfonated polymers have larger radii of gyration in solution due to electric repulsion among the sulfonic acid groups attached to the polymers.

In contrast to successful sulfonation of **4a** and **4b**, **4c** failed in sulfonation due to its lower solubility in dichloromethane. The soluble part in dichloromethane was sulfonated only to give brittle membranes insufficient for properties characterization. Figure 1 shows ^{1}H NMR spectra of **5b**. All peaks were well-assigned to the supposed chemical structure. We previously reported that the sulfonation of **4a** occurred selectively at 2,8-positions of cardo flurorene groups.[55,56] Under severer sulfonation conditions with more concentrated chlorosulfonic acid, phenylene groups in the main chain in addition to the fluorene groups were also sulfonated.

Synthesis of 6a–c and 7

Sulfonated polymers **6a–c** and **7** were synthesized by nucleophilic aromatic substitution reaction of pre-sulfonated difluoromonomer (SFPS) and azole-containing difluoromonomers with dihydroxy monomers as shown in Scheme 2 and Table 1. The molecular weights of **6a** and **6b** were high enough to form tough and flexible membranes, while **6c** and **7** resulted in somewhat low molecular weight. This is because of relatively lower solubility of **6c** and **7**, a part of which was precipitated during the polymerization reaction. It is surprising to note that bulky and unsymmetric 3-(trifluoromethyl)phenyl group on triazole caused poorer solubility in **5c** and **6c**. Trifluoromethyl groups may restrict molecular rotation of the polymer chains. The copolymer **6c** with the lowest molecular weight provided brittle membrane by solution casting, while flexible and self-standing membrane was obtained from **7**. Linear and rigid structure of biphenyl groups in **7** is likely to improve film forming capability. Similar results were obtained with other sulfonated aromatic polymers.[8,38]

IECs of **6a–c** and **7** polymers were targeted at 2.0 mequiv. g^{-1} similar to those of **5a–c**. The experimental IEC value was

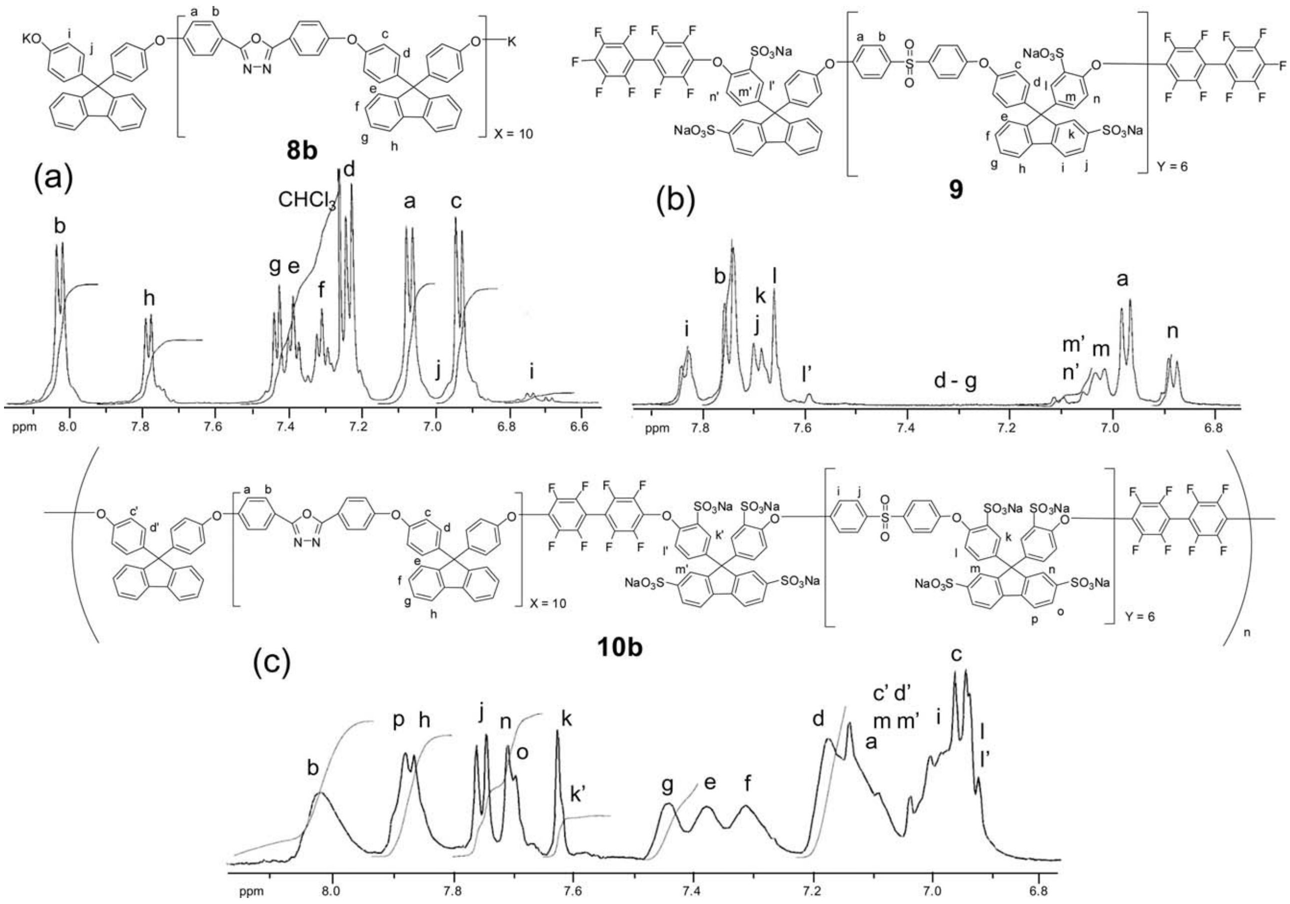


FIGURE 3 ^{1}H NMR spectra of (a) **8b** and (b) **9**, and (c) **10b**.

comparable for **6a** and **6b**, and lower for **7**. Differences in the reactivity between SFPS and **2** would be accountable. Figure 2 shows ^{1}H NMR spectra of **6a–c** and **7**. The observed peaks were well-assigned to their expected structures to support successful polymerization reaction.

Synthesis of 8, 9, and 10a–b

Oligomers **8** were synthesized under the similar conditions as for **4**. Degree of polymerization (X) of **8** was targeted at 10 by controlling the feed monomer ratio. ^{1}H NMR spectra showed successful oligomerization as shown in Figure 3(a) (**8b**) and S1 (**8a**). X value for **8a** was estimated to be about six from GPC data and five from NMR spectrum, respectively, which were in good accordance. Similarly, X value for **8b** was estimated to be about 10 from GPC data and 12 from NMR spectrum, respectively. DFB-terminated sulfonated oligomer (**9**) was synthesized by post-sulfonation, of which degree of polymerization (Y) was estimated to be about six by GPC [Fig. 3(b)]. Estimation of Y value from NMR spectrum was difficult due to overlap of end groups with main chains, but the spectrum of DFB-free OH-terminated oligomer (before end capping reaction) provided Y value of 5. Details on the synthesis and purification of **9** are available in the literature.[54] The block copolymerization of **8** and **9** was carried out at >120 °C for 24–72 h only to give insoluble gel-like products due to the cross-linking reactions via DFB. Therefore, lower temperature of 100 °C was applied for the block copolymerization to obtain **10** with better solubility. Polymer **10a** was yet little soluble in DMAc, DMSO, and NMP. In contrast, polymer **10b** showed reasonable solubility in DMAc to obtain self-standing membrane by solution casting. ^{1}H NMR spectra of **10b** in Figure 3(c) confirmed the presence of both hydrophobic and hydrophilic components and their composition.

Table 2 summarizes IEC and molecular weight of **10**. The experimental IEC of **10b** membrane by titration was lower than the expected value (2.0 mequiv. g^{-1}). This may be due to lower degree of polymerization (M_n) to induce broad distribution of IEC in polymer **10b**. Part of **10b** with high IEC

TABLE 2 IEC and Molecular Weight of **10**

Polymers	Experimental IEC (mequiv. g^{-1})[a]	Molecular Weight (kDa)[b]		Film[c]
		M_n	M_w	
10a	N/A	17	94	×
10b	1.5[a]	13	312	○

[a] Obtained from back-titration.

[b] Determined by GPC (calibrated by standard polystyrene samples).

[c] O, Self-standing film; X, Brittle film.

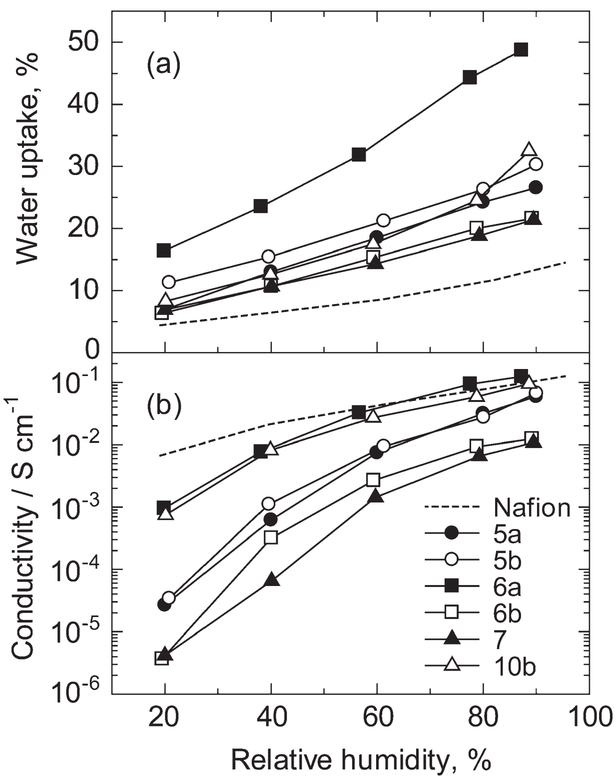


FIGURE 4 Humidity dependence of (a) water uptake and (b) proton conductivity of membranes **5–10** at 80 °C.

might have been lost during water washing purification step. In addition, the polydispersity index (M_w/M_n) was much higher than that expected from typical step growth polycondensation reaction. Although the polycondensation was carried out under rather mild conditions, it is considered that a small amount of cross-linking at DFB-terminal groups was contained.

Water Uptake and Proton Conductivity

Figure 4 shows water uptake (defined by weight of absorbed water divided by dry weight of polymer in percentage) and proton conductivity of the polymer membranes at 80 °C as a function of RH. Although most membranes have similar IEC values except **10b**, their water uptake values were different and dependent on the structure of hydrophobic and hydrophilic components. Membrane **6a** showed much higher water uptake than that of the other membranes. It is considered that oxadiazole groups with high affinity to water are responsible for such high water uptake. Similarly, membrane **10b** showed high water uptake taking its low IEC value into account. Comparison between **5a** and **5b** suggested that triazole groups also increased water uptake of the polymer membranes but the effect was much less pronounced compared to oxadiazole groups.

Proton conductivity of the membranes was approximately in the order of their water uptake. Membrane **6a** showed the highest proton conductivity. The conductivity of **6a** was comparable at >60% RH to that of Nafion. At 20% RH, **6a** was less conductive than Nafion (6.7 mS cm^{-1} for Nafion and 1.0 mS cm^{-1} for **6a**). When compared to **6b**, in which oxadiazole groups were replaced with triazole groups, **6a** showed much higher proton conductivity. The differences were more significant at low RH, for example, 26 times higher at 40% RH (7.7 mS cm^{-1} for **6a** and 0.3 mS cm^{-1} for **6b**) and 2700 times higher at 20% RH. Block copolymer architecture affected significantly the proton conductivity. Despite its lower IEC and lower water uptake, block copolymer membrane **10b** showed comparable proton conductivity to **6a** at all humidities examined.

For detailed discussion on proton conducting properties, proton diffusion coefficients (D_σ) are plotted as a function of water volume fraction (Φ) in Figure 5. The D_σ values are parameters taking both IECs and water uptake into account. Membrane **6a** showed much higher proton conductivity than that of the other membranes, however, its D_σ values were lower because of its significantly higher water uptake capability. Membranes **5a**, **5b**, **6b**, and **7** showed similar D_σ values at $\Phi = 0.2$–0.3, implying that the membranes have similar proton transport rate in this region. Membrane **10b** of a block copolymer showed the highest D_σ value in the wide range of Φ as expected from the data in Figure 4. It is concluded that the block copolymer structure containing oxadiazole groups in the hydrophobic blocks is effective for the sulfonated poly(arylene ether) membranes to make the most of absorbed water in proton transport.

Thermal and Mechanical Properties

Thermal stability of the membranes was tested by TGA in argon atmosphere as shown in Figure 6. The polymer membranes showed similar thermal behavior to our previously reported (SPEs).[56,57] Initial weight losses under about 150 °C are originated from the evaporation of hydrated water, of which amount was dependent of their IEC and structure. Amount of water uptake under atmosphere seems to affect the initial weight losses. The second weight loss commenced at around 250 °C, which was slightly different among the

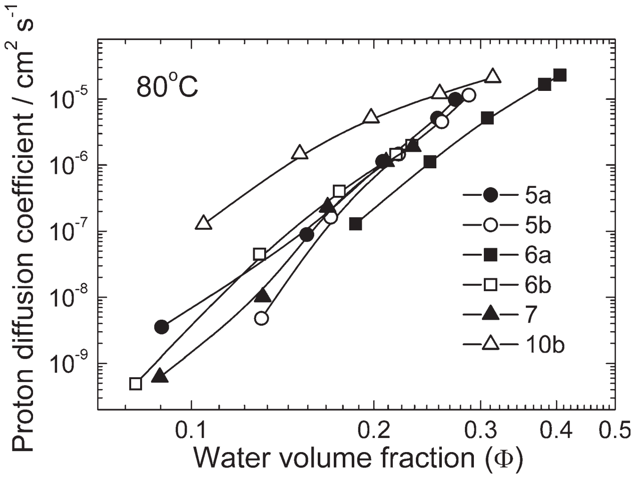


FIGURE 5 Proton diffusion coefficients of membranes **5–10** as a function of water volume fraction at 80 °C.

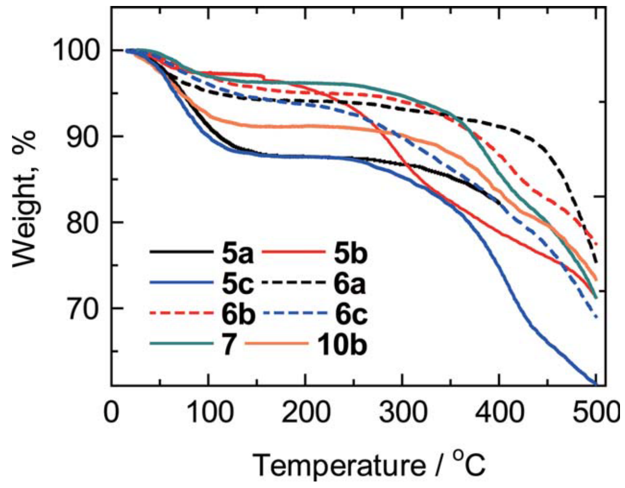


FIGURE 6 TGA curves of membranes **5–10** under argon atmosphere.

TABLE 3 Results of Elongation Test of Membranes **5–10** at 80 °C and 60% RH

Membrane	IEC (mequiv. g^{-1})	Maximum Stress at Break Point (MPa)	Young's Modulus (MPa)
5a	1.9	48	960
5b	2.0	34	640
6a	2.1	17	143
6b	1.9	32	665
7	1.7	52	970
10b	1.5	13	325
Nafion NRE212	0.91	16	50

membranes. The third step of the weight loss was observed above 400 °C due to the degradation of polymer backbones.

Stress versus strain curves of the polymer membranes were measured at 80 °C and 60% RH (simulating fuel cell operating conditions) and compared with that of Nafion NRE212 membrane in Figure 7 and Table 3. Nafion showed high elongation (430%) and maximum stress at break (16 MPa) with 50 MPa of Young's modulus. The sulfonated poly(arylene ether) membranes showed much lower strain, but higher maximum stress at break (32–52 MPa) and Young's modulus (640–970 MPa) except **6a** and **10b**. Membranes **5a** and **7** showed remarkably high Young's modulus. Oxadiazole groups affected negatively affected mechanical strength of the membranes. Comparison of **6b** and **7** suggested that linear biphenyl groups were more preferable for mechanical properties than fluorenyl groups (note that the former was of lower molecular weight). Membranes **6a** and **10b** showed lower stress, strain, and Young's modulus compared to those of the other membranes. Hydrophilic nature of oxadiazole groups may weaken hydrophobic intermolecular interaction among polymer chains. The membranes were flexible, however, relatively low elongation would have to be improved for practical fuel cell applications.

Oxidative and Hydrolytic Stabilities

Oxidative and hydrolytic stabilities are crucial parameters for fuel cell applications. We have tested our membranes under accelerated testing conditions. The results are summarized in Table 4. In the oxidative stability test, the membranes lost weight and molecular weight. Membrane **6b** and **7** was most oxidatively stable. These two polymers contain sulfonic acid groups on the main chains but not on the cardo fluorene groups. It is considered that sulfonic acid groups on aromatic rings with electron withdrawing sulfone groups are more stable to oxidation than those on fluorene groups.[58] We have obtained similar results previously.[57] The presence of oxadiazole groups deteriorated hydrolytic stability of the polymer membranes. Membranes **6a** and **10b** lost much of their molecular weight in the hydrolytic stability test, whereas losses in the weight and molecular weight were minor for the other membranes. As oxadiazole groups are more hydrophilic than

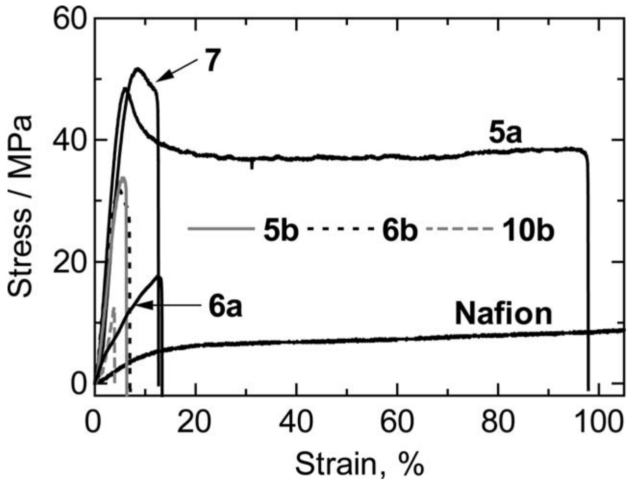


FIGURE 7 Strain–stress curves of membranes **5–10** at 80 °C and 60% RH.

TABLE 4 Oxidative and Hydrolytic Stability of Membranes **5–10**

	After Oxidative Stability Test[a]		After Hydrolytic Stability Test[b]	
Membrane	Residual Weight (%)[c]	Residual Molecular Weight (%)[d]	Residual Weight (%)[c]	Residual Molecular Weight (%)[d]
5a	35	24	99	95
5b	11	15	98	100
6a	20	18	95	15
6b	82	35	99	100
7	72	50	98	98
10b	15	20	93	13

[a] In Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C for 1 h.

[b] In pressurized water at 140 °C for 24 h.

[c] Residual weight percentage after the test.

[d] Residual percentage of molecular weight tested by GPC.

sulfone and triazole groups, water could have better access to the former groups to cause hydrolysis.

CONCLUSIONS

Effect of azole groups on the properties of sulfonated poly(arylene ether) membranes was investigated. From the standpoint of synthesis and film forming capability, oxadiazole, and triazole groups did not have effects. Trifluoromethylphenyltriazole groups, however, caused lower solubility and lower molecular weight of the resulting polymers. Incorporation of oxadiazole groups was effective for improving the proton conductivity due to its enhanced hydrophilicity. Combination of block copolymer structure and oxadiazole groups was desirable to balance absorbing and proton conductive properties. In contrast, oxadiazole groups have negative effects on mechanical properties and hydrolytic stability. These disadvantages need to be improved by introducing rigid-rod like hydrophobic component and protecting electronically and sterically oxadiazole groups, which are in our future agenda.

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