

# Synthesis and Characterization of Multiblock Copolymer Ionomers Containing Phthalazinone Ether Ketone and Fluorene Ether Ketone Moieties

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**ABSTRACT:** Two series of sulfonated multiblock copoly(ether-ketone)s containing phthalazinone ether ketone and fluorene ether ketone moieties have been synthesized successfully by two-step polycondensation. The water uptakes of the copolymers with varying sized sulfonated poly(phthalazinone ether ketone) block as hydrophilic blocks are moderate. In this series, polymer 10a gave the proton conductivity of  $1.20 \times 10^{-3}$  S/cm with IEC of 1.03. The water uptakes of the copolymers with varying sized sulfonated poly(fluorene ether ketone) blocks as hydrophilic blocks are high than 300%. These copolymers showed better proton conductivity. The copolymers with sulfonated poly(phthalazinone ether ketone) blocks had strong alcohol resistance at refluxing temperature. Whereas the copoly-

mers containing sulfonated poly(fluorene ether ketone) hydrophilic blocks were dissolved in methanol and ethanol. The cast films of the title ionomers were transparent, ductile, and flexible. Moreover, these copolymers demonstrated greatly improved oxidative and thermal stabilities. Especially, the copolymers comprising sulfonated poly(phthalazinone ether ketone) hydrophilic blocks and poly(fluorene ether ketone) hydrophobic blocks is a promising proton exchange membrane material for proton exchange membrane fuel cell used methanol or ethanol as fuel. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1100–1110, 2010

**Key words:** block-copolymers; ionomers; heteroatom-containing polymers; fluorine; step-growth polymerization

## INTRODUCTION

Perfluorosulfonic acid membranes, such as Nafion<sup>®</sup>, are the current state-of-the-art proton exchange membrane (PEM) for PEM fuel cells and direct methanol fuel cells because of their superior chemical and electrochemical stability, in addition to high proton conductivity of 98 mS/cm at room temperature with 100% RH and relatively low ion exchange capacity (IEC) of 0.91 mequiv/g. However, their critical drawbacks of high cost, high methanol crossover, and low proton conductivity as well as poor mechanical stability at elevated temperatures above 80°C are the hurdles for large-scale applications, which have led researchers to investigate promising alternatives.<sup>1–3</sup> Up to now, sulfonated aromatic poly-

mers as alternative proton exchange membrane have been well developed.<sup>4</sup> Unfortunately, it is very difficult to obtain an ideal balance between high proton conductivity and low water uptake. The randomly distributed sulfonic groups in the main chains result in dead-end ionic channels in the membranes, and these polymers require much higher IEC to get proton conductivity comparable with Nafion. Unlikely, high IEC results in high water uptake and the loss of mechanical properties. It is widely recognized that the superior proton conductivity of Nafion is attributed to the extensive nanoscale phase separation of ionic and nonionic domains. The model suggested by Kreuer for a sulfonated poly(ether-ketone) shows less pronounced ionic/nonionic separation than that of Nafion, that is, a morphology with narrower channels than those in Nafion, but with highly branched channels and many dead-end channels.<sup>2</sup> Therefore, in recent years, many researchers have started to investigate the synthesis of sulfonated aromatic copolymers with various architectures to mimic the morphology of Nafion.<sup>5–16</sup> Ghassemi et al.<sup>7</sup> synthesized multiblocks sulfonated-fluorinated poly(arylene ether)s with a promising morphological structure by a two-step polycondensation. Membranes with low IEC of 0.95 mequiv/g

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had water uptake of 40% but high proton conductivity of 80 mS/cm. Furthermore, a few recent reports say that sulfonated aromatic multiblock copolymers showed higher conductivities than the corresponding random copolymers,<sup>6,17–19</sup> probably due to better phase separation. However, the research on this class of copolymers is still in the initial stage, and the precise control of nanoscale morphology of multiblock copolymers may be restricted due to the polydispersity of each block.<sup>20</sup>

The research on the synthesis of ionomers with various architectures is of great interest for the reasons mentioned earlier. We have previously reported the synthesis of a novel class of ionomers, linear poly(phthalazinone ether ketone) ionomers. The heterocyclic N—C bond is ortho to the sulfonic acid group but not to the aromatic ether bond, such sulfonated polymers showed excellent thermal, chemical stability, and resistance to oxidation. Moreover, the membranes of the polymers had reasonable water affinity and good proton conductivity.<sup>21</sup> Novel poly(arylene ether)s with sulfonic acid groups attached onto pendent aromatic rings have been successfully synthesized in our group. These membranes showed excellent stabilities resistance to both oxidation and hydrolysis, as evidenced by subjecting to both Fenton's reagent test and immersion in boiling water.<sup>22,23</sup> Furthermore, we have also reported the successful synthesis of linear and crosslinked sulfonated fluorene-containing poly(arylene ether ketone)s. The results showed that the membranes had better mechanical, oxidative, and dimensional stabilities together with high proton conductivity ( $5.41 \times 10^{-2}$  S cm<sup>-1</sup>) at 80°C under 100% relative humidity.<sup>24,25</sup>

Herein, we report the synthesis and properties, the first example, of a series of sulfonated multiblock copolymers containing varying poly(phthalazinone ether ketone) and poly(fluorene ether ketone) blocks. These polymers have been synthesized by a two-step polycondensation. The sulfonic acid groups are attached to the deactivated aromatic rings in hydrophilic block segments. We investigated the effect of the varying hydrophilic block segments in the main chain on the thermal properties, proton conductivity, water uptake, ethanol uptake, and methanol uptake.

## EXPERIMENTAL SECTION

### Materials

Fluorenone, 4,4'-difluorobenzophenone (DFBP), and 4,4'-dihydrodiphenyl were purchased from Aldrich Chemical Company and used as received. 4,4'-(9-Fluorenylidene) diphenol (7) and diphenyl containing bisphthalazinone (12) were friendly supplied by Dr. Meng's research group, Sun Yet-sen University. Sulfonated 4,4'-difluorobenzophenone (9) (SDFBP)

were synthesized as outlined in Ref. 26. Reagent-grade *N,N'*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), chlorobenzene, toluene, methanol, concentrated hydrochloric acid (37.2%), anhydrous potassium carbonate, phthalic anhydride, and anhydrous aluminum chloride were obtained from commercial sources used without further purification. DMAc was dried over 4 Å molecule sieves and toluene was dried over sodium wire before use.

### Characterization

The <sup>1</sup>H-NMR spectra were recorded with a Bruker NMR instrument (Model: DRX 400 MHz) with dimethyl-*d*<sub>6</sub> sulfoxide (DMSO-*d*<sub>6</sub>) as a solvent with tetramethylsilane as the internal standard. Melting points were taken on a XT4A melting-point testing apparatus. Thermogravimetry (TGA) was performed on a Seiko SSC-5200 thermogravimetric analyzer at a heating rate of 20°C/min under N<sub>2</sub> atmosphere (flow rate of 200 mL/min), and *T*<sub>d5</sub> was reported as temperature at which 5% weight loss was observed. The glass transition temperatures (*T*<sub>g</sub>s) were determined on a modulated TA DSC instrument at a heating rate of 20°C/min under nitrogen protection. Inherent viscosity was determined for a solution of 0.5 g dL<sup>-1</sup> in DMSO at 30°C with a calibrated Ubbelohde viscometer. FTIR spectra were recorded on a Perkin-Elmer Spectrum100 Fourier transform spectrometer using film sample. Elemental analyses were performed on a Varios EL elemental analyzer for C, H, N, and S determination. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF MS) analyses were performed on a Bruker Reflex MALDI-TOF MS.

### Water uptake, methanol uptake, and ethanol uptake

The membrane was dried under vacuum at 80°C for 24 h. The weighed membrane was immersed in deionized water at 80°C for 24 h. Wet membrane was weighed quickly upon wiping up its surface water with tissue paper. The water uptake of membrane was calculated according to the following eq. (1):

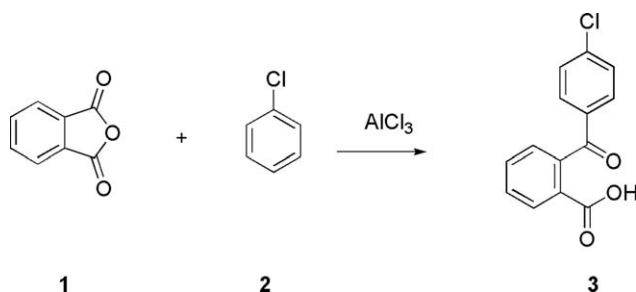
$$\text{water uptake (\%)} = (W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \cdot 100\% \quad (1)$$

where *W*<sub>wet</sub> and *W*<sub>dry</sub> are the weights of the wet membrane and dry membrane, respectively.

The methanol uptake and ethanol uptake of the prepared membrane were evaluated by measuring the weight change between dried and humidified states at refluxing temperature for 24 h.

### Proton conductivity

Proton conductivity measurement was performed on fully hydrated film samples at temperature 30°C at



**Scheme 1** Synthesis of 2-(4-chlorophenylbenzoyl)benzoic acid **3**.

100% relative humidity with a Solartron 1255B frequency response analyzer at an oscillating voltage of 10 mV, using a two probe method at frequency ranging from 1 MHz to 5 kHz. The proton conductivity ( $\sigma$ ) of the specimen in the transverse direction (across the membrane) was calculated from the impedance data according to following eq. (2):

$$\sigma = d/(RS) \quad (2)$$

where  $d$  and  $S$  are the thickness and the face area of the specimen, respectively, and  $R$  is derived from the low intersect of the high frequency semicircle on a complex impedance plane with the  $Re(Z')$  axis.

### Oxidative and hydrolytic stability

Oxidative stabilities were determined using Fenton's reagent (3 wt %  $H_2O_2$  + 2 ppm  $FeSO_4$ ) at 80°C. The

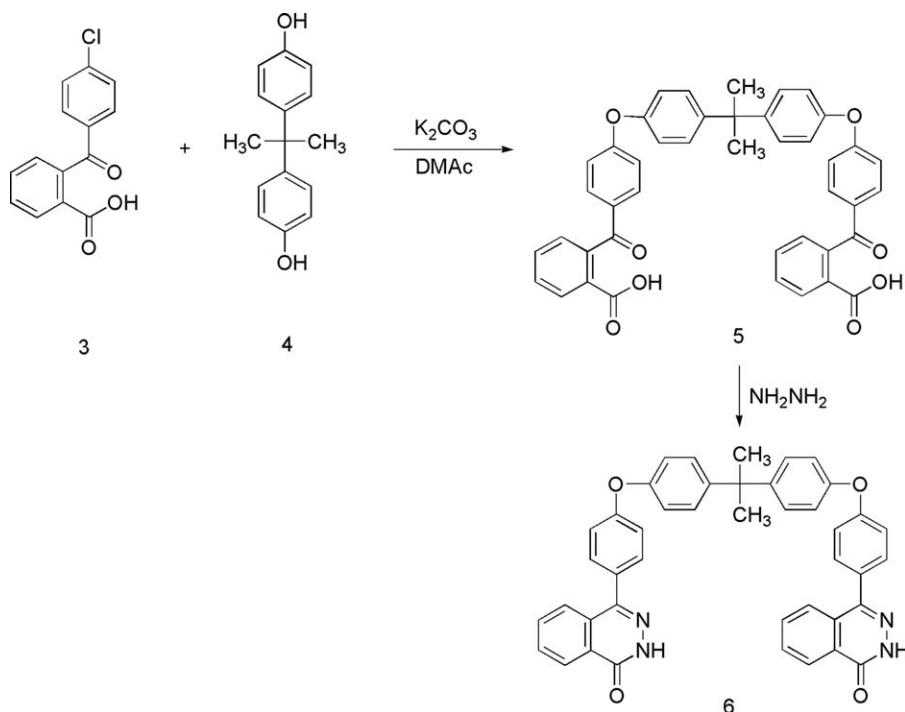
membranes were immersed in an Erlenmeyer flask containing Fenton's reagent. The flask was shaken vigorously once every 10 min until the membrane began to break.

### Synthesis of 2-(4-chlorophenylbenzoyl)benzoic acid **3** (Scheme 1)<sup>27</sup>

To a flask equipped with a Dean-Stark trap, phthalic anhydride **2** (29.6 g, 0.2 mol) were charged and dissolved in chlorobenzene **1** (120 mL). Aluminum chloride (80.0 g, 0.6 mol) was added to the above solution under stirring in the presence of nitrogen protection. The reaction mixture was refluxed and stirred for 4 h at 75–80°C. Upon cooling, the resulting mixture was poured into diluted HCl, agitated. At the beginning, white deposition was created, then the deposition dissolved and the resulting mixture became yellow and phase separation. 30 mL 40% KOH was added in to the obtained organic layer. Moved the water layer and acidized it with a large amount of 10% HCl water solution to precipitate the product. The resulting white powders were filtered off, dried, and recrystallized from chlorobenzene. Yield: 82.96% (43.25 g); mp: 150–152°C.

### Synthesis of BPA containing dicarboxylic acid **5** (Scheme 2)<sup>27</sup>

To a flask equipped with a Dean-Stark trap, 2,2-bis(4-hydroxyphenyl)propane **4** (0.02 mol, 4.56 g) and potassium carbonate (0.024 mol, 3.31 g) were



**Scheme 2** Synthesis of bisphthalazinone monomer **6**.

charged and dissolved in DMAc (40 mL) and toluene (40 mL) under stirring in the presence of nitrogen protection. The mixture was heated to 140°C for 2 h and then added 1,2-(4-chlorophenylbenzoyl)benzoic acid **3** (0.04 mol, 10.40 g), the toluene was finally removed by distillation after no additional water appeared. The reaction mixture was continued for 15 h at 168°C. Upon cooling, the resulting mixture was dissolved in 50 mL of H<sub>2</sub>O and poured into diluted HCl to precipitate the product. The resulting white powders were filtered off, dried, and recrystallized from aqueous glacial acetic acid. Yield: 90.81% (12.14 g); mp: 213–215°C. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 1.67 (s, 6H), 6.98–7.97 (m, 24H). MALDI-TOF-MS: single peak found: 676.81. Calcd. for C<sub>43</sub>H<sub>32</sub>O<sub>8</sub>: 676.71.

### Synthesis of BPA containing bisphthalazinone **6** (Scheme 2)<sup>27</sup>

To a flask equipped with a Dean-Stark trap containing **5** (0.02 mol, 4.56 g) dissolved in 200 mL ethanol, hydrazine hydrate (0.024 mol, 3.05 g) was slowly introduced. The reaction mixture was refluxed and stirred for 24 h at this temperature. At the beginning of the reaction, the reaction mixture appeared as a white emulsion. The mixture become clearer and clearer stepwise during heating. Compound **6** started to precipitate out from the solution in white color after 6 h. The reaction mixture was cooled down and filtered off, dried, and recrystallized from aqueous glacial acetic acid. Yield: 90.18% (12.14 g); mp: 320°C. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 1.67 (s, H), 7.05 (d, 4H), 7.13 (d, 4H), 7.30 (d, 4H), 7.58, 4H), 7.87 (d, 2H), 7.90 (m, 4H), 8.31 (d, 2H), 12.82 (s, 2H). MALDI-TOF-MS: single peak found: 669.00. Calcd. for C<sub>43</sub>H<sub>32</sub>N<sub>4</sub>O<sub>4</sub>: 668.74.

### Synthesis of polymer **10a** (Scheme 3)

To a 25 mL three-necked round-bottomed flask, fitted with a Dean-stark trap, a condenser, a nitrogen inlet/outlet, and a magnetic stirrer, **7** (0.85 mmol, 0.2976 g) and potassium carbonate (119 mmol, 0.1547 g) were charged and dissolved in DMAc (2 mL) and toluene (3 mL) under stirring in the presence of nitrogen protection. The mixture was then heated to 140°C for 2 h and then added **8** (0.80 mmol, 0.1744 g). The toluene was finally removed by distillation after no additional water appeared. The reaction mixture was continued for 20 h at 168°C.

Then the reaction mixture was cooled to room temperature, **6** (0.2673 g, 0.40 mmol) and potassium carbonate (0.56 mmol, 0.0728 g) were charged and added DMAc (2 mL) and toluene (5 mL) under stirring in the presence of nitrogen protection. The mixture was heated to 140°C for 2 h and then added **9**

(0.45 mmol, 0.1898 g). Toluene was finally removed by distillation after no additional water appeared. The reaction mixture was continued for 20 h at 168°C. Then the reaction mixture was cooled to room temperature and precipitated in 100 mL of mixture of methanol and water. The precipitates were filtered and wash with water thrice to remove inorganic salts. The fibrous polymer was collected and dried at 110°C under vacuum for 24 h.

<sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 1.65 (s, 72H), 7.02 (m, 160H), 7.11 (m, 100H), 7.28 (m, 104H), 7.61–7.68 (m, 130H), 7.85–7.95 (m, 154H), 8.38 (m, 50H). FTIR-ATR (film, cm<sup>-1</sup>): 3426, 2880, 2354, 1650, 1585, 1488, 1222, 1153, 998, 748. (C<sub>38</sub>H<sub>24</sub>O<sub>9</sub>S<sub>2</sub>·6H<sub>2</sub>O)(C<sub>38</sub>H<sub>24</sub>O<sub>3</sub>)<sub>13</sub>(C<sub>56</sub>H<sub>38</sub>N<sub>4</sub>O<sub>11</sub>S<sub>2</sub>·6H<sub>2</sub>O)<sub>12</sub>: Calcd. C, 68.68; H, 4.55; N, 3.19; S, 4.01. Found C, 68.14; H, 4.92; N, 3.96; S, 5.92.

### Synthesis of polymers **10b-c**, **11a-c** (Scheme 3)

Polymers **10b-c** and **11a-c** were synthesized followed the same procedure used for the preparation of polymer **10a**. The reactants molar ratios were list in Table I.

#### Polymer **10b**

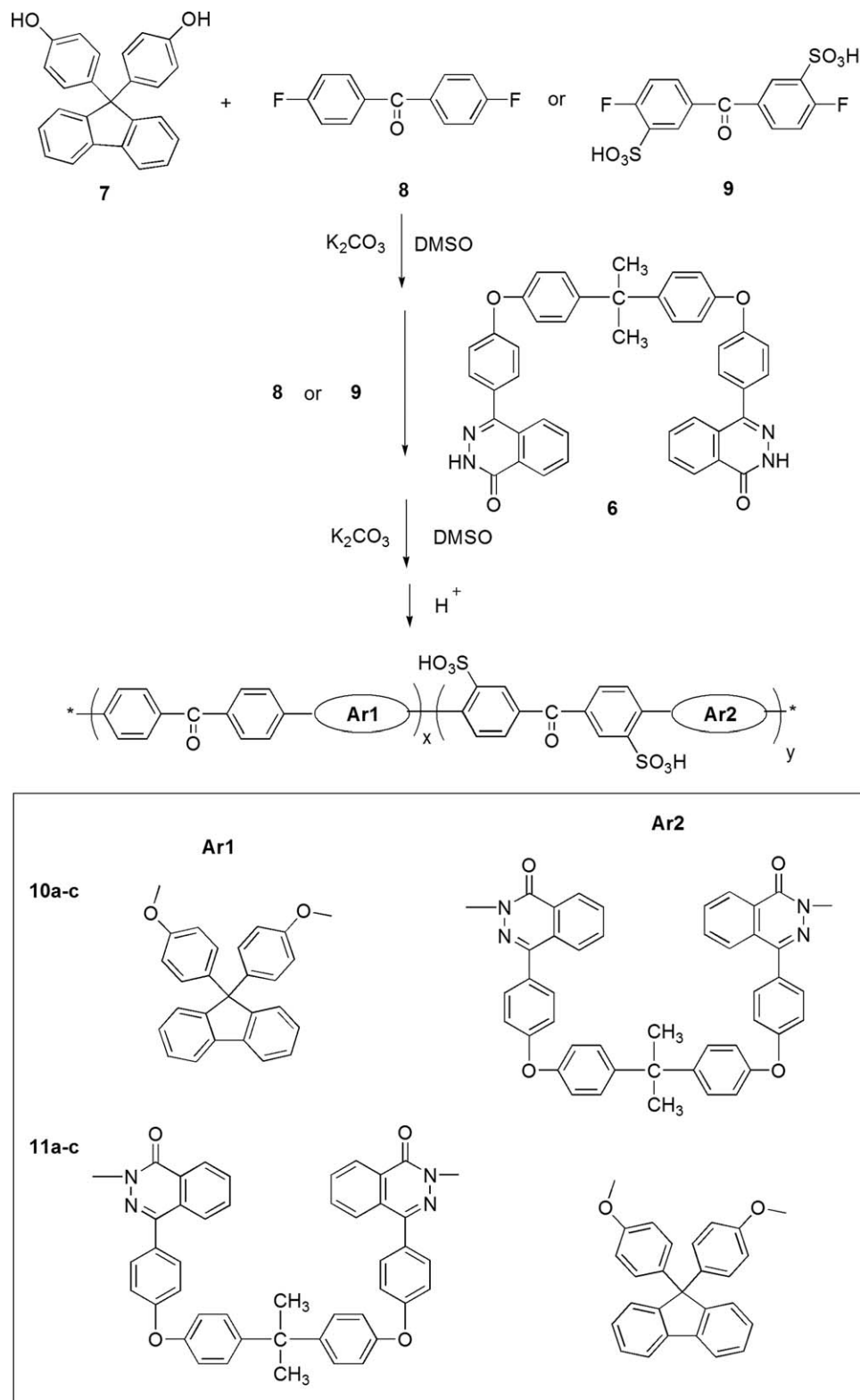
<sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 1.65 (s, 48H), 7.02–7.04 (m, 168H), 7.11–7.13 (m, 96H), 7.27–7.29 (m, 100H), 7.57–7.78 (m, 140H), 7.84–7.92 (m, 116H), 8.38 (m, 34H). FTIR-ATR (film, cm<sup>-1</sup>): 3412, 2894, 2594, 2429, 2036, 1903, 1650, 1590, 1472, 1221, 1007, 844, 731. (C<sub>38</sub>H<sub>24</sub>O<sub>9</sub>S<sub>2</sub>·6H<sub>2</sub>O)(C<sub>38</sub>H<sub>24</sub>O<sub>3</sub>)<sub>16</sub>(C<sub>56</sub>H<sub>38</sub>N<sub>4</sub>O<sub>11</sub>S<sub>2</sub>·6H<sub>2</sub>O)<sub>8</sub>: Calcd. C, 72.28; H, 4.55; N, 2.46; S, 3.23. Found C, 72.12; H, 4.96; N, 2.21; S 3.62.

#### Polymer **10c**

<sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 1.66 (s, 42H), 6.98–7.05 (m, 96H), 7.11–7.13 (m, 108H), 7.28–7.30 (m, 112H), 7.57–7.78 (m, 152H), 7.85–7.94 (m, 114H), 8.39 (m, 30H). FTIR-ATR (film, cm<sup>-1</sup>): 3406, 2894, 2354, 2050, 1925, 1643, 1584, 1472, 1221, 991, 732. (C<sub>38</sub>H<sub>24</sub>O<sub>9</sub>S<sub>2</sub>·6H<sub>2</sub>O)(C<sub>38</sub>H<sub>24</sub>O<sub>3</sub>)<sub>20</sub>(C<sub>56</sub>H<sub>38</sub>N<sub>4</sub>O<sub>11</sub>S<sub>2</sub>·6H<sub>2</sub>O)<sub>7</sub>: Calcd. C, 74.53; H, 4.56; N, 2.04; S, 2.72. Found C, 74.12; H, 5.06; N, 2.11; S, 3.32.

#### Polymer **11a**

<sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 1.67 (s, 30H), 6.86–6.88 (m, 80H), 6.96–7.00 (m, 100H), 7.17–7.19 (m, 80H), 7.34–7.42 (m, 122H), 7.49–7.51 (m, 36H), 7.62–7.64 (m, 62H), 7.93–7.95 (m, 76H), 8.16 (m, 42H). FTIR-ATR (film, cm<sup>-1</sup>): 3420, 2880, 2413, 1643, 1584, 1488, 1228, 1013, 845, 754. (C<sub>56</sub>H<sub>38</sub>N<sub>4</sub>O<sub>11</sub>S<sub>2</sub>·6H<sub>2</sub>O)(C<sub>38</sub>H<sub>24</sub>O<sub>9</sub>S<sub>2</sub>·6H<sub>2</sub>O)<sub>20</sub>(C<sub>56</sub>H<sub>38</sub>N<sub>4</sub>O<sub>5</sub>)<sub>4</sub>: Calcd. C, 61.11; H, 4.55; N, 1.37; S, 7.57. Found C, 61.29; H, 5.05; N, 2.04; S, 7.10.



**Scheme 3** Synthesis of polymers **10a-c** and **11a-c**.

**Polymer 11b**

$^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 1.66 (s, 60H), 6.85 (m, 64H), 6.96–7.00 (m, 104H), 7.15 (m, 112H), 7.34–7.40 (m, 98H), 7.48 (m, 76H), 7.60 (m,

74H), 7.91–7.93 (m, 108H), 8.14 (m, 34H). FTIR-ATR (film,  $\text{cm}^{-1}$ ): 3419, 3056, 2880, 2812, 2338, 1650, 1585, 1481, 1228, 1007, 844, 741.  $(\text{C}_{56}\text{H}_{38}\text{N}_4\text{O}_{11}\text{S}_2 \cdot 6\text{H}_2\text{O})$   $(\text{C}_{38}\text{H}_{24}\text{O}_9\text{S}_2 \cdot 6\text{H}_2\text{O})_{16}(\text{C}_{56}\text{H}_{38}\text{N}_4\text{O}_5)_9$ : Calcd. C, 65.28;

TABLE I  
The Synthesis of Sulfonated Multiblock Copolymers 10a–c, 11a–c, and 13

Polymer	The molar ratios of monomers 6 : 9 : 8 : 7	$\eta^a$ of oligomers (dL g <sup>-1</sup> )	$\eta^a$ (dL g <sup>-1</sup> )	Yield (%)	IEC <sup>b</sup> ( $\times 10^{-3}$ mol g <sup>-1</sup> )	IEC <sup>c</sup> ( $\times 10^{-3}$ mol g <sup>-1</sup> )
10a	12 : 13 : 13 : 14	0.53	0.85	94.88	1.32	1.03
10b	8 : 9 : 16 : 17	0.68	1.14	79.16	1.04	0.76
10c	7 : 8 : 20 : 21	0.82	2.08	64.85	0.87	0.66
11a	5 : 21 : 4 : 20	0.63	0.99	65.80	2.30	1.87
11b	10 : 17 : 9 : 16	0.52	1.30	55.45	1.73	1.76
11c	14 : 14 : 13 : 13	0.41	1.12	96.01	1.33	1.23
	7 : 8 : 12 : 9					
13	17 : 16 : 8 : 9	0.34	2.42	93.67	0.99	0.71
Nafion 117 <sup>d</sup>	–	–	–	–	0.91 <sup>d</sup>	0.83

<sup>a</sup> Tested in 0.5 g dL<sup>-1</sup> solution in DMSO at 25°C.

<sup>b</sup> Calculated IEC of the sulfonated multiblock copolymers.

<sup>c</sup> Measured IEC of the sulfonated multiblock copolymers.

<sup>d</sup> Ref. 25.

H, 4.55; N, 2.61; S, 5.82. Found C, 66.19; H, 5.12; N, 2.68; S, 5.92.

#### Polymer 11c

<sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 1.65 (s, 84H), 6.84 (m, 52H), 6.96–7.02 (m, 108H), 7.14 (m, 138H), 7.25–7.40 (m, 80H), 7.47 (m, 112H), 7.60–7.68 (m, 84H), 7.92 (m, 134H), 8.14 (m, 28H). FTIR-ATR (film, cm<sup>-1</sup>): 3413, 2916, 2598, 2435, 2325, 2043, 1903, 1650, 1585, 1481, 1228, 1007, 845, 731. (C<sub>56</sub>H<sub>38</sub>N<sub>4</sub>O<sub>11</sub>S<sub>2</sub>·6H<sub>2</sub>O)(C<sub>38</sub>H<sub>24</sub>O<sub>9</sub>S<sub>2</sub>·6H<sub>2</sub>O)<sub>13</sub>(C<sub>56</sub>H<sub>38</sub>N<sub>4</sub>O<sub>5</sub>)<sub>13</sub>: Calcd. C, 68.26; H, 4.54; N, 3.49; S, 4.57. Found C, 68.14; H, 4.92; N, 2.91; S, 5.23.

#### Synthesis of polymers 13 (Scheme 4)

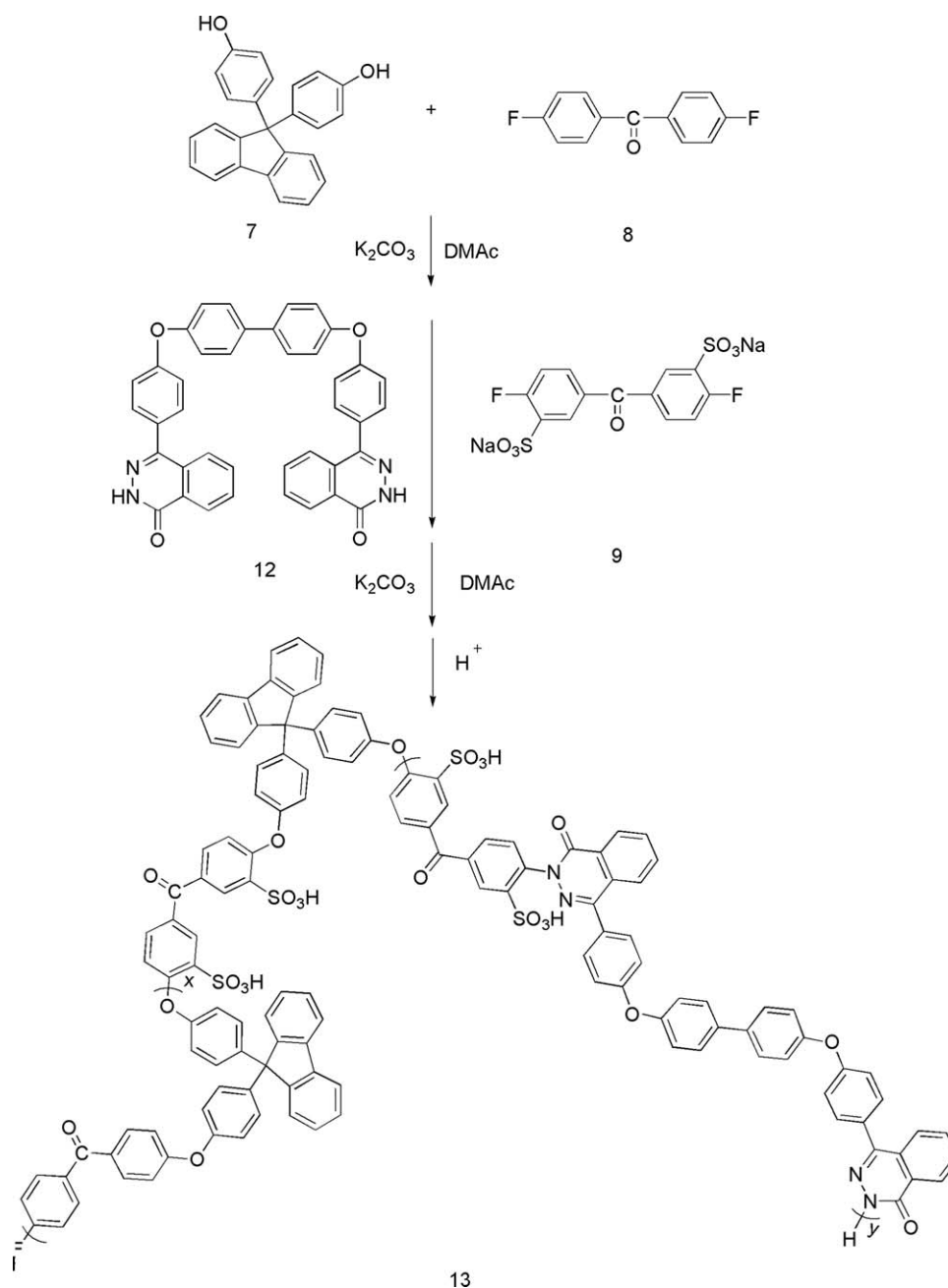
Synthesis of polymer 13 was performed followed the same procedure used for the preparation of polymer 10a. The dosages were 0.2505 g for 12, 0.1898 g for 9, 0.1744 g for 8, and 0.2976 g for 7. The corresponding molar ratio of 12 : 9 : 8 : 7 was 8 : 9 : 16 : 17. Yield: 93.67%. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 6.98–6.99 (m, 168H), 7.19 (m, 128H), 7.25–7.50 (m, 68H), 7.67–7.81 (m, 172H), 8.39 (m, 34H). FTIR-ATR (film, cm<sup>-1</sup>): 3456, 3049, 2034, 1903, 1647, 1589, 1487, 1231, 1151, 1010, 924, 837, 742. (C<sub>38</sub>H<sub>24</sub>O<sub>9</sub>S<sub>2</sub>·6H<sub>2</sub>O)(C<sub>38</sub>H<sub>24</sub>O<sub>3</sub>)<sub>16</sub>(C<sub>53</sub>H<sub>32</sub>N<sub>4</sub>O<sub>11</sub>S<sub>2</sub>·6H<sub>2</sub>O)<sub>8</sub>: Calcd. C, 72.03; H, 4.36; N, 2.51; S, 3.29. Found C, 72.70; H, 4.73; N, 2.18; S, 3.62.

## RESULTS AND DISCUSSION

### Synthesis of sulfonated multiblock copolymers 10a–c, 11a–c, and 13 containing phthalazinone ether ketone and fluorene ether ketone moieties

For the synthesis of sulfonated multiblock PEK with sequenced hydrophilic blocks and hydrophobic blocks, our methodology was the designed hydro-

philic blocks and hydrophobic blocks synthesized in different steps of a two-step reaction. One patent disclosed that the phthalazinone-based proton exchange membrane appears to have lower cross-over of methanol in a direct methanol fuel cell (DMFC).<sup>28</sup> The previous work<sup>21</sup> confirmed that the ionomers containing phthalazinone moiety with random distributed hydrophilic moieties and hydrophobic moieties showed excellent thermal, chemical stability, and resistance to oxidation. Miyatake published a series of their research works disclosed that the fluorene moieties can increase ionomers water retention ability at high temperatures and strengthen proton conductivity at temperature high as 120°C.<sup>29–31</sup> Thus, monomers containing phthalazinone or fluorene moiety are selected to synthesize ionomers to obtain high and stable proton conductivity. 2-(4-Chlorophenylbenzoyl)benzoic acid 3 is the key starting material of bisphthalazinone 6. Using common chemicals phthalic anhydride 2 and chlorobenzene 1 2-(4-chlorophenylbenzoyl)benzoic acid can be conveniently synthesized by typical electrophilic reaction depicted in Scheme 1. Scheme 2 discloses the two-step synthesis procedure of bisphthalazinone 6. The first step is to synthesize BPA containing dicarboxylic acid 5 by nucleophilic reaction. Then monomer 6 is produced by cyclization of Hydrazine hydrate and 5. Copolymers 10a–c, 11a–c, and 13 containing poly(phthalazinone ether ketone) and poly(fluorene ether ketone) blocks are synthesized via a two-step one-pot method as depicted in Schemes 3 and 4. The architecture of the sulfonated multiblock copolymers can be readily afforded by adjusting the molar ratios of reactants (Table I). The molecular weights of the fluorine-terminated poly(fluorenyl ether ketone), the fluorine-terminated sulfonated poly(fluorenyl ether ketone), and the copolymers are given in Table I. The  $\eta$  value of the oligomers can be changed and controlled by varying the molar ratio of bisphenol fluorine and



**Scheme 4** Synthesis of polymer 13.

difluoro-monomers. The oligomer synthesis step must be run a long time to guarantee the designed structure. The block segment length is calculated on the designed IEC of the sulfonated SPFEK. To eliminate oxidation, the reaction mixture should be carefully protected under a nitrogen flow. The polymerization results are listed in Table I. The inherent viscosity of the synthesized polymers ranged from 0.85 to 2.42 dL g<sup>-1</sup>, demonstrating very high molecular weight of the resulted polymers.

All the polymers were soluble in common aprotic solvents, such as DMSO, DMAc, dimethylformamide (DMF), and *N*-methylpyrrolidone (NMP). Tough

and smooth film was obtained by evaporating the solvent of the 5% solution in DMAc at 60°C in a dust-free environment. The <sup>1</sup>H-NMR spectra of polymer 10a and 11a are demonstrated in Figures 1 and 2, respectively, with all the peaks assigned to the molecular structures. The peak corresponding to adjacent hydrogen atom of sulfonated group in polymer 10a is at 8.39 ppm because of the electron withdraw action of nitrogen hybrid ring in phthalazinone unit. Whereas the peak corresponding to adjacent hydrogen atom of sulfonated group in polymer 11a locates at 8.16 ppm owing to the nucleophilic aromatic substitution taking place between the

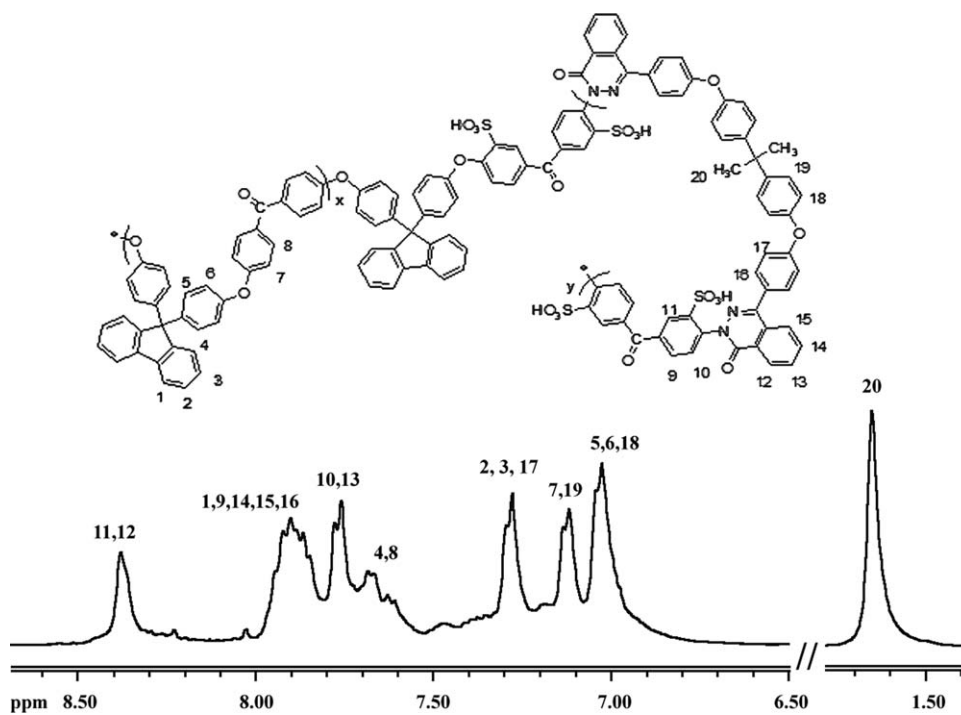
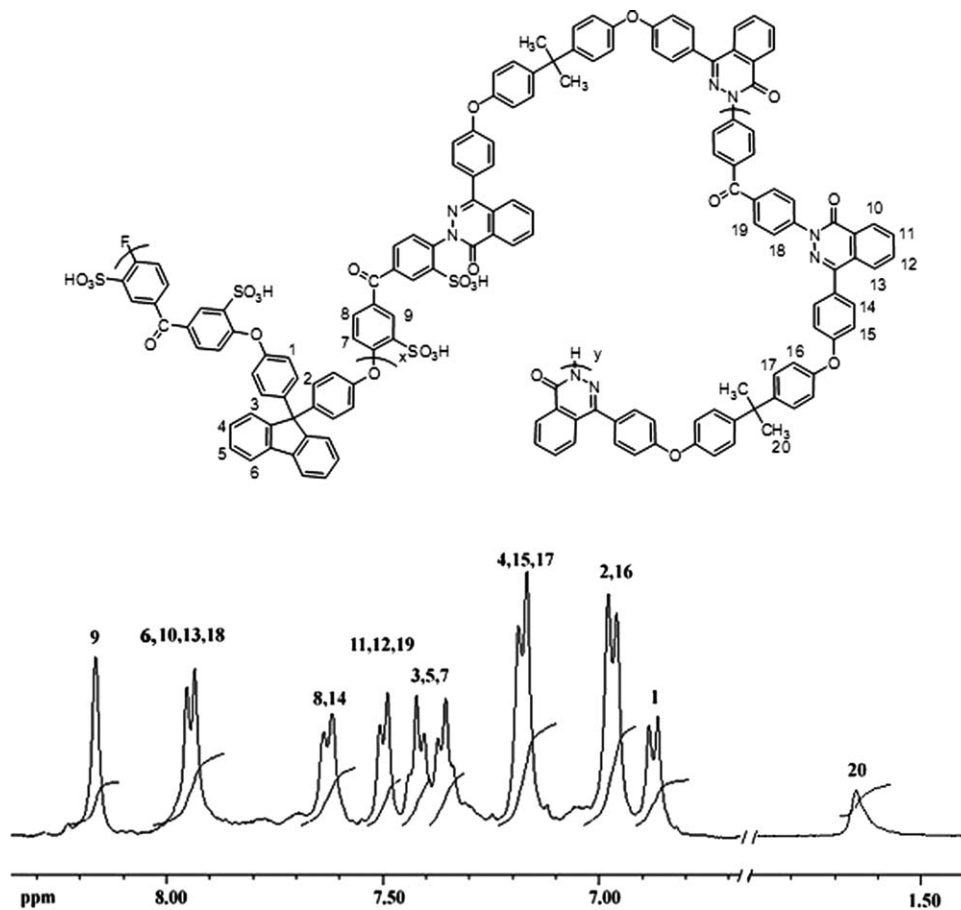
Figure 1  $^1\text{H-NMR}$  spectra of polymer 10a.Figure 2  $^1\text{H-NMR}$  spectra of polymer 11a.



TABLE II  
The Properties of Sulfonated Multiblock Copolymers 10a–c, 11a–c, and 13

Polymer	Resistance to oxidation <sup>a</sup> (h)		$T_{d5\%}$ (°C)	Water uptake <sup>b</sup> (%)	Methanol uptake <sup>c</sup> (%)	Ethanol uptake <sup>c</sup> (%)	Conductivity <sup>d</sup> (S/cm)
	$t_1$	$t_2$					
10a	F	e	253	26.4	4.2	7.7	$1.20 \times 10^{-3}$
10b	F	e	286	31.5	22.9	23.2	$3.16 \times 10^{-4}$
10c	F	e	267	25.1	6.1	14.2	$1.38 \times 10^{-4}$
11a	160	185	197	400.0	f	f	$6.54 \times 10^{-3}$
11b	F	e	157	371.3	f	f	–
11c	F	e	205	318.8	f	f	$2.14 \times 10^{-3}$
13	F	e	272	18.9	7.6	15.3	$1.22 \times 10^{-3}$
Nafion 117 <sup>g</sup>	–	–	–	42.3	–	–	$3.48 \times 10^{-3}$

<sup>a</sup>  $t_1$  and  $t_2$  refer to the expended time that the membrane began to rupture and disappeared in the solution.

<sup>b</sup> Measured at 80°C.

<sup>c</sup> Measured at refluxing temperature.

<sup>d</sup> Measured at 30°C, 100% relative humidity for hydrate membrane samples.

<sup>e</sup> Undegradable.

<sup>f</sup> Dissolved.

<sup>g</sup> Ref. 25.

sulfonated aryl halide and electron rich 4,4'-(9-fluorenylidene) diphenol. The aforementioned hydrogen peaks almost have no side-shoulder peak. The integration ratios of these peaks are well in accordance with the proposed molar ratios of each component (the feed molar ratio of monomers) of copolymers. All these <sup>1</sup>H-NMR results confirm that our proposed nucleophilic aromatic substitution taking place at a high extent.

### Water affinity and alcohol resistance

It is well known that water content, in proton exchange membranes, is one of key factors to determine the proton conductivity of the membrane. However, excess water uptake can lead to the mechanical property deteriorating of membrane due to the soluble nature of membrane in water. As can be seen from Table II, the water uptakes of copolymers with sulfonated poly(flourene ether ketone) blocks are 10–20 times higher than those copolymers with sulfonated poly(phthalazinone ether ketone) blocks. The water uptakes of the polymers in the same series increased with increasing IEC. As for polymers in different series, the relationship between IEC and water uptake changed. 10a has a designed IEC of 1.32. The designed IEC value of the polymer 11c is 1.33. The calculated IEC difference of these polymers is 0.2 according the data listed in Table I. The calculated water uptake difference of these polymers is 292.4% according the data listed in Table II. That is a proof the copolymers with sulfonated poly(flourene ether ketone) blocks demonstrate better hydrophilicity.

The methanol and ethanol uptakes results in Table II indicate copolymers with sulfonated poly(phthalazinone ether ketone) blocks have strong alcohol re-

sistance. Those copolymers with sulfonated poly(flourene ether ketone) blocks were dissolved in methanol and ethanol. It is no doubt that those ionomers with sulfonated poly(flourene ether ketone) blocks cannot be used in alcohol fuel cell.

### Oxidative and thermal stabilities

The oxidative stability to peroxide radical attack was investigated by measuring the elapsed time that a membrane began break after immersion of each sample in Fenton's reagent 3 wt % H<sub>2</sub>O<sub>2</sub> + 2 ppm FeSO<sub>4</sub>) at 80°C. The results are listed in Table II. These copolymers except polymer 11a exhibit more excellent oxidative stability when compared with the

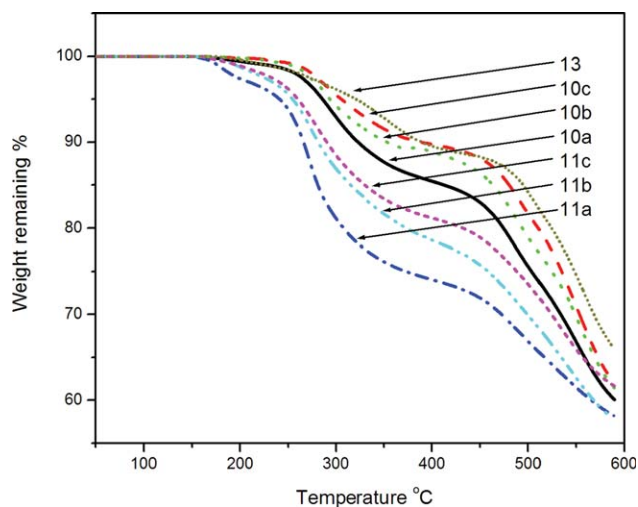


Figure 3 TGA trace of polymers 10a–c, 11a–c, and 13. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

reported fluorene-containing sulfonated poly(arylene ether sulfone)<sup>29</sup> and sulfonated poly(phthalazinone ether ketone)s.<sup>21</sup> It is also evident that the oxidative stabilities of copolymers decreased with increasing IEC value, especially in the case of IEC 2.30.

The thermal properties of polymers **10a-c**, **11a-c**, and **13** were investigated using TGA and DSC. All the polymers were preheated to remove moisture and solvent, and then TGA experiments were run from 30°C to 600°C at a heating rate of 20°C/min under nitrogen. Similar to other sulfonated polymers, two-step degradation profiles were observed for these polymers as shown in Figure 3. The first weight loss stages observed at 170–400°C were attributed to the elimination sulfonic acid groups. The second weight loss stages at 400–500°C can be attributed to the degradation of polymer main chain. Figure 3 also shows that sulfonated polymers with higher IEC values degrade more quickly than those with lower IEC values in the temperature range from 170°C to 400°C. There was no glass transition temperature observed from the DSC measurement of the polymers ranging from 60°C to 250°C due to their ionomer nature. The high thermal weight loss temperatures of the sulfonated multiblocks copolymers show excellent thermal chemical stability.

### Ion exchange capacity and proton conductivity

The ion exchange capacity (IEC) of the membrane was determined by titration. The membranes were first immersed in 2M NaCl solution for 24 h to exchange the sodium ions for protons. The resulting solution was then titrated with 0.1M NaOH using phenolphthalein as an indicator. The results are listed in Table I. The titration IEC values are lower than the designed values. This is because (1) it is not easy to get exact weight of the completely dried samples and (2) the proton exchange treatment might be incomplete. Especially in cases of high IEC polymers, these kinds of effect are more obvious.

Proton conductivities of the hydrated membranes were determined at 30°C and in 100% humidity. The results are tabulated in Table II. The highest value of proton conductivity of  $6.54 \times 10^{-3}$  S/cm was observed for polymer **11a**. The conductivity of Nafion 117 reported in the literature<sup>25</sup> was  $3.48 \times 10^{-3}$  S/cm at the same testing condition. Although the proton conductivity of the copolymers with sulfonated phthalazinone ether ketone blocks was still much lower than that of Nafion. Their strong alcohol resistance has encouraged us to study the properties of this class of polymers with higher IECs because the proton conductivity generally depends on the IEC.

### CONCLUSIONS

We have described the successful synthesis of sulfonated multiblock copoly(ether-ketone)s bearing poly(phthalazinone ether ketone) and poly(fluorene ether ketone) blocks by two-step polycondensation. The water uptakes of the copolymers with sulfonated poly(phthalazinone ether ketone) blocks are moderate. In this series, polymer **10a** gave the proton conductivity of  $1.20 \times 10^{-3}$  S/cm with IEC of 1.03. The water uptakes of the copolymers with sulfonated poly(fluorene ether ketone) blocks are high than 300%. These copolymers showed better proton conductivity. The copolymers with sulfonated poly(phthalazinone ether ketone) blocks had strong alcohol resistance at refluxing temperature. As the copolymers bearing sulfonated poly(fluorene ether ketone) blocks were dissolved in methanol and ethanol. The cast films of all the above copolymers were transparent, ductile, and flexible. Moreover, these copolymers demonstrated greatly improved oxidative and thermal stabilities. Especially, the copolymers bearing sulfonated poly(phthalazinone ether ketone) hydrophilic blocks and poly(fluorene ether ketone) hydrophobic blocks is a kind of promising proton exchange membrane material for proton exchange membrane fuel cell used methanol or ethanol as fuel.

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