# Synthesis and Sulfonation of Poly(aryl ethers) Containing Triphenyl Methane and Tetraphenyl Methane Moieties from Isocynate-Masked Bisphenols

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ABSTRACT: Wholly aromatic poly(aryl ethers) containing triphenylmethane and tetraphenylmethane moieties were successfully synthesized by aromatic nucleophilic substituting polycondensation from masked bisphenols and decafluorobiphenyl followed by sulfonation with chlorosulfonic acid. The sulfonation took place only at the para positions on the pendant phenyl rings due to the novel biphenol structures designed. For the synthesized polymers, the sulfonation content can be easily controlled and the water-takeup can be conveniently tailored by changing the amount of sulfonation agent. These sulfonated polymers are soluble in polar organic solvents, such as NMP, dimethylacetamide, dimethyl sulfoxide, dimethylformamide, and ethylene glycol monomethyl ether and can be readily cast into tough and smooth films from solutions. The films exhibited very high water absorption ability and superior mechanical strength. These polymers also showed high glass transition temperatures ranging from 176 to 203 °C compared with Nafion. The sulfonated polymers can be potentially used as the proton-exchange membranes for fuel cells.

### Introduction

In recent years there has been growing interesting in the development of a new proton exchange membrane to meet the requirement of fuel cells. It is generally accepted that among the many available kinds of proton conducting polymer electrolytes, poly(perfluoroalkylsulfonic acid) (Nafion) is the most preferable from the standpoint of chemical and thermal stabilities and physical and proton-conducting properties.  $^{\rm 1-3}$  However, its extremely high cost has limited to a large-scale practical use of Nafion. Many efforts have been devoted to developing cheaper proton-conducting polymers. Fluorine-free or partially fluorinated membranes have been shown to be potential candidates to substitute for the poly(perfluoroalkylsulfonic acid) membranes, as long as their mechanical, chemical, and electrochemical properties are comparable to Nafion. For instance, many fluorine-free polymers with sulfonic and/or phosphonic acid groups onto highly stable aromatic polymers have been reported. These include poly(ether ether ketone) (PEEK),<sup>4–8</sup> polysufone (PSF),<sup>9–11</sup> poly(aryl ether sulfone) (PES),<sup>12,13</sup> poly(aryl ether phthalazines),<sup>14</sup> and poly-(phenylene sulfide) (PPS).<sup>15,16</sup> Unfortunately, most of them failed to be used as proton-exchange membranes with reasonable lifetime, due to a combination of hydrolytic and oxidative degradation.<sup>17,18</sup>

To improve the durability of a polymer electrolyte membrane for fuel cells, many research works on

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partially fluorinated membranes have been disclosed in the literature. The most successful one is the sulfonated poly(trifluorostyene) membrane<sup>19,20</sup> developed by Ballard Advanced Materials Corp. Some properties of the membrane are almost the same as those of Nafion117.<sup>20,21</sup> Furthermore, the radiation grafting of styrene/divinylbenzene mixtures onto the backbone of fluorinated polymer has been extensively used to fabricate partially fluorinated polymer membranes.<sup>22–24</sup> Amarilla et al.<sup>25</sup> have reported a method for the preparation of thin composite membrane consisting of poly(vinylidene floride), linear sulfonated polystyrene, and antimonic acid. A similar polymer membrane synthesized from sulfonated polystyrene microspheres, poly(vinylpyrrolidone) and poly(vinylidene fluoride) also has been reported.<sup>26</sup> More recently, Miyatake and Hay<sup>27,28</sup> have designed aromatic copolymers containing sulfonated tetraphenylphenylene (or hexaphenylbiphenylene), fluorinated alkane, and perfluorophenylene moieties.

Despite a lot of new polymer membrane materials that have been synthesized, there is still no one candidate that is practically applicable for a proton exchange membrane having equivalent properties with Nafion. To meet the needs of fuel cell electrolytes, the polymers should exhibit chemical and electrochemical stability in the cell-operating environment, such as high resistance to oxidation, reduction, and hydrolysis. They should also possess reasonable mechanical strength and stability during the cell operation. Meanwhile, chemical properties compatible with the bonding requirements of the membrane electrode assembly (MEA) have to be achieved. Finally, the production costs of the polymers should be compatible with the application of fuel cells. In previous papers, we have reported the synthesis and properties of the polyaromatics with hindered and bulky

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groups that allowed the position-directed sulfonation.<sup>29</sup> These polymers showed high proton conductivity that could support high currents with minimal resistive losses and zero electronic conductivity.

It is well-known that poly(arylene ethers) are very stable structural materials; however, fuel cells assembled using these materials can only run a relatively short time due to membrane damage. Presumably, the damage results from a combination of hydrolytic and oxidative degradation. The degradation was documented to take place at the ether bonds in the backbone of aromatic polymers when there is a sulfonic acid group on the ortho position to the ether bond. However, the position-directed sulfonation of polyaromatics seems very difficult. Therefore, it is important to design and synthesize without the ortho-position-substituted sulfonic acid groups. In this respect, we report in this paper the synthesis of a series of partially fluorinated poly-(arylene ethers) and the sulfonation of these polymers with chlorosulfonic acid. The sulfonation took place only at the para positions on the pendant phenyl rings due to the novel bisphenol structures designed. These novel polymers were very soluble in common organic solvents and could be readily cast into tough and smooth films. It is expected that these partially fluorinated polymers should be more stable for use as membranes in fuel cells.

#### **Experimental Section**

**Materials.** All the chemicals used were reagent grade and purified by the standard methods. 2,6-Dimethylphenol, dichlorodiphenylmethane, and decafluorobiphenyl were obtained commercially from Aldrich Chemical Co. Dimethyl sulfoxide (DMSO), *N*,*N*-dimethyformamide (DMF), ethylene glycol monomethyl ether, chloroform, methylene chloride, toluene, methanol, phenol, and benzaldehyde were obtained from commercial sources and used as received. *N*,*N*-Dimethylacetamide (DMAc) was dried over 4 Å molecular sieves. Toluene was dried over sodium wire prior to being used. Anhydrous potassium carbonate was dried at 60 °C for 10 h in a vacuum oven.

**Characterization.** The glass transition temperatures ( $T_g$ 's) were determined on a Seiko 220 differential scanning calorimetry (DSC) instrument at a heating rate of 20 °C/min under nitrogen protection. The second scan was immediately initiated after the sample was cooled to room temperature. Thermal stability of the polymers from 30 to 600 °C was determined with a Seiko thermogravimetric analyzer (TGA/DTA; model

SSC-5200) under a protective nitrogen atmosphere (200 mL/ min). The heating rate used was 20 °C/min. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) analyses were carried out on a Kratos KOMPACT MALDI-TOF-MS. The analyte consisted of 1:4:2 (weight) of a sample, lithium bromide, and 1,8,9-trihydroxyanthracene (Dithranol) matrix. A sample with about 0.2  $\mu$ L of this analyte was spotted on the sample slot and dried at a temperature of about 50 °C. All spectra were recorded in the reflection mode. High-performance liquid chromatographic (HPLC) experiments were performed on a Milton Roy CM4000 multiple-solvent delivery system with a C8 Prime Sphere 4.6 mm  $\times$  250 mm column, with chloroform as the eluent, and with a UV detector at 254 nm. NMR data were recorded at 400 MHz on a Varian 400 Hz NMR instrument and are listed in parts per million downfield from tetramethylsilane. Melting points were taken on a XT4A melting point apparatus.

**Monomer Synthesis. (a) Preparation of Bis(4-hydroxyphenyl)phenylmethane (1a).** To a 50 mL, three-neck, roundbottom flask, equipped with a magnetic stirrer and a nitrogen inlet, containing 2.12 g (20.0 mmol) of benzaldehyde and 5.64 g (60.0 mmol) of phenol in 10 mL of toluene, 3.0 g of 60% sulfuric acid was added dropwise at 25 °C under nitrogen atmosphere with stirring (Scheme 1). The mixture was heated to 60–70 °C and maintained at that temperature for 8 h. Then the reaction mixture was cooled to room temperature to precipitate out a red brown solid. The solid was filtered and washed with water twice and a little toluene once and dried in a vacuum to yield 3.98 g of red brown solid as crude product (72.0% yield). It was recrystallized twice from toluene to obtain **1a** as a pale brown crystalline solid (m.p. 163–165 °C; 58% yield).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$  2.343 (s, 2H, OH); 5.408 (s, 1H, CH); 6.716–6.959 (t, 8H, 2C<sub>6</sub>H<sub>4</sub>); 7.147–7.171 (m, 5H, C<sub>6</sub>H<sub>5</sub>). MS: *m/e* 39, 55, 77, 94, 115, 152, 165, 181, 199, 228, 259, 276 (100%, M<sup>+</sup>).

(b) Preparation of Bis(3,5-dimethyl-4-hydroxyphenyl)phenylmethane (1b). The preparation of 1b was carried out using the same procedure as the synthesis of 1a except that phenol and 2,6-dimethylphenol were used. The crude product was recrystallized twice from toluene to afford 1b as a pale brown crystalline solid (m.p. 159–160 °C; 62% yield).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$  2.178 (s, 12H, CH<sub>3</sub>); 3.821 (s, 2H, OH); 5.292 (s, 1H, CH); 6.709 (s, 5H, C<sub>6</sub>H<sub>5</sub>); 7.093–7.284 (m, 4H, 2C<sub>6</sub>H<sub>2</sub>). MS: *m/e* 39, 65, 77, 91, 127, 152, 165, 181, 255, 317 (100%), 332 (M<sup>+</sup>).

(c) Preparation of Bis(4-hydroxylphenyl)diphenylmethane (1c). To a 50 mL, two-necked flask fitted with a condenser and a nitrogen inlet, dichlorodiphenylmethane (2.37 g, 10 mmol) and phenol (2.07 g, 22 mmol) were introduced. The mixture was stirred at room temperature until no gas was produced and then slowly heated to 150 °C followed by introducing nitrogen through the system for 20 min. Finally, the resulting mixture was distilled under reduced pressure for 30 min. Upon cooling to room temperature, the residue in the flask was subjected to recrystallization from ethanol. Pure **1c** was obtained as a pale yellow solid powder (2.1 g; m.p. 273–274 °C; 60.0% yield).

<sup>1</sup>H NMR (DMSO- $d_6$ , ppm):  $\delta$  6.656 (d, 4H), 6.868 (d, 4H), 7.067–7.269 (m, 10H, 2C<sub>6</sub>H<sub>5</sub>). MALDI-TOF-MS: found, 352.0; calcd for C<sub>25</sub>H<sub>20</sub>O<sub>2</sub>, 352.4.

(d) Preparation of Bis(3,5-dimethyl-4-hydroxyphenyl)diphenylmethane (1d). Using the same procedure as the synthesis of 1c, 1d was synthesized from dichlorodiphenylmethane (2.37 g, 10 mmol), 2,6-dimethylphenol (2.68 g, 22 mmol), and a catalytic amount of phenol (100 mg). The mixture was stirred at room temperature until no volatiles were produced. The reaction mixture was then heated to 50-60 °C and stirred at that temperature for 4 h. Then the temperature of the mixture was increased slowly to 150 °C, and nitrogen flow was allowed to pass through the system for 20 min. Thereafter, the resulting mixture was distilled under reduced pressure for 30 min. Upon cooling to room temperature, the resulting crude product was recrystallized from the mixture solvent of ethanol with petroleum ether to yield pure yellow product (2.8 g; m.p. 200-201 °C; 68.6% yield).

<sup>1</sup>H NMR (DMSO- $d_6$ , ppm):  $\delta$  2.11 (s, 12H, 4 CH<sub>3</sub>), 6.76 (s, 4H, 2C<sub>6</sub>H<sub>2</sub>), 7.127–7.24 (m, 10H, 2C<sub>6</sub>H<sub>5</sub>). MALDI-TOF-MS: found, 408.1; calcd for C<sub>29</sub>H<sub>28</sub>O<sub>2</sub>, 408.5.

(e) Preparation of Bis(4-propylcarbamoylphenyl)phenylmethane (2a). The synthesis procedure for 2a is as follows. A solution of 1a (5 mmol), *n*-propyl isocyanate (3.75 mL), and triethylamine (1 mL) in 20 mL of toluene was heated to 120 °C and kept at that temperature for 8 h. Upon the completion of the reaction, the mixture was rotavapped to ~8 mL using a rotavapor. White product powders were precipitated out from the solution after cooling to room temperature. The precipitate was filtered, washed twice with a minimum amount of toluene, and dried under vacuum at 60–70 °C for 24h. Compound 2a, as pure white powders, was obtained in a good yield (85.0%; m.p. 127–128 °C).

m.p. 127-128 °C). <sup>1</sup>H NMR (CDCI<sub>3</sub>, ppm):  $\delta$  0.95 (t, 6H,2CH<sub>3</sub>), 1.58 (m, 4H, 2CH<sub>2</sub>), 3.24 (m, 4H, 2CH<sub>2</sub>), 4.99 (b,2H,NH), 5.50 (s,1H,CH), 7.02-7.28 (m, 13H).

(f) Preparation of Bis(3,5-dimethyl-4-propylcarbamoylphenyl)phenylmethane (2b). A solution containing 1b (2 mmol), *n*-propyl isocyanate (1.7 mL), and triethylamine (0.5 mL) in 10 mL of toluene was heated to 120 °C and kept at that temperature for 10 h. After the reaction, the mixture was concentrated to 5 mL using a rotavapor and cooled to room temperature. White product powders were precipitated out from the solution. The precipitates were filtered, washed twice with a minimum amount of toluene, and dried under vacuum at 60–70 °C for 24h. Compound **2b**, as pure white powders, was obtained in good yield (73.6%; mp. 173–174 °C).

<sup>1</sup>H NMR (CDCI<sub>3</sub>, ppm):  $\delta$  0.96 (t, 6H,2CH<sub>3</sub>), 1.59 (m, 4H, 2CH<sub>2</sub>), 2.11 (s,12H,4CH<sub>3</sub>), 3.24 (m, 4H, 2CH<sub>2</sub>), 6.76 (b, 4H, 2C<sub>6</sub>H<sub>2</sub>), 7.11–7.28 (m, 5H, C<sub>6</sub>H<sub>5</sub>).

(g) Preparation of Bis(4-propylcarbamoylphenyl)diphenylmethane (2c). A solution of 1c (4.0 mmol), *n*-propyl isocyanate (3.75 mmol), and triethylamine (1 mL) in 10 mL of toluene was heated to 120 °C and kept at that temperature for 8 h. The mixture was concentrated to 5 mL by evaporating the solvent. White product powders were precipitated out from the solution after cooling to room temperature. The precipitates were filtered, washed twice with a minimum amount of toluene, and dried under vacuum at 60-70 °C for 24 h. Compound 2c, as pure white powders, was obtained in good yield (82.2%; m.p. 190–191 °C).

<sup>1</sup>H NMR (CDCI<sub>3</sub>, ppm):  $\delta$  0.96 (t, 6H, 2CH<sub>3</sub>), 1.58 (m, 4H, 2CH<sub>2</sub>), 3.23 (m, 4H, 2CH<sub>2</sub>), 6.98 (b, 4H, 2C<sub>6</sub>H<sub>2</sub>), 7.14–7.24 (m, 14H).

(h) Preparation of Bis(3,5-dimethyl-4-propylcarbamoylphenyl)diphenylmethane (2d). A solution of 1d (3.6 mmol), *n*-propyl isocyanate (3.1 mL), and triethylamine (1 mL) in 15 mL of toluene was heated to 120 °C and maintained at that temperature for 10 h. The mixture was rotavapped to ~6 mL, and cooled to room temperature. White product powders were precipitated out from the solution after cooling to room temperature. The precipitates were filtered, washed twice with a minimum amount of toluene, and dried under vacuum at 60–70 °C for 24 h. Compound **2d**, as pure white powders, was obtained in good yield (90.48%; m.p. 204–205 °C).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$  0.96 (t, 6H, 2CH<sub>3</sub>), 1.59 (m, 4H, 2CH<sub>2</sub>), 2.11 (s,12H, 4CH<sub>3</sub>), 3.23 (m, 4H, 2CH<sub>2</sub>), 5.05 (b, 2H, 2NH), 6.87 (s, 4H, 2C<sub>6</sub>H<sub>2</sub>), 7.15–7.24 (m, 10H, 2C<sub>6</sub>H<sub>5</sub>).

Synthesis of Poly(arylene ethers). (a) Synthesis of **Polymer 3a.** A typical polymerization procedure is given as follows. To a 25 mL, three-neck, round-bottom flask equipped with a magnetic stirrer, a Dean–Stark trap, condenser, and nitrogen inlet, 2a (0.2777 g, 0.62 mmol), decafluorobiphenyl (0.2079 g, 0.62 mmol), and potassium carbonate (0.1289 g, 0.93 mmol) in DMAc (2.0 mL) were added. The reaction mixture was heated to 80-90 °C and kept at that temperature for 8 h. The reaction mixture was diluted with DMAc (3 mL) when it became too viscous. After cooling to room temperature, the solution was poured slowly into methanol (60 mL) containing a few drops of hydrochloric acid. The polymer was precipitated out and washed successively with water (20 mL) and methanol (20 mL). The obtained polymer was redissolved in 30 mL of chloroform. After depositing for more than 5 h, the solution was filtered through a thin layer of Celite. The filtrate was concentrated to 4 mL, and poured slowly into 60 mL of methanol with stirring. The polymer was precipitated out and then filtered, washed with methanol, and dried at 120  $^\circ\mathrm{C}$ under vacuum for 24 h. White fibrous polymer 3a was obtained in a yield of 84.3%.

<sup>1</sup>H NMR (400 MHz; ppm):  $\delta$  6.945 (d, 4H), 7.076 (d, 6H), 7.193–7.240 (m, 1H), 7.285 (m, 2H).

(b) Synthesis of Polymer 3b. Polymer 3b (Figure 1) was synthesized from 2b and decafluorobiphenyl using the same procedure as the synthesis of polymer 3a. White fibrous polymer 3b was obtained in a yield of 85.0%.

<sup>1</sup>H NMR (400 MHz; ppm): δ 2.1525 (s, 12H), 6.741 (s, 4H,), 7.073 (d, 2H), 7.260(d, 1H), 7.288 (m, 2H).

(c) Synthesis of Polymer 3c. A typical polymerization procedure is as follows. Compound 2c (0.5220 g, 1 mmol), decafluorobiphenyl (0.3343 g, 1 mmol), and potassium carbonate (0.2087 g, 1.5 mmol) and DMAc (3.50 mL) were introduced into a 25 mL, three-neck, round-bottom flask equipped with a magnetic stirrer, a Dean-Stark trap, condenser, and nitrogen inlet. The reaction mixture was heated to 150-160 °C and maintained at that temperature for 18 h. The reaction mixture was diluted with DMAc (5 mL) when it became too viscous. After cooling to room temperature, the solution was poured slowly into methanol (60 mL) containing a few drops HCl. The polymer was precipitated out and washed with methanol. The obtained polymer was redissolved in 30 mL of chloroform. After depositing for more than 5 h, the solution was filtered through a thin layer of Celite. The filtrate was rotavapped to 4 mL and then poured slowly into 60 mL of methanol with stirring. The polymer was precipitated out and filtered, followed being washed with methanol and dried at 120 °C under vacuum for 24 h. White fibrous polymer 3c was obtained in a yield of 85.5%

<sup>1</sup>H NMR (400 MHz; ppm):  $\delta$  6.907 (d, 4H,), 7.145–7.196 (m, 10H), 7.224–7.260 (m, 4H).

(d) Synthesis of Polymer 3d. Polymer 3d (Figure 2) was synthesized from decafluorobiphenyl and 2d using the same procedure as the synthesis of polymer 3c. White fibrous polymer 3d was obtained in good yield (94.8%).

<sup>1</sup>H NMR (400 MHz; ppm):  $\delta$  3.229 (s, 12H), 6.824 (d, 4H), 7.159–7.179 (m, 6H), 7.240–7.255 (m, 4H).

(e) Synthesis of Copolymer 3e. Copolymer 3e was synthesized from the copolymerization decafluorobiphenyl with 2d (0.5 mmol) and 2b (0.5 mmol) using the same procedure as the synthesis of polymer 3c. White fibrous polymer 3e was obtained in yield (0.6069 g; 91.4%).

<sup>1</sup>H NMR (400 MHz; ppm):  $\delta$  6.947 (d, 4H,), 7.028 (d, 4H), 7.196–7.217 (m,10H), 7.240–7.273 (m, 4H), 7.764 (d, 4H).





Sulfonation of Poly(arylene ethers). A typical procedure for the sulfonation of polymers is given as follows: To the solution of 3a (0.25 mmol) in 25 mL of methylene chloride, 2.5 mL of 0.8 M chlorosulfonic acid in methylene chloride was added dropwise at room temperature over 1 h. The mixture was stirred vigorously for 6 h until the pale brown products precipitated out from the solution. The precipitates were collected and washed with hexane three times and redissolved in 5 mL of DMSO. To the solution was added 10 mL of 3 wt %potassium hydroxide aqueous solution. After 6 h reaction, the mixture was acidified with 100 mL of 5 vol % hydrochloric acid. The aqueous solution was dialyzed for 2 days. The sulfonated product 4a was recovered by evaporation of the water. All of the products were characterized by both FT-IR and <sup>1</sup>H NMR. The results of characterization of the sulfonated polymers are listed as follows.

(a) Polymer 4a. <sup>1</sup>H NMR (DMSO- $d_6$ ; ppm):  $\delta$  7.112–7.230 (br, 7H), 7.614 (m, 4H). FT-IR (KBr): 1035.9 ( $\nu_{SO_3H}$  sym), 1190.8 ( $\nu_{SO_3H}$  asym).

**(b) Polymer 4b** (Figure 3). <sup>1</sup>H NMR (DMSO- $d_6$ ; ppm):  $\delta$  2.138(s, 12H, 4CH<sub>3</sub>), 5.533 (s, 1H), 6.871 (s, 4H,) 7.079 (d, 2H), 7.533 (d, 2H). FT-IR (KBr): 1030.0 ( $\nu_{SO_3H}$  sym), 1211.4 ( $\nu_{SO_3H}$  asym).

(c) Polymer 4c. <sup>1</sup>H NMR (DMSO- $d_6$ ; ppm):  $\delta$  7.103–7.227-(br, 8H), 7.476(br, 4H), 7.740(2H). FT-IR (KBr): 1036.0 ( $\nu_{SO_3H}$  sym), 1228.4 ( $\nu_{SO_3H}$  asym).

(d) Polymer 4d (Figure 4). <sup>1</sup>H NMR (DMSO- $d_6$ ; ppm):  $\delta$  2.154 (s, 12H, 4CH<sub>3</sub>), 6.901 (s, 4H), 7.156 (d, 4H), 7.573 (d, 4H). FT-IR (KBr): 1036.0 ( $\nu_{SO_3H}$  sym), 1226.5 ( $\nu_{SO_3H}$  asym).

(e) Polymer 4e. <sup>1</sup>H NMR (DMSO- $d_6$ ):  $\delta$ (ppm) 2.142–2.168 (m, 24H, 8 CH<sub>3</sub>), 6.966 (s, 8H), 7.132–7.295 (br, 6H), 7.577 (br, 6H). FT-IR (KBr): 1036.5 ( $\nu_{SO_3H}$  sym), 1190.3 ( $\nu_{SO_3H}$  asym).

## **Results and Discussion**

**Syntheses of Bisphenols 1.** Novel bisphenols **1a,b** were readily synthesized from benzaldehyde and the phenols using 75% sulfuric acid as catalyst. The bisphenols tend to be easily oxidized, even though the reactions were performed under nitrogen atmosphere. A 50% excess of phenol in stoichiometric ratio was added in order to afford bisphenols in high yields. The bisphenols **1c,d** were synthesized by the reaction of dichlorodiphen-ylmethane with different phenols. The reaction should be carried out under nitrogen atmosphere with 10%



Figure 4. <sup>1</sup>H NMR spectrum for polymer 4d.

excess of phenol used, because the phenols were easily oxidized and dichlorodiphenylmethane was easily hydrolyzed. To get a good yield, the reaction temperature needed to be slowly raised and carefully controlled.

**Syntheses of the Masked Bisphenols 2.** The aforesaid and synthesized bisphenols **1** are extremely unstable and can be easily oxidized during the polymerization with decafluorobiphenyl, even though under the protection of nitrogen atmosphere. The reaction of isocyanates with alcohols to give *N*-carbamates has been widely employed to prepare polyurethanes.<sup>29,30</sup> Therefore, an alternate approach to stabilize bisphenols **1** is to react isocyanates with **1** to give *N*-carbamates, which can be easily purified by recrystallization. Urethanes usually decompose to alcohols at temperatures above 220 °C to give free isocyanate and alcohol or free amine, carbon dioxide, and olefin. For phenolic urethanes, the decomposition begins at temperatures as low as 150

 $^{\circ}C.^{31}$  So, they can decompose at 150  $^{\circ}C$  and could be polymerized with activated dihalo aromatic compounds to form high molecular polymers. It is preference to afford purer polymers via this method due to lower polycondensation temperature used.

The syntheses of *N*-carbamates are a simple addition reaction without any byproducts formation, and side reactions can be minimized under the appropriate conditions.<sup>32</sup> Various catalysts can speed up this reaction, and in this study triethylamine was adapted. To ensure the completed protection of hydroxyl groups of bisphenols **1**, a large excess of *n*-propyl isocyanate was added. After the reaction, the excess *n*-propyl isocyanate and solvent (toluene) were easily removed by distillation under reduced pressure.

**Syntheses and Properties of Polymers 3.** Hay et al.<sup>33</sup> have reported that the carbamates of bisphenol A, which could be rapidly cleaved by K<sub>2</sub>CO<sub>3</sub> to generate

#### Scheme 2. Syntheses of Polymers 3a-e



potassium phenoxide in situ, could be directly polymerized with dihalo aromatic compounds in DMAc to form high molecular weight poly(arylene ethers). Therefore, the carbamate method is quite useful for the preparation of poly(arylene ethers), especially when unstable bis-phenols are involved in the polymerization.

In previous work,<sup>29</sup> we have synthesized a series of fluorine-free and wholly aromatic polymers from bisphenols and activated dihalo aromatic compounds, such as bis(4-fluorophenyl)sulfone, 4,4-difluorobenzophenone, or 1,3(4)-bis(4-fluorophenzoyl)benzene. Since the polymers showed poorer solubility and precipitated out from the solution during the polymerization, it is difficult to obtain very high molecular weight polymers. Using decafluorobiphenyl, which is more reactive in nucleophilic substitution reaction and makes the polymers more soluble than the above difluoride monomers, allows the polymerization to take place at lower temperatures (Scheme 2). Moderately high molecular weight polymers ( $M_n = 10\ 000-15\ 000$ ) were obtained at 170 °C under a basic condition (K<sub>2</sub>CO<sub>3</sub> in DMAc). However, since oxidative reaction with a trace amount of oxygen in the system was inevitable, the polymers obtained exhibited a slightly dark color. As is well-known, there are three advantages using masked biphenols.<sup>15</sup> They are that (1) monomers can be purified by simple recrystallization, (2) no water is generated during polymerization, and (3) high molecular weight polymers are readily formed in a short period of time under mild conditions. Using the propylcarbamoyl-masked biphenol, high molecular weight polymers were synthesized with molecular weights  $(M_n)$  ranging from 26 159 to 49 983 Da that corresponded to inherent viscosities from 0.34 to 0.47 dL/g (Table 1).

The synthesized polymers are very soluble in common organic solvents, such as acetone, tetrahydrofuran (THF), and CHCI<sub>3</sub> and could be cast into smooth and flexible film from solutions. The molecular structures of the polymers were confirmed by <sup>1</sup>H NMR as stated in the Experimental Section.

Table 1. Molecular Weights of Polymers 3a-e

	3a	3b	3c	3 <b>d</b>	3e
$\eta_{ m inh}{}^a$ (dL/g)	0.40	0.46	0.43	0.47	0.34
$M_{ m n}{}^b$	32 378	45 306	39 714	49 983	26 159
$M_{ m w}{}^b$	83 468	97 276	70 315	319 263	70 899
MDI $^c$	2.58	2.15	1.77	6.39	2.71

 $^a$  0.5 g/dL in CHCl3 at 25 °C.  $^b$  Determined by GPC using polystyrenes as standards.  $^c$  Molecular weight distribution index.

Table 2. Thermal Properties for Polymers 3a-e

		_		-	
	3a	3b	<b>3c</b>	3d	3e
<i>T</i> <sub>g</sub> (°C)	176.0	195.2	200.9	203.3	190.8
TGA (N <sub>2</sub> )					
$T_{-5\%}$ (°C)	336.5	396.6	513.2	438.1	401.0
$T_{-10\%}$ (°C)	360.1	424.1	544.7	453.9	424.1

Polymers 3c-e were synthesized at higher temperature than polymers 3a,b. Presumably, it is because the steric hindrance of 2c,d is greater that that of 2a,b, and the propylcarbamoyl groups in 2c,d are more difficult to eliminate than that in 2a,b. Therefore, the in-situ deprotection and polymerization of 2c,d took place at higher temperature.

Thermal properties of the synthesized polymers are listed in Table 2. It can be seen that the polymers exhibited high glass transition temperatures and excellent thermal stabilities.  $T_{g}$ 's ranged from 176.0 to 203.3 °C, and 5% weight loss temperatures ranged from 340 to 510 °C, respectively.

The incorporation of bulky methyl groups onto the polymer backbone led to the increase in the  $T_g$ 's of the resulting polymers. Thus, the polymers derived from methyl-containing bisphenols **1b**,**d** exhibited higher  $T_g$ 's than their counterparts derived from bisphenols **1a**,**c**. It is apparent that the tetraphenyl-containing polymers **3c**,**d** exhibited better thermal stability than the triphenyl-containing polymers **3a**,**b**. It is believed that the poor thermal stability resulted from the presence of methyl groups on the polymer backbone. Scheme 3. Sulfonation of Polymer 3b



#### Scheme 4. Sulfonation of Polymer 3d





Table 3. Elemental Analyses of 4b,d,e

	found				calcd		
	Ce	He	$S_{ m e}$	Ct	Ht	$S_{ m t}$	$S_{ m r}$
4b	53.75	4.22	4.06	58.09	3.04	4.43	4.39
<b>4d</b>	45.85	4.36	6.06	54.91	2.90	7.14	7.25
<b>4e</b>	51.41	3.85	5.07	53.15	2.80	5.60	5.24

Syntheses and Properties of Sulfonated Polymers. All the polymers were sulfonated using chlorosulfonic acid in methylene chloride. The sulfonation completed at room temperature in a few hours. Because of the insolubility of the resulted products, chlorosulfonic acid must be added as slowly as possible under acutely stirring. Residual sulfonyl chloride was neutralized with aqueous potassium hydroxide in DMSO. Upon treatment with hydrochloric acid followed by dialysis, brownish polymers were obtained after evaporating the water. Based on the FT-IR spectra, strong absorption bands of sulfonic acid groups were observed at  $\sim 1035~{
m cm^{-1}}$ ( $\nu_{SO_{3}H}$  symmetric) and  $\sim 1220$  cm<sup>-1</sup> ( $\nu_{SO_{3}H}$  asymmetric). In the <sup>1</sup>H NMR spectrum, a peak at 7.20–7.30 ppm for **3b**, **d**, **e** disappeared and a new peak was observed at 7.50–7.60 ppm, indicating that the sulfonation occurred at only the para position of the pendant phenyl rings, as depicted in Schemes 3–5. For the polymers **3a 3c**, as expected, the sulfonation reaction was confirmed from the <sup>1</sup>H NMR spectrum to take place on the ortho position to ether bonds of phenylene groups. Elemental analyses were further performed to determine the sulfonation degrees of 4b,d,e. From Table 3, we can see that the hydrogen contents from elemental analyses

4e

**Table 4. Properties of Sulfonated Polymers** 

		water-take-up content, wt % in 80 °C	
polymer	$\mathrm{EW}^{a}$	(12 h)	solubility
4b	788	45.0	DMSO, DMAc, DMF, NMP
<b>4d</b>	528	75.3	DMSO, DMAc, DMF, NMP
<b>4e</b>	631	62.7	DMSO, DMAc, DMF, NMP

were greater than those from calculation. This behavior was resulted from the strong water absorption ability of the sulfonated polymers. To eliminate the effect of water, the sulfur contents were generally calculated using the following equation:

# sulfur content $(S_r) = C_t S_e / C_e$

where  $S_e$  and  $C_e$  are the sulfur and carbon contents respectively based on elemental analyses and  $C_t$  represents the theoretical carbon content calculated from the repeating unit of sulfonated polymer.

The solubility and the water-take-up content of sulfonated polymers **4b**,**d**,**e** are summarized in Table 4. All the sulfonated polymers were soluble in polar solvents such as DMSO, DMAc, DMF, and NMP. Polymers **4b**,**d**,**e** were swelled in water showing good water affinity. As expected, the water-take-up ability increased with the decrease of equivalent molecular weight (EW). Self-supporting, flexible, and transparent films can be obtained from these sulfonated polymers by casting from DMSO. Unlike other sulfonated polymers, which completely lose their mechanical strength after absorbing water, the as-made polymer films showed good mechanical strength. Poorer mechanical strength was resulted from the extensive sulfonation on the backbone of polymers. Furthermore, the films from 4b,d,e showed much higher water affinity (Table 4) than commercial Nafion film (about 25%). In this respect, these films showed potential application as proton-exchange membranes for fuel cells.

#### Conclusion

High molecular weight poly(arylene ethers) containing triphenylmethane and tetraphenylmethane moieties were prepared using the masked bis-phenols. These polymers had high glass transition temperatures ranging from 176.0 to 203.3 °C, when compared with Nafion. The sulfonation of these polymers took place only at the para positions on the pendant phenyl rings. The sulfonation content of these polymers can be easily controlled and the water-take-up can be conveniently tailored by changing the amount of the sulfonation agent. These sulfonated polymers are soluble in polar organic solvents and can be readily cast into tough and smooth films from solutions. These films exhibited good water affinity and superior mechanical strength. These polymers showed much higher water affinity than commercial Nafion film. Therefore, they can be potentially used as the proton-exchange membranes for fuel cells because of their comprehensive properties in stable structure, high water-take-up ability, and mechanical strength.

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#### **References and Notes**

- (1) Eisenberg, A.; Yeagger, H. L. *Perfluorinated Ionomer Mem-branes*, ACS Symposium Series 180; American Chemical Society: Washington, DC, 1982.
- (2) Grot, W. G. *Macromol. Symp.* **1994**, *82*, 161.
   (3) Shoesmith, J. P.; Collins, R. D.; Oakley, M. J.; Stevenson, D. K. J. Power Source 1994, 49, 129.

- (4) Bishop, M. T.; Karasz, F. E.; Russo, P. S.; Langley, K. H. Macromolecules 1885, 18, 86.
- Jin, X.; Bishop, M. T.; Ellis, T. S.; Karasz, F. E. Br. Polym. J. 1985, 17, 4.
- (6) Shibuya, N.; Porter, R. S. Macromolecules 1992, 25, 6495.
- Jia, L.; Xu, X.; Zhang, H.; Xu. J. J. Appl. Polym. Sci. 1996, 60, 1231.
- Trotta, F.; Druoli, E. G.; Moraglio, E.; Baima, P. J. Appl. Polym. Sci. 1998, 70. (9) Noshay, A.; Robenson, L. M. J. Appl. Polym. Sci. 1976, 20,
- 1885.
- (10) Johnson, B. C.; Yilgor, I.; Tran, C.; Iqbal, M.; et al. Polym. Chem. 1984, 22, 721.
- (11) Lufrano, F.; Squadrito, G.; Patti, A.; Passalacqua, E. J. Appl. Polym. Sci. 2000, 77.
- (12) Notle, R.; Ledjeff, K.; Bauer, M.; Mulhaupt, R. J. Membr. Sci. 1993, 83, 211.
- (13) Meng, Y. Z.; Tjong, S. C.; Hay, A. S.; Wang, S. J. J. Polym. Sci., Part A: Polym. Chem. 2001, 39, 3218.
  (14) Hiao, S. H.; Yang, C. Y. J. Polym. Sci., Part A: Polym. Chem.
- 1977, 35, 2801.
- (15) Miyatake, K.; Iyotani, H.; Yamamoto, K.; Tsuchida, E. Macromolecules 1996, 29, 6969.
- (16) Miyatake, K.; Shoyji, E.; Yamamoto, K.; Tsuchida, E. Macromolecules 1997, 30, 2941.
- (17) Steck, A. E. New Mater. Fuel Cell Syst. I, Proc. Int. Symp. 1995, 74.
- (18) Steck, A. E.; Stone, C. New Mater. Fuel Cell Syst. II, Proc. *Int. Symp.* **1997**, 792. (19) Basura, V. I.; Beattie, P. D.; Holdcroft, S. *J. Electroanal.*
- Chem. 1998, 458, 1.
- (20) Agostino, D.; Lee, J. Y., Jr.; Cook, E. H. [P]. U.S. Pat., 4012303, 1977-3-15.
- (21) Basura, V. I.; Beattie, P. D.; Holdcroft, S. J. Electroanal. Chem. 1999, 468, 180.
- (22) Nasef, M. M.; Saidi, H.; Dessouki, A. M.; El-Neser, E. M. Polym. Int. 2000, 49, 399.
- (23) Brack, H. P.; Buchi, F. N.; Rota, M.; Scherer, G. G. Polym. Eng. Sci. 1998, 77, 368.
- (24) Nasef, M. M.; Saidi, H.; Dessouki, A. M. J. Membr. Sci. 2003, 216, 27.
- (25) Amarilla, J. M.; Rojas, R. M.; Rojo, J. M.; Cubillo, M. J.; Linares, A.; Acosta, J. L. *Solid State Ionics* **2000**, *127*, 133.
- (26) Chen, N. P.; Hong, L. Solid State Ionics 2002, 146, 377.
- (27) Miyataka, K.; Oyaizu, k.; Tsuchida, E.; Hay, A. S. Macromoleculaules 2001, 34, 2065.
- (28) Miyatake, K.; Hay, A. S. J. Polym. Sci., Part A: Polym. Chem. 2001, 39, 3211.
- (29) Wang, S. J.; Meng, Y. Z.; Hlil, A. R.; Hay, A. S. Macromol-ecules, in press. Wang, L.; Meng, Y. Z.; Wang, S. J.; Xiao, M.; Hay, A. S. J. Polym. Sci., Part A: Polym. Chem., in press. (30) Bayer, O. Angew Chem. 1947, 59, 275.
- (31) Dyer, E.; Newborn, G. E. J. Am. Chem. Soc. 1958, 80, 5495.
- (32) Lyman, D. J. J. Polym. Sci. 1960, 45, 49.
- (33) Wang, Z. Y.; Carvalho, H. N.; Hay, A. S. J. Chem. Soc., Chem. Commun. 1991, 1221.

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