

# Synthesis and Properties of Sulfonated Aromatic Fluoro-Polymers

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**ABSTRACT:** Polycondensation of perfluorobiphenyl with  $\alpha,\alpha$ -bis(4-hydroxyphenyl)ethylbenzene and/or 9,9-bis(4-hydroxyphenyl)fluorene was investigated. The polycondensation of perfluorobiphenyl with  $\alpha,\alpha$ -bis(4-hydroxyphenyl)ethylbenzene and/or 9,9-bis(4-hydroxyphenyl)fluorene proceeded at low-temperature to give high-molecular weight and thermal stable polymers. The  $^{19}\text{F}$ -NMR spectra of the polymers indicate that the polymers consist of predominantly 1,4-phenylene structure with respect to the perfluoroaromatic compound. The sulfonation of the polymers

obtained from the polycondensation occurred at the phenyl groups and fluorenyl side chain. A tough and smooth film was prepared by a casting method from DMF solution of the sulfonated polymer. The films showed hydrolytic and oxidative stabilities, and a high-proton conductivity. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1582–1588, 2010

**Key words:** polycondensation; perfluorobiphenyl; bis(hydroxyphenyl); sulfonated fluorine polymers; electrolyte membrane

## INTRODUCTION

Proton conducting polymers have been recently developed,<sup>1–3</sup> and many polymers with sulfuric and/or phosphonic acid groups onto thermal stable aromatic polymers that include poly(ether ether ketone),<sup>4,5</sup> polysulfone,<sup>6,7</sup> poly(aryl ether sulfone),<sup>8</sup> poly(aryl ether phthalazines),<sup>9</sup> and poly(phenylene sulfide)<sup>10,11</sup> have been reported. Although the polymers have a higher thermal stability and glass transition temperature ( $T_g$ ) than those of Nafion ( $T_g = 115^\circ\text{C}$ ), most of them failed to be used as proton conducting membranes with enough lifetime. This may be presumably, because of a combination of hydrolytic and oxidative degradation documented to occur at ether or sulfide bonds in the backbone of aromatic polymers, and the degradations may be explained by the presence of a sulfonic acid group at the *ortho*-position to the ether bonds by increasing nucleophilicity for the displacement reaction, which contribute to the lower stability of the materials.<sup>12,13</sup> Thus, the design of the molecular structure for using as polyelectrolyte membrane is important to improve the durability.<sup>14</sup>

However, fluoro-polymers usually show thermal and chemical stabilities. Among the partially fluorinated polymer membranes that have been reported, the most successful one is a sulfonated poly(trifluoro-

styrene) membrane,<sup>15</sup> whose some properties are almost equal to those of Nafion. Amarilla et al.<sup>16</sup> synthesized thin composite polymer membranes consisting of poly(vinylidene fluoride) segment, a linear sulfonated polystyrene units, and antimonate acid groups. Similar polymer membranes were synthesized from sulfonated polystyrene microspheres, poly(vinyl pyrrolidone), and poly(vinylidene fluoride).<sup>17</sup>

The polymers should have chemical stabilities such as high-resistance to oxidation, reduction, and hydrolysis to use as fuel cell polymer electrolytes.<sup>1</sup> Taking the reported results into consideration, the sulfonated fluoro-poly(arylene ether)s obtained from polycondensation with perfluoroaromatic compound will be expected to have good properties as a polymer electrolyte membrane. We have reported, the synthesis of polymer consisting of 2,2-bis(4-hydroxyphenyl)hexafluoropropane or bisphenol-A (BPA) with perfluorobiphenyl or hexafluorobenzene.<sup>18</sup> However, such polymer is not suitable to the design of sulfonation of phenyl position in the chain. In this article, we synthesize the polymer obtained from the polycondensation of perfluorobiphenyl with  $\alpha,\alpha$ -bis(4-hydroxyphenyl)ethylbenzene and 9,9-bis(4-hydroxyphenyl)fluorene. Moreover, the sulfonation reaction of the fluorine-containing polymers and the some properties of the sulfonated polymers were investigated.

## Experimental

### Materials

Perfluorobiphenyl,  $\alpha,\alpha$ -bis(4-hydroxyphenyl)ethylbenzene, 9,9-bis(4-hydroxyphenyl)fluorene, dimethylsulf-

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oxide (DMSO), *N,N*-dimethylacetamide (DMAc), dimethyl formamide (DMF), and chlorosulfonic acid purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan, were used as received. Methylene chloride and other reagents were used after purification by conventional methods.

### Polymerization procedure

To a solution of perfluorobiphenyl (1.0 mmol) and bisphenol derivative (1.0 mmol) in 10 mL of DMAc was added sodium hydride (2.5 mmol) at 0°C for 3 h under nitrogen atmosphere. The mixture was then warmed up to reaction temperature (30°C). After the reaction, the products were poured into 200 mL of 3% hydrochloric acid to precipitate the polymer formed. The isolated polymer was purified by reprecipitation from THF/methanol of 3% hydrochloric acid, and dried under high-vacuum at room temperature overnight. Polymer yield was determined by gravimetry.

### Sulfonation of polymers

A typical procedure for sulfonation of the polymers is as follows; to the solution of the polymer (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 a few hours at room temperature until the pale brown products precipitated. The precipitate was collected and washed with an excess of hexane three times, and dissolved in 5 mL of DMSO. To the solution was added 100 mL of 3 wt % potassium hydroxide aqueous solution. After the reaction for 6 h, the products were acidified with 5 mL of concentrated hydrochloric acid, and concentrated by evaporation. The white product was filtered, and washed with an excess of water. The polymer was dried under high-vacuum overnight.

### Characterization of polymers

The number-average molecular weight ( $M_n$ ), the weight-average molecular weight ( $M_w$ ), and the polydispersity index ( $M_w/M_n$ ) of the polymers were determined by gel permeation chromatography (GPC) using a Tosoh 8000 series system in THF at flow rate of 1 mL/min at 38°C. Standard polystyrenes were used for molecular weight calibration. The  $^{19}\text{F}$ -NMR spectra of the polymers were measured in  $\text{CDCl}_3/\text{CF}_3\text{COOH}$ . The  $^1\text{H}$ -NMR spectra of the sulfonated polymers were measured in  $\text{CDCl}_3$  with TMS as an internal standard using a JEOL A-400 spectrometer. IR spectra of the polymer were measured using a JASCO FT/IR-430 spectrometer.

Thermal analysis was performed by the thermogravimetry (TG) using a SEIKO TG/DTA 6200 in nitrogen atmosphere at a heating rate of 10°C/min in the range from 25 to 500°C. The differential scanning calorimetry (DSC) was measured using a SEIKO DSC 6200 in nitrogen atmosphere at a heating rate of 20°C/min in the range from 25 to 250°C. The proton conductivity of sulfonated polymers was measured by four-probe electrochemical impedance spectroscopy using a Solartron S1 1280B.

### Production of polymer film

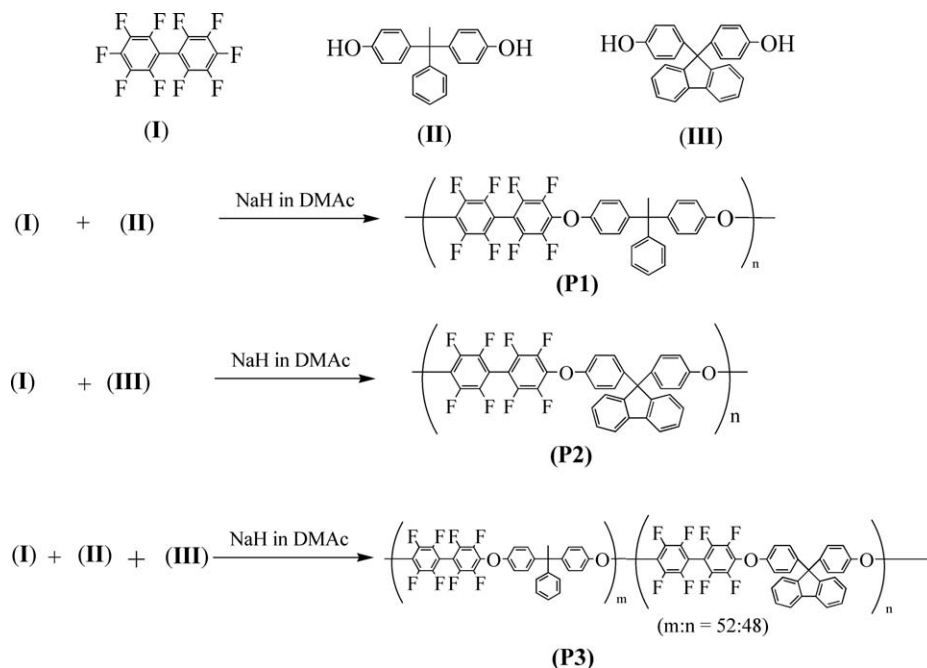
The films of the sulfonated polymers were prepared by a casting method. The sulfonated polymers (0.1 g) were dissolved in 4 mL of dimethylformamide (DMF), and casted on a teflon plate to give light brown films by heating at 60°C under high-vacuum.

## RESULTS AND DISCUSSION

### Synthesis of parent polymers

Polycondensation of perfluorobiphenyl with  $\alpha,\alpha$ -bis(4-hydroxyphenyl)ethylbenzene (**II**) and/or 9,9-bis(4-hydroxyphenyl)fluorene (**III**) in the presence of NaH as a base in DMAc at 30°C for 3 h was carried out (Scheme 1), and the results are listed in Table I. The polycondensation proceeded even at low-temperature to give high-molecular weight polymers in high-yields. It was reported that the polycondensation of bisphenol derivatives with bis(4-fluorophenyl)sulfone and 4,4-difluorobenzophenone did not give high-molecular weight polymer.<sup>19</sup> However, when perfluorobiphenyl was used as a fluorine compound, high-molecular weight polymers were formed easily, which is in an agreement with the previously reported results.<sup>18</sup> The resulting polymers afforded an unimodal in the GPC elution curves, and the molecular weights of the polymers were independent on the bis(4-hydroxyphenyl) compounds in the monomer feed.

The contents of (**II**) and (**III**) units in the resulting polymers were determined by  $^1\text{H}$ -NMR spectroscopy. The  $^1\text{H}$ -NMR spectra of the polymers are shown in Figure 1. In the NMR spectra of the polymers, no signals were observed based on perfluorobiphenyl, but the peaks based on (**II**) and (**III**). Each signal based on (**II**) and (**III**) in the polymers can be assigned as indicated in Figure 1. These peak intensities were used to determine the contents of the polymer. The  $\alpha,\alpha$ -bis(4-hydroxyphenyl)ethylbenzene content of the ternary components polymer (**P3**) was estimated to be 48 mol %, which is in a good agreement with the content of  $\alpha,\alpha$ -bis(4-hydroxyphenyl)ethylbenzene in the comonomer. This means that the nucleophilicity of  $\alpha,\alpha$ -bis(4-hydroxyphenyl)



**Scheme 1** Polycondensation of perfluorobiphenyl with bisphenol derivatives.

ethylbenzene and 9,9-bis(4-hydroxyphenyl)fluorene seems to be a similar in the polymerization.

Figure 2 shows the  $^{19}\text{F}$ -NMR spectra of the polymers obtained from the polycondensation of perfluorobiphenyl with  $\alpha,\alpha$ -bis(4-hydroxyphenyl)ethylbenzene (P1) and with 9,9-bis(4-hydroxyphenyl)fluorene (P2). In the polycondensation of perfluorobiphenyl with  $\alpha,\alpha$ -bis(4-hydroxyphenyl)ethylbenzene, two peaks appeared at  $-138.8$  ppm and  $-153.6$  ppm based on perfluorobiphenyl unit, but other peaks were not observed, indicating that the copolymer consists of the predominantly 1,4-phenylene structure without defect structures such as branching or cross-linking. In the  $^{19}\text{F}$ -NMR spectrum of the polymer obtained from the polycondensation of perfluorobiphenyl with 9,9-bis(4-hydroxyphenyl) flu-

orene, only two peaks appeared at  $-138.9$  and  $-153.6$  ppm based on perfluorobiphenyl unit, indicating that the copolymer predominantly also consists of the 1,4-phenylene link.

$T_g$  of the polymer was estimated from DSC measurement. The DSC charts are shown in Figure 3 and the values of  $T_g$  are also listed in Table I. All the polymers measured showed high  $T_g$ , suggesting that the polymers have a rigid structure. Then, a thermal

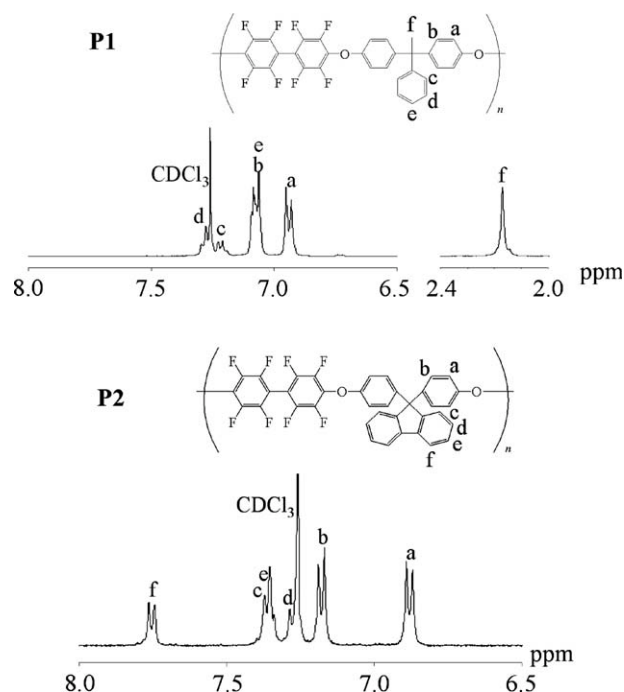
**TABLE I**  
Polycondensation of Perfluorobiphenyl with  $\alpha,\alpha$ -bis(4-hydroxyphenyl)ethylbenzene and/or 9,9-bis(4-hydroxyphenyl)fluorene at  $30^\circ\text{C}$  for 3 h<sup>a</sup>

Monomer feed (mmol)		Polymer <sup>b</sup>	Polymer yield (%) <sup>c</sup>	$M_n \times 10^{-4}$	$M_w/M_n$	$T_g$ ( $^\circ\text{C}$ )	
I <sup>b</sup>	II <sup>b</sup>						
1	1.0	-	<b>P1</b>	94	9.0	2.3	177
1	-	1.0	<b>P2</b>	92	11.5	2.4	259
1	0.25	0.75	-	96	11.4	3.0	
1	0.5	0.5	<b>P3</b>	96	11.9	3.7	217
1	0.75	0.25	-	93	10.8	3.2	

<sup>a</sup> NaH was used as base, dimethylacetamide was used as a polymerization solvent.

<sup>b</sup> Abbreviation is indicated in Scheme 1.

<sup>c</sup> Calculated from methanol insoluble part.



**Figure 1**  $^1\text{H}$ -NMR spectra of P1 and P2.

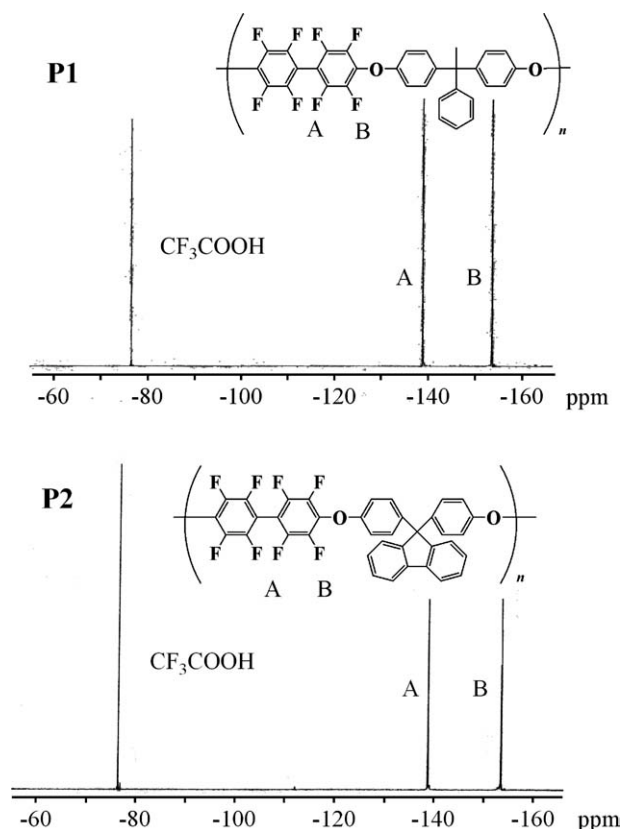


Figure 2  $^{19}\text{F}$ -NMR spectrum of P1 and P2.

stability of the polymers formed was checked by TGA measurement. The results are shown in Figure 4. The decomposition temperature of all the polymers examined was not observed up to *ca* 450°C, and the temperature of 5% weight loss of polymer ( $T_{d5\%}$ ) was similar to all the polymers obtained in this study. Namely, thermally stable polymers were synthesized.

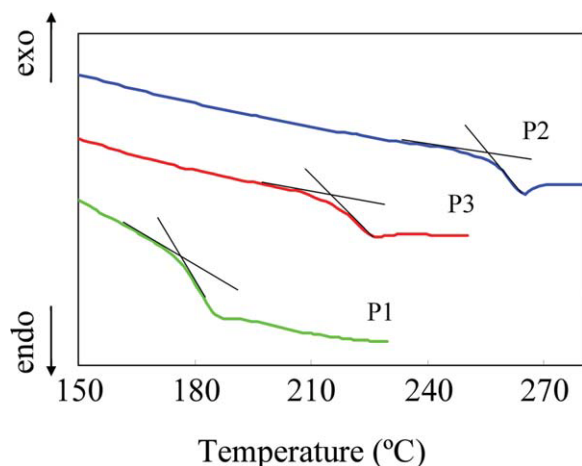


Figure 3 DSC charts of the polymers at a heating rate of 20°C/min. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

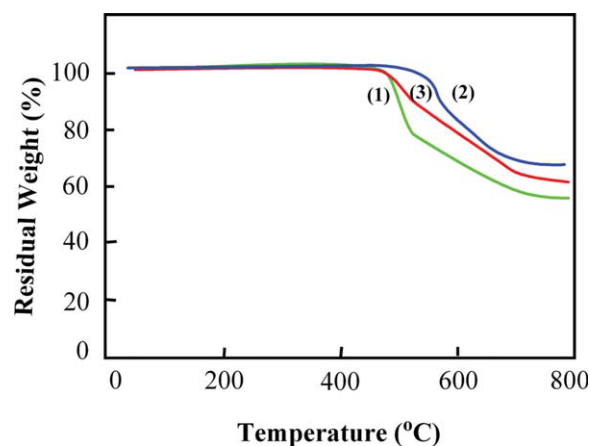


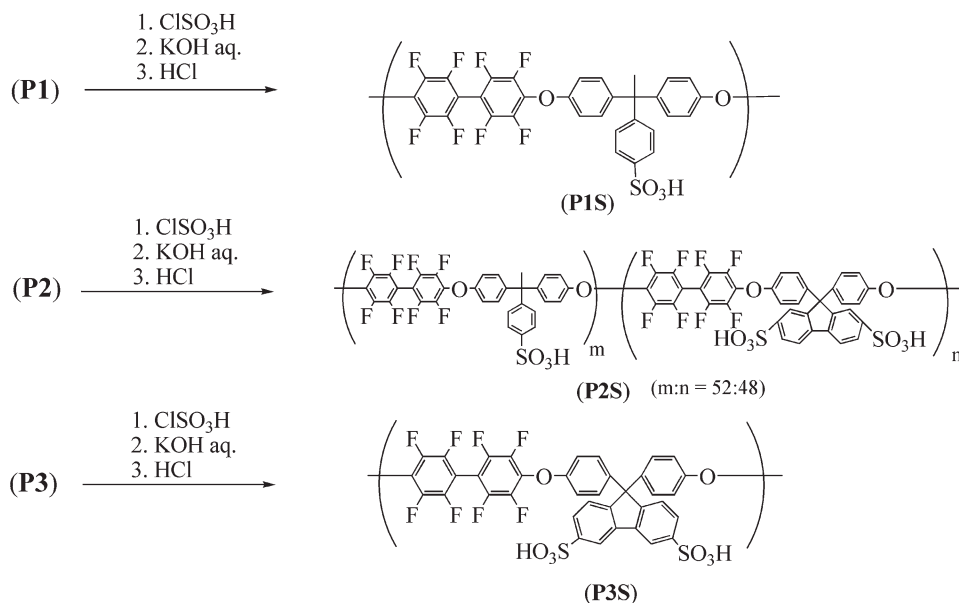
Figure 4 TGA curves of polymers at a heating rate of 10°C/min; P1 (1), P2 (2), and P3 (3). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

### Sulfonation of the polymers

The sulfonation of the polymers was carried out using chlorosulfonic acid in methylene chloride as indicated in Scheme 2. The reaction induced to give chlorosulfonated polymers as an intermediate of a sulfonated polymer. The chlorosulfonated polymers were hydrolyzed in an aqueous KOH in the presence of a small amount of DMSO, followed by acidification by hydrogen chloride to give corresponding sulfonated polymers.

The introduction of sulfonic acid groups in the polymer after the sulfonation was checked by the  $^1\text{H}$  and  $^{19}\text{F}$ -NMR spectroscopy. The  $^1\text{H}$ -NMR spectra of the sulfonated polymer are shown in Figure 5. In the  $^1\text{H}$ -NMR spectra of SP1, two sets of doublet peaks of aromatic proton based on 1,4-disubstituted phenylene structure were observed besides two doublet peaks attributed to the polymer main chain. In the spectrum of SP2, two broad peaks and a single peak of aromatic proton based on 1,2,4-trisubstituted phenylene structure were observed. The results suggest that the sulfonic acid groups were introduced predominantly at *p*-position of phenyl group and 2,7-position of fluorenyl group, respectively. However, small signals appeared as the proton "e" of P1 and the proton "d" of P2 (Fig. 1) were observed in the sulfonated polymers, indicating sulfonation reaction did not proceed completely. This was confirmed by the  $^{19}\text{F}$ -NMR spectra of the sulfonated polymers. The  $^{19}\text{F}$ -NMR spectra of the sulfonated polymers are shown in Figure 6. In addition to peaks based on the sulfonated polymers consist of mainly 1,4-phenylene structure with respect to perfluorobiphenyl group, two small peaks (A' and B') were also observed, and the signals of the main peaks (A and B) were shifted to the upfield, indicating that the complete sulfonation of the polymers did not occur under the



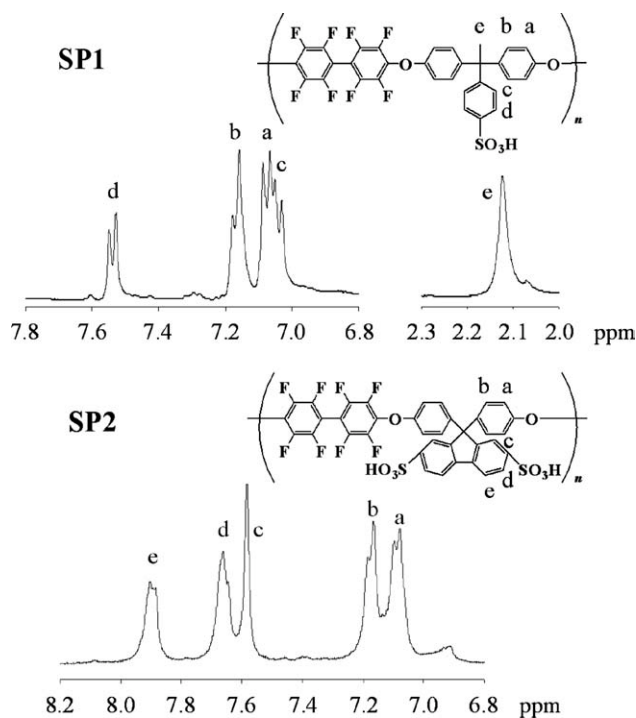
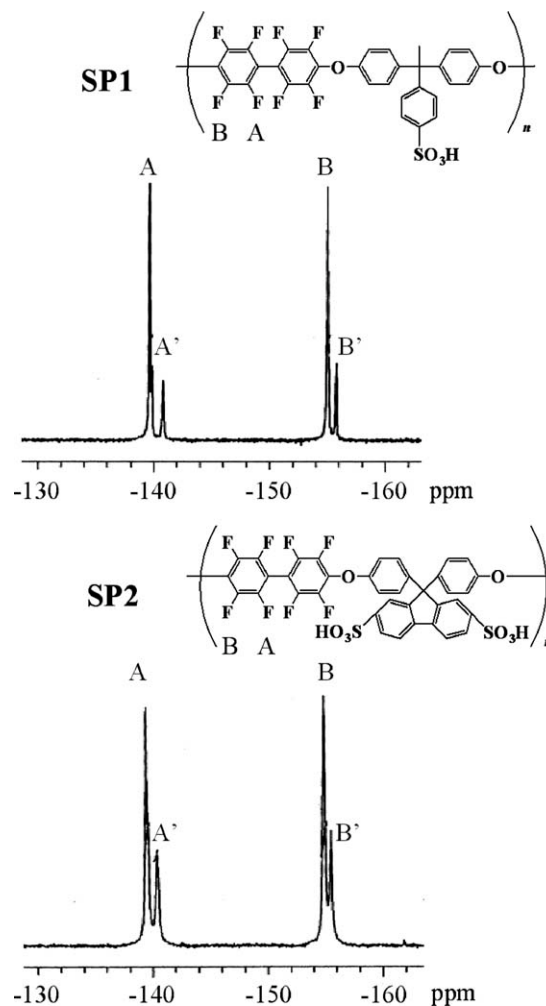


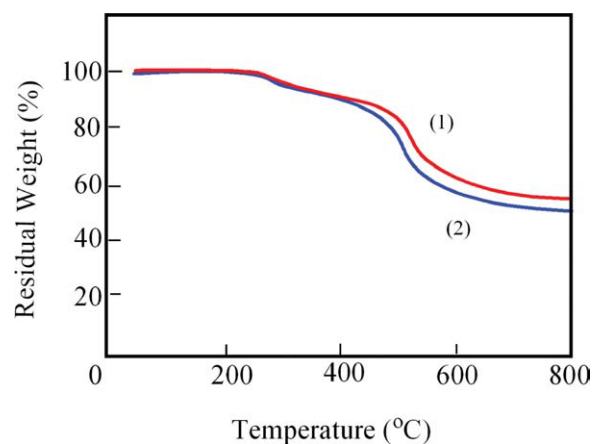
Scheme 2 Sulfonation reaction of the polymers.

experimental conditions. Although it is not clear reason why the complete sulfonation did not proceed, it may be related to that the solubility of the polymer is changed, and that more prolong reaction time is required.

### Properties of sulfonated polymers

A thermal stability of the sulfonated polymers after drying at 120°C for 30 min was estimated by TGA.

Figure 5  $^1\text{H-NMR}$  spectra of SP1 and SP2.Figure 6  $^{19}\text{F-NMR}$  of SP1 and SP2.



**Figure 7** TGA curves of **SP1** (1) and **SP2** (2). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

The results are shown in Figure 7, and the determined decomposition temperatures of the sulfonated polymers are listed in Table II. Two-stage weight loss pattern was observed for the sulfonated polymers examined. The weight loss of the sulfonated polymers was 9.5% for **SP1** and 14.0% for **SP2** in the first stage, corresponding to 69% for **SP1** ~ 79 % for **SP2** of the calculated value of sulfonic acid contents in the corresponding polymers. Namely, the first weight loss may be attributed to the elimination of sulfonic acid groups. The second stage of weight loss was associated with the degradation of the sulfonated polymers, suggesting that the introduction of sulfonic acid groups in the polymers decreased the thermal stability of the polymers as comparison with each parent polymers.

### Properties of the films

The solubility test of the sulfonated polymer was examined, and the results are listed in Table III. All the sulfonated polymers examined were insoluble in chloroform, THF, and toluene, but they were soluble in DMAc, DMF, and DMSO. As shown in Figure 8,

**TABLE II**  
Thermal Stability of the Sulfonated Polymers

Polymer structure	$T_{in}$ (°C) <sup>a</sup>	$T_{d5\%}$ (°C) <sup>b</sup>	$W_f$ (%) <sup>c</sup>	dSO <sub>3</sub> (%) <sup>d</sup>
<b>SP1</b>	230	307	9.5	12.0
<b>SP2</b>	231	302	14.0	19.9
<b>SP3</b>	233	285	11.7	16.2

<sup>a</sup> Temperature at which polymer begins to decompose under nitrogen atmosphere.

<sup>b</sup> Temperature for 5% weight loss under nitrogen atmosphere.

<sup>c</sup> Weight loss at first step.

<sup>d</sup> Theoretical weight loss of SO<sub>3</sub>.

**TABLE III**  
Solubility and Water Absorbed Capacity of the Sulfonated Polymers

Polymer structure	Solubility <sup>a</sup>					Water-uptake content, wt % <sup>b</sup>
	CHCl <sub>3</sub>	THF	DMAc	DMSO	DMF	
<b>SP1</b>	–	–	+	+	+	48.0
<b>SP2</b>	–	–	+	+	+	67.2
<b>SP3</b>	–	–	+	+	+	57.7

<sup>a</sup> +, soluble; –, insoluble.

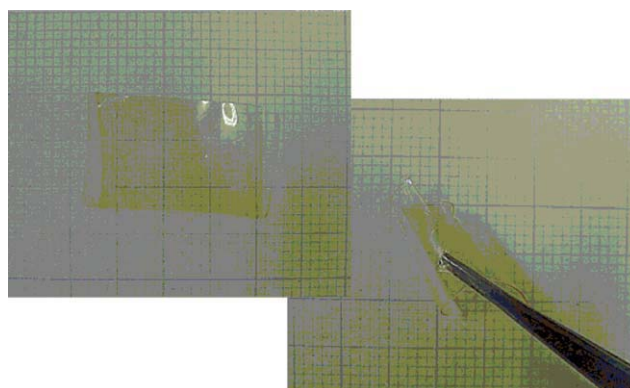
<sup>b</sup>  $(W_{wet} - W_{dry}) / W_{dry} \times 100$ , in water at room temperature for 24 h.

the cast films with a tough and smooth can be prepared from DMF solution.

To examine water-uptake contents of the sulfonated polymers, the films were soaked in water at room temperature for 24 h, and the results are also listed in Table III. All the films were swelled in a water, and show a good water affinity (48.0 ~ 67.2%). The water-uptake ability increased with a decrease of equivalent molecular weight per sulfonic acid group (EW).

The stabilities of the sulfonated polymers on a hydrolysis and an oxidation reaction were examined, and the results are listed in Table IV. The films of the sulfonated polymer (0.5 × 1.0 cm) were heated in boiling water at 100°C, 120°C, and 140°C for 24 h using a static autoclave. Although no weight loss of the films was observed at 100°C and 120°C, the hydrolytic degradation of the film was observed when the test was carried out at 140°C, the films kept the original form.

The films were soaked in Fenton's reagent (30 ppm Fe<sub>2</sub>SO<sub>4</sub> in 30% H<sub>2</sub>O<sub>2</sub>) as a strong oxidant at room temperature. All the sulfonated polymer films were stable in Fenton's reagent for a few hours, and the color disappeared into solution after 6 h. These results suggest that the sulfonated polymers have



**Figure 8** Image of the sulfonated polymer film of **SP2**. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE IV**  
**Properties of the Sulfonated Polymers**

Polymer structure	EW <sup>a</sup>	Hydrolytic resistance <sup>b</sup>			Oxidative resistance	$\rho$ (S/cm) <sup>c</sup>
		100°C	120°C	140°C		
<b>SP1</b>	663	+	+	–	3.5 h	0.06
<b>SP2</b>	402	+	+	–	2.0 h	0.16
<b>SP3</b>	488	+	+	–	2.5 h	0.03

<sup>a</sup> Theoretical equivalent weight per sulfonic acid group.

<sup>b</sup> Tested in a autoclave for 24 h: +, stable; –, degradation.

<sup>c</sup> Proton conductivity of the sulfonated polymers at 20°C.

high-stabilities against hydrolytic and oxidative reaction.

Proton conductivity of the sulfonated polymer films at 20°C was measured, and the results are also shown in Table IV. Among the sulfonated polymers used, the proton conductivity of **SP1** and **SP3** was lower than that of Nafion (0.1 S cm<sup>-1</sup>), but **SP2** was higher than that of Nafion. This demonstrates that the sulfonated polymers synthesized have potentially to use as a polyelectrolyte membrane. The reason why the proton conductivity of **SP2** is higher than that of **SP1** and **SP3** is not clear, but the flexibility of the polymer may be related to the proton conductivity.

### CONCLUSION

Polycondensation of perfluorobiphenyl with  $\alpha,\alpha$ -bis(4-hydroxyphenyl) ethylbenzene and/or 9,9-bis(4-hydroxyphenyl)fluorene proceeded to a give high-molecular weight polymer, and the polymers showed a thermal stability. The polymers consists predominantly of 1,4-phenylene structure with

respect to the bis(hydroxyphenyl) group. The sulfonation of the polymers occurred at the phenyl and fluorenyl side chain to give the corresponding sulfonated polymers. A tough and smooth film was prepared by a casting from DMF solution, and showed good properties for hydrolytic and oxidative stabilities, and a high-proton conductivity.

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