

# Proton-Conductive Membranes of Sulfonated Polyphenylsulfone

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**ABSTRACT:** Polyphenylsulfone was sulfonated by two different methods: reaction with  $\text{SO}_3$  and reaction with  $(\text{CH}_3)_3\text{SiSO}_3\text{Cl}$ . The products were characterized, and the advantages of both methods are discussed. Much more homogeneous products were obtained from the reaction with  $(\text{CH}_3)_3\text{SiSO}_3\text{Cl}$ , along with better control of the sulfonation degree. An alternative method of membrane preparation led

to an asymmetric structure, which allowed the combination of high mechanical stability and high proton conductance. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2820–2827, 2002

**Key words:** functionalization of polymers; modification; membranes

## INTRODUCTION

Ion-conductive membranes are the central components of technologies such as electro dialysis, chlor-alkali processes, and fuel cells. In fuel cells, the membrane is simultaneously an electrolyte for the transport of protons produced at the anode to the cathode and a barrier between the fuel (usually hydrogen or methanol for direct methanol fuel cells) and the oxygen fed to the cathode side. High proton conductivity, low fuel and oxygen permeability, and high chemical stability are requirements for a good fuel cell membrane.

Most proton-conductive membranes are made of sulfonated polymers.<sup>1–3</sup> Carboxylation<sup>4</sup> has been used for the preparation of cation exchange membranes to a lesser extent. More recently, polymers containing basic groups, such as polybenzimidazole, doped with acids have become important for proton conduction above 100°C.<sup>5</sup> Among those with sulfonic groups, Nafion, the perfluorosulfonic acid membrane produced by DuPont, and Flemion, an analogous membrane produced by Asahi Glass, are the best choices for several electrochemical applications because of their high proton conductivity and chemical stability. However, their production costs are very high, and other disadvantages such as high methanol permeability do not favor their application in direct methanol fuel cells, for instance, stimulating the development of alternative nonfluorinated polymers with lower costs.

In this study, polyphenylsulfone was sulfonated by two different methods and characterized for applica-

tions as proton-conductive membranes. Polyphenylsulfone was chosen because of its high stability with respect to other available polysulfones.

The sulfonation of polymers has been described in the literature by many methods, which differ in their ease of application, the homogeneity of the reaction medium, their cost, and their toxicity. Polysulfones and polyethersulfones have been sulfonated with the following sulfonating agents:  $\text{H}_2\text{SO}_4$ ,<sup>6</sup>  $\text{SO}_3$  in  $\text{CH}_2\text{Cl}_2$ ,<sup>7</sup>  $\text{SO}_3$ /triethylphosphate (TEP),<sup>8,9</sup> and  $(\text{CH}_3)_3\text{SiSO}_3\text{Cl}$ .<sup>10,11</sup> The functionalization of polyphenylsulfone has been much less considered in the literature, although the possibility of sulfonation has been mentioned in a few patents. Sulfonation with  $\text{ClSO}_3\text{H}$  up to a sulfonation degree (SD) of 0.6 has been claimed for applications on hemodialysis membranes.<sup>12</sup> Sulfonation with  $\text{SO}_3$ /TEP complexes has been claimed for applications as dental plaque barriers.<sup>9</sup> The sulfonation of polyphenylsulfone with butyllithium (BuLi) was described with further oxidation to sulfonic groups.<sup>13,14</sup>

In Table I, the advantages and disadvantages of the different methods for the sulfonation of polysulfone are compared. In this work, the chosen sulfonating agents were  $\text{SO}_3$  and  $(\text{CH}_3)_3\text{SiSO}_3\text{Cl}$ . For the choice of  $\text{SO}_3$ , the main factor considered was its relatively low cost. The second method was chosen because of the possibility of better reaction control. The weak points and advantages of both methods are discussed. The main goal was to obtain a polymer with high proton conductivity that was still insoluble in water and methanol. Membranes prepared with sulfonated polyphenylsulfone had their proton conductivity and methanol/water permeability evaluated, these being important parameters for applications in electrochemical devices such as direct methanol fuel cells.

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**TABLE I**  
**Methods for the Sulfonation of Polysulfones**

Sulfonating agent	H <sub>2</sub> SO <sub>4</sub>	SO <sub>3</sub>	SO <sub>3</sub> /TEP	ClSO <sub>3</sub> H	BuLi	(CH <sub>3</sub> ) <sub>3</sub> SiSO <sub>3</sub> Cl
Advantages	Inexpensive	Very reactive, not expensive	Sulfonation may be too mild with high TEP content	Not expensive	Only method for sulfonation of electron-deficient rings	Homogeneous reaction with better control
Disadvantages	Production of water with agent dilution during reaction; weakening the reactivity	Side reactions with crosslinking are possible; heterogeneous reaction	Minimization of crosslinking	Chain cleavage, branching, or crosslinking reactions are possible; heterogeneous reaction (affect reproducibility)	Expensive	Relatively expensive
Sulfonated aromatic ring	Electron-rich	Electron-rich	Electron-rich	Electron-rich	Electron-deficient	Electron-rich
References	6	7	8, 9	12	13, 14	10, 11

## EXPERIMENTAL

### Materials

The polyenylsulfone Radel R-5000 was supplied by BP Amoco, Sunbury-on-Thames, England. SO<sub>3</sub> and trimethylsilylchlorosulfonic acid [(CH<sub>3</sub>)<sub>3</sub>SiClSO<sub>3</sub>H] were produced by Aldrich, Diesenhofen, Germany.

### Sulfonation with SO<sub>3</sub>

Solid SO<sub>3</sub> was carefully heated at 40°C for about 3–4 days under Ar for depolymerization of the β-SO<sub>3</sub> form. The resulting liquid SO<sub>3</sub> was dissolved in dichloromethane. The polyphenylsulfone was previously dried and separately dissolved in dichloromethane. A solution of dichloromethane/SO<sub>3</sub> was then slowly dropped into the polymer solution under cooling. After about 48 h, the system was poured into ice, and the precipitated polymer was separated.

### Sulfonation with (CH<sub>3</sub>)<sub>3</sub>SiClSO<sub>3</sub>H

The polyphenylsulfone was previously dried and dissolved in dichloromethane at room temperature. Trimethylsilylsulfonic acid was carefully added to the solution at 40°C. A reaction followed for 24–98 h while Ar was bubbled into the solution. The solution was then cooled to room temperature and poured into methanol. The precipitated polymer was further washed with methanol and later washed with water in a Soxhlet extractor for 16 h. The product was dried at 75°C.

### Polymer characterization

#### SD

The polymer was characterized by <sup>1</sup>H-NMR, elemental analysis (from S and C contents), thermogravimet-

ric analysis (TGA), and titration to determine SD. SD is here defined as the molar ratio of sulfonic groups to monomer units of polyphenylsulfone.

#### Thermal analysis

TGA was performed with Netzsch equipment (TG cell 209) (Selb, Germany).

#### Titration

A defined weight of the polymer was dissolved in dimethylformamide (DMF). After the addition of water, the resulting emulsion was titrated with 0.1M KOH, with phenolphthalein as an indicator.

#### <sup>1</sup>H-NMR

The nuclear resonance spectra of the modified polymers were obtained with a Bruker 300-MHz spectrometer (Karlsruhe, Germany) after polymer dissolution in deuterated dimethyl sulfoxide (DMSO).

#### Molecular weight

The molecular weight of the polymer before and after sulfonation was determined by gel permeation chromatography (with a Jasco GPC/HPLC chromatograph, calibrated with polystyrene standards, with a UV detector) (Gross-Umstadt, Germany) to evaluate any eventual degradation. The solvent was DMF containing 50 mmol of ammonium acetate per liter of DMF.

### Membrane preparation

Dense, homogeneous membranes 40–80 μm thick were obtained by the slow evaporation of the solvent

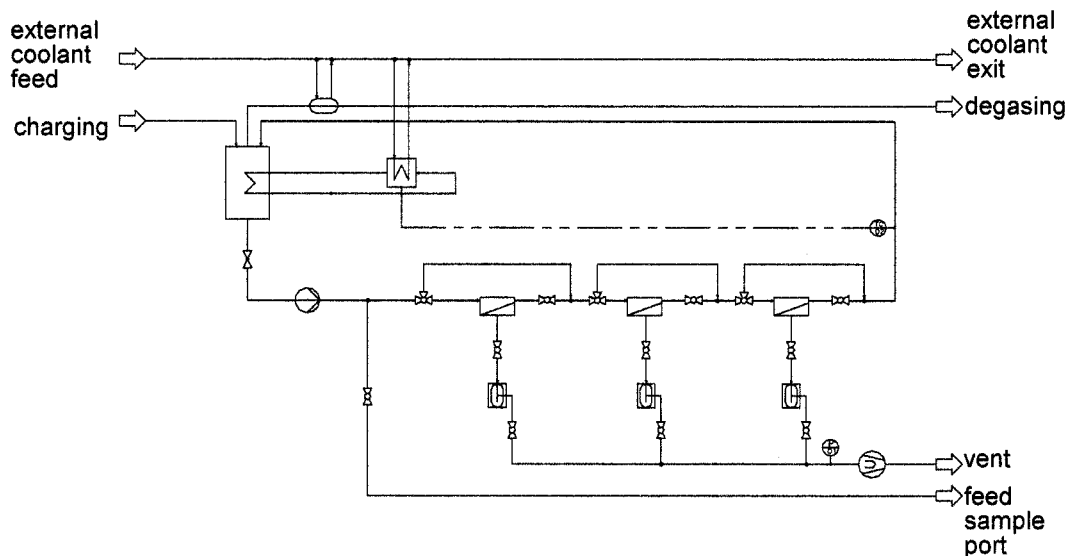


Figure 1 Equipment used for pervaporation.

of a DMF/polymer solution on a carefully leveled glass plate at about 75°C.

Asymmetric, structured membranes were obtained from an 8 wt % polymer solution in DMSO. The solution was filtered, and concentrated H<sub>2</sub>SO<sub>4</sub> was added in a molar ratio of about 3:1 (H<sub>2</sub>SO<sub>4</sub> to sulfonic groups in the polymer) before the membrane was cast onto a glass plate and the solvent was evaporated.

### Membrane characterization

The membranes were characterized with respect to their proton conductivity and permeability to liquid methanol and water. The morphology of the films was controlled by electron microscopy.

### Impedance spectroscopy

The intrinsic proton conductivity of the sulfonated polymer membrane was evaluated with impedance spectroscopy. The membrane was characterized in water via heating from 20 to 80°C, followed by a decrease in the temperature to 20°C.

### Pervaporation

The permeability of the membrane to liquid water and methanol was evaluated by pervaporation with the equipment described in Figure 1. A 20 wt % methanol solution in water was used as the feed, circulating at 55°C on one side of the membrane. The permeate side was evaluated, and the permeate was collected and weighed in traps immersed in liquid nitrogen. The permeate and feed compositions were determined with refraction indices.

### Electron microscopy

The homogeneity of the membranes was evaluated with field emission scanning electron microscopy (FESEM). The membranes were fractured in liquid nitrogen and then immersed at room temperature in a 5% solution of AgNO<sub>3</sub> for about 20 h. They were washed with water, dried, and coated with carbon. The membrane surface was then imaged with back-scattered electrons in a JEOL 6400 field emission scanning electron microscope (Eching, Germany). Bright regions revealed the presence of silver attached to the surface, on which the sulfonic groups were preferentially located.

## RESULTS AND DISCUSSION

The sulfonation of polyphenylsulfone with SO<sub>3</sub> always led to two fractions, a water-soluble and highly sulfonated (SD > 1.5) fraction and a water-insoluble fraction with SD < 0.7 (0.7 sulfonic groups per monomeric unit).

Table II compares the SD values obtained after the analysis by different methods for the same sample.

TABLE II  
SD of Polyphenylsulfone Modified with SO<sub>3</sub> (1 mol of SO<sub>3</sub>/mol of Monomer Unit of Polyphenylsulfone)

Method	SD	
	Water-insoluble	Water-soluble
TGA	0.59	2.23
Elemental analysis	0.65	2.63
<sup>1</sup> H-NMR	0.59	2.10
Titration	0.48	1.47

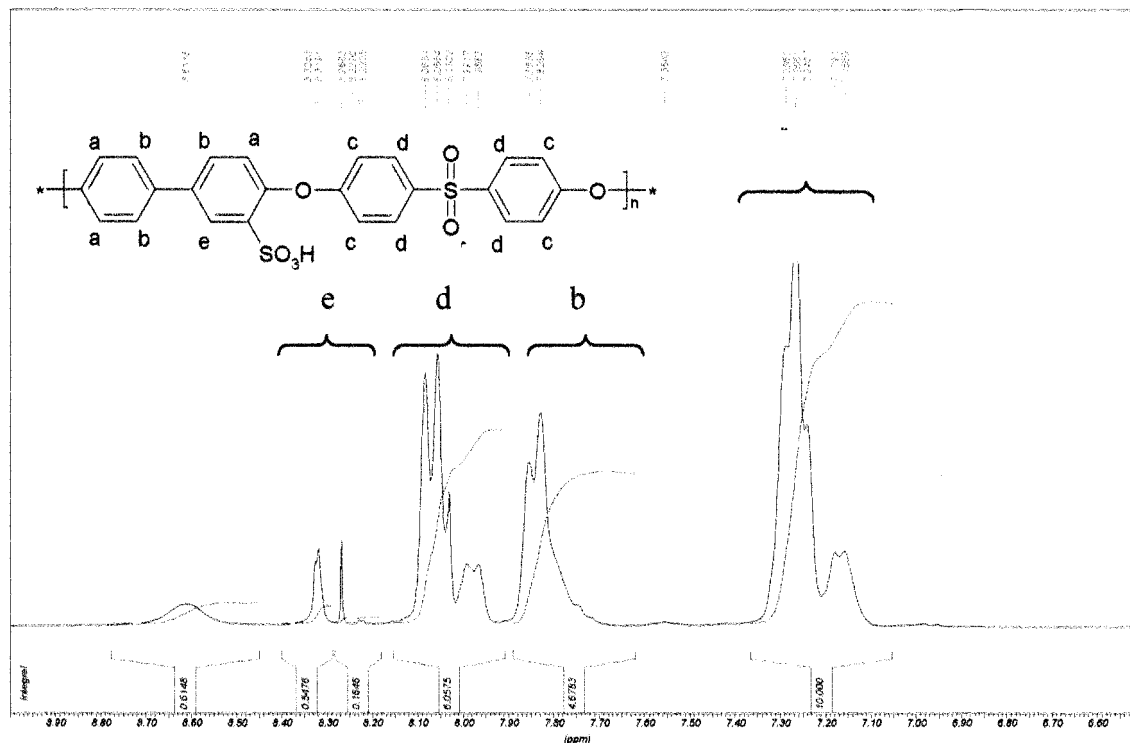


Figure 2  $^1\text{H-NMR}$  spectrum of polyphenylsulfone sulfonated with  $\text{SO}_3$  ( $\text{SD} = 0.6$ ).

By thermoanalysis, after the remaining water and solvent were released, we found that at  $180^\circ\text{C}$ , the sulfonic group started to be eliminated, with a 0–25% weight loss up to  $340^\circ\text{C}$  and a further 20% weight loss up to  $500^\circ\text{C}$  before the degradation of the main chain began. We then estimated the SD, taking into account the weight loss between 180 and  $500^\circ\text{C}$ .

By NMR, we estimated the SD with a method analogous to that reported by Noshay and Robeson<sup>15</sup> for sulfonated polysulfone. In this case, SD is

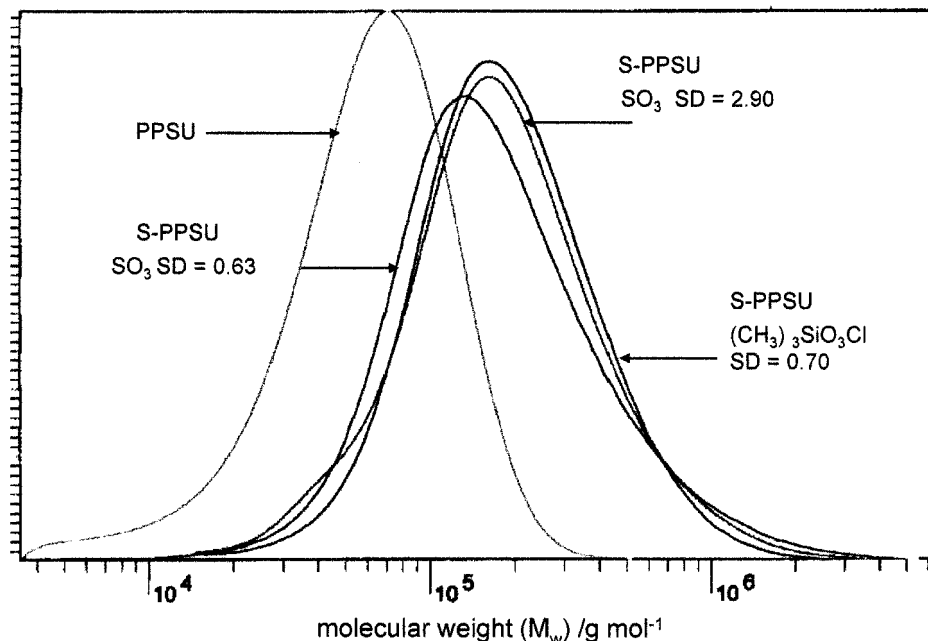
$$\text{SD} = (12 - 4A_{abc}/A_{de}) / (2 + A_{abc}/A_{de}) \quad (1)$$

where  $A_{abc}$  and  $A_{de}$  are the sums of the areas of peaks due to a, b, and c protons and d and e protons, respectively (see Fig. 2). Figure 2 shows an example of  $^1\text{H-NMR}$  for sulfonated polyphenylsulfone with  $\text{SD} = 0.6$  (sulfonation with  $\text{SO}_3$ ).

Different experiments were performed, with the amount of  $\text{SO}_3$  varied from 0.5 to 2.0 mol/mol of polyphenylsulfone monomer units. In each experiment, water-soluble ( $\text{SD} > 1.5$ ) and water-insoluble fractions were obtained. Even under more drastic conditions, with the  $\text{SO}_3$  concentration and reaction time increased, fractions that were water-insoluble could not be obtained with SD values greater than 0.7. Target products, which combine insolubility and high ionic contents, should have an intermediate SD ( $0.7 < \text{SD} < 1.5$ ) and could not be obtained by this first method.

As shown in Figure 3, no molecular weight decrease was detected by gel permeation chromatography, and this could be evidence of chain degradation after the reaction with  $\text{SO}_3$ . However, an apparent increase in the molecular weight was observed after sulfonation. Sulfonation of 70–100% of the monomer units of polyphenylsulfone ( $0.7 > \text{SD} > 1.0$ ) would theoretically lead to an increase of 12–17% of the molecular weight due to the inclusion of  $\text{SO}_3\text{H}$  groups. The observed increase, however, was higher than this. It is known that the coils of polyelectrolytes expand as a result of intramolecular repulsive forces. The effect can be minimized by the addition of salts, which increase the ionic strength of the medium. The sulfonated polyphenylsulfone behaves as a polyelectrolyte in DMF. Although salt was also added to the solution, the concentration was probably not enough to hinder the repulsive effect of the sulfonic groups. The effect is higher if the SD increases, as observed in the literature for other sulfonated polymers.<sup>16</sup> This was the case for the highly sulfonated fraction of polyphenylsulfone, which was soluble in water (see also Fig. 3). However, for this highly sulfonated fraction, a shoulder can be seen in the molecular weight curve, probably indicating partial degradation.

The ion conductivity values of films obtained with the polymer sulfonated with  $\text{SO}_3$  were less than 6 mS/cm at  $80^\circ\text{C}$  and, therefore, not suitable for applications such as fuel cells.



**Figure 3** Gel permeation chromatography curves of polyphenylsulfone before and after sulfonation with  $\text{SO}_3$  (SD = 0.63 and 2.90) and  $(\text{CH}_3)_3\text{SiClSO}_3\text{H}$  (SD = 0.70).

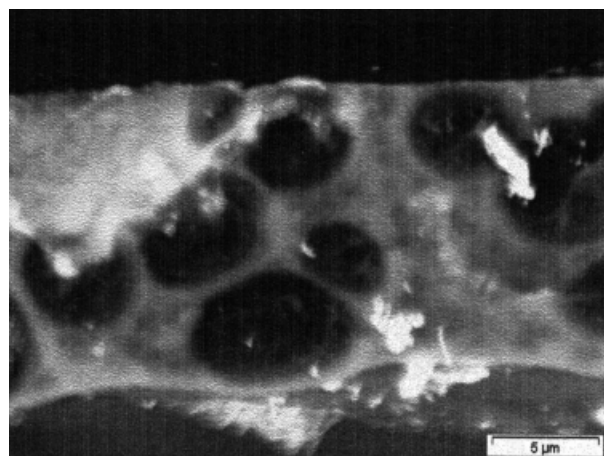
The homogeneity of the polymer films was then evaluated by electron microscopy. Figure 4 shows the surface fractures of membranes prepared from polymers sulfonated with  $\text{SO}_3$  after staining with  $\text{Ag}^+$ .

$\text{Ag}^+$  was preferentially located in regions rich in  $\text{SO}_3^-$ , giving bright spots in images obtained by backscattered electrons. It is clear that the film was highly heterogeneous, with large regions with lower concentrations of  $\text{SO}_3^-$ . The sulfonation led to a heterogeneous product because, as soon as part of the polymer reacted with  $\text{SO}_3$ , it became insoluble in the apolar solvent, and the sulfonation had to be further con-

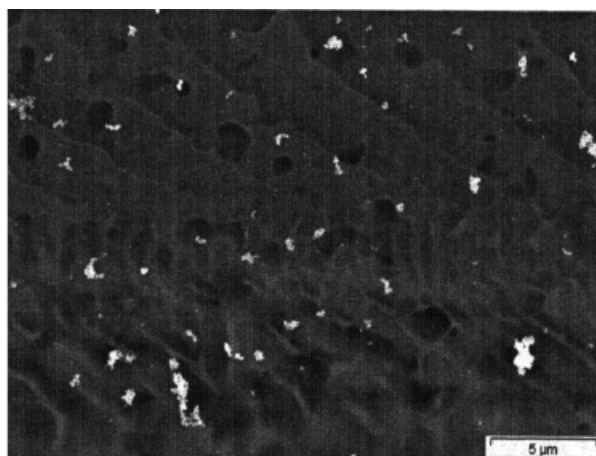
ducted in a dispersed system rather than homogeneously in solution up to the end of the reaction.

The problem of product heterogeneity was solved by the sulfonation being conducted by the reaction of the polymer with  $(\text{CH}_3)_3\text{SiClSO}_3\text{H}$ . Better control of the sulfonation was possible because the sulfonated polymer (still containing silylated groups) remained in solution until the end of the reaction. Quite homogeneous films were obtained, as can be seen via FESEM in Figure 5(b) for samples stained with  $\text{Ag}^+$ .

Sulfonated polymers, which were insoluble in water, could be obtained with higher SDs (up to 1.2),



(a)



(b)

**Figure 4** FESEM images with backscattered electrons of a membrane fracture after staining with  $\text{Ag}^+$ : polyphenylsulfone sulfonated with (a)  $\text{SO}_3$  (SD = 0.6) and (b)  $(\text{CH}_3)_3\text{SiClSO}_3\text{H}$  (SD = 1).

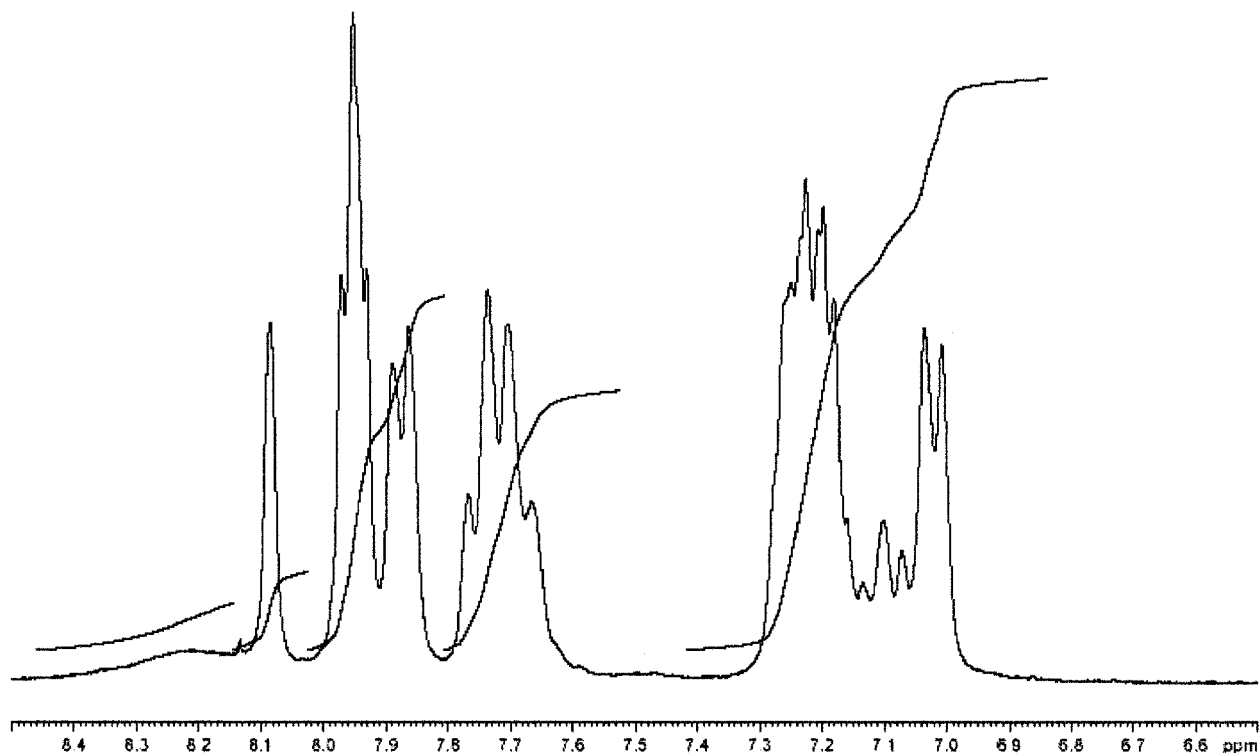


Figure 5  $^1\text{H-NMR}$  spectrum of polyphenylsulfone sulfonated with  $(\text{CH}_3)_3\text{SiClSO}_3\text{H}$  ( $\text{SD} = 0.54$ ).

which could be better controlled by changes in the amount of the sulfonating agent and the reaction time. Some values are shown in Table III.

A higher SD ( $\text{SD} = 1.76$ ) was obtained by the reaction being conducted in dichloroethane, which allowed heating up to  $75^\circ\text{C}$ . However, the polymer obtained was already water-soluble.

Gel permeation chromatography curves of samples sulfonated with  $(\text{CH}_3)_3\text{SiClSO}_3\text{H}$  are shown in Figure 4. No chain scission was observed. The apparent increase in the molecular weight was also here due to the presence of ionic groups, which caused chain expansion in a medium of insufficient ionic strength.

The  $^1\text{H-NMR}$  spectrum of the homogeneously sulfonated polymer with  $\text{SD} = 0.54$  is shown in Figure 5. Here also, the phenyl rings far from the  $-\text{SO}_2-$  group were the most susceptible to sulfonation.

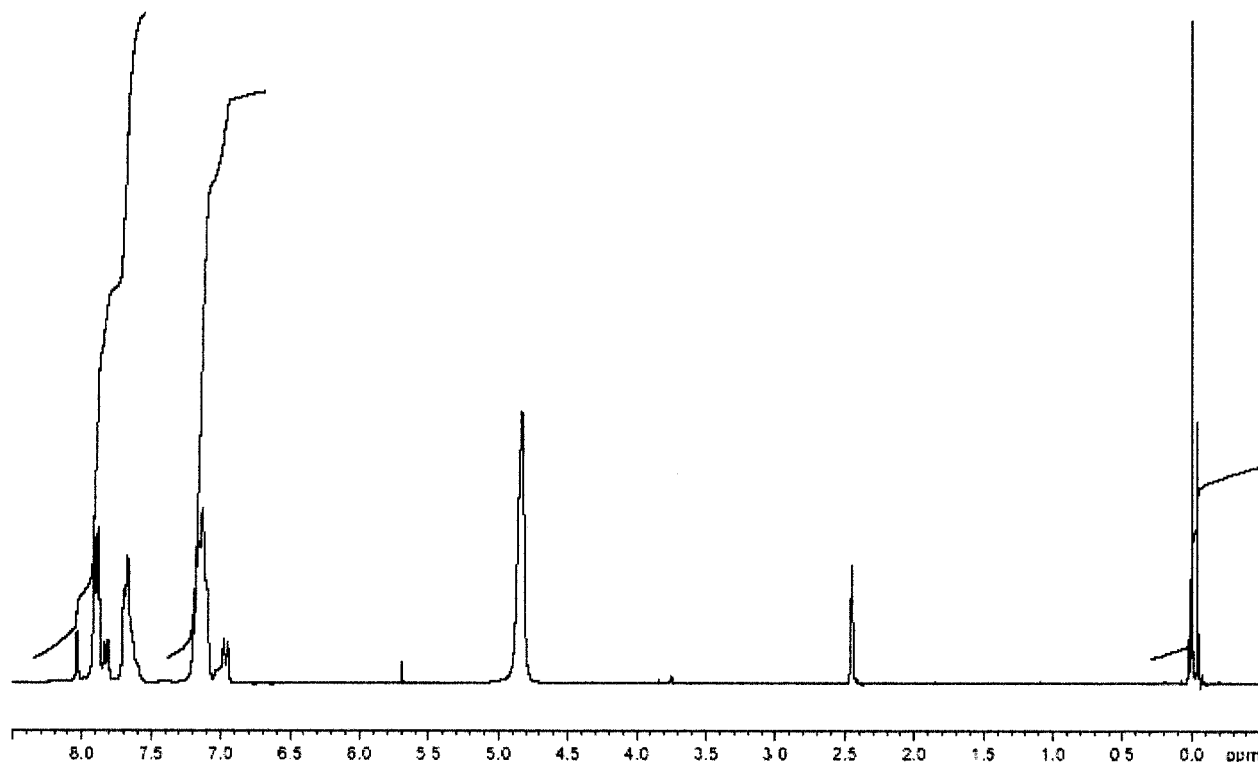
The  $^1\text{H-NMR}$  spectrum of the same polymer before the completion of hydrolysis in methanol is shown in Figure 6. In this case, the silyl ether groups can still be seen.

The sulfonated products were evaluated with respect to their permeability to methanol and water. Pervaporation experiments are shown in Table IV. The membranes with  $\text{SD} = 1.0$  had methanol and water permeability much lower than that of Nafion, even

TABLE III  
SD of Polyphenylsulfone Reacted With  $(\text{CH}_3)_3\text{SiClSO}_3\text{H}$

Sulfonation agent/ monomer unit (mol/mol)	Temperature ( $^\circ\text{C}$ )	Reaction time (h)	SD			
			Method			
			TGA	Elemental analysis	$^1\text{H-NMR}$	Titration
1.0	25	72	0.37			
1.4	40	24	0.69			
2.0	40	24	0.64	0.70	0.54	0.65
2.9	40	24	0.59			
3.1	40	48	0.98		1.40	
1.4	40	60	1.06	0.59	1.10	
0.7	40	96	0.54			
1.0	40	96	1.19			
2.5 <sup>a</sup>	75 <sup>a</sup>	96 <sup>a</sup>	1.76 <sup>a</sup>			

<sup>a</sup> Reaction in dichloroethane.



**Figure 6**  $^1\text{H-NMR}$  spectrum of polyphenylsulfone sulfonated with  $(\text{CH}_3)_3\text{SiClSO}_3\text{H}$  ( $\text{SD} = 0.54$ ) before hydrolysis is complete (the polymer still contains 25% silyl ether groups).

when the thickness was one-third that of Nafion films. Low methanol permeability is a required characteristic for applications such as direct methanol fuel cells.

The specific ion conductivities of sulfonated polyphenylsulfone with  $\text{SD} = 0.7$  and  $1.0$  as a function of temperature are shown in Figure 7. The proton conductivity values of dense films with  $\text{SD} = 1.0$  were about  $14 \text{ mS/cm}$ , which is still relatively low.

To improve the proton conductance of polyphenylsulfone films, we prepared them in a different way. Concentrated  $\text{H}_2\text{SO}_4$  was added to the polymer casting solution. As the solvent evaporated to form the films, phase separation seemed to occur, analogously to the conventional process of the preparation of porous membranes for ultrafiltration.<sup>17,18</sup> The polymer-

rich phase gave rise to the membrane dense matrix, and the solvent-rich phase developed into cavities dispersed in the polymer matrix, forming the asymmetric structure shown in Figure 8. The cavities were closed cells, not connected to one another, and might have helped to keep the water during the operation in the electrochemical cells. The polymer matrix was dense and did not allow a high methanol or water flow across the membrane. Although having less polymer material (because of the presence of the cavities), the membranes showed mechanical stability comparable to that of a completely dense membrane of the same thickness. The main advantage is the superior proton conductance across the membrane. Figure 7 shows values of the proton conductivity of a dense membrane of sulfonated polyphenylsulfone ( $\text{SD} = 1$ ) as a function of temperature and values of the apparent conductivity (calculated from conductance values normalized by the whole membrane thickness) for the asymmetric membrane of the same polymer material. The proton transport across the asymmetric membrane was about four times faster than that across the dense membrane.

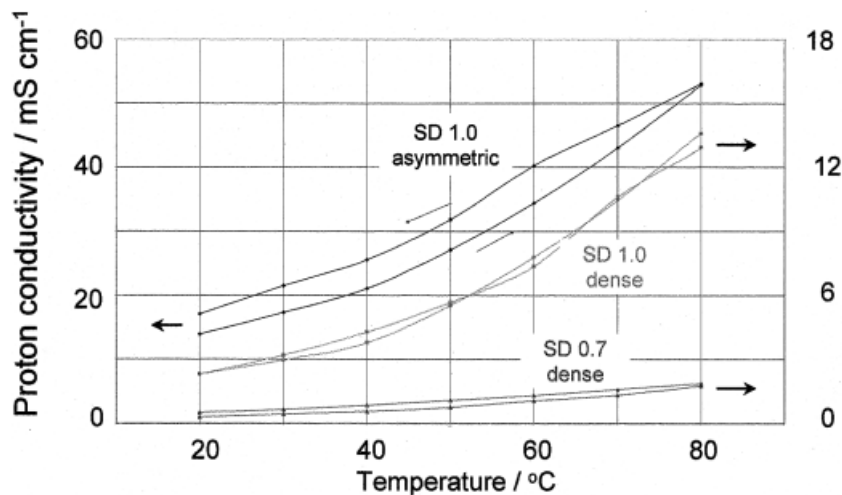
## CONCLUSIONS

Polyphenylsulfone was sulfonated by reactions with  $\text{SO}_3$  and  $(\text{CH}_3)_3\text{SiClSO}_3$ . The former sulfonation agent led to a quite heterogeneous product. However, the

**TABLE IV**  
Pervaporation of Sulfonated Membranes with a Feed Containing 20 wt % Methanol in Water at  $55^\circ\text{C}$

Membrane		Thickness ( $\mu\text{m}$ )	Flux ( $\text{g h}^{-1} \text{m}^{-2}$ )	
Sulfonation method	SD		Methanol	Water
	0	40	2	24
$\text{SO}_3$	0.45	30	566	2580
$(\text{CH}_3)_3\text{SiClSO}_3\text{H}$	0.54	50	79	750
	0.70	41	83	835
	1.00	38	120	1249
	1.00 <sup>a</sup>	61	192	2204
Nafion 117		175	658	2862

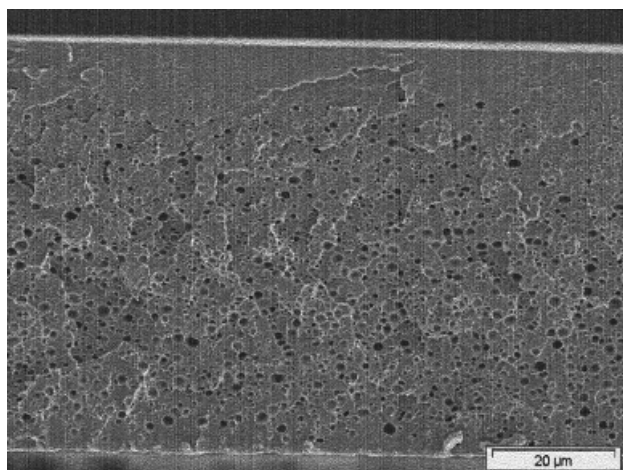
<sup>a</sup> Asymmetric structure.



**Figure 7** Proton conductivity as a function of temperature for sulfonated polyphenylsulfone: dense membranes (SD = 0.7 and 1.0) and asymmetric membranes (SD = 1.0).

reaction with  $(\text{CH}_3)_3\text{SiClSO}_3$  gave a homogeneous sulfonated polymer with interesting characteristics for electrochemical applications. SD could be well controlled, and water-insoluble products were obtained with SD values as high as 1.0. Asymmetric membranes were prepared with a proton conductivity of about 55 mS/cm at 80°C.

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**Figure 8** Asymmetric membrane prepared from sulfonated polyphenylsulfone (SD = 1.0).

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