

# Phosphonated and sulfonated polyphenylsulfone membranes for fuel cell application

Ethel Parceró<sup>a,b</sup>, Rafael Herrera<sup>b</sup>, Suzana P. Nunes<sup>a,\*</sup>

<sup>a</sup> GKSS Research Centre, Institute of Polymer Research, Max-Planck-Str. 1, D-21502 Geesthacht, Germany

<sup>b</sup> Universidad Nacional Autónoma de México, Facultad de Química, México

Received 19 September 2005; received in revised form 21 December 2005; accepted 25 December 2005

Available online 30 August 2006

## Abstract

Membranes of phosphonated polyphenylsulfone with functionalization degree up to 88–106% were prepared by reaction in the presence of Pd(0)-complexes. Membranes of phosphonated and sulfonated polyphenylsulfone were also prepared by sulfonating previously phosphonated polyphenylsulfone. The membrane proton conductivities were evaluated by impedance spectroscopy at the temperature range between 50 and 150 °C. While sulfonated membranes had higher proton conductivity at 100% relative humidity, they swell much more than the phosphonated films in water and have a much higher permeability to water and methanol. Phosphonated films are thermally more stable.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Phosphonated; Ion-exchange; Fuel cell

## 1. Introduction

The development of ion-exchange membranes for electro-dialysis or more recently for fuel cells has stimulated the functionalization of polymers with the incorporation of acid groups. In most of the cases they are sulfonic or in less extent carboxylic groups. Phosphonation has been much less explored. The synthesis of phosphorus-containing polymers was in the past mainly connected to the development of flame retardant materials. Phosphonated polystyrene and polyolefins have been early reported [1,2]. Phosphonation has also been applied to improve the blood compatibility of polymers [3].

In the last years the research on alternative materials for fuel cell has grown. There is however still a lack of polymeric materials suitable for the proton transport in a temperature range between 100 and 160 °C. Operating at this temperature range would improve the reaction kinetics and decrease the catalyst poisoning by CO. From the engineering point of view there would be also advantages connected to heat and water management. However, most of the ion-exchange polymers start to lose water above 100 °C, suffering then from a decrease

of proton conductivity. The innovative approaches for membrane preparation, which are currently followed by different groups worldwide, were reviewed in recent publications [4–6]. Researchers are looking for polymers able to transport protons by alternative mechanisms in the absence of water or materials able to keep water up to higher temperatures.

Phosphonic groups are believed to keep the water more than sulfonic groups [7,8]. Besides, phosphonic groups are more thermally stable. This has motivated the synthesis of new phosphonated polymers. Table 1 summarizes most of the papers on phosphonated polymers. One of the first groups to propose the use of phosphonated polymers for membranes and later more specific for the fuel cell application was the group of Cabasso and coworkers [7,8]. They phosphonated poly(phenylene oxide) using the Michaelis–Arbuzov reaction [9]. This is the reaction of an ester of trivalent phosphorus with alkyl halides and it is one of the most versatile ways to form a carbon–phosphorus bond. In the presence of nickel or palladium halides as catalysts aryl halides also react. The route has been reported for the functionalization of poly(4-phenoxybenzoyl-1,4-phenylene) [10]. Analogous strategy has been used also for the synthesis of new phosphonated fluoromonomers [11] and their further polymerization [12]. In a previous paper of our group [13], the Michaelis–Arbuzov reaction showed to be ineffective for the phosphonation of polyphenylsulfone. A successful

\* Corresponding author. Tel.: +49 4152 872440.

E-mail address: [nunes@gkss.de](mailto:nunes@gkss.de) (S.P. Nunes).

Table 1  
Phosphonated polymers

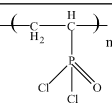
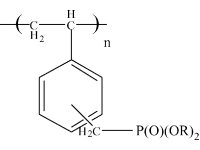
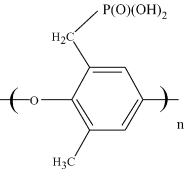
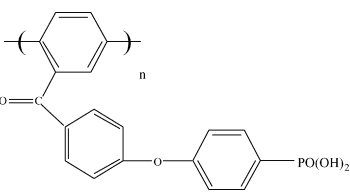
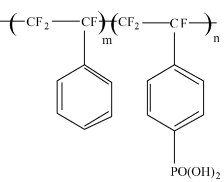
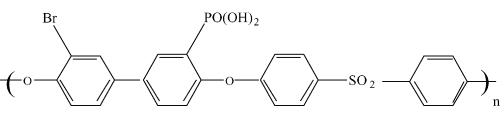
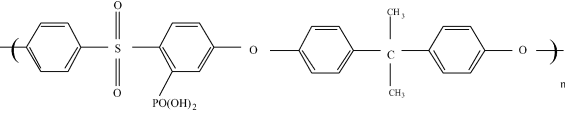
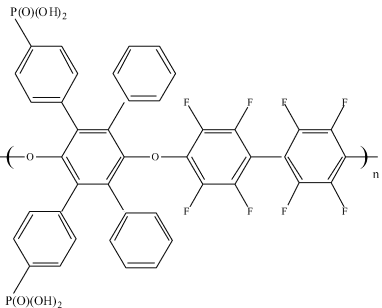
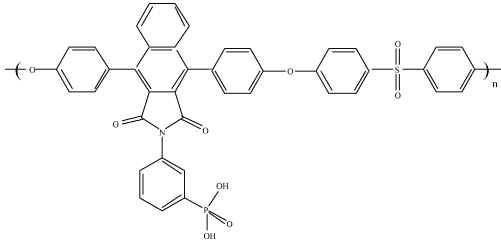
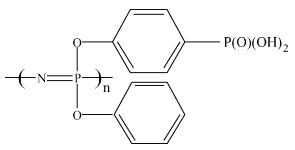
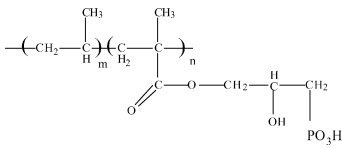
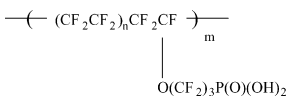
Polymer	Reaction or reactants	Proton conductivity (mS/cm)	References
	PCl <sub>3</sub> /O <sub>2</sub>		[2]
	Michaelis–Arbuzov		[2]
	Michaelis–Arbuzov		[7,8,20]
	Michaelis–Arbuzov	0.1	[10]
	Polymerization of phosphonated vinylstyrene	1–10	[12,19]
	Pd catalyst/HP(O)(OEt) <sub>2</sub>		[13]
	BuLi/CIP(O)(OEt) <sub>2</sub>		[15]
	Pd(PPh <sub>3</sub> ) <sub>4</sub> /HP(O)(OEt) <sub>2</sub>		[16]

Table 1 (Continued)

Polymer	Reaction or reactants	Proton conductivity (mS/cm)	References
	Nucleophilic polycondensation	0.001–0.01	[21]
	BuLi/CIP(O)(OEt) <sub>2</sub>	28	[17,18]
	$\gamma$ -Radiation, grafting of epoxy group and treatment with H <sub>3</sub> PO <sub>4</sub>		[3,22]
	Copolymerization of phosphonated fluorinated vinyl ethers	6–76	[23]

alternative method was the P–C coupling reaction catalysed by Pd(0)-complexes, which we reported before [13,14]. By this procedure a phosphonation degree up to 90% was obtained. More recently, Lafitte and Jannasch [15] reported the phosphonation of polysulfone up to 50% using lithiation. The direct lithiation in the presence of diphenyl or diethyl chlorophosphate led to the functionalization of the biphenyl sulfone segment, while the lithiation preceded by the bromination enable the phosphonation of the bisphenol A segment.

A reaction analogous to that reported for the polyphenylsulfone using Pd catalysts was used by Miyatake and Hay [16] to obtain phosphonated polyphenyloxides and by Souza et al. [11] to obtain phosphonated monomers. A great advantage of this procedure is the possibility of binding the phosphonic group directly to the aromatic ring without any spacer, which could decrease the stability of the polymer in the presence of oxidizing agents. Other classes of reported phosphonated polymers are polyphosphazenes [17,18] and grafted polymers obtained by  $\gamma$ -radiation [3,22]. Grafted polymers were prepared for electro dialysis [22] by  $\gamma$ -irradiation of polyolefins followed by reaction with glycidyl methacrylate and further conversion of the epoxy group by treatment with concentrated phosphoric acid.

Characterization of phosphonated films in terms of their proton conductivity has been reported for few of the men-

tioned phosphonated polymers: polyphosphazene [18], trifluoropolystyrene [19], poly(4-phenoxybenzoyl-1,4-phenylene) [10]. Relatively low conductivity values were reported for most of the polymers prepared up to now. The values for polyphosphazene and for perfluorocarbon polymers [23] were quite encouraging. Poly(phenylene oxide) [8] was evaluated in fuel cell tests.

In this paper a mixed functionalization of polyphenylsulfone, incorporating phosphonic and/or sulfonic groups is reported. The characterization of films with different degrees of functionalization is discussed. Also blends of sulfonated and phosphonated polymers were considered.

## 2. Experimental

### 2.1. Materials

Polyphenylsulfone Radel<sup>®</sup> R-5000 was supplied by BP Amoco, Sunbury-on-Thames, England. Tris(dibenzylideneacetone)dipalladium(0)-chloroform-adduct (Pd<sub>2</sub>(dba)<sub>3</sub>), triethylamine 99.5%, hydrobromic acid 48%, *o*-dichlorobenzene 99%, diphenyl ether 99%, and trimethylsilylchlorosulfonic acid were obtained from Aldrich. Diethyl phosphite >99% was purchased from Fluka. The chemicals were used as received and the polymer was previously dried in vacuum.

## 2.2. Phosphonation of polyphenylsulfone

The phosphonation was conducted as described before [13]. The polymer was first brominated according to a procedure reported by Guiver et al. [24], leading to a degree of substitution close to two Br atoms per repeating unit. A solution of 0.3 g ( $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ ) in a mixture of 50 mL *o*-dichlorobenzene, 20 mL diethyl phosphite and 5 mL triethylamine was heated to 90 °C under argon atmosphere. A solution containing 10.0 g of the brominated polymer in 75 mL of the same solvent mixture was added dropwise and the solution was heated to 120 °C for 96 h in the dark. During this time further 0.2 g of the catalyst in 60 mL of diethyl phosphite and 10 mL triethylamine were added in different portions. The polymer was then precipitated in methanol, redissolved in chloroform, reprecipitated in methanol and dried at 50 °C in vacuum.

The phosphonated polymer was suspended in concentrated hydrobromic acid and heated under reflux for 48 h. The polymer was then filtered, washed with water and dried under vacuum at 45 °C.

## 2.3. Sulfonation of polyphenylsulfone

The sulfonation followed a procedure also reported before [25]. The polyphenylsulfone was dissolved in dichloromethane at room temperature. Trimethylsilylchlorosulfonic acid was carefully added to the solution at 40 °C. A reaction followed for up to 98 h while argon 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 50 °C.

## 2.4. Membrane preparation

The membranes were prepared in *N*-methyl pyrrolidone, using polymer, which was previously washed with water for several days. Membranes were cast on heating plates at 50–60 °C and were dried in vacuum before characterization.

## 2.5. Functionalization degree

The average degree of phosphonation (PD) and sulfonation (SD) was estimated by  $^1\text{H}$  NMR and by elemental analysis.

The  $^1\text{H}$  NMR spectra were obtained using a Bruker DCX-300 spectrometer. The spectra were recorded in  $d_6$ -DMSO and referenced to tetramethylsilane (TMS) as internal standard.

The elemental analysis was carried out at the Fraunhofer Institute for Applied Polymer Research at Golm, Germany, with a Carlo Erba CHNS-O Analyzer Model EA 1110 and 1108.

The functionalization degree was calculated taking in account the number of moles of phosphorus, sulphur and carbon. The phosphonation was directly calculated from both the molar ratio of phosphorus to sulphur and of phosphorus to carbon. Both ratios led to similar values of phosphonation degree. The sulfonation degree was calculated from the sulphur/carbon molar ratio. For polymers containing both phosphonic and sulfonic

groups only elemental analysis was used, taking in account the phosphorus/carbon and sulphur/carbon molar ratios.

## 2.6. Thermal analysis

The polymers were characterized by thermogravimetric analysis in a NETZSCH TG 209 equipment, heating the samples from 20 to 900 °C under argon atmosphere at a heating rate of 10 K/min.

## 2.7. Water uptake

The ability of the membrane to absorb water was estimated by immersion of pieces of about 0.1 g of polymer films in water at 50 °C during hours and weighting in analytical balance.

The ability of the membrane to absorb water was estimated by gravimetric analysis. Previously weighted polymer film (ca. 0.1 g) was immersed in water at 50 °C during 24 h and then carefully surface dried and weighted in an analytical balance.

## 2.8. Permeability to methanol

The permeability of the membranes to methanol was evaluated according to a procedure reported before [25]. A 20 wt% methanol solution at 55 °C in water was used as feed in a pervaporation set-up. The permeate side was evacuated. The permeate was collected after 1 h and weighted in traps immersed in liquid nitrogen. The composition was determined by refraction index measurements.

## 2.9. Proton conductivity measurements

The proton conductivity was measured by impedance spectroscopy using a Zahner IM6 spectrometer, which allowed measurements at  $10^6$  to 10 Hz. The measuring cell was analogous to that reported by Alberti et al. [26]. The membranes were exhaustively washed in water. The membranes were immersed in boiling water during 1 h before measuring. In the cell they were pressed between two carbon electrodes and the conductivity was measured across the membrane at 100% relative humidity, varying the temperature from 50 to 150 °C. The proton conductivity was estimated by impedance values at phase angle zero.

## 3. Results and discussion

The reaction in the presence of Pd (0)-complex catalyst made possible the phosphonation of polyphenylsulfone up to a functionalization degree of 88–106%. The estimation of phosphonation degree (PD) using data from elemental analysis comes to very similar values either by taking in account P/C or P/S ratios. These values are however slightly higher than those obtained using the NMR characterization.

Figs. 1 and 2 show the  $^1\text{H}$  NMR spectra of polyphenylsulfone respectively with 88% phosphonation and 84% sulfonation degree. The solvent  $d_6$ -DMSO led to the peak at 2.5 ppm. The presence of water is responsible for the peak at 3.4 ppm. Both in Figs. 1 and 2 a series of peaks can be seen between 7 and

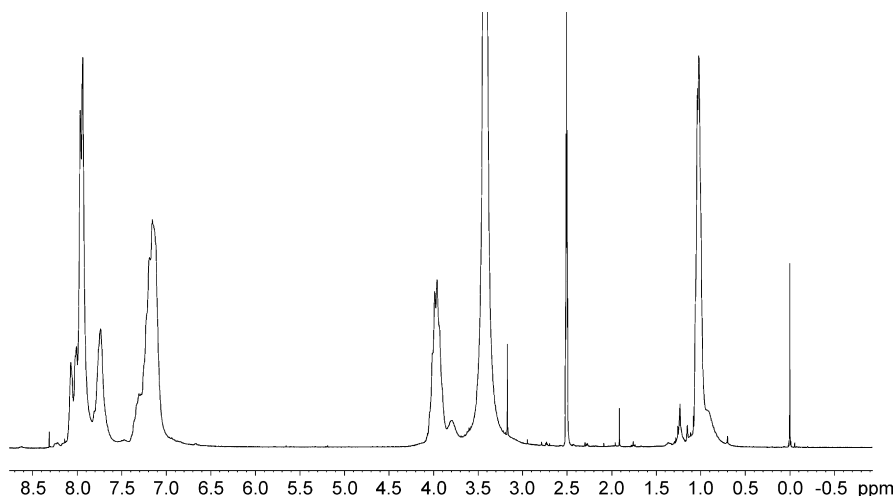
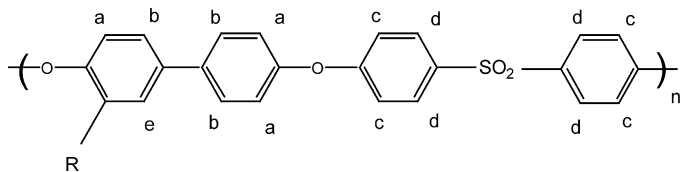


Fig. 1.  $^1\text{H}$  NMR spectrum of polyphenylsulfone with 88% phosphonation degree.

8 ppm. These peaks are assigned to protons of the aromatic rings, according to the following chemical structure:



where  $\text{R} = \text{PO}(\text{CH}_2\text{CH}_3)_2$  for Fig. 1 and  $\text{R} = \text{SO}_3\text{H}$  for Fig. 2.

The assignment followed previous papers of our group for sulfonated [25] and phosphonated [13] polysulfones.

For the determination of the sulfonation degree the intensity of the peak relative to the proton (proton “e” in Fig. 2) bonded to the carbon adjacent to that linked to the sulfonic group was compared to the peak relative to protons directly near the sulfone group (proton “d” in Fig. 2).

Before submitting the phosphorus-containing polymer to hydrolysis, the  $\text{CH}_2$  protons of the phosphonic ester can be

detected in the form of peaks at 4.1 ppm and at 1 ppm in Fig. 1. After the hydrolysis the peaks disappeared, confirming that the acid form was obtained.

For the estimation of the phosphonation degree, the ratio between the integrated peak at 4.1 ppm before the hydrolysis and the integrated peaks of protons at the main aromatic chain between 7.6 and 8.2 ppm was taken into consideration. This ratio between the integrated peaks gave the data listed in Table 2.

Similar results of the sulfonation degree were obtained from both  $^1\text{H}$  NMR and elemental analysis and they are listed in Table 3. Table 4 lists data of polymers which were first phosphonated and then sulfonated; in these cases the degree of functionalization was determined only by elemental analysis.

The independent phosphonation or sulfonation led to high degrees of substitution. However, the attempts of sulfonating previously phosphonated polymers were not very effective. This was the case for instance of polymers with phosphonation degree of about 60%, which were submitted to post-sulfonation. The sulfonation degree was not higher than 9% and could not be

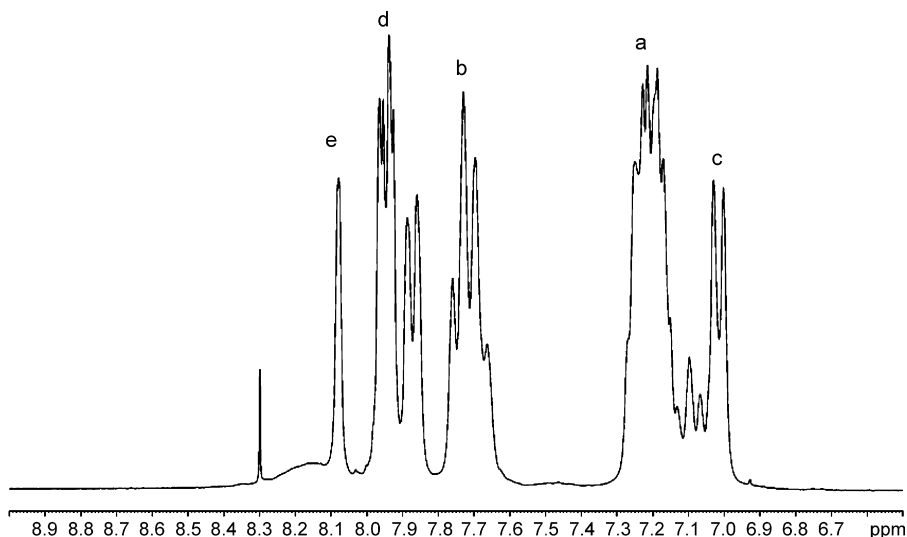


Fig. 2.  $^1\text{H}$  NMR spectrum of polyphenylsulfone with 82% sulfonation degree.

Table 2  
Phosphonated polyphenylsulfone

Polymer	Time of reaction (h)	Degree of phosphonation (%)	
		NMR	Elemental analysis <sup>a</sup>
P12	96	12	19
P30	96	30	30
P47	96	47	54
P59	96	59	66
P61	96	61	87
P88	96	88	106

<sup>a</sup> Calculated from P/S ratios.

Table 3  
Sulfonated polyphenylsulfone

Polymer	Time of reaction (h)	Degree of sulfonation (%)	
		NMR	Elemental analysis
S12	48	–	12
S44	24	44	–
S84	48	84	80
S88	96	88	86

increased by changing the reaction conditions. The reason for this low sulfonation degree could be the following. The sulfonation procedure [25] is based on an electrophilic agent that modifies the electron-rich aromatic rings in the chain. The sulfone group has a remarkable electron withdrawing effect. Therefore, the rings near the sulfone groups are less susceptible to sulfonation. The sulfonation would preferentially occur in rings linked to the ether groups, which are poor in electrons. When the polymer was previously phosphonated, exactly these rings near the ether group have been already functionalized with bromine, which later partially react, giving rise to phosphonic groups. A high degree of bromination is conducted to increase the yield of the phosphonation. As a consequence, the phosphonated polymers contain excess of non-reacted bromine attached to the aromatic rings. Halogens are known as deactivating agents for electrophilic aromatic substitution. This explains the low substitution degree obtained with the sulfonation. A sulfonation using lithiation [27,28] could be an alternative to modify the previously phosphonated polymers, since the rings near the sulfone group would then be preferred for the nucleophilic attack.

Since only a low degree of sulfonation was possible by reacting the phosphonated polymer with trimethylsilylchlorosulfonic, a blend of highly sulfonated polyphenylsulfone with the phosphonated polymer was used to prepare a membrane.

Table 4  
Phosphonated and sulfonated polyphenylsulfone

Polymer	Time of phosphonation reaction (h)	Time of sulfonation reaction (h)	Degree of functionalization (elemental analysis) (%)	
			Phosphonation	Sulfonation
P12S24	96	72	12	24
P59S8	96	24	59	8
P61S4	96	24	61	4
P61S9	96	48	61	9
Blend P88S84	96	96	44	42

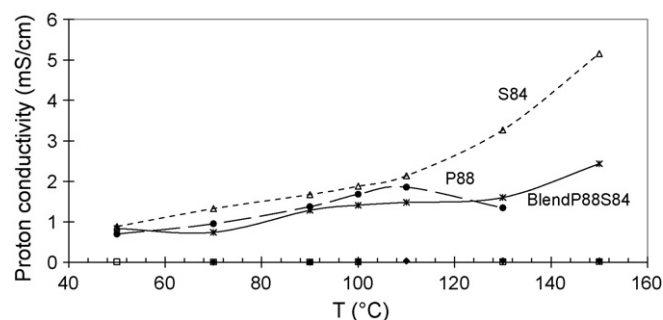


Fig. 3. Proton conductivity at 100% RH as a function of temperature: polymers with ( $\Delta$ ) 84% sulfonation, ( $\bullet$ ) 88% phosphonation and ( $\times$ ) a blend with equal amounts of both polymers.

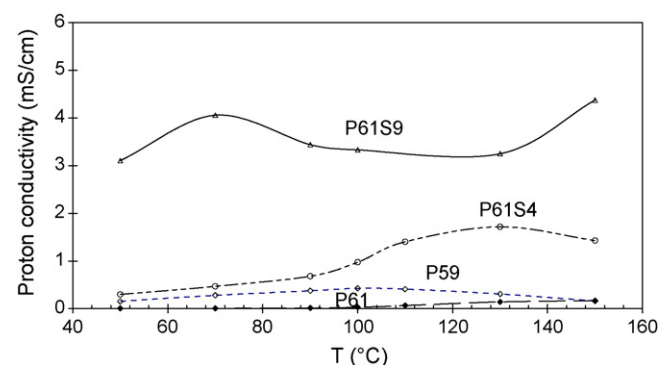


Fig. 4. Proton conductivity at 100% RH as a function of temperature: polymers with ( $\diamond$ ) 59% or ( $\blacklozenge$ ) 61% phosphonation degree and additionally ( $\circ$ ) 4% and ( $\Delta$ ) 9% sulfonation.

Its characterization is also compared to the other functionalized membranes.

Polyphenylsulfone membranes with degree of functionalization (phosphonation or sulfonation) lower than 45% had a proton conductivity lower than 0.1 mS/cm. Fig. 3 compares 88% phosphonated membranes with 84% sulfonated membranes, as well as with a blend, containing 50% of the phosphonated polymer (with 88% phosphonation degree) and 50% of the sulfonated polymer (with 84% sulfonation degree). They all have the same range of proton conductivity, with the sulfonated membrane having the highest values even above 100 °C. The total degree of functionalization is similar for the blend. However, the whole degree of phosphonation or sulfonation is each half of that of the other membranes. A Nafion<sup>®</sup> 117 membrane measured in the same conditions had proton conductivity between 12 and 22 mS/cm. Fig. 4 compares now polymers, which have been only

Table 5  
Pervaporation of 20 wt% methanol solution in water at 55 °C (feed at 1 atm and permeate side under vacuum) through phosphonated and sulfonated polyphenylsulfone membranes

Functionalization degree (%)		Membrane thickness ( $\times 10^{-6}$ m)	Water flux ( $\times 10^{-7}$ kg s $^{-1}$ m $^{-2}$ )	Methanol flux ( $\times 10^{-7}$ kg s $^{-1}$ m $^{-2}$ )
Phosphonation	Sulfonation			
0			86	5
12		35	161	11
12	24	49		56
30		62	1368	35
47		39	1270	33
61		45	1164	30
61	4	95		550
88		98	2435	338
	84	62		1220
44	42 <sup>a</sup>	66		128

<sup>a</sup> Blend with equal amounts of 88% phosphonated and 84% sulfonated polymers.

phosphonated (59–61% degree of phosphonation) and those, which have been phosphonated and additionally modified with 4 and 9% of sulfonation. Polymers with 59 and 61% sulfonation degree have similar proton conductivities, the difference being attributed to experimental error. A clear increase of proton conductivity was observed even with relatively small extent of sulfonation.

Fig. 5 shows the capability of the membranes to absorb water at 50 °C. Comparing membranes with similar degree of functionalization, it is confirmed that at least at temperatures as low as 50 °C the sulfonated membranes swells more in water than the phosphonated films.

Since the direct methanol fuel cells is a potential application for proton conductive membranes, the permeability of different sulfonated and phosphonated films to methanol and water was evaluated in pervaporation experiments. The results are presented in Table 5 and are coherent with the results of water absorption. As expected the permeability increases with the degree of functionalization. The sulfonated films are clearly more permeable to both water and methanol than the phosphonated membranes. However, a small extent of sulfonation additionally to phosphonation (e.g.: membrane with 61% phosphonation) increases dramatically the permeability. Quite interesting is the result for the blend. As mentioned before and from Fig. 3, this blend keeps a value of proton conductivity at least as high as the polymer with 88% phosphonation degree. The

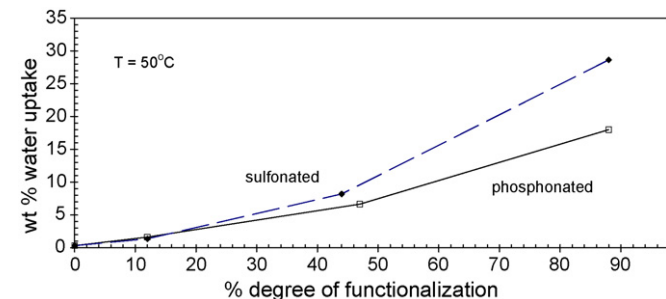


Fig. 5. Water uptake in equilibrium at 50 °C: comparison between phosphonated and sulfonated membranes.

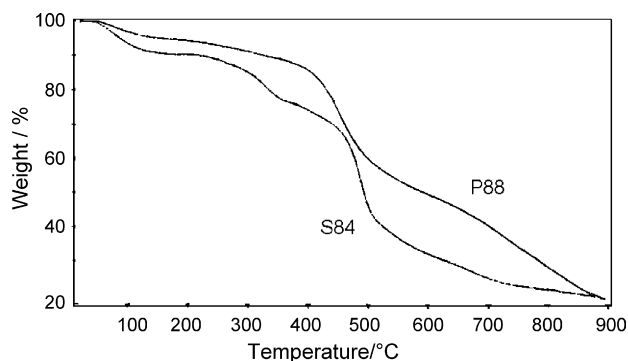


Fig. 6. Thermogravimetric analysis of polyphenylsulfones with 88% degree of phosphonation and 84% degree of sulfonation.

methanol permeability was however much lower than that of the individual polymers used in the blend preparation.

The thermal stability of phosphonated and sulfonated polymers with similar degree of functionalization is compared in Fig. 6. Both polymers are highly functionalized and therefore quite hydrophilic. Although the membranes were dried before the characterization a weight loss at about 100 °C corresponding to water evaporation can be detected for both films. After this for the sulfonated membrane a further weight loss is measured at about 250 °C, corresponding to the desulfonation and later at 450 °C, corresponding to the degradation of the main chain. For the phosphonated polymer the first decomposition step starts at about 400 °C and before this the dephosphonation is not evident.

#### 4. Conclusion

Polyphenylsulfone with degree of phosphonation up to 88–106% was obtained using Pd(0)-catalysts. Polymers with mixed functionalization could be obtained by sulfonation of previously phosphonated polymers. The sulfonation degree was as high 24%, when the samples were previously phosphonated. The pure phosphonated polymers were thermally more stable than polymers with similar sulfonation degree. From measurements performed at 100% relative humidity and temperatures as high as 150 °C, it was

observed that the proton conductivity of sulfonated membranes was slightly higher than that of phosphonated films. The sulfonated membranes swell clearly much more than the phosphonated. They are also much more permeable to water and methanol. Promising results with high proton conductivity but relatively low swelling and permeability were observed for blends of sulfonated and phosphonated polymers.

### Acknowledgements

The authors thank M. Eggers and Dr. N. Scharnagl for recording the thermal analysis and NMR spectra, Hugo Silva for the conductivity measurements and particularly Dr. Kai Jakoby for the discussions in the initial stage of this work. The experimental work was conducted at GKSS Research Centre in the frame of the Master Degree of Ethel Parceró obtained in 2004 at the Universidad Nacional Autónoma de México.

### References

- [1] M. Sander, E. Steininger, Phosphorus-containing resins, *J. Macromol. Sci. C2* (1968) 1–26.
- [2] M. Sander, E. Steininger, Phosphorylation of polymers, *J. Macromol. Sci. C2* (1968) 57–72.
- [3] Y.C. Nho, O.H. Kwon, C. Jie, Introduction of phosphoric acid group to polypropylene film by radiation grafting and its blood compatibility, *Radiat. Phys. Chem.* 64 (2002) 67–75.
- [4] Q. Li, R. He, J.O. Jensen, N.J. Bjerrum, Approaches and recent development of polymer electrolyte membranes for fuel cells operating above 100 °C, *Chem. Mater.* 15 (2003) 4896–4915.
- [5] G. Alberti, M. Casciola, Solid state protonic conductors, present main applications and future prospects, *Solid State Ionics* 145 (2001) 3–16.
- [6] W.H.J. Hogarth, J.C. Diniz da Costa, G.Q. Lu, Solid acid membranes for high temperature (>140 °C) proton exchange membrane fuel cell, *J. Power Sources* 142 (2005) 223–237.
- [7] I. Cabasso, J. Jagur-Grodzinski, D. Vofsi, Synthesis and characterization of polymers with pendent phosphonate groups, *J. Appl. Polym. Sci.* 18 (1974) 1969–1986.
- [8] X. Xu, I. Cabasso, Preliminary study of phosphonate ion exchange membranes for PEM fuel cells, *J. Polym. Mater. Sci.* 120 (1993) 68.
- [9] A.K. Bhattacharya, G. Thyagarajan, The Michaelis–Arbuzov rearrangement, *Chem. Rev.* 81 (1981) 415–430.
- [10] S. Yanagimachi, K. Kaneko, Y. Takeoka, M. Rikukawa, Synthesis and evaluation of phosphonated poly(4-phenoxybenzoyl-1,4-phenylene), *Synth. Met.* 135–136 (2003) 69–70.
- [11] R. Souzy, B. Amenduri, B. Boutevin, D. Virieux, Synthesis of new aromatic perfluorovinyl ether monomers containing phosphonic acid functionality, *J. Fluorine Chem.* 125 (2004) 1317–1324.
- [12] R. Souzy, B. Amenduri, Functional fluoropolymers for fuel cell membranes, *Progr. Polym. Sci.* 30 (2005) 644–687.
- [13] K. Jakoby, K.V. Peinemann, S.P. Nunes, Palladium-catalyzed phosphonation of polyphenylsulfone, *Macromol. Chem. Phys.* 204 (2003) 61–67.
- [14] K. Jakoby, S.P. Nunes, K. Peinemann, Proton conductive membrane for electrochemical applications, CA2412310, 2004.
- [15] B. Lafitte, P. Jannasch, Phosphonation of polysulfones via lithiation and reaction with chlorophosphonic acid esters, *J. Polym. Sci., Part A: Polym. Chem.* 43 (2005) 273–286.
- [16] K. Miyatake, A.S. Hay, New poly(arylene ether)s with pendant phosphonic acid groups, *J. Polym. Sci., Part A: Polym. Chem.* 39 (2001) 3770–3779.
- [17] H.R. Allcock, M.A. Hofmann, R.M. Wood, Phosphonation of aryloxyphosphazenes, *Macromolecules* 34 (2001) 6915–6921.
- [18] M.V. Fedkin, X. Zhou, M.A. Hofmann, E. Chalkova, J.A. Weston, H.R. Allcock, S.N. Lvov, Evaluation of methanol crossover in proton-conducting polyphosphazene membranes, *Mater. Lett.* 52 (2002) 192–196.
- [19] C. Stone, T.S. Daynard, L.Q. Hu, C. Mah, A.E. Steck, Phosphonic acid functionalized proton exchange membranes for PEM fuel cells, *J. New Mater. Electrochem. Syst.* 3 (2000) 43–50.
- [20] T.P. Jauhiainen, Effect of bromine and phosphorous substituents on the glass transition properties of some substituted poly(oxy-1,4-phenylenes), *Angewandte Makromolekulare Chemie* 104 (1982) 117–127.
- [21] Y.Z. Meng, S.C. Tjong, A.S. Hay, S.I. Wang, Synthesis and proton conductivities of phosphonic acid containing poly-(arylene ether)s, *J. Polym. Sci., Part A: Polym. Chem.* 39 (2001) 3218–3226.
- [22] S.H. Choi, Y.H. Jeong, J.J. Ryoo, K.P. Lee, Desalination by electrodialysis with the ion-exchange membrane prepared by radiation-induced graft polymerization, *Radiat. Phys. Chem.* 60 (2001) 503–511.
- [23] S.V. Kotov, S. Pedersen, W. Qiu, Z.M. Qiu, D.J. Burton, *J. Fluorine Chem.* 82 (1997) 13–19.
- [24] M.D. Guiver, O. Kutowy, J.W. Simon, Functional-group polysulfones by bromination metalation, *Polymer* 30 (1989) 1137–1142.
- [25] A. Dyck, D. Fritsch, S.P. Nunes, Proton-conductive membranes of sulfonated polyphenylsulfone, *J. Appl. Polym. Sci.* 86 (2002) 2820–2827.
- [26] G. Alberti, M. Casciola, L. Massinelli, B. Bauer, Polymeric proton conducting membranes for medium temperature fuel cells (110–160 °C), *J. Membr. Sci.* 185 (2001) 73–81.
- [27] W. Schnurberger, J. Kerres, S. Reichle, G. Eigenberger, Modifying thermoplastic polymers insoluble in organic dispersants, DE 19622338, 1997.
- [28] M.D. Guiver, G.P. Robertson, M. Yoshikawa, C.M. Tam, in: I. Pinnau, B. Freeman (Eds.), *Membrane Formation and Modification*, American Chemical Society, Washington, DC, 1999.