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Publisher's version / Version de l'éditeur:
https://doi.org/10.1002/marc.200600337
Macromolecular Rapid Communications, 27, pp. 1411-1417, 2006

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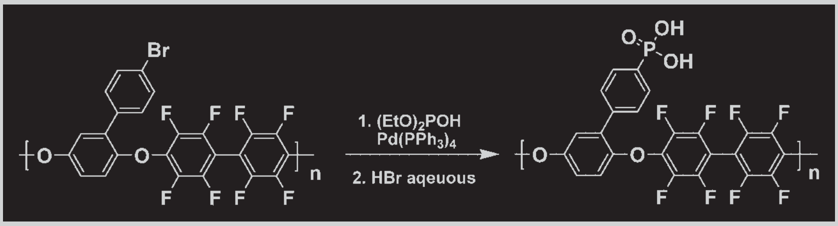
Summary: A high-molecular-weight fluorinated poly(aryl ether) with a 4-bromophenyl pendant group has been synthesized based on a bromo-bisphenol. A phosphonic acid derivative is readily prepared from this in high conversion yield. The phosphonated polymer possesses excellent thermal, oxidative, and dimensional stability, low methanol permeability, and reasonable proton conductivity, and may be a candidate polymeric electrolyte membrane for fuel cell applications.



Synthesis of a poly(aryl ether) with a phosphonic acid group.

Fluorinated Poly(aryl ether) Containing a 4-Bromophenyl Pendant Group and its Phosphonated Derivative

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Received: May 12, 2006; Revised: July 5, 2006; Accepted: July 6, 2006; DOI: 10.1002/marc.200600337

Keywords: fluoropolymers; membranes; phosphonation; proton exchange membrane

Introduction

Poly(aryl ether)s are a class of high-performance polymers known for their outstanding combination of chemical, physical, and mechanical properties.[1,2] Fluorinated aromatic polymers have been widely used in many high-technology fields, such as low loss waveguide devices,[3] low dielectric constant insulators,[4] and highly efficient separation membranes, because of their unique properties.[5]

Bromine-containing polymers are of interest because of their good thermal, optical, and flame-retarding properties. Bromine in polymers may also be converted readily into various functional groups, such as trimethylsilyl, phosphonate, and many others.[6,7] Bromine-containing polymers are often prepared either by post-bromination or by the polymerization of brominated monomers.[8]

Compared with sulfonic acid units, phosphonic acid units are known for their higher chemical and thermal stability and greater ability to retain water.[9] Phosphonated polymers are anticipated as potential proton exchange membranes (PEMs) for possible high-temperature fuel cell applications, which will enhance the kinetics of the electrode reactions and reduce the risk of catalyst poisoning.[10] However, only a few phosphonated polymers have been studied as PEM materials because the synthetic methods for preparing phosphonated polymers are limited and less familiar. Furthermore, a high degree of phosphonation (DP) is required to achieve sufficient proton conductivity because of the lower acidity of phosphonic acid.[11,12]

Recently, Miyatake and Hay[13] and Nunes and coworkers[14] reported successful phosphonation reactions based on the conversion of bromo-poly(aryl ethers) and poly(ether sulfone)s, respectively, using a palladium catalyst. However, properties related to proton conductivity were not reported. In the present study, a highly fluorinated poly(aryl ether) containing a 4-bromophenyl pendant group is prepared, and its phosphonation reaction is investigated. The properties related to PEM applications are evaluated.

Experimental Part

Materials

Decafluorobiphenyl, (4-bromo)aniline, 1,4-benzoquinone, zinc powder, diethylphosphite, triethylamine, and tetrakis(triphenylphosphine)palladium, were obtained from Sigma Aldrich Ltd., and used as received. *N*,*N*-Dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO) were purchased from Sigma Aldrich Ltd., purified by stirring with CaH_2 for several hours and distilled under reduced pressure, and kept over 5 Å molecular sieves before use. Anhydrous potassium carbonate (K_2CO_3) was ground into fine powder and stored in a vacuum oven at 120 °C before use.

Instrumentation

FT-IR spectra were performed on a Nicolet 520 Fourier-transform spectrometer. One-dimensional ^{1}H, ^{13}C, ^{19}F, ^{31}P, and two-dimensional COSY, HSQC, and HMBC NMR spectra were recorded on a Varian Unity Inova NMR spectrometer at the following frequencies: ^{1}H 399.945 MHz, ^{13}C 100.575 MHz, ^{19}F 376.282 MHz, and ^{31}P 161.900 MHz. The NMR solvents $CDCl_3$ and DMSO-d_6 were used as the reference for ^{1}H (7.25 and 2.50 ppm, respectively) and ^{13}C NMR (77.00 and 39.43 ppm, respectively) spectroscopy. Fluoroform ($CFCl_3$) was used as the internal reference (0 ppm) for ^{19}F NMR spectroscopy. The signal of H_3PO_4 85% in water was used as the external reference (0 ppm) for ^{31}P NMR spectroscopy. DSC measurements were performed on a TA Instrument 2920 DSC at a heating rate of 10 °C · min^{-1} under nitrogen. Melting points were obtained in the first run, and the glass transition temperature (T_g) was taken from the DSC curve in the second heating run. Thermogravimetric analysis (TGA) was performed on a TA Hi-Res TGA 2950 thermal analyzer system at 10 °C · min^{-1} in air. Gel permeation chromatography (GPC) was obtained by a Waters 410 instrument with tetrahydrofuran (THF) as the eluent and polystyrene as standards. Mechanical properties of thin dry and wet films were evaluated on an Instron 5565 instrument at a strain rate of 10 mm · min^{-1}, and a 500 N load cell was used. The samples were cut into standard dumbbell shapes (DIN-53504-S3A). The proton conductivities of the membranes were measured in the longitudinal direction and were obtained by alternating current (AC) impedance spectroscopy (Solartron 1260A) over a frequency range of 1 to 10^7 Hz at different relative humidities.

Synthesis of 4-Bromophenylquinone (Br-PQ) and 4-Bromophenylhydroquinone (Br-PH)

Br-PQ and Br-PH were synthesized according to a previously reported synthetic procedure using (3,5-ditrifluoromethyl)-phenylquinone and (3,5-ditrifluoromethyl)phenylhydroquinone.[15]

Br-PQ: Yield: 80%. Mp: 115 °C (DSC). IR (powder): 1 649 cm^{-1} (C=O).

^{1}H NMR (DMSO-d_6): $\delta = 7.66$ (d, 2H, $J = 8.4$Hz), 7.48 (d, 2H, $J = 8.4$ Hz), 6.99 (d, 1H, $J = 10$ Hz), 6.98 (d, 1H, $J = 2.4$ Hz), 6.83(dd, 1H, $J_1 = 10$ Hz, $J_2 = 2.4$ Hz).

^{13}C NMR (DMSO-d_6): $\delta = 187.32$, 185.90, 143.82, 137.06, 135.86, 132.08, 131.73, 131.23, 131.00, 123.31.

Br-PH: Yield: 78%. Mp: 131 °C (DSC). IR (powder): 3 220 cm^{-1} (–OH).

^{1}H NMR (DMSO-d_6): $\delta = 8.92$ (s, 2H), 7.57 (d, 2H, $J = 8.4$ Hz), 7.49 (d, 2H, $J = 8.4$ Hz), 6.78 (d, 1H, $J = 8.4$ Hz), 6.69 (d, 1H, $J = 2.8$ Hz), 6.63 (dd, 1H, $J_1 = 8.4$ Hz, $J_2 = 2.8$ Hz).

^{13}C NMR (DMSO-d_6): $\delta = 149.96$, 146.48, 137.75, 130.91, 130.64, 126.53, 119.58, 116.78, 116.00, 115.34.

Synthesis of the Fluorinated Poly(aryl ether) with a 4-Bromophenyl Pendant Group (8F-PAE-Br)

Into a 100 mL three-necked flask equipped with a magnetic stirrer, an argon inlet, and a Dean-Stark trap, were added Br-PH (2.65 g, 0.01 mol), anhydrous K_2CO_3 (2.01 g, 0.015 mol), DMAc (25 mL), and toluene (20 mL). The mixture was allowed to reflux for 5 h, and then the toluene was removed. After cooling to room temperature, 3.34 g (0.01 mol) of decafluorobiphenyl was added and the reaction mixture was heated to 80 °C. After stirring at 70–80 °C for 48 h, the viscous solution was poured into methanol. The flexible threadlike polymer was pulverized and the resulting powder was refluxed several times with deionized water and methanol, and dried at 100 °C for 48 h. IR (film): 1 071 (Ar–O–Ar), 724 cm^{-1} (F–Ar).

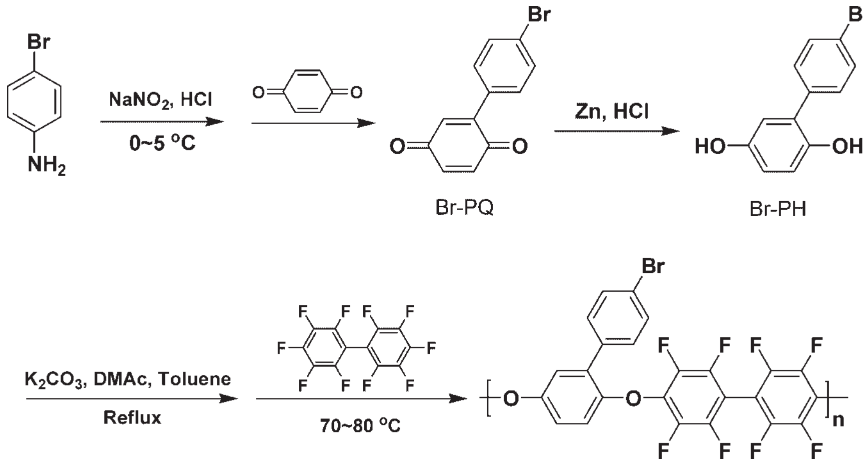
Synthesis of the Fluorinated Poly(aryl ether) Phosphonated Ester (8F-PAE-P-Ester)

Brominated polymer, 8F-PAE-Br (1.18 g, 2 mmol), was added into a stirred mixture of 5.15 mL of diethylphosphite, 5.57 mL of triethylamine, 0.6 mmol of tetrakis(triphenylphosphine)-palladium, and 10 mL of DMSO under an argon atmosphere. The polymer slowly dissolved in the mixture, and the reaction temperature was increased to 100 °C. After precipitation of the polymer from the homogenous mixture, an additional 5 mL of DMSO was added into the reaction solution to allow the polymer to redissolve. The mixture was poured into 150 mL of methanol that contained 10 vol.-% concentrated hydrochloric acid (37%) to obtain a fibrous product after several hours. The polymer that contained the catalyst was washed in hot methanol and water several times. After drying in a vacuum oven, the polymer powder was dissolved in chloroform, and reprecipitated into methanol that contained 10 vol.-% concentrated hydrochloric acid. The polymer was thoroughly washed with hot water and methanol to obtain the phosphonated ester polymer, 8F-PAE-P-Ester.

IR (film): 1 066 (Ar–O–Ar), 1 057 (P–O–C), 724 cm^{-1} (F–Ar).

Hydrolysis of the 8F-PAE-P-Ester

The membranes in acid form were obtained by soaking the 8F-PAE-P-Ester film in concentrated HBr solution (48%) at reflux for 72 h. The films were thoroughly washed with water over



Scheme 1. Synthesis of a highly fluorinated poly(aryl ether) that contains a bromine group.

48 h to remove excess acid, and then dried at 120 °C for 12 h. IR (film): 3 200–2 500 (phosphonic acid), 1 064 (Ar–O–Ar), 726 cm^{-1} (F–Ar).

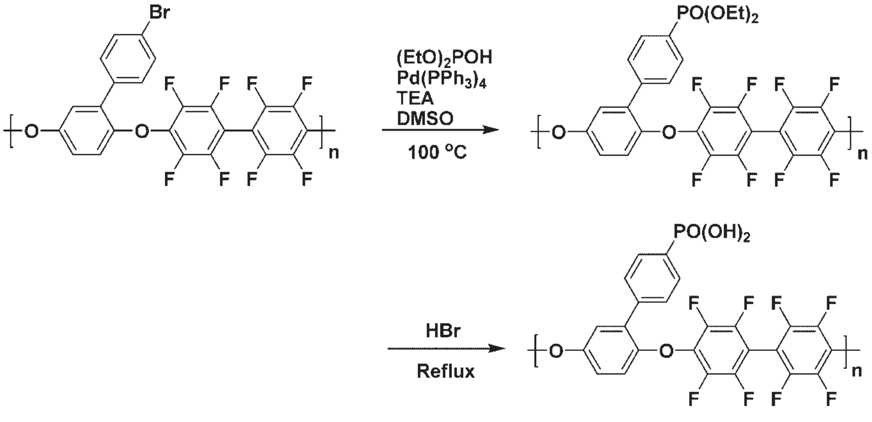
Results and Discussion

Bisphenol monomer, Br-PH, has been synthesized by a coupling reaction in high yield, as shown in Scheme 1. The structures of Br-PQ and Br-PH are in good agreement with their FT-IR, ^1H, and ^{13}C NMR spectra. To avoid possible branching and crosslinking caused by the more activated fluorine atoms of decafluorobiphenyl, a two-stage reaction procedure that involves initial phenolate formation of Br-PH with K_2CO_3 in DMAc, followed by low temperature polycondensation of phenolate with decafluorobiphenyl is used. High-molecular-weight polymer is readily obtained, as shown by GPC, with an apparent number-average molecular weight ($\overline{M}_n$) of 34 000, and a weight-average molecular weight ($\overline{M}_w$) of 110 000, relative to polystyrene standards.

Several methods have been reported to introduce phosphonic acid groups into low-molecular-weight aromatic compounds, but some of them are not readily adaptable for polymers because of poor solubility and possible side reactions.[13] In this study, a Pd^0 complex has been selected as a catalyst to convert brominated poly(aryl ether) into a phosphonated derivative (Scheme 2). DMSO is used as the solvent because the 8F-PAE-Br polymer is readily soluble in hot DMSO.

It is interesting to note that the substitution reaction proceeds quickly. For example, the conversion reaches 41% after 3 min and 95% (by NMR calculation) after 6 min when 30 mol-% palladium catalyst is used. Both the substitution reaction time and catalyst amount are far lower than the results published in the literature.[13] It is obvious that the short reaction time is helpful to minimize side reactions and chain degradation.

In this reaction, a higher DP (≈100%) can be easily obtained. The DP is much higher than a previously reported phosphonated poly(ether sulfone) (PES) (≈58%) under similar reaction conditions.[14]



Scheme 2. Synthesis of a poly(aryl ether) with a phosphonic acid group.

The phosphonated poly(aryl ethers) in their ester forms are readily converted into their acid forms by hydrolysis with concentrated hydrobromic acid, as evidenced by FT-IR and NMR spectra. Absorption bands between 3 200 and 2 500 cm^{-1} that arise from the phosphonic acid group are observed in the FT-IR spectra.

All three polymers have been fully characterized by NMR. Table 1 lists all the assigned signals observed in the ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra. In the ^{1}H NMR spectra, the presence of the phosphoric ester was noted by the ethoxy CH_2 (4.13 ppm) and CH_3 (1.33 ppm) signals at lower frequencies, and also by the new P–H couplings between P and H2 ($^3J = 13.0$ Hz) as well as P with the CH_2 ($^2J =$ 19.1 Hz). Conversion of the phosphoric ester into the phosphoric acid is confirmed by the disappearance of the ethoxy signals, which are replaced by a broad phosphoric acid hydrogen signal at 6.57 ppm. Three bond and even four bond P–H couplings between P–H2 ($^3J = 12.6$ Hz) and P–H3 ($^4J = 3.2$ Hz) indicate the presence of a phosphorous atom. ^{13}C NMR signals have all been unambiguously assigned (Table 1) by using two-dimensional HSQC and HMBC spectroscopy. The phosphorous atom causes splitting of the carbon signals through P–C couplings for the aromatic C1, C2, and C3 of both the phosphoric ester and acid derivatives as well as with the CH$_3$ of the ester derivative. Strong C–F couplings (250 Hz) are also evident. Fluorine and phosphorous NMR spectra confirm the presence of these heteroatoms as expected from the structures. Figure 1 shows ^{1}H and ^{13}C NMR spectra of the expanded aromatic regions for 8F-PAE-P-Acid.

DSC and TGA have been performed to evaluate the thermal properties of the polymers. The T_g values of 8F-PAE-Br and 8F-PAE-P-Ester are 174 and 161 °C, respectively. The DSC curve of 8F-PAE-P-Acid shows no obvious T_g because of the effect of phosphonic acid groups, which have a strong interaction that hinders the molecular chain motion. No melting endotherms are observed in the DSC traces, which suggests the amorphous nature of the polymers.

Figure 2 is a TGA comparison of 8F-PAE-Br, 8F-PAE-P-Ester, and 8F-PAE-P-Acid in air. 8F-PAE-P-Br has excellent thermal stability and its 5% weight loss temperature is as high as 503 °C, which is attributable to its aromatic chains and thermally stable C–F and C–Br bonds. As a comparative sample, 8F-PAE-P-Ester has two obvious decomposition stages around 307 and 467 °C, the initial one is associated with the loss of ester ethyl groups. Polymer 8F-PAE-P-Acid has much better thermal stability than the phosphonic ester, and no obvious decomposition is observed until the main-chain decomposition at ≈420 °C.

Table 1. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR data for polymers.

Atom number	8F-PAE-Br in CDCl$_3$ $\delta$$^{a)}$	8F-PAE-P(O)(OEt)$_2$ in CDCl$_3$ $\delta$$^{a)}$	8F-PAE-P(O)(OH)$_2$ in DMSO-d_6 $\delta$$^{a)}$
	ppm	ppm	ppm
H2	7.56 (d, $^3J_{HH}$ 8.0)	7.88 (dd, $^3J_{PH}$ 13.0, $^3J_{HH}$ 8.0)	7.78 (dd, $^3J_{PH}$12.6, $^3J_{HH}$ 8.2)
H3	7.44 (d, $^3J_{HH}$ 8.0)	7.68 (d, $^3J_{HH}$ 8.0)	7.68 (dd, $^3J_{HH}$ 8.2, $^4J_{PH}$ 3.2)
H7	6.93 (d, $^3J_{HH}$ 8.0)	6.90–6.97 (m)	7.35 (d, $^3J_{HH}$ 9.0)
H8	7.01 (dd, $^3J_{HH}$ 8.0, $^4J_{HH}$ 2.0)	6.99–7.07 (m)	7.29 (d, $^3J_{HH}$ 9.0)
H10	7.11 (br s)	7.11–7.17 (m)	7.45 (d, $^4J_{HH}$ 2.0)
P(O)O*H*	–	–	6.57 (br)
CH_2	–	4.13 (dt $^2J_{PH}$ 19.1, $^3J_{HH}$ 7.2)	–
CH_3	–	1.33 (t $^3J_{HH}$ 7.2)	–
C1	122.50 (s)	128.20 (d, $^1J_{CP}$ 192.0)	133.70 (d, $^1J_{CP}$ 182.15)
C2	131.52 (s)	131.86 (d, $^2J_{CP}$ 9.8)	130.43 (d, $^2J_{CP}$ 9.8)
C3	130.82 (s)	129.39 (d, $^3J_{CP}$ 14.9)	128.75 (d, $^3J_{CP}$ 14.7)
C4	134.74 (s)	140.02 (s)	137.63 (s)
C5	132.12 (s)	132.23 (s)	131.48 (s)
C6	149.84 (s)	150.02 (s)	149.47 (s)
C7	116.84 (s)	116.81 (s)	117.34 (s)
C8	116.19 (s)	116.63 (s)	116.72 (s)
C9	153.11 (s)	153.23 (s)	152.70 (s)
C10	118.66 (s)	118.92 (s)	118.31 (s)
C11	135.2–135.7 (m)	135.3–135.8 (m)	134.7–135.1 (m)
C12	141.52 and 141.09 (dd, $^1J_{CF}$ 252.8, $^2J_{CF}$ 14.1)	141.60 and 141.25 (d, $^1J_{CF}$ 251.9)	141.06 and 140.76 (d, $^1J_{CF}$ 247.4)
C13	144.63 (d, $^1J_{CF}$ 252.8)	144.72 (d, $^1J_{CF}$ 252.3)	144.19 (d, $^1J_{CF}$ 250.5)
C14	102.0–103.0 (m)	102.0–103.0 (m)	101.3–102.2 (m)
$\underline{C}H_2$	–	62.25	–
CH$_3$	–	16.33 (d, $^3J_{CP}$ 6.0)	–
F12	−153.13 to −153.93 (m)	−152.80 to −154.20 (m)	−153.00 to −154.00 (m)
F13	−137.80 to −138.43 (m)	−137.50 to −138.80 (m)	−137.50 to −138.30 (m)
P	–	18.80	13.49

[a] In parentheses: multiplicity and *J*/Hz.

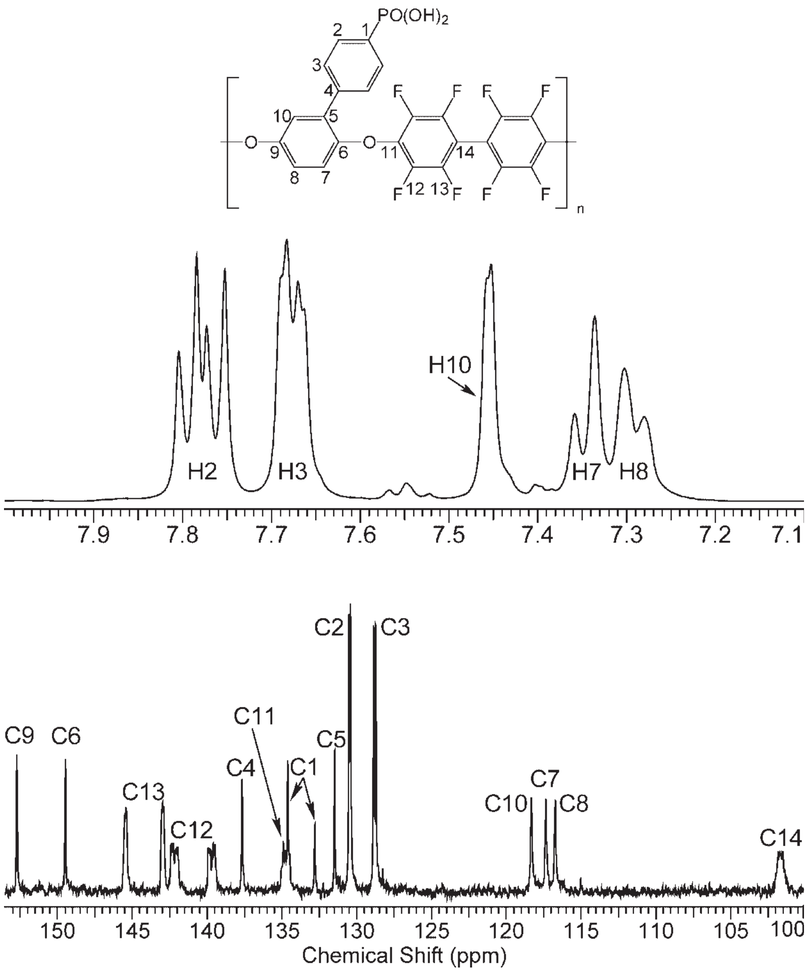


Figure 1. ^{1}H and ^{13}C NMR spectra of 8F-PAE-P-Acid.

Its 5% weight loss temperature is as high as 461 °C, which is much higher than those of the sulfonated polymers (≈250 °C).[16] In comparison, the surface color changes to a darker tone for Nafion 117 at 120 °C while the color of 8F-PAE-P-Acid film remains unchanged at 150 °C for more than 6 h.

8F-PAE-PAE-Br and 8F-PAE-P-Ester are readily soluble in aprotic polar solvents such as NMP, DMAc, and DMF, as well as in the less polar solvents such as chloroform and tetrahydrofuran (THF). 8F-PAE-P-Acid is readily soluble in DMAc, DMF, DMSO, and NMP. The high solubility of all the polymers enable thin films to be readily prepared.

Good mechanical properties are one of the necessary requirements of polymers for their application as PEM materials. However, the highly fluorinated poly(aryl ether)s often show poor tensile properties because of their relatively lower molecular weights that can arise from limitations of the polymerization conditions. The 8F-PAE-Br film has a tensile stress at maximum load of 86.2 MPa, Young's moduli of 1.45 GPa, and elongation at break of 20%. In the dry state, 8F-PAE-P-Acid shows a tensile stress of 81.2 MPa and Young's moduli of 1.66 GPa. In comparison to the dry sample, the wet one exhibits a lower tensile strength and a higher elongation at break. These mechanical data show they are strong membrane materials (see Table 2 for a summary).

Because of their higher temperature stability than their $-SO_3H$ analogues and the possibility of conductivity at low humidity levels, polymers with phosphonic acid groups ($-PO_3H_2$) have been studied as potential candidates for use as PEM materials. Additional requirements are good dimensional stability (low swelling ratios) in humidified environments, and high proton conductivity (closely related to acid content and water uptake). Fluorine-containing moieties impart a higher degree of hydrophobicity than non-fluorinated groups, which improves the dimensional stability of the sulfonated polymer in water.

As expected, the swelling ratio and water uptake increases with the temperature. It exhibits a far lower dimensional swelling and water uptake than Nafion 117. The water uptake and swelling ratio of Nafion 117 increases dramatically at around 80 °C, which implies that it is in a state above the percolation threshold. However, 8F-PAE-P-Acid still maintains an extremely low swelling ratio and water uptake even at 100 °C. The swelling ratio of this film is below 5.0% after

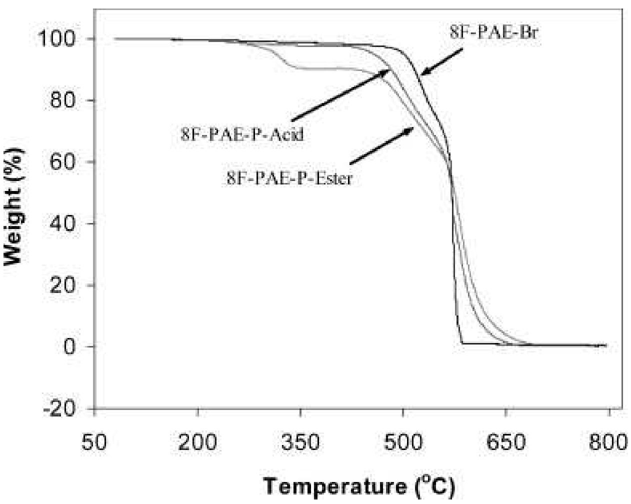


Figure 2. A TGA comparison of 8F-PAE-Br, 8F-PAE-P-Ester, and 8F-PAE-P-Acid.

immersion in boiling water for 96 h. Its water uptake is 3.0, 7.3, and 14.6% at 22, 80, and 100 °C, respectively.

The oxidative stability of the polymers has been evaluated in Fenton's reagent at 80 °C. This method is regarded as a standard test to gauge relative oxidative stability and to simulate accelerated fuel cell operating conditions. The phosphonated polymer membrane maintains 98.7% weight after treatment with Fenton's reagent at 80 °C for 1 h, and maintains its dimensional shape and flexibility after 48 h, which indicates a relatively higher oxidative stability compared with other reported sulfonated polymers.[17]

Proton conductivity has been tested as a function of temperature and relative humidity. Phosphonated polymers have a lower proton conductivity compared with Nafion 117. 8F-PAE-P-Acid has a proton conductivity up to $2.6 \times 10^{-3}\ \mathrm{S \cdot cm^{-1}}$ in water at room temperature, and $6.0 \times 10^{-3}\ \mathrm{S \cdot cm^{-1}}$ at 95% relative humidity at 80 °C. Proton conductivities measured at higher temperatures and lower relative humidity levels are considerably lower. Proton conductivities are $2.9 \times 10^{-6}\ \mathrm{S \cdot cm^{-1}}$ at 45% relative humidity, and $2.0 \times 10^{-6}\ \mathrm{S \cdot cm^{-1}}$ at 25% relative humidity at 120 °C, respectively. To improve the proton conductivities of the phosphonated polymers, it will be necessary to increase the DP beyond that at present.

Membranes intended for direct methanol fuel cells (DMFC) must possess both high proton conductivity and be effective barriers for methanol crossover from the anode to the cathode compartment.[18] Among the most significant of Nafion's drawbacks is its high methanol permeability in the DMFC application. This limitation is associated with Nafion microstructure, where interconnected ionic domains strongly contribute to its high proton conductivity, but at the same time contribute to fast methanol diffusion.

In order to compare the methanol permeability of the prepared membranes with that of Nafion 117, the latter has been tested under the same conditions of 10 vol.-% (2.47 M) methanol at 30 °C. 8F-PAE-P-Acid reveals a methanol permeability of $1.07 \times 10^{-8}\ \mathrm{cm^2 \cdot s^{-1}}$, which constitutes a significant reduction (>100×) compared with Nafion, with a value of $1.55 \times 10^{-6}\ \mathrm{cm^2 \cdot s^{-1}}$.

Table 2. Mechanical properties of 8F-PAE-Br and 8F-PAE-P-Acid films.

Polymer	Tensile strength	Young's modulus	Elongation at break
	MPa	GPa	%
8F-PAE-Br	86.2	1.45	20
8F-PAE-P-Acid (dry)	81.2	1.66	14
8F-PAE-P-Acid (wet)	63.7	1.08	20

Conclusion

A novel, highly fluorinated, high-molecular-weight polymer that contains (4-bromo)phenyl side groups has been synthesized. It has good solubility, high thermal stability, and good tensile strength. It can be readily transformed into a phosphonated polymer with a high degree of phosphonation. The polymer with a (4-phosphonic acid)phenyl pendant group possesses excellent mechanical properties, thermal stability, and oxidative resistance. It shows promising conductivity up to $2.6 \times 10^{-3}\ \mathrm{S \cdot cm^{-1}}$ in water at room temperature, and $6.0 \times 10^{-3}\ \mathrm{S \cdot cm^{-1}}$ at 95% relative humidity at 80 °C. It also exhibits an extremely low methanol permeability value of $1.07 \times 10^{-8}\ \mathrm{cm^2 \cdot s^{-1}}$.

Acknowledgements: Financial support for this project, provided by the joint research cooperation program between the *National Science Council of Taiwan (ROC)* and the *National Research Council of Canada*, is gratefully acknowledged (NRCC publication No. 47899).

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