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# Phosphonated poly(arylene ether)s as potential high temperature proton conducting materials

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### ABSTRACT

The preparation and characterization of new phosphonated polymeric ionomers based on a fully aromatic poly(arylene ether) backbone with applications as proton exchange membranes for fuel cell is reported. The high-molecular-weight polymers were obtained by the polycondensation of the phosphonated monomers with decafluorobiphenyl in high yields with inherent viscosities up to 0.58 dL g<sup>-1</sup>. The hydrolysis of the phosphonated ester into phosphonic acid groups was carried out quantitatively under acidic conditions. The polymers were studied by TGA after hydrolysis and showed10% weight loss above 430 °C. Membranes with total ion-exchange capacities above 6 meq/g showed proton conductivities of approximately92 mS/cm at 25 °C and 100% relative humidity increasing to ca.150 mS/cm at 140 °C. Their conductivity under dry condition showed values over 2 mS/cm at 120 °C which upon doping with phosphoric acid jumped to nearly 100 mS/cm.

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# 1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are under consideration as future power sources for transport, stationary and portable applications [1–3]. While there are continuing improvements in advancing the PEMFC technology, one of the present challenges is the development of new durable membranes that allow operation at higher temperatures and low humidity [3,4]. Because of their excellent chemical and physical properties and well-studied synthesis, membrane based on sulfonic acid containing polymers, have drawn much interest and are often regarded as the material of choice for use as solid electrolyte membranes in PEMFCs [5,6]. However, their shortcomings at temperatures above 90 °C or at low relative humidity motivate the search for ionomers with alternative acidic moieties, such as phosphonic acid, which have higher chemical and thermal stabilities than sulfonic acid [7]. Aromatic phosphonic acids have lower acidity but better chemical and thermal stability and greater ability to retain water compared with their sulfonic acids analog [8-12].

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Studies on model compounds have shown higher thermal and electrochemical stability for phosphonic acid based compounds compared with their sulfonic acid analogue. The high degrees of selfdissociation and hydrogen bonding in phosphonated compounds lead to high proton conductivities in moderate temperature and low humidity [8,13,14]. It has been suggested that the significant proton donor and acceptor properties combined with the high dielectric constant of phosphonic acid result in high degrees of selfdissociation [13]. Formation of water due to the self-condensation equilibrium between phosphonic acid groups especially at higher temperatures may help their conductivity under very dry conditions. It has been proposed that the conductivity of phosphonate dionomers under nearly zero humidity may mainly be due to the presence of this small amount of water [15].

Although phosphonic acid containing polymers show some advantages relative to sulfonic acid containing polymers for higher temperature application in PEMFC, they are not well studied due to relatively limited synthetic procedures and the required high degree of phosphonation (DP) in order to achieve sufficient proton conductivity [7,16,41–44,47]. Lower acidity and a higher degree of hydrogen bonding of the phosphonated polymers compared with the sulfonated systems lead to reductions in the number of absorbed water molecules per acid group ( $\lambda$ ) in a phosphonated



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membrane. Therefore, synthesizing phosphonic ionomers with increased acidity and ion exchange capacity (IEC) may lead to high proton conductivities required for the successful application of such materials as electrolyte in PEM fuel cell at high temperature and low humidity.

The majority of the phosphonic acid containing ionomers reported to date have low IEC value and proton conductivity. Some examples of these materials include: poly(arylene ether)s [17–20], poly(ethersulfone)s [21–24], polyphosphazenes [25,26], poly(4-phenoxybenzoyl-1,4-phenylene)s [27] and polymers with per-fluorinated backbones [7,12,28]. Proton conduction in these systems is water dependent, similar to observed behavior with sulfonated polymers. Since the preparation of phosphonated ionomers with very high IEC value is achievable compared to sulfonic ionomers, it is desirable to design phosphonic ionomers with increased acidity and IEC.

In this study, we report new poly(arylene ether)-containing phosphonic acid substituents on the main chains of ionomers. We initially prepared diphosphonated bisphenol and biscarbamate monomers and subsequently polymerized them with decafluorobiphenyl to produce the corresponding phosphonatedpoly(arylene ether)s. The presence of highly concentrated acid groups next to perfluorinated biphenyl rings should increase acidity and aggregation of phosphonic acids which may provide a better condition for higher proton conductivity. The synthesis, structure, and some properties of the phosphonated ionomers as well as phosphoric acid doped membrane are reported.

### 2. Experimental

### 2.1. Instrumentation

<sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, and <sup>31</sup>P NMR spectra were measured on a Bruker model DRX 500 AVANCE apparatus at the following frequencies: <sup>1</sup>H 500 MHz,  $^{13}$ C 125 MHz,  $^{19}$ F 470 MHz, and  $^{31}$ P 202 MHz. The signal of H<sub>3</sub>PO<sub>4</sub> 85% in water was used as the external reference (0 ppm) for <sup>31</sup>P NMR spectroscopy. Elemental analysis for C, H and N performed by a Perkin Elmer 2004 (II)analyzer. Melting points (uncorrected) were measured with an Electrothermal Engineering LTD 9200 apparatus. Inherent viscosities ( $\eta_{inh} = \ln \eta_r/c$  at concentration of  $0.5 \text{ g } \text{dL}^{-1}$ ) were measured with an Ubbelohde suspended-level viscometer at 30 °C using N,N-dimethylacetamide (DMAc) as solvent. Thermogravimetric analyses (TGA) were conducted with a Stanton Redcraft STA-780 (London, UK) thermal analysis under nitrogen atmosphere at a heating rate of 10 °C min<sup>-1</sup>. The experimental ion exchange capacity (IECexp, meq PO3H2/gof dried polymer) of the membranes determined via titration using the following procedure: Initially membrane samples were vacuum dried at 80 °C until constant weight, and then the samples were individually immersed in 30 mL of 0.1 N NaOH/0.1 M NaCl mixed aqueous solution (1/3 by volume) and stirred for 24 h, to convert the membrane from the H<sup>+</sup> to the Na<sup>+</sup> form completely. Subsequently, 15 mL of 0.10 N HCl solutions was added, and the excess amount of HCl was titrated using 0.025 N NaOH solution with phenolphthalein as a pH indicator. IECexp was calculated according to the following equation.

$$IEC_{exp} = 0.025(V_{NaOH} - V_B)/W_{dry}$$

where  $V_{\text{NaOH}}$  is the volume of 0.025 N NaOH aqueous solutions for the volumetric titration,  $V_{\text{B}}$  is the volume of NaOH aqueous solution for blank titration, and  $W_{\text{dry}}$  is dry weight of the membrane. Also the theoretical IEC value for membrane (IEC<sub>cal</sub>) was also calculated as follows:  $IEC_{cal} = equivalents of$ 

– OH per unit/repeat unit molecular weight

To obtain water uptake values, membranes were dried for 24 h at 100 °C, weighed ( $W_{dry}$ ), and immersed in deionized water at room temperature until reading a constant mass (2 days). The wet membranes were blotted dry and immediately weighed ( $W_{wet}$ ). The water uptake is reported as a percentage and determined by taking the equilibrium weight difference between the wet film ( $W_{wet}$ ) and the dry film ( $W_{drv}$ ) and dividing by the dry film ( $W_{drv}$ ) weight.

The acid doping level of membranes was determined by immersing samples in 85% phosphoric acid for various doping times (1–14 days) at room temperature. The samples were weighed before and after the immersion and the weight gain was obtained, and the acid doping level of the membrane was calculated as the moles of phosphoric acid per phosphonic acid group.

The proton conductivity of the phosphonated polymeric membranes was measured by placing the membranes between two platinum electrodes held by two polytetrafluoroethylene (PTFE) frames. A homemade chamber was used to equilibrate the samples for conductivity measurement. An impedance spectrum was recorded from 10 MHz to 10 Hz using an Autolab PGSTAT 30in fully hydration and water-free conditions at various temperatures. The proton conductivity ( $\sigma$ ) is the reciprocal of the resistance (R) and reported in units of milli-Siemens per centimeter (mS/cm) from:  $\sigma = L/RS$  where L and S are the thickness and area of the membrane, respectively.

#### 2.2. Materials

Diisopropylamine (Aldrich) was dried over KOH and distilled just before use under nitrogen atmosphere. Triethylamine (Aldrich) was dried by refluxing over sodium hydroxide pellets for several hours, distilled and then stored over potassium hydroxide pellets. Diethyl phosphite distilled before use under argon.

Decafluorobiphenyl (Sigma Aldrich) was used as received. *N*,*N*-Dimethylacetamide (DMAc) (Sigma Aldrich) was purified by stirring over CaH<sub>2</sub> for several hours and distilled under reduced pressure. Anhydrous potassium carbonate ( $K_2CO_3$ ) (Aldrich) was ground into fine powder and stored in a vacuum oven at 120 °C before use.

### 2.3. Monomer synthesis

### 2.3.1. Tetraethyl 1,4-phenylene diphosphate(O-Ph)

A mixture of hydroquinone (30 mmol, 3.3 g), diethyl phosphite (62 mmol, 8.56 g, 8 mL), and 18 mL of carbon tetrachloride was stirred and cooled to 0 °C. 8.7 mL (62 mmol, 6.3 g) of triethylamine was then added drop-wise to the reaction mixture cooled in ice bath over a period of 1 h so that the temperature was maintained below 5 °C. After addition, the reaction mixture was stirred at 0 °C for 1 h, then the ice bath was removed and the mixture was stirred overnight at room temperature. Water (20 mL) was added, the reaction mixture was filtered, and the organic layer was dried over anhydrous sodium sulfate. By removal of solvent on a rotary evaporator 9.75 g (85%) of colorless liquid was obtained: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>);  $\delta$  1.33–1.36 (t, 12H, <sup>3</sup>*J* (H–H) = 7 Hz), 4.18–4.23 (m, 8H), 7.18 (s, 4H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>);  $\delta$  16.45 (d, <sup>3</sup>*J* (C–P) = 6.9 Hz), 65.07 (d, <sup>2</sup>*J* (C–P) = 6.2 Hz), 121.48 (d, <sup>3</sup>*J* (C–P) = 4.7 Hz), 147.95 (d, <sup>2</sup>*J* (C–P) = 7.5 Hz) ppm; <sup>31</sup>P NMR (202 MHz, D<sub>2</sub>O):  $\delta$  –5.83 to –5.68 (m) ppm.

### 2.3.2. Tetraethyl (2,5-dihydroxy-1,4-phenylene) diphosphate (C-Ph)

A solution of lithium diisopropylamide (LDA) was prepared as follows: To a solution of diisopropylamine (25.4 mmol, 2.57 g,

4711

3.58 mL) in THF (15 mL) at -78 °C under argon was added *n*butyllithium (25 mmol, 10 mL) and the mixture was stirred for 30 min A solution of O-Ph (6 mmol, 2.3 g) in dry THF (10 ml) was slowly added with a syringe to a solution of LDA. After stirring for 1 h at -78 °C, the solid carbon dioxide-acetone bath was removed and the mixture was allowed to warm up to room temperature and stir for an additional 1 h. A mixture of saturated solution of ammonium chloride (15 mL) and diethyl ether (20 mL) was then added, and the organic layer was separated and the aqueous layer was extracted with diethyl ether and methylene chloride for several times. The combined organic layers were washed with water and dried over MgSO<sub>4</sub>.The solvent was removed in vacuo to give a yellowish solid as crude product. Recrystallization from acetone/ water yields 2.42 g (68%) white crystalline solid. Mp 219–220 °C; <sup>1</sup>H NMR (500 MHz, CDC1<sub>3</sub>) 1.37–1.40 (t, 12H, <sup>3</sup>J (H–H) = 7 Hz), 4.08-4.16 (m, 4H), 4.18-4.25 (m, 4H), 7.01-7.05 (dd, 2H, <sup>2</sup>J (H-P) = 15.7 Hz,  ${}^{3}J$  (H-P) = 7.4 Hz), 9.75 (s, 2H, (b, OH, exchangeable with  $D_2O$ ), ppm; <sup>13</sup>C NMR (125 MHz, CDC1<sub>3</sub>);  $\delta$  16.58 (d,  ${}^{3}J(C-P) = 7.0$  Hz), 63.60 (d,  ${}^{2}J(C-P) = 5.4$  Hz), 116.84 (d,  ${}^{1}J$ (C-P) = 173.0 Hz, 119.82 (dd, <sup>2</sup>J(C-P) = 14.1 Hz, <sup>3</sup>J(C-P) = 6.1 Hz), 153.02 (dd,  ${}^{2}J$  (C–P) = 17.8 Hz,  ${}^{3}J$  (C–P) = 6.3 Hz), ppm;  ${}^{31}P$  NMR (202 MHz, CDCl<sub>3</sub>); δ 19.79–19.98 (m) ppm, Anal. Calcd. for C<sub>14</sub>H<sub>24</sub>O<sub>8</sub>P<sub>2</sub>: C, 43.97; H, 6.28. Found: C, 43.90; H, 6.20.

# 2.3.3. Bis-propylcarbomate-masked derivative: (2,5-bis(diethoxy-phosphoryl)-1,4-phenylene bis(propylcarbamate)) (C-Ph-BC)

To a solution of C-Ph (2 mmol, 0.764 g) in 25 mL of methylene chloride was added 1 mL of *n*-propylisocyanate and 0.7 mL of triethylamine. The mixture was stirred at room temperature for 3 days to obtain a white precipitate. The solvent was removed and a crude product was washed with methylene chloride to obtain C-Ph-BC in a 70% yield. Mp: 170–172 °C, <sup>1</sup>H NMR (500 MHz, MeOH-*d*<sub>4</sub>);  $\delta$  0.99–1.02 (t, 6H, <sup>3</sup>*J* (H–H) = 7.4 Hz), 1.34–1.37 (t, 12H, <sup>3</sup>*J* (H–H) = 7 Hz), 4.14–4.20 (m, 8H), 4.34 (s, (amide NH and water in methanol)), 7.63–7.68 (dd, 2H, <sup>3</sup>*J* (H–P) = 15 Hz, <sup>4</sup>*J* (H–P) = 6.7 Hz), ppm; <sup>13</sup>C NMR (125 MHz, MeOH-*d*<sub>4</sub>);  $\delta$  10.58, 15.57 (d, <sup>3</sup>*J* (C–P) = 6.5 Hz), 22.91, 42.99, 63.58 (d, <sup>3</sup>*J* (C–P) = 6.1 Hz), 127.16 (d,

<sup>1</sup>*J* (C–P) = 185.5 Hz), 129.71 (m), 149.60 (d, <sup>2</sup>*J* (C–P) = 18.5 Hz), 154.89 ppm; <sup>31</sup>P NMR (202 MHz, DMSO- $d_6$ );  $\delta$  12.77 ppm (at 350 K).

# 2.4. Polymer synthesis

# 2.4.1. Synthesis of the phosphonated poly(aryl ether) with bisphenol method (PAE-1)

A three-necked round bottom flask equipped with a magnetic stirrer, an argon inlet, and a dean-stark trap was charged with decafluorobiphenyl (0.6682 g, 2 mmol), anhydrous potassium carbonate (0.83 g, 6 mmol), diphosphonate diester(C-Ph)(0.7644 g, 2 mmol), NMP 10 mL, and 4 mL of toluene. The reaction mixture was heated at 115 °C for 20 h (during which the toluene was removed and the solution became viscous). The temperature was raised slowly to 140 °C and stirred for 2 h to obtain a light brown viscous solution. The solution was cooled to room temperature and poured into 200 mL deionized water containing 2 mL hydrochloric acid. The precipitated polymer was filtered, washed several times with deionized water to remove salts, and finally vacuum dried at 100 °C for 24 h yield 90%. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>); δ1.15–1.24 (t, 12H), 4.11 (b, 8H), 7.63 (b, 2H) ppm; <sup>19</sup>F NMR (470 MHz, DMSO-*d*<sub>6</sub>);  $\delta$  – 139.1 and – 154.5 (major peaks), – 140.7, – 156.7, – 161.4 ppm; <sup>31</sup>P NMR (202 MHz, DMSO-*d*<sub>6</sub>); δ6.98, 10.32, 10.73 ppm. Anal. Calcd.forC<sub>26</sub>H<sub>22</sub>F<sub>8</sub>O<sub>8</sub>P<sub>2</sub>: C, 46.17; H, 3.28; Found: C, 46.01%; H, 3.22%.

# 2.4.2. Synthesis of the phosphonated poly(aryl ether) with bicarbamate method (PAE-2)

In a procedure similar toPAE-1, a mixture of C-Ph-BC (1.105 g, 2 mmol) and decafluorobiphenyl (0.6682 g, 2 mmol) were dissolved in 10 mL of DMAc. Potassium carbonate (0.55 g, 4 mmol) was added and the reaction temperature was raised slowly to 130 °C and stirred for 5 h under an argon atmosphere. The brown viscous solution was cooled to room temperature and poured into 200 mL deionized water containing 2 mL hydrochloric acid. The precipitated polymer was filtered, washed several times with deionized water to remove salts, and finally vacuum dried at 100 °C for 24 h yield 95%. <sup>31</sup>P NMR (202 MHz, DMSO- $d_6$ ); 12.20, 12.80 ppm. Anal.



Scheme 1. Preparation of phosphonate ester functionalized bisphenol (C-Ph) and bis-propylcarbamate derivative (C-Ph-BC).

Calcd. for  $C_{26}H_{22}F_8O_8P_2$ : C, 46.17; H, 3.28; Found: C, 46.09%; H, 3.29%. (H, and F NMR data was similar toPAE-1).

# 2.5. Dealkylation

The membranes in their acid forms were obtained by soaking the PAE-1 or PAE-2 ester films in concentrated HCl solution. In a typical reaction, 1 g of PAE-2 was placed in 50 mL of hydrochloric acid (38%). After 10 days of reflux, the membrane was filtered off and water repeatedly added and removed in vacuum to remove excess acid, and then dried at vacuum for 12 h yield more than 98% (based on <sup>1</sup>H NMR spectrum). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>);  $\delta$  7.23–7.48 (2H, aromatic H), 9.40 (b, 4H, phosphonic acid); <sup>31</sup>P NMR (202 MHz, DMSO-*d*<sub>6</sub>);  $\delta$ 5.58–5.63 (d) ppm. Anal. Calcd.forC<sub>18</sub>H<sub>6</sub>F<sub>8</sub>O<sub>8</sub>P<sub>2</sub>: C, 38.32; H, 1.07; Found: C, 39.14%; H, 1.35%.

# 3. Results and discussion

# 3.1. Monomer synthesis

As shown in Scheme 1 phosphonated monomer (C-Ph) was prepared by a two-stage synthetic procedure starting from diphosphorylation of hydroquinone by diethylphosphate using simplified Atherton—Todd method [30], followed by phosphate—phosphonate rearrangement in the presence of strong base [31]. Finally the prepared diphosphonated compound was reacted with *n*-propylisocyanate to give the corresponding bispropylcarbamate-masked compound (C-Ph-BC).

The structure of these compounds was confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>31</sup>P NMR and elemental analysis. The preparation of the (C-Ph) was confirmed using NMR spectroscopy. Proton NMR



Fig. 1. <sup>1</sup>H NMR spectrum of C-Ph-BC in MeOH-d<sub>4</sub>.

showed shift of the protons on the aromatic ring from  $\delta$  7.18 ppm (s) to  $\delta$  7.03 ppm (dd), and the appearance of a new peak at  $\delta$  9.75 ppm corresponding to the phenol OH groups. The appearance of a new peak at  $\delta$  116.84 ppm (d) with <sup>1</sup>J (173 Hz) corresponding to the C<sub>Aromatic</sub>–P bond in the <sup>13</sup>C NMR spectrum, and shift of the phosphorus from  $\delta$  –5.7 ppm to  $\delta$  + 19.85 ppm in the <sup>31</sup>P NMR were observed.

Masked bisphenols often give much better results in nucleophilic substitution polymerization reactions compared with their parent bisphenols [29], therefore phosphonated bisphenol (C-Ph) was converted to its corresponding biscarbamate (C-Ph-BC) as shown in Scheme 1.

Preparation of bis-propylcarbamate derivative (C-Ph-BC) was confirmed by the disappearance of signals at  $\delta$  9.75 ppm, corresponding to the protons of OH group and the appearance of new peaks at  $\delta$  0.99–1.02 (triplet, 6 protons), 1.60–1.65 (multiplet, 4 protons), and 3.17-3.20 (triplet, 6 protons) corresponding to the protons of *n*-propyl group in the <sup>1</sup>H NMR spectroscopy (Fig. 1). Also the appearance of 3 new peaks in the aliphatic region in the <sup>13</sup>C NMR corresponds to the propyl group confirms the formation of C-Ph-BC compound (Fig. 2). The <sup>31</sup>P NMR spectrum of C-Ph-BC at ambient temperature consists of two multiplet signals at 12.20 and 12.80 ppm with the relative intensities of 7:1. The variable temperature spectrum at 202 MHz showed line shape changes over a temperature range of 50 °C. At 321 K and below, the <sup>31</sup>P spectrum for C-Ph-BC consist of two octets (Fig. 3). At higher temperatures, the two signals broaden and eventually merge to a singlet at around 340 K. As shown in Fig. 3, the minor peak at 12.80 ppm appears to merges into the high frequency signal (at 12.20) as the temperature is raised.

### 3.2. Polymer synthesis

Nucleophilic aromatic substitution has been employed successfully in the synthesis of various high-molecular-weight poly(arylene ether)s [32,33].It is well known that aromatic bisphenol with electron withdrawing groups at the ortho position are not highly reactive in nucleophilic substitution polycondensation reaction with bis(halides).We first investigated the polymerization of the phosphonated bisphenol and masked bicarbamate with 4,4'-difluorodiphenyl sulfone under different nucleophilic substitution conditions by changing solvent, temperature, base, etc. However, these attempts were not successful and low molecular weight oligomers formed presumably due to the low reactivity of the bisphenol monomer. Therefore, we have examined the more reactive decafluorobiphenyl monomer (Scheme 2) which is known to form linear poly(arylene ether)s under relatively mild condition [34].Careful dehydration during polymerization is required to obtain high-molecular-weight polymers and it can be achieved through azeotropic distillation. Another option is using masked-bisphenol and run the reaction under completely anhydrous condition. In both cases, the reaction temperature has to be controlled carefully to suppress possible side reactions such as branching or crosslinking. Two parafluorines in decafluorobiphenyl are more reactive and preferentially react to form linear chain.

The new fluorinated poly(arylene ether)s containing phosphonic ester groups were synthesized by polycondensation reaction between the substituted hydroquinones and decafluorobiphenyl (Scheme 2).

The reaction was carried out in DMAc under argon atmosphere and temperatures below 140 °C. The polycondensations proceeded



Fig. 2. <sup>13</sup>C NMR spectrum of C-Ph-BC in MeOH- $d_4$ .



Fig. 3. <sup>31</sup>P variable temperature NMR of spectrum of C-Ph-BC in DMSO-*d*<sub>6</sub>.

readily in a homogeneous solution and tough and stringy materials formed when the viscous polymer solutions were trickled into the stirring methanol/water (1/1) mixture. As shown in Table 1, the inherent viscosities of polymers in the ester form were 0.45 and 0.58 dL  $g^{-1}$  PAE-1 and PAE-2, respectively. The elemental analysis values were in good agreement with the calculated values for the proposed structures of polymers. Structural features of these polymers were verified by H, F, and P NMR spectroscopies.

The <sup>19</sup>F NMR spectrum of the PAE-1 polymer shows two major peaks at -139.1 and -154.5 ppm, which were assigned to the *meta*and *ortho*-fluorine atoms on the polymer main chain. It also revealed three smaller other peaks at -140.7, -156.7 and -161.4 ppm for the end-groups. By comparing the integral intensity of the peaks of the main chain fluorines with those on the end units, the degree of polymerization (n) and the number average molecular weight ( $M_n^{NMR}$ ) was calculated (Table 2). Based on this comparison, values of 42 and 56 have been estimated for the degree of polymerization (n) corresponding to a number average molecular weight ( $M_n^{NMR}$ ) of 28,400 and 37,900 Da for the bisphenol and biscarbamate methods, respectively. Advantages of the carbamate method over the conventional bisphenol method are shorter reaction time under mild conditions, no water generation during the polymerization, and formation of higher molecular weight polymers.

Polymers in the ester form (PAE-1 and PAE-2) were hydrolyzed to their corresponding acid form (PAA-1 and PAA-2) after treating with hydrochloric acid (HCl) for 10 days and dealkylated products were characterized by <sup>1</sup>H, <sup>31</sup>P, and <sup>19</sup>F NMR spectroscopies. <sup>1</sup>H NMR spectrum revealed only small residue of ethyl groups in the aliphatic region. Phosphorus peaks at 6.98, 10.32, 10.73 ppm correspond to the phosphonate esters in the <sup>31</sup>P NMR spectrum were disappeared, and a new peak appeared at 5.61 ppm which was assigned to phosphonic acid. These changes along with the CHN analysis indicated the completion of the dealkylation reaction.



Scheme 2. Synthesis of the polymers in the ester form and hydrolysis to the corresponding acid form.

Thermal stability, solubility, and viscosity of phosphonated poly (arylene ether)s in ester, acid and salt forms.									
Polymer	Yield (%)	Thermal stability	Inherent viscosity <sup>b</sup>	Solubility <sup>a</sup>					

Polymer		Yield (%)	stability		Inherent viscosity <sup>5</sup>	Solubility"					
			<i>T</i> <sub>10</sub> (°C) <sup>c</sup>	Cy <sup>d</sup> (%)	$rac{\eta_{ ext{inh}}}{( ext{dl/g})}$	DMAc	DMSO	THF	MeOH	H <sub>2</sub> O	CHCl <sub>3</sub>
Ester Derivatives	PAE-1	90	298	53 <sup>e</sup>	0.45	+ +	+ +	+	+	-	±
	PAE-2	95	299	58 <sup>e</sup>	0.58	+ +	+ +	+	±	_	S
Acid Derivatives	PAA-1	97 <sup>f</sup>	426	33	_	+	+	_	_	_	_
	PAA-2	98 <sup>f</sup>	430	32	_	+	+	_	_	_	_
Salt Derivatives	PAS-1	_	430	63	_	_	_	_	_	S	_
	PAS-2	_	428	65	-	_	_	_	_	S	-

(++) Soluble at room temperature, (+) soluble after heating,  $(\pm)$  partially soluble after heating, (S) swell, (-) insoluble.

<sup>a</sup> Solubility: measured at a polymer concentration of 0.05 g/ml.

<sup>b</sup> Measured at a polymer concentration of 0.5 g/dl in DMAc at 30 °C.

<sup>c</sup> Temperature at which 10% weight loss occurred under nitrogen atmosphere.

<sup>d</sup> Char yield calculated as the percentage of solid residue after heating from room temperature to 700 °C under nitrogen.

e In 500 °C

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<sup>f</sup> Obtained from <sup>1</sup>H NMR (Hydrolysis yield).

### 3.3. Solubility properties

Solubility of the polymers was tested qualitatively in various solvents and the results are presented in Table 1. Polymers PAE-1 and PAE-2 with phosphonic ester groups showed very good solubility in a variety of solvents such as NMP, DMF, THF and methanol. However, after hydrolysis solubility of the polymers decreased and PAS-1 and 2 with disodium phosphonate groups became insoluble in all the above solvents and PAA-1 and 2 with phosphonic acid groups were only soluble in high boiling solvents such as DMSO and DMAc. PAS polymers in the salt form were prepared by neutralizing PAA polymers with sodium hydroxide. Both PAA-1 and 2 formed tough films after casting from DMSO or DMAc solution. Strong interaction between the phosphonic acid groups is believed to be responsible for low solubility of phosphonated polymers. It has been reported that phosphonated polysulfone having more than 0.75 phosphonic acid group per repeating unit were not completely soluble in DMAc or DMSO [21], and poly(arylene ether)s having two phosphonic acid groups per repeating unit were found to only swell in DMSO even at 100 °C [19].

### 3.4. Thermal properties

High thermal stability is a key property for the membranes in fuel cell application. Thermal stability of the phosphonated polymers in the ester, salt and proton forms was investigated by TGA measurements. The temperatures which 10% weight loss ( $T_{10}$ ) occur and char yields at 750 °C under nitrogen were determined from the original thermograms and tabulated in Table 1. As expected and is clearly shown in Fig. 4, the polymers with ester groups show lower thermal stability compared with the polymers in their acid and salt form. The temperature for 10% weight loss recorded around 290 °C for PAE samples which was due to the loss of four ethyl groups. Similar TGA results have been reported for polymers containing phosphonic esters [19,35].

Table	2
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Physica	al prope	rties of	PAA	polym	ers.
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Polymer	Polymerization degree (n) <sup>a</sup>	M <sup>NMR</sup> <sub>n</sub>	Water uptake (%)					IEC	IEC
			25 (°C)	40 (°C)	60 (°C)	80 (°C)	100 (°C)	experimental	theoretical
PAA-1	42	23,700	36.5	39.1	44.6	53.1	61.0	6.23	7.09
PAA-2	56	31,600	33.8	35.4	39.3	46.3	55.6	6.05	7.09

<sup>a</sup> Based on NMR data.

<sup>b</sup> Phosphonic acid is considered a diprotic acid.

As seen in Fig. 4, the decomposition occurred for PAS and PAA samples in at least three distinctive temperature ranges. The very slow mass loss in the salt and proton form occurred in the temperature range of 100–300 °C is due to the loss water. Water may be absorbed or involved in condensation even in nominally dry materials (two phosphonic acid groups form a P–O–P bond producing water). The next weight loss step is observed from 435 to 480 °C and is most probably connected with the cleavage of the C–P bond. The final step of the degradation which starts around 480 °C, and should be due to the degradation of the main chain.

For the acid derivatives the 10% weight loss under nitrogen atmosphere occurred around 430 °C and the polymer produced more than 30 wt% char residue at 750 °C. PAS polymers showed  $T_{10}$ value around 430 °C similar to PAA samples. However, the char yields at 750 °C were higher (around65%) under similar conditions.

# 3.5. Degree of phosphonation and IEC

<sup>1</sup>H NMR was used to determine the degree of hydrolysis or phosphonation and subsequently amount of repeat units with residual phosphonate ester groups in the membranes. The degree of hydrolysis was determined from residual ethyl groups of phosphonate ester, resonants at 1.2 ppm ( $-CH_3$ ) and 4.1 ppm ( $-CH_2$ ) after hydrolysis of PAE polymers. The following equation was used to calculate degree of hydrolysis by using integration values of ethyl and aromatic region. As shown in Table 1, degree of hydrolysis was 97% and 98% for PAA-1 and PAA-2, respectively.

Degree of Hydrolysis = 
$$\left\{ \left[ (10 \times H_{aromatic}) - H_{ethyl} \right] / (10 \times H_{aromatic}) \right\} \times 100$$

Experimental ion exchange capacity (IEC) was determined by titration of the membranes in acid form with sodium hydroxide. The results show IEC values around 6.2 mmol/g compared to the theoretical value of 7.0 which is calculated by considering both



Fig. 4. TGA comparison of PAE-2 (ester form), PAA-2 (acid form), and PAS-2 (salt form).

protons of each phosphonic acid group in the repeat unit (Table 2). The small deviation between experimental and theoretical IEC values may come from the fact that the second proton of phosphonic acid is less acidic and may not be completely neutralized during titration.

# 3.6. Water and phosphoric acid uptake

Proton conductivity in polymeric electrolytesrelies strongly on the concentration of water as mobile phase and sharply decreases as the water content decreases. On the other hand, high water uptake causes excessive swelling and dimensional changes and therefore decreases in the mechanical strength. The diphosphonated PAA samples were tested for their water uptake by comparing the weight of the membranes in dry state and after submerging in deionized water. The PAA-1 membrane exhibited slightly higher water uptake (36.5 wt %) than that of the PAA-2 membrane (33.8 wt %) which is in agreement with the higher IEC value of PAA-1.This moderate level of water uptake at 100% RH corresponds to  $\lambda$  (the number of water molecules per acid group) of about 5-6. Sulfonated polymers with similar structure and number of acid groups per repeat unit have much higher water uptake and may even be water soluble [36-38]. Similar observation and comparison between phosphonated and sulfonated ionomers are reported in the literature [39]. Because of low number of water molecules per phosphonic acid groups it is very important to reach high degree of phosphonation in order to obtain ionomers with properties useful for fuel cell application. This usually becomes a limiting factor for post-phosphonation reactions which only one phosphonic per repeat unit may form even at nearly 100% yield.

It is highly desirable to run PEM fuel cells at temperatures exceeding 100 °C for better efficiency and less technical complexity. The system should therefore be able to operate under dryer condition that is a critical limitation for almost all PEMs which their proton conductivity depends heavily on minimum level of hydration. Polybenzimidazole (PBI) doped with phosphoric acid as mobile phase is one of the best choice for high temperature (up to 200 °C) PEM fuel cells. To investigate proton conductivity of the PAA membranes at high temperature and water-free conditions, they were soaked in 85% phosphoric acid at room temperature (membrane thickness was about 40  $\mu$ m). The level of phosphoric acid uptake increase over time and reach high level of around 3.5 mol of phosphoric acid per phosphonic group after 14 days (Fig. 5).

# 3.7. Proton conductivity

Proton conductivity of the phosphonated membranes was measured under both fully hydrated and dry conditions. The



Fig. 5. Time dependence doping level of PAA-2 membrane.

conductivity value for PAA-2 membrane reached 92 mS/cm when fully hydrated at ambient temperature which is comparable with standard perfluorosulfonic acid membranes [40] and substantially higher among the reported phosphonated polymers [14,24,39,41-44]. For example, proton conductivity of highly phosphonated polysulfone has been reported around 12 mS/cm at 100 °C under fully hydrated conditions [44] and for phosphonated poly(N-phenylacrylamide) with very high IEC of 6.7 was 88 mS/cm under 95% relative humidity and 80 °C [41]. High proton conductivity of PAA clearly demonstrates that the high and localized concentration of phosphonic acids was effective for water-assisted proton transport.

It was also found that the level of conductivity of the PAA-2 membrane under fully hydrated condition increased by temperature and reached150 mS/cm around 100 °C and stays almost constant up to 140 °C (Fig. 6). This behavior might partially be due to the different amounts of water absorbed by the membrane at various temperatures (see Table 2). At high temperatures, the conductivity was seemingly constant with the temperature possibly due to the large water uptake of the membrane under fully immersing conditions. Water uptake measurement above 100 °C did not result reproducible data because of technical difficulties.

Proton conductivity of PAA membrane under dry (no external humidification) condition increased exponentially by temperature from nearly  $2 \times 10^{-3}$  mS/cm at 25 °C to 2.2 mS/cm at 120 °C (Fig. 7) which is remarkably high for a non-fluorinated hydrocarbon membrane. Because of their amphoteric character phosphonic



**Fig. 6.** Temperature dependence of proton conductivity of phosphoric acid doped PAA-2 membrane ( $[PO_4H_3]/[-PO_3H_2] \sim 3.5$ ) ( $\blacksquare$ ) and PAA-2 in the fully hydrated conditions ( $\blacktriangle$ ).



Fig. 7. Proton conductivity vs temperature for PAA-2 membrane under dry condition.

acids can form strong hydrogen bonding which allows structure diffusion of protons through formation of a hydrogen bond network with fast hydrogen bond breaking and forming processes. This phenomena results in high water retention for phosphonated membranes at elevated temperatures and high proton conductivity in a low humidity condition [48].

As expected the proton conductivity of diphosphonated membranes after doping with phosphoric acid under dry condition increased significantly and jumped almost three orders of magnitude to 1 mS/cm at 30 °C and 100 mS/cm at 140 °C (Fig. 6). Similar behavior has been reported for PBI/Phosphoric acid system which shows strong relationship between conductivity and temperature and level of doping [45,46]. The values of proton conductivity reported for phosphoric acid doped PBI membranes (6.5H<sub>3</sub>PO<sub>4</sub> molecules per PBI repeat unit) at 140 °C and 5% and 30% RH are 22 and 50 mS/cm, respectively [45]. High proton conductivity of PAA membrane with relatively low level of doping indicates that phosphonic acid groups and phosphoric acid molecules effectively participate in the conductivity process by formation of a hydrogen bonding network.

### 4. Conclusions

In the present study, we report successful synthesis of highly phosphonated poly(arylene ether)s from diphosphonated hydroquinone. The phosphonation took place on the hydroquinone ring at two positions and polymerization with the decafluorobiphenyl following with acidic hydrolysis lead to polymers with inherent viscosities up to 0.58 dL  $g^{-1}$ . The resulting polymers were soluble in polar aprotic solvents and could be readily cast into tough and clear films. The thermal stability of these membranes based on TGA study showed  $T_{10\%}$  at about 430 °C. The high phosphonic acid content membrane reached a conductivity of around 150 mS/cm at about 100 °C under fully hydrated and 2.2 mS/cm at 120 °C under dry condition. Once impregnated with phosphoric acid proton conductivity jumped to near 100 mS/cm under no external humidification. The combination of all these properties makes this phosphonated polymeric electrolyte potentially useful in fuel cell technology.

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