

Article

Synthesis and Characterization of a Phosphonated Graft Copolyimide

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Abstract. A new synthesis route of phosphonated multi-block, branched copolyimide is proposed in this research. The synthesis and characterization of the series of new phosphonated graft copolyimides were prepared by combination of one-step high temperature polymerization and phosphonation method by lithiation and reaction with excess diethylchlorophosphate. The phosphonate ester product was converted to the phosphonic acid by hydrolysis. A branched polyimide structure was achieved by coupling the two polyimides with 3, 3'-diaminobenzidine. A phosphonated branched copolyimide with 32 % mol phosphonation exhibited high thermal stability, with a decomposition temperature in nitrogen of ~475°C. Proton exchange membranes prepared from these copolyimides had proton conductivity of 0.02 – 0.03 S/cm at 100% humidity over a temperature range of 40 – 100°C.

Keywords: Copolyimide, phosphonic acid, PEM fuel cell.

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1. Introduction

Renewed interest in hydrogen fuel cells during the last decade has led to increased research of ionomers. Despite the large research activity directed at development of ionomers for proton exchange membranes (PEMs), there is still no suitable polymeric material for use in fuel cells at elevated temperatures, e.g., between 100°C – 120°C, which is desirable for transportation applications. Most membranes lose water above 100°C, which decreases the proton conductivity. Blends and composite membranes have shown some improvement in conductivity above 100°C, but, in general, single ion materials do not retain sufficient amounts of water at such temperatures to provide sufficient conductivity.

Historically, the acid functionalities used in ionomers for PEMs have been primarily carboxylic and sulfonic acids. Sulfonated polyimides have excellent thermal, oxidative stability and mechanical properties. Many works reported the advantages and disadvantages of polyimide membranes. The normal five-membered ring in phthalic polyimides showed poor hydrolytic stability under the strongly acidic conditions of fuel cell [1, 2]. In comparison, the six-membered ring in naphthalic polyimides displayed better thermal and chemical stability, along with improved mechanical strength than phthalic polyimides. Although their properties are excellent, naphthalic polyimides are more difficult to synthesize and cast into membrane because of their low solubility in common organic solvents [3].

Phosphonic acid-containing ionomers have been much less studied than carboxylate and sulfonate ionomers [4]. Early work on phosphonated polyolefin ionomers was done in 1970-1980 using a chlorophosphorylation reaction [5-10]. More recently, Emery and Savignac reviewed the synthesis of phosphonates by nucleophilic substitution of phosphorus using organolithium compounds, which minimizes the formation of side products [11]. Lafitte and Jannasch [12] phosphonated polysulfone up to 50% by lithiation. Direct lithiation in the presence of diphenyl or diethyl chlorophosphate led to the phosphonation of the biphenyl sulfone segment, while lithiation following bromination of the polymer produced phosphonation of the bisphenol A groups. Those authors [13] also made phosphonated polysulfone by lithiating the polymer, reacting it with methyl iodobenzoates and then running a CuBr-mediated cross-coupling reaction between the iodinated polymer and [(diethoxyphosphinyl)-difluoromethyl]ZnBr. The product was dealkylated with bromotrimethylsilane to produce the phosphonic acid group.

In addition to the choice of acid groups, the microstructure of the polymer also affects the properties of PEMs, and various different chain architectures and/or morphologies have been considered for PEMs. These include block copolymers composed of hydrophobic and hydrophilic domains [14], the latter promoted proton transfer; Graft-block copolymers, e.g., poly(sodium styrene sulfonate) grafted to a polystyrene backbone, exhibited higher proton conductivity than a random copolymer with the same composition [15]. Lee et al. [11] prepared sulfoalkylated graft polyimides and found that the ionomers with the longest side chains had the best durability and chemical resistance. Cheng et al. [16] reported that sulfonated polyimides prepared from 4,4'-ketone dinaphthalene 1,1' and 8,8'-tetracarboxylic dianhydride had good solubility in common aprotic solvents and crosslinked membranes formed from this material exhibited good mechanical properties and water stability.

The research described above suggests that grafting hydrophilic chains onto a hydrophobic main-chain may represent the optimum approach for providing high mechanical strength and good transport properties. This paper describes the synthesis and characterization of multi-block, branched copolyimides containing phosphonic acid groups.

2. Experimental

2.1. Materials

1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) and m-cresol were purchased from Sigma-Aldrich. Triethylamine (Et₃N), 4,4'-diaminodiphenylether (4,4'-ODA), 3,3'-diaminobenzidine, aniline, n-butyllithium, diethylchlorophosphate (DECP) bromo-trimethylsilane (TMSBr) Tetrahydrofuran (THF) and 2-propanol were purchased from Acros Organics.

2.2. Synthesis of Polyimide Based on NTDA-ODA

To a 250 mL three-neck flask, equipped with a dean stark trap and a N₂ inlet and outlet, was added 6.01 g (30 mmol) of 4,4'-ODA and 100 mL of m-cresol. After the 4,4'-ODA completely dissolved, 8.15 g (30.4 mmol) of NTDA, and 1.46 g (14.4 mmol) of triethylamine were added and then stirred at 80°C for 4 h, then at 180°C for 16 h and finally at 200°C for 4 h. When the reaction was completed, the reaction mixture was precipitated with 2-propanol, filtered, washed with acetone and dried at 80°C in a vacuum oven overnight (13.10 g, 92% yield). That product is hereafter denoted as PI-A. The reaction is shown in Fig.1 (section 2.2).

2.3. Synthesis of Phosphonated Polyimide

The synthesis of the phosphonated polyimide, to be used as the side-chains of the copolyimide, involved four reaction steps, see Fig. 1 (section 2.3).

Step 1: The first step was a polycondensation reaction. To a 125 mL three-neck flask, equipped with a dean stark trap and a N₂ inlet and outlet, 2 g (10 mmol) of 2,2'-dibromo-4,4'-diaminodiphenyl ether and 30 mL of m-cresol were added. After the 2,2'-dibromo-4,4'-diaminodiphenyl ether had completely dissolved, 2.79 g (10.4 mmol) of NTDA, and 0.88 g (8.6 mol) of triethylamine were added and the solution was stirred at 80°C for 2 h. 0.02 g (0.2 mmol) of aniline was then added to the solution and the solution was stirred for another 2 h. The polymer was imidized at high temperature by heating the reaction mixture to 180°C for 16 h and then 200°C for 4 h. The 30 ml of toluene was added during the thermal imidization step. When the reaction was complete, the polymer was precipitated with 2-propanol (100 mL), filtered, washed with acetone and dried overnight at 80°C in a vacuum oven. The polyimide product (PI-B) was a brown powder (4.53 g, 95% yield).

Step 2: PI-B was chain-extended using 3,3'-diaminobenzidine, which has 4 reactive amine groups that can react with the anhydride end-group of the PI-B. The aniline provided a non-functional end-group to the PI-B, so that only a dimer was formed. The proper stoichiometric molar ratio of 3,3'-diaminobenzidine and PI-B and the steric hindrance of PI-B can control the reaction to occur at only 2 amines of the 3,3'-diaminobenzidine. To a 100 mL three-neck flask, equipped with a N₂ inlet and outlet, was added 0.04 g (0.18 mmol) 3,3'-diaminobenzidine and 5 mL of m-cresol. After the diaminobenzidine dissolved, 2 g (0.18 mmol) of PI-A in 25 mL m-cresol was slowly added dropwise and stirred at 150°C for 6 h. When the reaction was complete, the product (PI-C) was precipitated with 2-propanol (100 mL), filtered, washed with acetone and dried overnight at 80°C in a vacuum oven. PI-C was a dark brown powder (1.53 g, 75% yield).

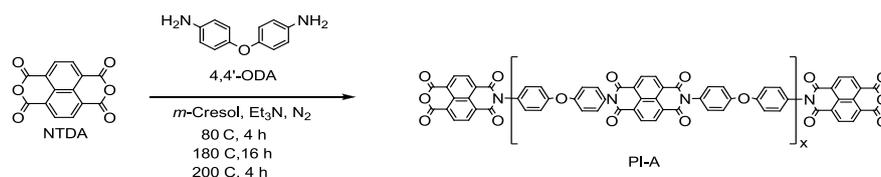
Step 3: PI-C was phosphonated using a 100 mL three-neck flask, equipped with a N₂ inlet and outlet. A 1% solution of PI-B (1 g, 4.45 mmol) in THF (110 ml) was cooled to -78°C using a dry ice/2-propanol mixture. Desired n-BuLi was slowly added and stirred for 30 min. Then, a 200% molar excess amount of diethylchlorophosphate (DECP) was quickly added and stirred for 3 h. The reaction was terminated with 2 mL 2-propanol and the product (PEPI-C) was precipitated in 2-propanol (100 mL), filtered, washed with acetone and dried overnight at 80°C in a vacuum oven (0.67 g, 67% yield).

Step 4: The PEPI-C was converted to the phosphonic acid derivative by suspending in THF (1 g/20 mL) adding a 5% excess of bromotrimethylsilane and mixing the solution at room temperature for 24 h. The reaction mixture was then added to a 50% HCl solution in deionized (DI) water and stirred for 24 h. The hydrolyzed polyimide (paPI-C) was then filtered, washed with DI water many times and dried overnight at 50°C in a vacuum oven.

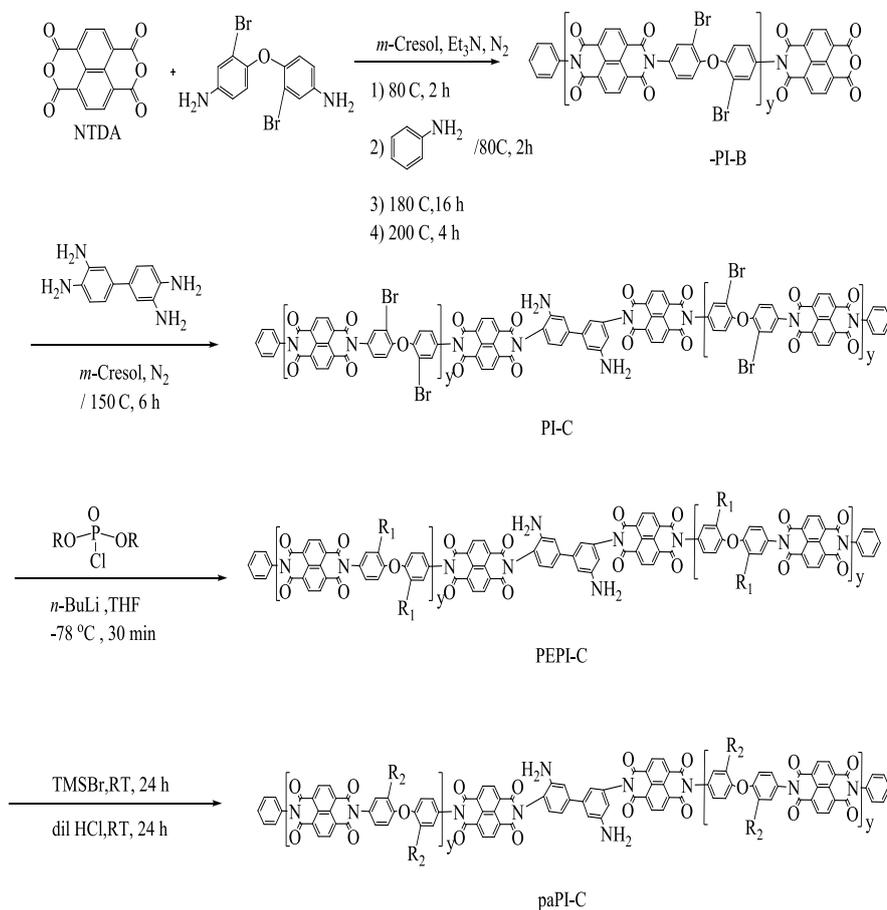
2.4. Synthesis of Phosphonated Graft Copolyimide

To a 250 mL three-neck flask, equipped with a N₂ inlet and outlet was added an equimolar amount of a PI A solution and a pa-PI-C solution solution in m-cresol and stirred at 150°C for 6 h. An additional 15 mL of m-cresol was added to dilute the viscous solution. A reaction between the two polymers occurred at the remaining two amines from the chain extension of PI-B step. When the reaction was complete, the product was precipitated with 2-propanol (100 mL), filtered, washed with acetone and dried overnight at 80°C in a vacuum oven. The resulting branched phosphonated graft-block copolymer, denoted as PBPI, was a dark brown powder. The reaction is shown in Fig. 1 (section 2.4). All synthesis route of phosphonated graft copolyimide from section 2.2 to 2.4 were presented in Fig. 1.

Section 2.2



Section 2.3



Section 2.4

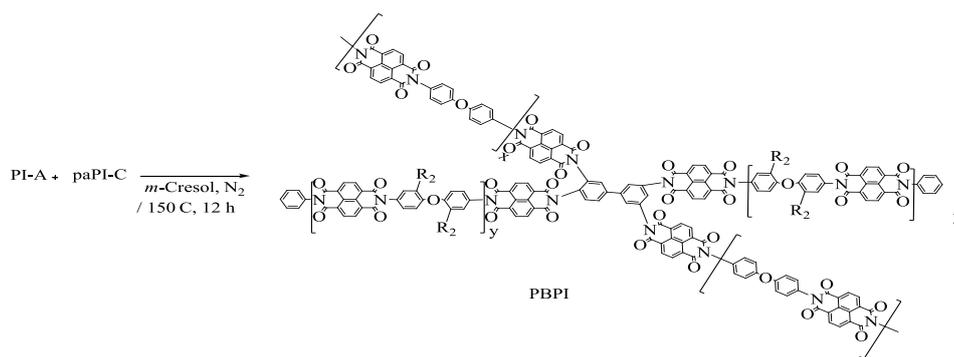


Fig.1. Synthesis Route of the phosphonated graft copolyimide described in section 2.2 to section 2.4.

2.5. Characterization

Fourier transform infrared (FT-IR) spectra were obtained with a Nicolet FTIR Spectrophotometer using powder samples and a spectral range of 400-4000 cm⁻¹. Nuclear Magnetic resonance (NMR) was performed using a Bruker 400 Ultrashield instrument, model AV400, operating at 400 MHz and using deuterated dimethylsulfoxide (DMSO-d₆) as a reference. Thermogravimetric Analysis (TGA) was used to assess the

thermal stability of the polymers under nitrogen, using a heating rate of 20°C/min. Intrinsic viscosity measurements were conducted with a Ubbelohde viscometer using m-cresol at 45°C.

2.6. Preparation of Membrane Electrode Assembly and Proton Conductivity Measurement

The blends of PBPI and pure polyimide based on NTDA-ODA with 4:1 w/w was completely dissolved in m-cresol at 120°C and cast in the clean petri-dishes, and then dried in oven at 80°C until the films were completely dried, yield the PBPI membranes, which had 160-180 μm thickness. Then, the film was pressed by hot-pressed at 60°C for 3-5 min to smooth the films.

Membrane electrode assemblies (MEAs) were prepared as follows; a 40 wt% Pt/C catalyst/Nafion™ solution from Alfa Aresa was used for preparation of the electrodes and graphite media (Sigracet®) from Ion Power were used for the gas-diffusion layers. The Pt/C catalyst concentration at the anode and cathode were 0.4 and 0.2 mg Pt/cm², respectively. The catalyst was air-brushed onto the membrane (5 cm²) and then hot-pressed the membrane by 120°C, 1000 psi for 10 s.

The experiments with MEA were kept at control condition in a humidifier for 24 h at room temperature and then the proton conductivities were determined with a Scribner 850e Fuel Cell Station. The 0.2 L/min of H₂ and air were fed to anode and cathode respectively. Due to short ohmic period in polarization curve of phosphonated membrane samples, the constant current at 0.2 A was applied for all membrane samples including Nafion@117. The Impedance spectra were recorded at 10⁻¹ to 10⁴ Hz in the range between 40 and 100°C and at 100% humidity by setting the temperature of cathode humidifier, cell and anode humidifier to the same value (Notation XX//YY//ZZ refers to the temperature of cathode humidifier (XX) cell (YY) anode humidifier (ZZ)). The proton conductivity was defined as the ratio of thickness to resistance, which determined from the complex plane or Nyquist plot, and reported in units of S/cm.

3. Result and Discussion

The structures of the polyimides were confirmed by ¹H-NMR and FTIR. As presented in Fig. 2, the completion of the imidization step was confirmed by the absence of anhydride carbonyl peaks in the FTIR spectra in the regions around 1780 cm⁻¹ and 1740 cm⁻¹ and the appearance of the naphthalimide carbonyl absorptions at 1710 cm⁻¹ (asymmetric) and 1670 cm⁻¹ (symmetric). The C-N-C vibration was observed around 1345 cm⁻¹. In comparison with the main-chain polyimide, PI-A, PEPI-C showed three new peaks at 2980 cm⁻¹, 1030 cm⁻¹ and 965 cm⁻¹. The band at 2980 cm⁻¹ was attributed to C-H stretching of ethyl group, the 1030 cm⁻¹ band was assigned to (P)-O-C stretching and the band at 965 cm⁻¹ was assigned to the P-O-(C) vibration of the ethyl groups [17]. The absorptions arising from (EtO)₂P=O decreased after hydrolysis, whereas the new bands between 2580-2670 cm⁻¹ are due to -P(O)(OH)₂ [18].

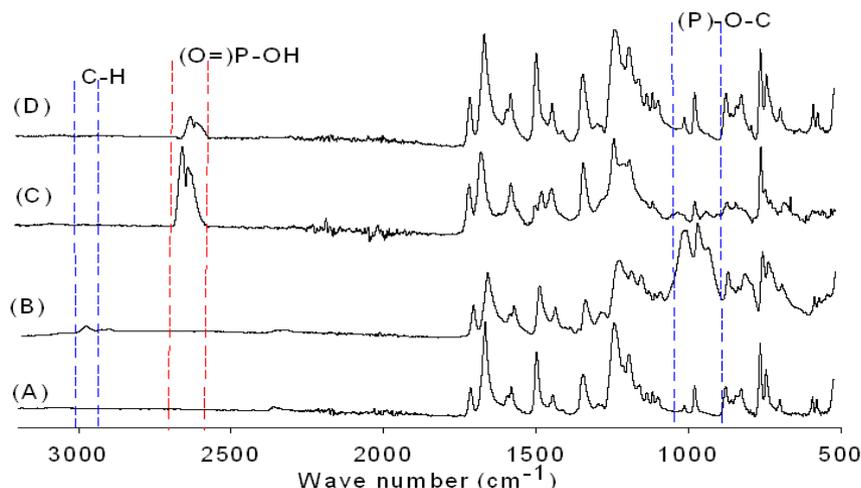


Fig. 2. FT-IR spectra of polyimide samples; (A) PI-A, (B) PEPI-C, (C) paPI-C and (D) PBPI.

The $^1\text{H-NMR}$ spectra of the PI-A polyimide, the phosphonic acid derivative of the phosphonated polyimide, paPI-C and the phosphonated graft copolyimide, PBPI was shown in poor resolution, due to the poor solubility of the polyimides in DMSO-d_6 . In the $^1\text{H-NMR}$ spectra for the copolyimides, the formation of naphthaimide were confirmed by the chemical shifts at 8.7-8.8 ppm, which corresponded to the naphthalene protons. The remaining unreacted $-\text{NH}_2$ groups showed up at 6.55 ppm and the resonance of the aromatic protons in 3,3'-diaminobenzidine were at 7.54 ppm. This confirmed the chain extension of PI-B. The grafting step was confirmed by the disappearance of the $-\text{NH}_2$ resonance at 6.55 ppm.

The % phosphonation, i.e., concentration of phosphonic acid groups, was estimated from the $^1\text{H-NMR}$ by calculating from the integration ratio from the sum of the integrated area of the protons of ethyl groups at 4.1 ppm and the methyl groups at 1.29 ppm divided by the integrated area of aromatic proton between 7.1 to 8.7 ppm [19]. Figure 3 shows the $^1\text{H-NMR}$ for PEPI-C, the phosphonate ester derivative of PI-C, for which the %phosphonation was calculated to be $\sim 32\%$ mol. The IEC_{nmr} of paPI-C calculated from $^1\text{H-NMR}$ by Eq.(1) was approximately 1.48 meq/g.

$$\% \text{phosphonation} = \frac{40X}{24 + 20X} \quad (1)$$

where X is degree of polymerization.

The IEC of paPI-C determined from titration, was about 1.45 meq/g. It can be concluded that IEC of phosphonate polyimide samples determined by titration were agreeing well with the calculation from $^1\text{H-NMR}$ of phosphonate ester derivative polyimide.

Due to the poor solubility of PBPI in DMSO-d_6 solvent, the IEC of the PBPI graft copolymer was only determined by titration method which had value about 1.02 meq/g. The phosphonate graft copolyimide, PBPI, had lower IEC than phosphonate polyimide samples, paPI-C. The decreases in the IEC of PBPI versus paPI-C were consistent with the dilution of the phosphonic acid groups due to the grafting of the paPI-C to the unphosphonated polyimide PI-A.

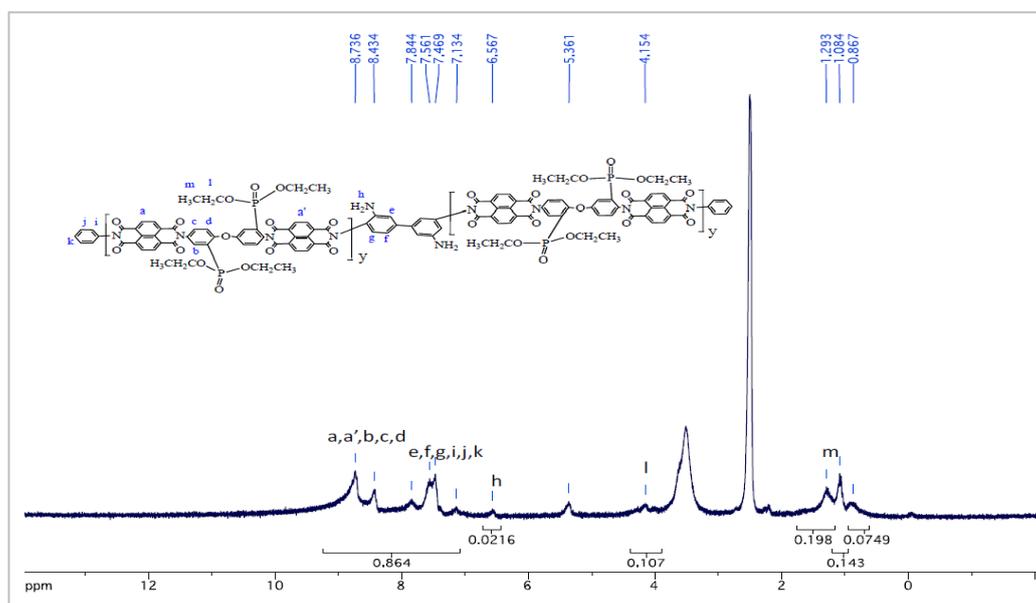


Fig. 3. $^1\text{H-NMR}$ of PEPI-C sample ($\sim 32\%$ Phosphonation) in DMSO-d_6 .

GPC analysis was not possible for molecular weight determination, because of their poor solubility of the polymers in any solvent other than m-cresol. Viscosity average molecular weights could not be determined since no Mark-Houwink constants are available for branched polyimides described in this paper. In order to estimate the molecular weight of the graft-copolyimide, PBPI, a comparison of the intrinsic viscosities in m-cresol at 45°C and the theoretical molecular weight of synthesized polymers were studied. The theoretical molecular weight was calculated based on 100% conversion of the reactions, see Table 1. Although the data in Table 1 cannot be used to confirm the exact structure of the PBPI, they were consistent with the grafting of paPI-C to PI-A, as shown in Fig. 1 (section 2.4).

Table 1. Comparison of intrinsic viscosity and theoretical molecular weights of the polyimides.

Sample	Degree of polymerization	Theoretical Mn ^a (g/mol)	[η] (g/dL)
PI-A	149	33,000	9.30
paPI-C	49 ^b	22,000	8.16
PBPI	-	55,000	12.48

Remark ^a The molecular weight is calculated assuming 100% conversion of monomers.

^b paPI-C was prepared from PI-B with degree of polymerization = 49 (see Fig.1 in section 2.4).

A comparison of the thermal stability of PI-A, paPI-C and PBPI is shown in Fig. 4. All of the polymers were stable to at least 400°C, because of the excellent stability of the imide groups. PI-A was stable to ~550°C, where degradation of the imide groups occurred. The paPI-C was less stable, probably as a result of the phosphonic acid groups. Both the paPI-C and the PBPI showed a two stage degradation process with the first mass loss occurring at about 475°C, due most likely to degradation of the phosphonic acid groups, and a second mass loss above 570°C due to the degradation of the polyimide.

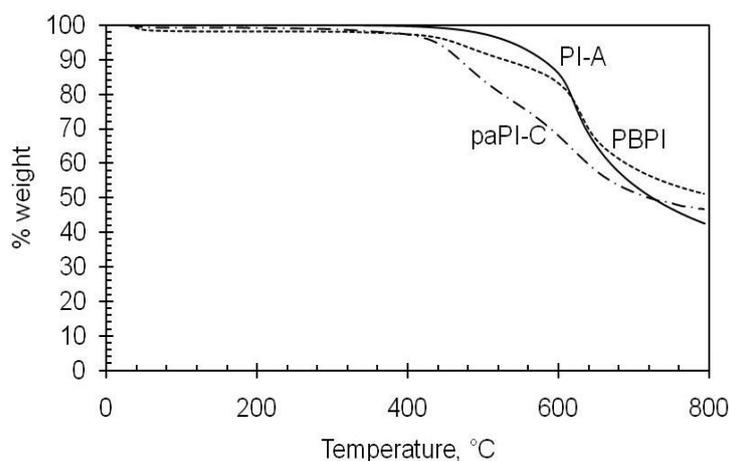


Fig. 4. TGA of the polyimides in a nitrogen atmosphere.

The phosphonated polymers also had a small mass loss below 100°C, which was most likely water. The phosphonated polymers had higher char than the PI-A, which was not unexpected since phosphorous compounds are often used for flame retardancy, a property due to char formation that prevents the release of volatile gases and smoke during a fire. The reason for why PBPI had higher char than paPI-C, which had the highest phosphorous concentration, was not known, but may be due simply to differences in the particle sizes of the powders used for the TGA experiments.

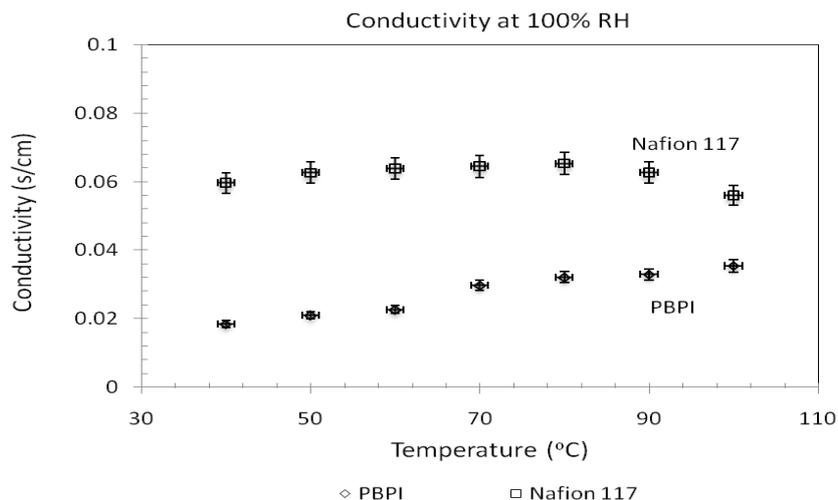


Fig. 5. Proton conductivity vs. temperature of PBPI and Nafion®117. (Remark: At 100% RH and 100°C, the temperature of fuel cell test system was set at 98//100//98.)

The proton conductivity of PBPI membranes measured at various temperatures using 100% humidity was shown in Fig. 5. Data for Nafion®117 were also shown for comparison. The conductivity of the phosphonated polyimide membrane was comparable, though a little lower than that of Nafion®117. The conductivity of the membrane appeared to slightly increase with increasing temperature, while Nafion started to fall off at 100°C. However, polymer blend technique was used for preparation of PBPI membrane, so if the pure PBPI were made as the membranes instead of blending, the higher proton conductivity would be attained.

4. Conclusions

A new phosphonated branched-block copolyimide was synthesized using a combination of polycondensation and lithiation reactions and a tetra-amine coupling compound. The synthetic route was relatively simple and allowed for facile adjustment of molecular weight of the backbone and side chains, as well as the phosphonation concentration. The phosphonated branched copolyimide was thermally stable to at least 475°C and membranes of the polymer had proton conductivity of 0.02-0.03 S/cm at 100% humidity. The fuel cell performance of these membranes will be discussed in a future paper.

References

- [1] B. R. Einsla, Y. T. Hong, S. Kim, F. Wang, N. Gunduz, and J. E. Mcgrath, "Sulfonated naphthalene dianhydride based polyimide copolymers for proton-exchange-membrane fuel cells. I. Monomer and copolymer synthesis," *Journal of Polymer Science, Part A Polymer Chemistry*, vol. 42, no. 4, pp. 862-874, 2004.
- [2] B. R. Einsla, Y. S. Kim, M. A. Hickner, Y. T. Hong, M. L. Hill, B. S. Pivovar, and J. E. Mcgrath, "Sulfonated naphthalene dianhydride based polyimide copolymers for proton-exchange-membrane fuel cells II. Membrane properties and fuel cell performance," *Journal of Membrane Science*, vol. 255, no. 1-2, pp. 141-148, 2005.
- [3] O. Savadogo, "Emerging membranes for electrochemical systems: (I) solid polymer electrolyte membranes for fuel cell systems," *Journal of New Materials for Electrochemical Systems*, vol. 1, no. 1, pp. 47-66, 1998.
- [4] R. Souzy and B. Ameduri, "Functional fluoropolymers for fuel cell membranes," *Progress in Polymer Science*, vol. 30, no. 6, pp.664-687, 2005.
- [5] J. P. Schroder and W. P.Sopchak, "The reaction of phosphorus trichloride and oxygen with polymers," *Journal of Polymer Science*, vol. 47, no. 149, pp. 417-433, 1960.
- [6] P. J. Phillips, F. A. Emerson, and W. J. MacKnight, "Structure and properties of polyethylene modified with phosphonic acid side groups. I. Mechanical and thermal studies," *Macromolecules*, vol. 3, no. 6, pp.767-771, 1970.

- [7] P. J. Phillips, F. A. Emerson, and W. J. MacKnight, "Structure and properties of polyethylene modified with phosphonic acid side groups. II. Dielectric properties," *Macromolecules*, vol. 3, no. 6, pp. 771-777, 1970.
- [8] B. W. Delf and W. J. MacKnight, "Structure of some ethylene-phosphonic acid copolymers," *Journal of Polymer Science: Polymer Physics*, vol. 11, no. 3, pp. 571-585, 1973.
- [9] R. A. Weiss, R. W. Lenz, and W. J. MacKnight, "Properties of polyethylene modified with phosphonate side groups. I. Thermal and mechanical properties," *Journal of Polymer Science: Polymer Physics*, vol. 15, no. 8, pp. 1409-1425, 1977.
- [10] R. A. Weiss, R. W. Lenz, and W. J. MacKnight, "Phosphonate ionomers based on phosphonylated ethylene-propylene copolymer," *Journal of Polymer Science: Polymer Chemistry*, vol. 18, no. 9, pp. 2887-2899, 1980.
- [11] F. Eymery, B. Iorga and P. Savignac, "Synthesis of phosphonates by nucleophilic substitution at phosphorus: The $S_NP(V)$ reaction," *Tetrahedron*, vol. 55, no. 46, pp. 13109-13150, 1999.
- [12] B. Lafitte and P. J. Jannasch "Phosphonation of polysulfones via lithiation and reaction with chlorophosphonic acid esters," *Journal of Polymer Science Part A: Polymer Chemistry*, vol. 43, no. 2, pp. 273-286, 2005.
- [13] B. Lafitte and P. J. Jannasch, "Polysulfone ionomers functionalized with benzoyl(difluoromethylenephosphonic acid) side chains for proton-conducting fuel-cell membranes," *Journal of Polymer Science Part A: Polymer Chemistry*, vol. 45, no. 2, pp. 269-283, 2007.
- [14] G. Maier and M. Gross, "Preparation of block polymers for PEM applications," US Patent Application, US2008027151, 2008.
- [15] J. Ding, C. Chuy, and S. Holdcroft, "Enhanced conductivity in morphologically controlled proton exchange membranes: Synthesis of macromonomers by sfp and their incorporation into graft polymers," *Macromolecules*, vol. 35, no. 4, pp. 1348-1355, 2002.
- [16] X. Chen, Y. Yin, P. Chen, H. Kita, and K. I. Okamoto, "Synthesis and properties of novel sulfonated polyimides derived from naphthalenic dianhydride for fuel cell application," *Journal of Membrane Science*, vol. 313, no. 1-2, pp. 106-119, 2008.
- [17] P. Chhabra and V. Choudhary, "Synthesis and characterization of sulfonated naphthalenic polyimides based on 4,4'-diaminodiphenylether-2,2'-disulfonic acid and bis[4-(4 aminophenoxy) phenylhexafluoropropane] for fuel cell applications," *European Polymer Journal*, vol. 45, no.5, pp. 1467-1475, 2009.
- [18] G. Socrates, "Organic phosphorus compounds," in *Infrared and Raman Characteristic Group Frequencies Table and Chart*, 3rd ed. West Sussex, England: John Wiley & Sons Ltd., 2001, pp. 233.
- [19] P. Sysel, M. Sochurek, and P. Holler, "Preparation of fluorine containing polymer," *Polymer*, vol. 39, no. 20, pp. 4751-4755, 1998.

