

# Crosslinked Electrolytes Based on Poly(butoxy-Methylenenorbornene) for Proton Exchange Membrane

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**ABSTRACT:** The poly(butoxymethylenenorbornene-*co*-norbornenemethyl acetate) (PBN/NA) were successfully synthesized via the vinyl addition copolymerization of 2-butoxymethylene norbornene (BN) and norbornene-2-methyl acetate (NA). The poly(butoxymethylenenorbornene-*co*-norbornenemethanol) (PBN/NOH) was obtained by the de-esterification of PBN/NA. After doping with 4,5-imidazole dicarboxylic acid (IDA) and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), the proton exchange membranes with crosslinked structure were obtained and the corresponding morphology, water uptake, proton conductivity, methanol permeability, thermal stability, as well as tensile properties were

investigated. The results indicate that the crosslinked membranes showed higher proton conductivity at higher temperatures and lower methanol permeability after incorporation of more content of IDA and H<sub>3</sub>PO<sub>4</sub>. The PNIH membranes showed lower tensile strength, elongation at break as well as the elastic modulus than pristine PBN/NOH. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3225–3233, 2012

**Key words:** proton exchange membrane; polynorbornene; vinyl-copolymerization

## INTRODUCTION

The proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) will be potentially used in a wide range of portable and mobile applications. The proton exchange membrane (PEM) is one of the key components determining the performance of the fuel cells. There has been considerable effort focusing on the development of alternative low-cost, high-temperature, polymer-based electrolytes membranes.<sup>1–8</sup>

The vinyl-type polynorbornene (PNB) exhibits excellent optical transparency, high thermal stability, high glass transition temperature and low moisture absorption. However, the poor solubility in common organic solvents, mechanical brittleness and low adhesion property limit the further application of PNB.<sup>9</sup> Thus, many researchers incorporated different functional pendant groups such as alkoxysilyl, alkyl,

and ester groups into the PNB backbone to improve the properties of PNB.<sup>10</sup> It is noticed that the solubility of the PNB could be significantly improved after incorporation of functional groups.<sup>11,12</sup> The sulfonated polynorbornene derivatives have been successfully prepared, and they are mainly used for the gas transport and ionic transport applications. Additionally, they were prepared by the ring opening metathesis polymerization (ROMP), followed by the treatment of sulfonating agents of acetyl sulfate or hydrogenation of the main chains.<sup>13–15</sup>

As far as we know, there is no literature reporting on the application of PNB and its derivatives used as the PEM. In this article, due to the relatively high thermal and dimensional stability of PNB, we are aimed to develop a novel proton exchange membrane based on the PNB derivatives. According to our previous work,<sup>12,16</sup> we have synthesized the PNB derivatives containing hydroxyl groups and ether groups. The hydroxyl and butoxy derived polynorbornene (PBN/NOH) copolymer could be crosslinked with 4,5-imidazole dicarboxylic acid (IDA) via the esterification.<sup>17,18</sup> In this article, the crosslinked proton conducting membranes were prepared by doping with phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) to form imidazole-H<sub>3</sub>PO<sub>4</sub> complexes. The properties of the cross-linked membranes using as the PEMs were carefully investigated.

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## EXPERIMENTAL

### Materials

5-norbornene-2-methanol (NBMOH) (98%) was purchased from Chongqing Hi-Tech Chemical and was used as received without further purification. The bis( $\beta$ -ketone aphthyl-amino) nickel(II) catalyst was prepared according to the previous procedure.<sup>19</sup> Tris(pentafluorophenyl)borane ( $B(C_6F_5)_3$ , 95%) was purchased from J&K company and used directly. 4,5-imidazole dicarboxylic acid (IDA) and sodium hydride (NaH, 60%) were provided by Aladdin. The phosphoric acid ( $H_3PO_4$ , 85%), pyridine ( $C_5H_5N$ ), acetic anhydride ( $Ac_2O$ ) were purchased from Tianjin Damao chemical. The above chemicals were used directly without further purification.

### Monomer synthesis

#### Norbornene-2-methyl acetate (NA)

The NBMOH<sup>20</sup> (6.0 mL, 0.05 mol) was charged into a 250-mL three-necked flask containing 100 mL of pyridine under nitrogen protection at room temperature. Then, acetic anhydride (4.8 mL, 0.05 mol) was added into the flask by a dropping funnel in 1 h under vigorous stirring. The mixture was heated and refluxed for 3 h, and poured into the ice water. The crude product was extracted with diethyl ether and washed by 10% aqueous HCl solution and sodium carbonate solution. The organic layer was dried over anhydrous sodium sulfate and evaporated to obtain 7.7 g of NA (yield, 92.8%).

#### 2-butoxymethylene norbornene (BN)

The NaH<sup>21</sup> (4.8 g, 0.2 mol) was charged into a 250-mL three-necked flask containing 100 mL of THF, followed by the addition of NBMOH (6.0 mL, 0.05 mol) under vigorous stirring at room temperature. After refluxing for 2 h, the bromobutane (11.0 mL, 0.1 mol) was added dropwise, and the mixture was stirred for additional 24 h at 60°C. Then, the mixture was washed by deionized water, and the organic layer was separated and dried with magnesium sulfate for 24 h. After removing the magnesium sulfate, the solution was concentrated by evaporation. The raw product was purified by the column chromatography with eluant of petroleum ether and ethyl acetate (4/1 in v/v). After evaporation, 7.83 g of BN (yield, 87%) was finally obtained.

### Copolymerization of BN and NA

The copolymerization of BN and NA was carried out in a 100-mL two-necked, round-bottom flask with a magnetic stirring bar. All the monomers were dried over  $CaH_2$ , and vacuum distilled prior to poly-

merization. After sufficiently purging with nitrogen, the homogeneous bis( $\beta$ -ketonaphthylamino)Ni(II) pre-catalyst with  $B(C_6F_5)_3$  as cocatalyst was added. The mole feed ratio of BN and NA was 9 : 1 and the polymerization was performed according to the previous literature.<sup>12,16</sup> All procedures for polymerization were carried out under a purified argon atmosphere. A typical polymerization procedure was as follows. Into a 50-mL, two-necked, round-bottom flask containing a magnetic stirring bar, the appropriate  $B(C_6F_5)_3$  solid and toluene as a solvent were added in turn and shaken to obtain a homogeneous solution, and then 2.5 mL of an BN and NA solution (0.0425 mol/L) was injected. After an appropriate amount of a fresh Ni(II) catalyst solution (in toluene, 0.005 mol/L) was injected into the reaction solution to initiate the polymerization while an appropriate amount of the solvent was supplied to maintain a total reaction volume of 10 mL, the mixture stood at a constant temperature for a definite reaction time. The polymerization was terminated by addition of 5% HCl/MeOH (v/v) solution, and the resulting PBN/NA copolymer was filtered and washed by fresh methanol and deionized water. The received polymer was then dried in vacuum at 60°C for 48 h, and the number-average molecular weight ( $M_n$ ) of the copolymer was determined to be about 57,000 g/mol with the polydispersity of 2.2 as measured by gel permeation chromatography (GPC).

### De-esterification of PBN/NA

The PBN/NA (2.0 g) was dissolved in 40 mL of THF/EtOH (5/1 in v/v) solution, followed by the addition of 10 mL of KOH solution (5 mol/L) in 1 h. Then, the mixture was refluxed for 24 h, and the organic layer was separated. The organic solution was added into the 5% HCl/MeOH (v/v) solution, and the PBN/NOH copolymer was obtained. After washing by methanol and deionized water, the polymer was dried in vacuum at 60°C for 48 h. The received PBN/NOH copolymer (1.8 g) showed a  $M_n$  of 56 000 g/mol and polydispersity of 1.8 as determined by GPC.

### Membrane preparation

The PBN/NOH copolymer, IDA and  $H_3PO_4$  with different molar ratios were mixed together, and cast onto a clean glass slide and reacted at 110°C for 2 h to form the crosslinked membrane with different molar ratios of PBN/NOH, IDA and  $H_3PO_4$  as shown in Table I.<sup>17,18</sup> The corresponding membranes are named as PNIH211, PNIH222, PNIH233, and PNIH244, respectively.

**TABLE I**  
**Water Uptake, Proton Conductivity, Methanol Permeability, Tensile Strength, Elongation at Break, and Elastic Modulus of the Membranes**

| Samples              | [OH] :<br>[IDA] : [H <sub>3</sub> PO <sub>4</sub> ] | Thickness<br>(mm) | Water<br>uptake<br>(wt %) | Proton<br>conductivity<br>at 80°C<br>(S cm <sup>-1</sup> ) (×10 <sup>-3</sup> ) | Methanol<br>permeability<br>at 20°C<br>(cm <sup>2</sup> s <sup>-1</sup> ) (×10 <sup>-6</sup> ) | Tensile<br>strength<br>at break<br>(MPa) | Elongation<br>at break<br>(%) | Elastic<br>modulus<br>(MPa) |
|----------------------|---|-------------------|---------------------------|---|--|--|-------------------------------|-----------------------------|
| PBN/NOH              | 2 : 0 : 0   | 0.135             | 0.2                       |   | 0.62   | 18.0                                     | 32.8                          | 670.5                       |
| PNIH211 <sup>a</sup> | 2 : 1 : 1 <sup>b</sup>                              | 0.227             | 2.8                       | 0.39  | 0.42   | 10.5                                     | 21.8                          | 455.6                       |
| PNIH222              | 2 : 2 : 2   | 0.297             | 5.2                       | 1.17  | 0.39   | 8.6                                      | 13.8                          | 326.7                       |
| PNIH233              | 2 : 3 : 3   | 0.310             | 12.0                      | 1.88  | 0.35   | 5.3                                      | 9.9                           | 253.3                       |
| PNIH244              | 2 : 4 : 4   | 0.360             | 13.6                      | 3.05  | 0.25   | 4.2                                      | 6.7                           | 179.6                       |
| Nafion115            |   | 0.143             | 33.4                      | 84.4  | 2.34   |  |                               |                             |

<sup>a</sup> The PNIH is the PBN/NOH copolymer crosslinked by IDA and H<sub>3</sub>PO<sub>4</sub>.

<sup>b</sup> The molar ratio of the added PBN/NOH : [IDA] : [H<sub>3</sub>PO<sub>4</sub>].

### Water uptake

$$\delta = I/(RA) \quad (2)$$

Water uptake was determined by weighing vacuum dried membrane and fully equilibrated membrane with water. The surface of the membrane sample was quickly wiped with an absorbent tissue to remove the excess of water and the sample was then weighed. The water uptake of the membrane was determined from:

$$\text{Water uptake}(\%) = (W_s - W_d)/W_d \times 100\% \quad (1)$$

where  $W_d$  and  $W_s$  are the weights of dried and wet membranes, respectively.

### Proton conductivity

The proton conductivities ( $\delta$ ) of the membranes at different temperatures were evaluated using three-electrode electrochemical impedance spectra. The impedance measurements were carried out on a CHI660 electrochemical workstation (CH Instruments) coupled with a computer. A PTFE diffusion cell composed of two symmetrical chambers was divided by a membrane sample. The cells were filled with the electrolyte composed of sulfuric acid (0.5M). The two platinum wires using as working electrode and counter electrode, as well as a Ag/AgCl electrode functionalized as the reference electrode were introduced into the electrolyte solution. The impedance spectra were recorded with the help of ZPlot/ZView software under an ac perturbation signal of 10 mV over the frequency range of 0.1 MHz to 1 Hz. The electron resistant of the system (without membrane divided) was measured as  $R_1$ , and the electron resistant of the system (with membrane divided) was measured as  $R_2$ . Electron resistant of membrane under variable temperature (20–80°C) at 100 % humidity was obtained as the dispersion of  $R_2$  and  $R_1$ . The proton conductivity  $\delta$  of the membrane was calculated from the following equation:

where  $\delta$ ,  $I$ ,  $R$ , and  $A$  represent the proton conductivity, thickness of membranes, the resistance of the membrane and the cross-sectional area of the membrane, respectively.

### Methanol permeability

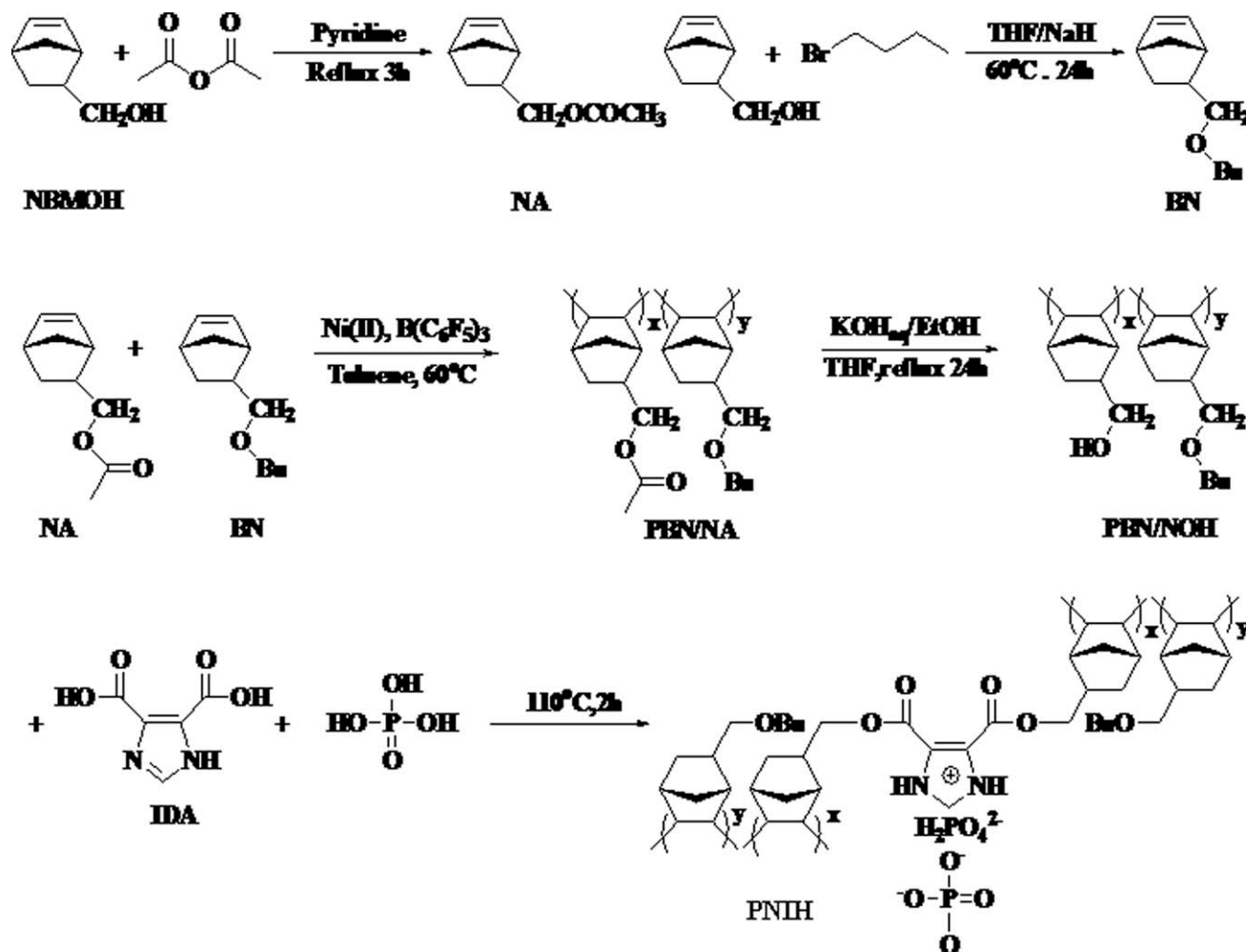
An organic glass diffusion cell was used to obtain the methanol permeability of the membranes. The diffusion cell was composed of two chambers divided by a membrane sample. One chamber of the cell ( $V_1$ ) was filled with a 1.0M ( $C_1$ ) methanol solution in deionized water. The other chamber ( $V_2$ ) was filled with deionized water. A sample (effective area 0.385 cm<sup>2</sup>) was clamped between the two chambers. Both compartments were stirred by a magnetic follower during the experiment. The concentration of methanol in solution was estimated using a differential refractometer (WellChrom K-2401). The refractometer is highly sensitive to methanol, which can be measured continuously during the test. The methanol permeability was calculated from the slope ( $S$ ) of the straight line plot of methanol concentration versus time. The measurement was performed at room temperature. And the membrane permeability ( $P$ ) was calculated from the following equation:

$$P = SV_2l/AC_1 \quad (3)$$

where  $A$  (cm<sup>2</sup>) is the membrane area,  $l$  (cm) is the membrane thickness,  $C_1$  is the methanol concentration, and  $V_2$  is the volume of deionized water.

### Characterization

The Fourier transform infrared (FTIR) spectra were measured on a Shimadzu IRPrestige-21 FT-IR spectrophotometer. The proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra were recorded on a Bruker



**Scheme 1** Synthesis of BN, NA, PBN/NA and PBN/NOH, and the preparation of PNIH crosslinked membranes.

ARX 400 NMR spectrometer with deuterated chloroform as solvent and tetramethylsilane ( $\delta = 0$ ) as internal reference. The thermal gravimetric analysis (TGA) was performed using a Perkin-Elmer instruments TGA 7 at a heating rate of  $20^\circ\text{C min}^{-1}$  under a nitrogen atmosphere ( $50 \text{ mL min}^{-1}$ ). Tensile strength, elongation at break, and Elastic modulus were measured with a CMT8502 Machine model GD203A (Shenzhen Sans Testing Machine, China) at a speed of  $5 \text{ mm min}^{-1}$ . The membrane was cut into a sheet of 50 mm in length and 20 mm in width. The thickness of the membrane was about 0.01 mm. The cross section morphology of the membranes were investigated by scanning electron microscope (SEM), using an Environmental Scanning Electron Microscope (ESEM, FEI Quanta 200). All the samples were soaked in the liquid nitrogen and fractured, followed by the sputtering of a thin layer of gold. The cross-section of the membranes was then observed by the SEM with an accelerating voltage of 5 kV. The gel permeation chromatography (GPC) was carried out on a Breeze Waters system using chloroform as the eluent at a flow rate of  $1.0 \text{ mL}$

$\text{min}^{-1}$ . The instrument was calibrated with monodisperse polystyrene standards.

## RESULTS AND DISCUSSION

### Structure and morphology

The synthesis of the copolymers is illustrated in Scheme 1. The norbornene derived monomers of BN and NA were copolymerized in the presence of Nickel catalyst and  $\text{B}(\text{C}_6\text{F}_5)_3$  cocatalyst via the vinyl addition polymerization. The received copolymer of PBN/NA was further converted into PBN/NOH via the de-esterification. After reacting with IDA and doping with  $\text{H}_3\text{PO}_4$ , the crosslinked electrolytes based on PBN/NOH was obtained.

The structure of the monomers and polymers was analyzed by FTIR as shown in Figure 1. For the BN and NA monomers, the absorption peaks at  $3060$  and  $1650 \text{ cm}^{-1}$  are attributed to the stretching vibration of  $-\text{C}=\text{C}-\text{H}$  and  $\text{C}=\text{C}$  bonds, respectively. The peak at  $1740 \text{ cm}^{-1}$  is associated with the carbonyl vibration of ester group, and the peaks at  $1240$

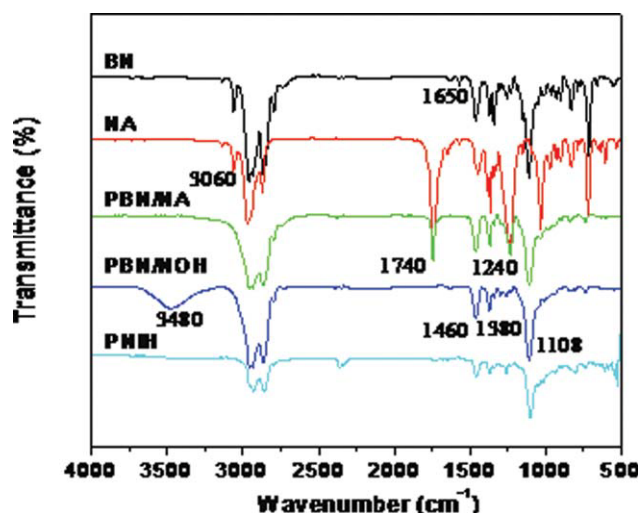


Figure 1 FTIR spectra of BN, NA, PBN/NA and PBN/NOH. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

and  $1033\text{ cm}^{-1}$  are ascribed to the asymmetric and symmetric stretching vibration of C—O—C bond of ester group of NA. The peak at  $1108\text{ cm}^{-1}$  is attributable to the asymmetric stretching vibrations of

C—O—C bond of BN. After copolymerization, the absorption peaks of the double bonds disappeared in PBN/NA, confirming of the mechanism of vinyl addition polymerization rather than ROMP. After the de-esterification of PBN/NA, the appearance of absorption peak at  $3480\text{ cm}^{-1}$  and the disappearance of the absorption peak at  $1740\text{ cm}^{-1}$  are observed, suggesting that the PBN/NOH copolymer was successfully obtained. The PNIH exhibits the absorption peaks similar to those of PBN/NOH copolymer except for the peak at around  $3480\text{ cm}^{-1}$ , showing that the hydroxyl groups disappears after the reaction with IDA and doping with  $\text{H}_3\text{PO}_4$ .

The  $^1\text{H-NMR}$  was further applied to investigate the chemical structure of the monomers and polymers as shown in Figure 2. For the BN monomer,<sup>21,22</sup> the reflection signals between 5.6 and 6.2 ppm are attributable to the protons connected to the double bond in norbornene. The signals from 2.7 to 2.9 are ascribed to the protons of bridge carbons (C1, C4), and the broad signal ranging from 2.9 to 3.5 ppm corresponds to the protons of  $-\text{CH}_2\text{OCH}_2-$  group. The signal at 0.85 ppm is attributed to the protons in  $-\text{CH}_3$  group, and the other signals at 2.3, 1.8, 1.6, 1.5, 1.4, 1.2, 1.1, 1.0, and 0.4 ppm are

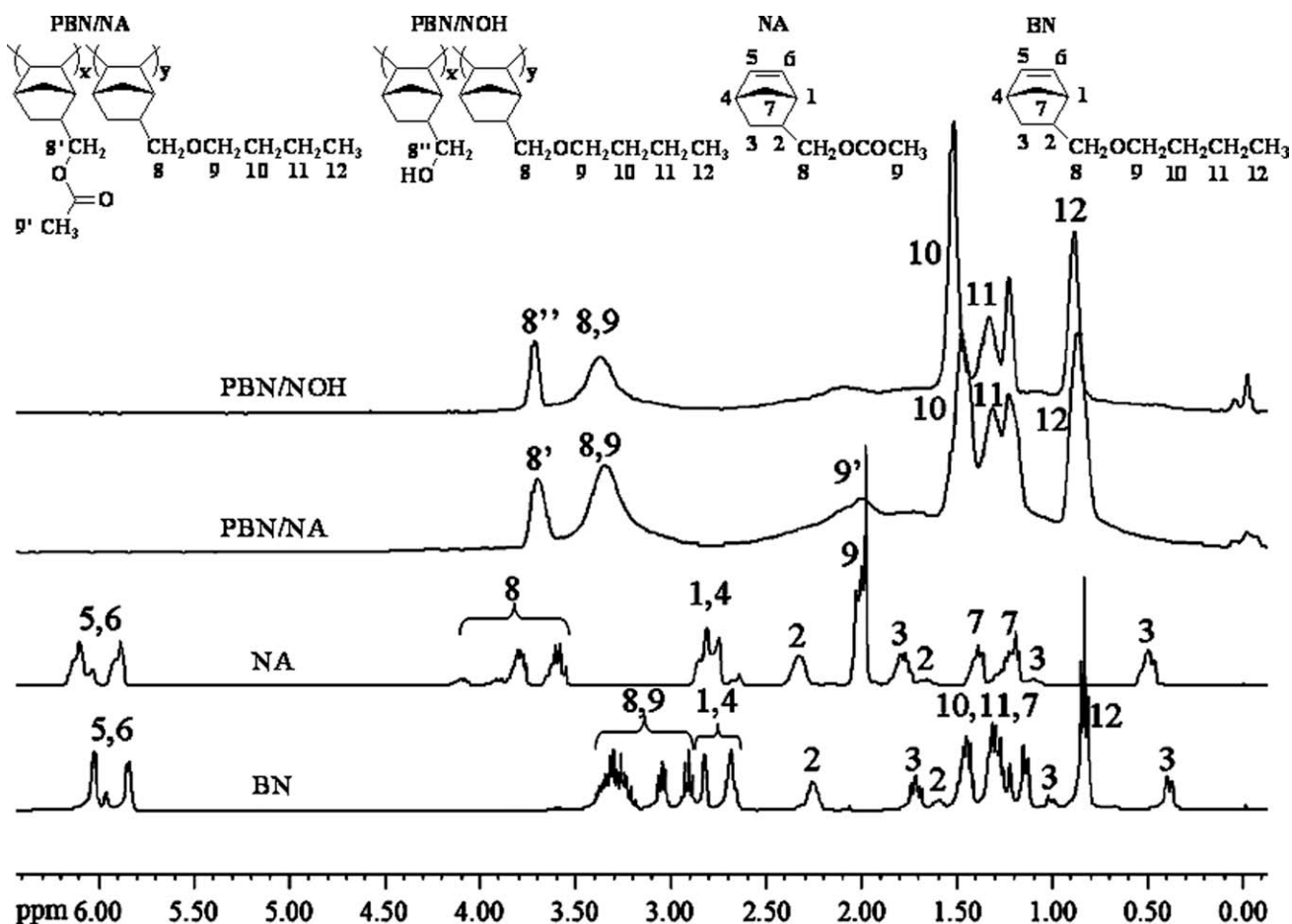
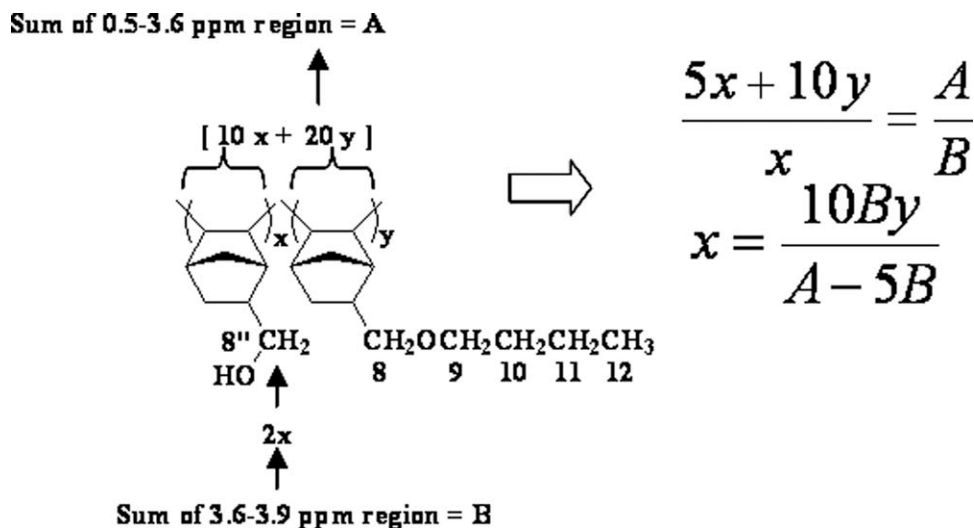


Figure 2 The  $^1\text{H-NMR}$  spectra of BN, NA, PBN/NA, and PBN/NOH.



**Figure 3** The composition analysis of the PBN/NOH copolymer based on the <sup>1</sup>H-NMR results.

corresponded to other protons as illustrated in Figure 2, respectively. In comparison with BN, the protons of NA shift to lower field probably due to the  $\pi$ - $\pi$  conjugation effect of carbonyl group.<sup>20,22</sup> The signals between 5.6 and 6.4 ppm are attributed to the protons of double bond, and the broad signals between 3.5 and 4.2 ppm correspond to the protons of  $-\text{CH}_2-\text{OCO}-$  group. The signals from 2.6 to 2.9 ppm are attributed to the bridge carbon (C1, C4) protons, and the other signals at 2.3, 2.0, 1.8, 1.7, 1.4, 1.2, 1.1, and 0.5 ppm correspond to the protons as shown in Figure 2. After the copolymerization of BN and NA, the signals between 5.6 and 6.4 ppm are not discerned, confirming of the vinyl addition polymerization mechanism. In addition, the four reflection signals below 2.0 ppm are indicative of the typical vinyl-addition type polynorbornene.<sup>12,16</sup> Furthermore, the reflection signals at about 2.0 ppm are ascribed to the protons of methyl group (C9') connected to carbonyl group in PBN/NA. The signals located at 3.4 and 3.8 ppm should be corresponded to the protons (C8, C9, C8') as illustrated in Figure 2. It is noticed that the signals of PBN/NOH are similar to those of PBN/NA except for the disappearance of signal at about 2.0 ppm ascribed to protons of methyl group (C9'). It is suggested that the ester groups were successfully converted to the hydroxyl groups after de-esterification. On the basis of the FTIR and NMR results, it is believed that the copolymers were successfully synthesized via the vinyl addition polymerization of BN and NA.

To further calculate the content of hydroxyl norbornene monomer (NBMOH) in the PBN/NOH copolymer, the structure of the copolymers was carefully investigated as shown in Figure 3. As indicated in Figure 2, the three broad signals at 0.5–3.0 ppm, 3.0–3.6 ppm, and 3.6–3.9 ppm are attributed to the protons of norbornene (NB) skeleton, C8-H, C9-H,

and C8''-H, respectively. The block length of NBMOH is assumed to be  $x$ , and the block length of BN is assumed to be  $y$ . The area of the signals ranging from 0.5 to 3.6 ppm is assumed to be  $A$ , and area of the signals ranging from 3.6–3.9 ppm is assumed to be  $B$ . Therefore, the areas of  $A$  and  $B$  have the relationship as following:

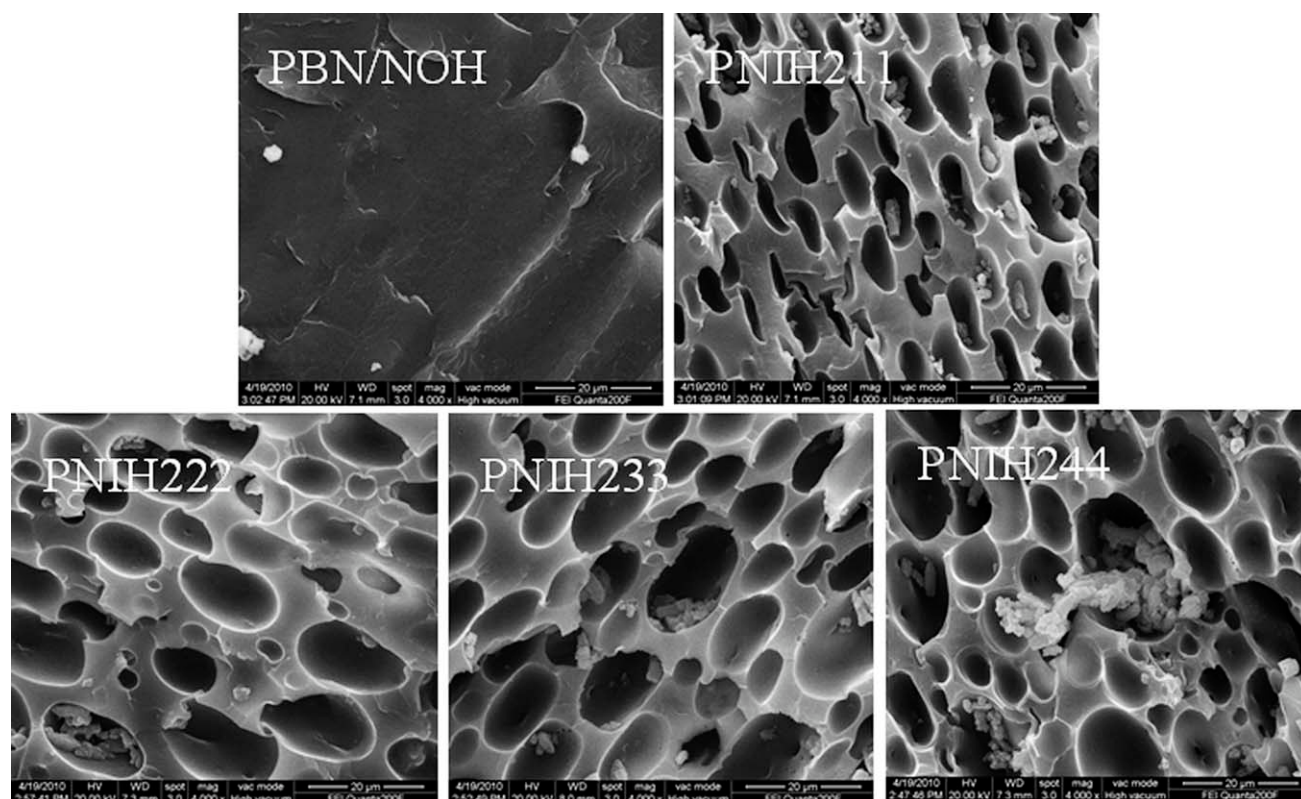
$$A/B = (10x + 20y)/(2x) \quad (4)$$

From the above equation,  $x$  could be calculated as  $10By/(A-5B)$ , and the NBMOH content is calculated to be about 6.85%.<sup>23</sup> It is indicated that there is about 6.85% of NBMOH in the copolymers.

The cross section morphology of the membranes analyzed by the SEM is shown in Figure 4. It is observed that the PBN/NOH membrane exhibits a relatively smooth surface, indicating of the brittle fracture mechanism by the treatment of liquid nitrogen. However, the surfaces of other membranes are full of micro pores, with the diameters ranging from 5 to 20  $\mu\text{m}$ . The pore sizes tend to increase as the IDA and  $\text{H}_3\text{PO}_4$  content increases. It is indicated that the incorporation of IDA and  $\text{H}_3\text{PO}_4$  facilitates the formation of crosslinking structure in the membranes, and the appearance of the micro pores might be concerned with the crosslinking structure and phase separation. The above morphology will eventually affect the transport properties and mechanical properties of the membranes.

#### Water uptake, proton conductivity, and methanol permeability

Water uptake and swelling ratio of PEMs are closely related to proton conductivity, dimensional stability, and mechanical strength. The water within the



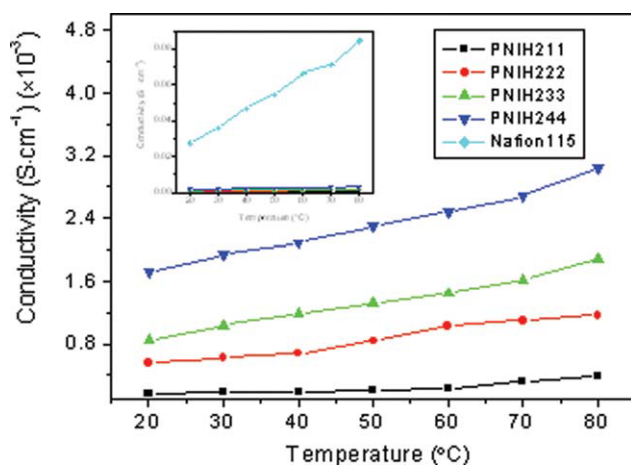
**Figure 4** The cross-sectional SEM images of PBN/NOH and PNIH membranes.

membrane provides a carrier for the proton and maintains high proton conductivity. However, excessive water uptake in a PEM leads to unacceptable dimensional change or loss of dimensional shape, which could lead to weakness or dimensional mismatch when incorporated into a membrane electrode assembly. As shown in Table I, the water uptake of the crosslinked membranes increases from 2.8 to 13.6 wt % with the increase of IDA and  $\text{H}_3\text{PO}_4$  complex feed ratios. It is suggested that the incorporation of  $\text{H}_3\text{PO}_4$  facilitated the improvement of the hydrophilicity of the membranes. It is noted that there is almost no size change of the pristine polynorbornene membrane and the crosslinked membranes after immersion in deionized water for 10 days, due to the rigid molecular chains and the crosslinking structure of the membranes by the introduction of IDA. According to Kim's research work,<sup>24</sup> it is suggested that the crosslinked membranes could be used as the candidate for the high temperature proton conductive membrane.

It is generally accepted that the proton conductivity is dependent on the experimental approaches, as well as the instruments. In this article, Nafion 115 membrane was chosen to measure the proton conductivity under the same conditions for comparison. In Figure 5, it is observed that the proton conductivities of the PNIH crosslinked membranes and Nafion 115 membrane increase gradually as the temperature

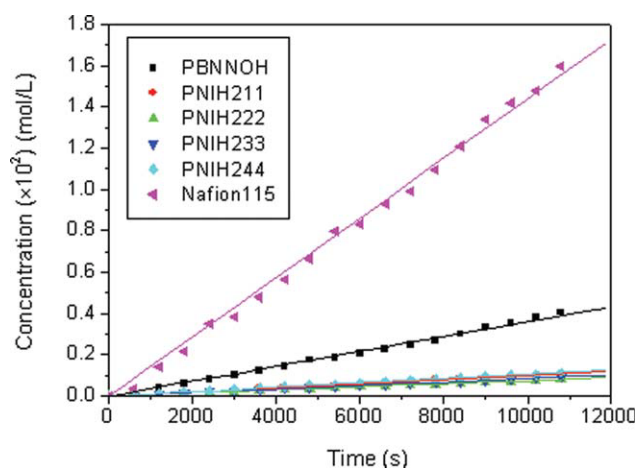
increases. At  $80^\circ\text{C}$ , the Nafion 115 membrane exhibit the proton conductivity of about  $0.084 \text{ S cm}^{-1}$ , and the PNIH244 membrane show the proton conductivity of  $3.05 \times 10^{-3} \text{ S cm}^{-1}$ . Furthermore, the proton conductivity of the PNIH crosslinked membranes is dependent on the content of  $\text{H}_3\text{PO}_4$ . The incorporation of high content of  $\text{H}_3\text{PO}_4$  leads to the higher proton conductivity of the membranes. Based on the SEM results, the pore sizes tend to increase as the IDA and  $\text{H}_3\text{PO}_4$  content increases. It is indicated that the proton conductivity of the membranes are influenced by the formation of pores and the pore sizes. The formation of bigger pores facilitates the increase of the proton conductivity of the membranes. The temperature dependence of proton conductivity in  $\text{H}_3\text{PO}_4$  doped membranes fit well with the Arrhenius equation.<sup>24</sup> It is suggested that the norbornene derived polymer electrolytes could be used as the polymer electrolyte membrane at relatively high temperatures.

Methanol permeability and proton conductivity are the two transport properties, determining the fuel cell performance. Low methanol permeability and high proton conductivity are required for direct methanol fuel cells. As seen in Table I, the methanol permeability of the PNIH crosslinked membranes is ranging from  $4.2 \times 10^{-7}$  to  $2.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ , which is about one order of magnitude lower than that of Nafion 115. In Figure 6, the concentration of



**Figure 5** The proton conductivity for different membranes as a function of temperature. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

methanol increases gradually as the time increases, and the methanol concentration for Nafion115 and PBN/NOH membranes are much higher than those of the PNIH membranes during the whole process. Furthermore, the methanol permeability decreases as the IDA and  $H_3PO_4$  content increases. Based on the above results, it is suggested that the incorporation of more content of IDA and  $H_3PO_4$  not only improves the proton conductivity but also decreases the methanol permeability of the membranes. The relatively low methanol permeability of the PNIH membranes is supposed to be related with the formation of crosslinked structure, which restricts the crossover of methanol molecules. The appearance of the micro pores as observed by SEM might be another factor for the low methanol permeability. However, the incorporation of too much IDA and



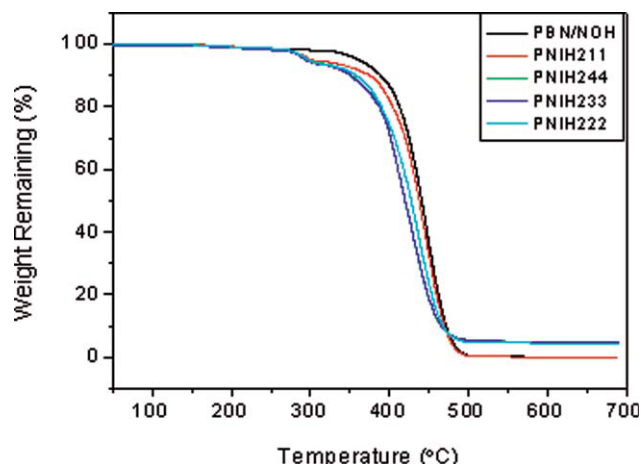
**Figure 6** The methanol permeation concentration for different membranes as a function of time. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

$H_3PO_4$  may eventually deteriorate the thermal and mechanical properties of the membranes.

### Thermal and mechanical properties

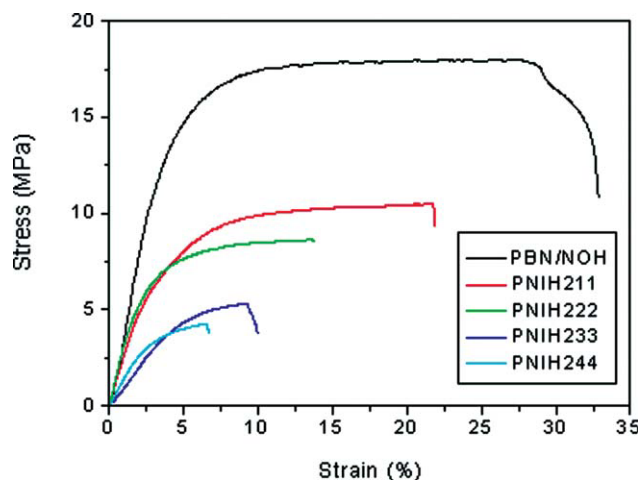
The thermal stability of the membranes was analyzed by TGA and the corresponding results are shown in Figure 7. It is observed that all the membranes including the pristine PBN/NOH and the PNIH crosslinked membranes are thermally stable below  $270^\circ\text{C}$ , showing of no significant weight loss. The PNIH crosslinked membranes exhibit about 7.0 wt % weight loss as the temperature increases from 270 to  $340^\circ\text{C}$ , in comparison with 3.0 wt % weight loss of pristine PBN/NOH. It is suggested that the incorporation of  $H_3PO_4$  makes the polynorbornene membranes less stable. The formation of the micro pores as observed by SEM confirms that there might be phase separation in the PNIH membranes, which decreases thermal stability of the membranes.

The tensile properties of the PBN/NOH and PNIH crosslinked membranes were also investigated, and the results are shown in Figure 8 and Table I. It is noted that the pristine PBN/NOH membrane exhibits the highest values of tensile strength, elongation at break, as well as the elastic modulus. However, the incorporation of  $H_3PO_4$  deteriorates the mechanical properties of the membranes. The values of tensile strength, elongation at break and the elastic modulus significantly decrease to 4.2 MPa, 6.7% and 179.6 MPa for the PNIH244 membrane, respectively. The formation of the crosslinked structure makes the polymer chain less flexible, leading to the decrease of elongation at break. Furthermore, the incorporation of inorganic IDA and  $H_3PO_4$  deteriorates the mechanical strength of the membranes, leading to the decrease of both tensile



**Figure 7** The TGA curves of PBN/NOH and PNIH membranes. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 8** Stress and strain curves of PBN/NOH and PNIH membranes. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

strength and elastic modulus. Furthermore, the weak tensile strength should be related with the micro pores as observed by SEM.

### CONCLUSIONS

The norbornene-derived PBN/NA and PBN/NOH copolymers were successfully synthesized via the vinyl addition polymerization and de-esterification, as confirmed by both FTIR and NMR analysis. The PNIH membranes exhibited lower water uptake and proton conductivity as compared with Nafion 115 membrane. The PNIH membranes showed much lower methanol permeability, which is about one order of magnitude lower than that of Nafion 115. The PBN/NOH and PNIH membranes were thermally stable and started to decompose at about 270°C, but the incorporation of IDA and H<sub>3</sub>PO<sub>4</sub> deteriorated the thermal stability of the membranes. The PNIH membranes showed lower tensile strength, elongation at break as well as the elastic modulus than pristine PBN/NOH. The butoxy-methylene group on polynorbornene has tuned mechanical properties of final membranes with comparison to unmodified polynorbornene. This article demonstrates a novel proton exchange membrane

based on polynorbornene derived copolymers. It is expected that the PNIH membranes could be potentially used as PEM at relatively high temperatures.

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