

Vinyl-Addition Type Norbornene Copolymers Containing Flexible Spacers and Sulfonated Pendant Groups for Proton Exchange Membranes

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ABSTRACT: Novel sulfonated poly(2-butoxymethylenenorbornene-co-2-(6-phenoxy-hexyloxymethylene)-5-norbornene [sP(BN/PhHN)]) were prepared successfully through vinyl-addition type polymerization and then sulfonated with concentrated sulfuric acid (98%) as sulfonating agent in a component solvent. The sP(BN/PhHN)-40 with the maximal degree of sulfonation of 40% can be obtained by controlling the sulfonating reaction time from 8 to 20 h, and a proton conductivity of 3.35×10^{-3} S/cm was achieved at 70°C. The methanol permeabilities of these membranes were in the range from 0.26 to 6.58×10^{-7} cm²/s, which were remarkably lower than Nafion (2.36×10^{-6} cm²/s). TEM analysis revealed that these side-chain type membranes have a microphase separated structure composed of hydrophilic side-chain domains and hydrophobic polynorbornene main chain domains. Sulfonated polynorbornene containing soft spacers displayed better properties, such as lower water uptake, high thermal properties, mechanical properties, and low methanol permeability. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) are one of the most attractive technologies as the clean, quiet, and portable power sources. Proton exchange membranes (PEMs) are the critical component of PEMFCs. Criteria for a practical PEM are chemical stability, good electrode adhesion properties, high proton conductivity, and low methanol permeability. Up to now, Nafion, a perfluorinated membrane made by Du Pont, has been used extensively as commercial PEMs. However, several disadvantages such as low operating temperature, high methanol permeability, and high cost seriously hindered its commercial applications.¹

To settle the problems mentioned above, many new materials have been investigated. During the last two decades, extensive efforts have been made to develop alternative hydrocarbon-based polymer electrolyte membranes. Various kinds of sulfonated aromatic hydrocarbons have been studied, especially sulfonated aromatic polymer, which include sulfonated poly(arylene ether sulfone)s,² poly(arylene ether ketone)s,³ polyimides,⁴ and polybenzimidazoles.⁵ All sulfonated aromatic polymers materials are among the most promising candidates due to their high thermal and chemical stability, low methanol permeability

and high proton conductivity,¹ which depend on their degree of sulfonation (DS). In general, for the sulfonated polymer membrane require high sulfonation level to achieve sufficient proton conductivity. Unfortunately, such high sulfonation level usually makes them excessively swollen in water or aqueous methanol solution. In this case, highly sulfonated polymer membranes lose their properties and become unsuitable for PEMFC or direct methanol fuel cell (DMFC) applications.⁶ Hence, there is a need to develop a membrane material that can deliver a high proton conductivity combined with low methanol permeability.

A strategy to improve the properties of sulfonated aromatic polymer is to develop a new membrane material that can deliver a high proton conductivity combined with low methanol permeability. Recently, polynorbornene (PNB) has attracted the interest of material desired for the application in gas transport and ionic transport. Because of their high thermal stability (the decompose temperature up to 400°C), good mechanical properties, low moisture absorption, plasma etching, and a low dielectric constant. In recent 10 years, several sulfonated PNB derivatives with high proton conductivities used as PEMs have been synthesized by ring-opening metathesis polymerization, followed by the treatment of sulfonating agents of acetyl sulfate or hydrogenation

of the main chains.^{7,8} Compared to ring-opening metathesis polymerization of norbornene, the vinyl-addition polymerization of norbornene yields a PNB with better performance. In particular, the vinyl-type PNBs show higher ideal methanol to water permeability selectivity with somewhat lower methanol permeability,⁹ which evoked people's interest in its application in DMFCs. However, the vinyl-type PNB has rarely been reported in the PEM. In 2001, Toyota¹⁰ used vinyl-type PNB in PEM for the first time, but without subsequent reported due to its poor solubility. In our previous study,¹¹ we have synthesized the vinyl-type PNB with side-chain-containing sulfonic acid groups or imidazole-H₃PO₄ complexes, they all have good properties for PEMs, such as high proton conductivity, low methanol permeability, good mechanical properties, and excellent thermal stability.

The hydrophilic–hydrophobic microphase separation morphology is particularly important for PEM materials because it affects the water uptake and the proton transport pathway in the ionomer membranes.¹² Membranes with the sulfonic acid moieties incorporated directly onto the backbones generally suffer from high water swelling and poor hydrolytic stability, especially when DS is high.^{13,14} To improve the osmotic and hydrolytic stability of the sulfonated polymers, it is previously suggested to increase the hydrophilic–hydrophobic separation by locating the sulfonic acid groups further away from the polymer main chains.^{15,16} So sulfonic acid groups on side chain are better than them on main chain for PEM. In this article, a new functionalized norbornene monomer containing phenyl group on the pendant side chain was prepared and copolymerized with 2-butoxymethylene norbornene (BN) catalyzed by bis-(β -ketonaphthylamino)nickel(II)/B(C₆F₅)₃ catalytic system. The obtained copolymers were further sulfonated by using concentrated sulfuric acid (98%) as a sulfonating agent and DS was controlled by varying the reaction time. The properties of sulfonated copolymer membranes, such as proton conductivity, methanol permeability, mechanical strength, water uptake, IEC and thermal stability were evaluated and discussed. The sulfonated copolymer membrane with DS of 40% possesses good mechanical properties and excellent thermal stability, low methanol permeability, which were remarkably lower than Nafion® 117 membranes.

EXPERIMENTAL

Materials

5-Norbornene-2-methanol (86.4% endo, 13.7% exo) (Chongqing Hi-Tech chemical Co., 98%) was used as obtained from the manufacturer. The catalyst bis(β -ketonaphthylamino)nickel (II) was synthesized according to the method reported in our previous work.¹⁷ Tris(pentafluorophenyl)borane (B(C₆F₅)₃, 97%) was purchased from J&K (Tianjing, China). 6-Bromo-1-hexanol (90%) was provided by Beijing Isomersyn Technology Co., *N*-butyl bromide (99%), triphenylphosphine (TPP, 95%), diethyl azodicarboxylate (40% in toluene) (DEAD, 98%), and sodium hydride (NaH, 60%) was provided by Aladdin. Calcium hydride (CaH₂), sodium (Na), hydrochloride (HCl), phenol, and concentrated sulfuric acid (H₂SO₄, 95–98%) were purchased from Sinopharm Chemical Reagent Co.

Characterization

The FTIR spectrum spectroscopy was measured on a Shimadzu IR Prestige-21 FTIR spectrophotometer. The nuclear magnetic resonance (NMR) spectra were collected on a Bruker ARX 600 NMR at ambient temperature, with deuterated chloroform as the solvent and with tetramethylsilane ($\delta = 0$) as the internal standard. The thermal gravimetric analysis (TGA) was performed on a SDT Q600 for thermogravimetry. Measurements were made by heating from room temperature to 600°C at a heating rate of 10°C min⁻¹ under a nitrogen atmosphere. The mechanical strength of the membrane was by a CMT8502 Machine model GD203A (Shenzhen Sans Testing Machine Co., China) at a speed of 10 mm min⁻¹. Tensile tests were carried out at room temperature and ambient humidity conditions. The wide-angle X-ray diffraction (WXR) curves were recorded on a Bruker D8 Focus X-ray diffractometer, operating at 40 kV and 40 mA with a copper target ($\lambda = 1.54 \text{ \AA}$) and at a scanning rate of 2°/min. Transmission electron microscopy (TEM) image was obtained using a JEOL JEM-2010 (HR) microscope operated at 200 kV. Samples were stained by immersing films in silver nitrate aqueous solution for 24 h, thoroughly washed with water, and dried at room temperature. Silver nitrate is used to exchange the H⁺ of sulfonic acid groups with Ag⁺, enabling hydrophilic regions to be observed as darker areas. For the TEM analysis, the polymer sample was dissolved in THF (2 mg/mL), and then a drop of this solution was placed onto a standard copper grid.

The proton conductivities (δ) 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 (0.5 M). The two platinum wires used as working electrode and counter electrode, as well as 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 alternating-current 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 (20–70°C) at 100% humidity was obtained as the dispersion of R_2 and R_1 . The proton conductivity δ of the membrane was calculated from the following equation:

$$\delta = I/(RA) \quad (1)$$

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

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 5 M (C_1) methanol

solution in distilled water. The other chamber (V_2) was filled with equivalent water. A sample (effective area, 0.385 cm^2) was clamped between the two chambers. Methanol permeates across the membrane by the concentration difference between the two chambers. The methanol concentration in the receiving chamber as a function of time is given by:

$$C_2(t) = [ADKC_1(t - t_0)] / (V_2l) \quad (2)$$

where A (cm^2) is the membrane area, l (cm) is the membrane thickness, D is the methanol diffusivity, and K is the partition coefficient between the membrane and the adjacent solution. The product DK means the membrane permeability (P):

$$P = (C_2(t)V_2l) / [AC_1(t - t_0)] \quad (3)$$

C_2 is measured several times during the permeation experiment and the methanol permeability is obtained from the slope of the straight line. The methanol concentration was measured by using a gas chromatography of Agilent GC 6820 equipped with a FID detector.

The ion exchange capacities (IEC) were determined by titration. The dried composite membranes were immersed in $2 \text{ M H}_2\text{SO}_4$ (aq.) at room temperature for 24 h and then thoroughly washed with water. Then they were equilibrated in 2.0 M NaCl solution for 2 days to exchange the protons with sodium ions and were then removed and were washed by deionized water. The rinse water was collected and combined with the NaCl solution. The acidity of the NaCl solution was titrated by 0.005 mol L^{-1} NaOH solution using 0.5% phenolphthalein solution in ethanol/water as the end-point indicator. The IEC (in mequiv g^{-1}) was calculated as the ratio of exchangeable protons to the weight of the dry membrane (M , g):

$$\text{IEC} = \frac{V_{\text{NaOH}} \times C_{\text{NaOH}}}{M_{\text{(membrane)}}} \quad (4)$$

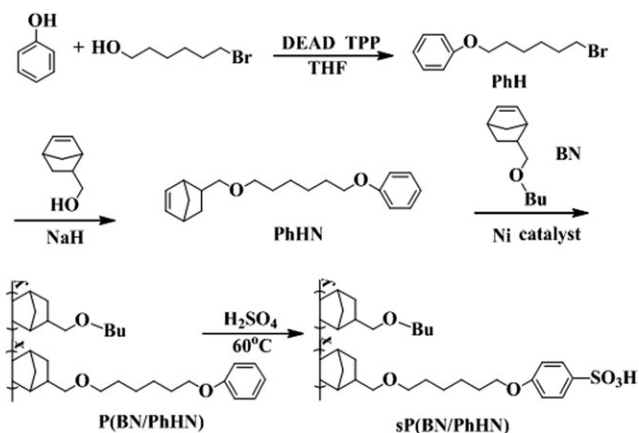
The water uptake was determined by measuring the difference in weight between dry and hydrated membranes. The membrane was dried under vacuum at 100°C for 10 h until constant weight and then immersed into deionized water at room temperature for at least 48 h. Then the membrane was taken out, wiped with tissue paper and quickly weighted on a microbalance. Water uptake of the membranes was calculated from the following equation:

$$\text{Water uptake}(\%) = (W_w - W_d) / W_d \times 100\% \quad (5)$$

where W_d and W_w are the weights of dry and corresponding water-swollen membranes weight, water uptake of the samples were estimated from the average value of at least three measurements for each membrane.

Synthesis of Functional Norbornene Monomer

2-Butoxymethylene Norbornene. 2-BN monomer was synthesized according to the method reported in our previous work.¹¹ Yield: 7.83 g (87%). $^1\text{H-NMR}$ (CDCl_3 , δ): 6.15–5.90 (m, 2H, $\text{CH}=\text{CH}$), 3.8–3.2 (m, 4H, $-\text{CH}_2-\text{O}-\text{CH}_2-$), 3.06–0.82 (m, 7H, norbornene-7H), 1.11 (t, 3H, $-\text{CH}_3$).



Scheme 1. Illustration of procedure for synthesis of sP(NB/PhHN).

2-(6-Phenoxy-hexyloxymethylene)-5-Norbornene (PhHN). The monomer, phenyl functionalized norbornene [2-(6-phenoxy-hexyloxymethylene)-5-norbornene] was synthesized via the etherification reaction as shown in Scheme 1. A solution of phenol (3.76 g, 40 mmol) and DEAD (17.4 g, 20 mmol, 40 wt % in toluene) in THF (50 mL) was added slowly to a solution of TPP (10.6 g, 40 mmol) and 6-bromo-1-hexanol (5.43 g, 30 mmol) in THF (50 mL) by a pressure-equalized dropping funnel under nitrogen at 0°C . The reaction mixture was stirred for 24 h. Then the solvent was evaporated, and the crude product was purified by column chromatography. Intermediate product **PhH** was obtained as light yellow oily liquid by column chromatography.

A 250-mL glass reactor was loaded with 2.4 g (0.1 mol) of NaH and 100 mL of THF, and then 1.2 g (0.01 mol) of 5-norbornene-2-methanol was added under stirring at room temperature, and refluxing for 2 h, then 2.57 g (0.01 mol) of **PhH** was added slowly. The reaction was continued to stir for 24 h at 70°C . After being washed with deionized water, the product was purified by column chromatography (petroleum ether/ethyl acetate = 200/1 v/v). The product was obtained as yellow-green oily liquid. Yield: 2.8 g (78.4%) of product. $^1\text{H-NMR}$ (CDCl_3 , δ): 6.88–7.28 (m, 5H, $\text{C}_6\text{H}_5-\text{O}-$), $\text{CH}=\text{CH}$), 3.9–3.96 (t, 2H, $\text{C}_6\text{H}_5-\text{O}-\text{CH}_2-$), 3.35–3.4 (m, 4H, $-\text{CH}_2-\text{O}-\text{CH}_2-$), 2.39–0.84 (m, 7H, norbornene-7H), 1.64–1.21 (m, 8H, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$).

Copolymerization

All procedures were carried out under purified nitrogen atmosphere. A typical copolymerization procedure is as follows: a toluene solution of BN and PhHN (molar ratio BN/PhHN = 8/2) was added via a syringe into a 100-mL two-necked round-bottomed flask containing a magnetic stirrer, the complexes solution was then introduced followed by 1-mL $\text{B}(\text{C}_6\text{F}_5)_3$ solution (0.1 mol/L) and 1-mL homogeneous bis(β -ketonaphth-ylamino)Ni(II) solution (5×10^{-3} mol/L). The total volume was kept constant at 10 mL. The polymerization was performed at 60°C for 30 min. The polymerization was quenched by ethanol/HCl (v/v = 9/1) solution and stayed overnight. The polymers were then obtained through filtration or centrifugation and washed by ethanol several times and were dried at 40°C for

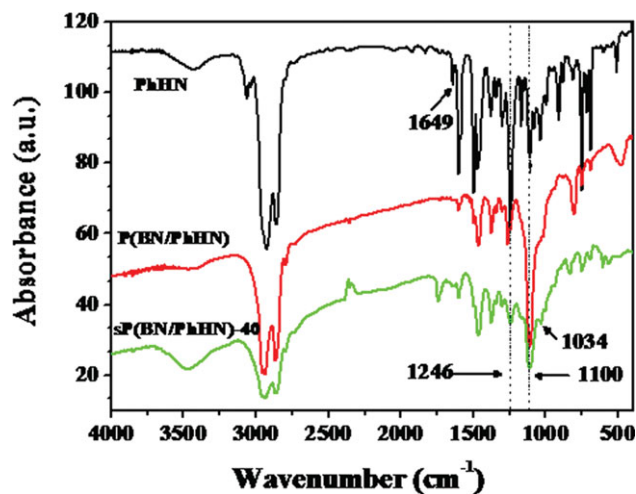


Figure 1. FTIR spectra of (a) PhHN, (b) P(BN/PhHN), and (c) sP(BN/PhHN)-40. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

24 h in a vacuum oven. The copolymerization procedure is also shown in Scheme 1.

Sulfonation of the Copolymer

In a two-necked round-bottomed flask, 0.2 g of the copolymer P(BN/PhHN) was dissolved in 20 mL of cyclohexane and 20 mL of ethyl acetate under nitrogen. Five milliliters of concentrated sulfuric acid (98%) was added slowly to the polymer solution at 60°C. After the desired reaction time, which was 8, 12, 16, and 20 h, 100 mL of methanol was slowly added to stop the reaction. The sulfonated PNB copolymer with different DS, sP(BN/PhHN)-20, sP(BN/PhHN)-28, sP(BN/PhHN)-33, and sP(BN/PhHN)-40, were prepared successfully. The sulfonated copolymer was filtered, washed with deionizer water until neutral pH value. The final product was dried in vacuum at 37°C for 2 days.

Membrane Preparation

Membranes were prepared by casting 10 wt % chlorobenzene solutions of corresponding copolymer P(BN/PhHN) and sulfonated copolymers sP(BN/PhHN) onto a clean glass plate. The solvent was evaporated at 60°C. The dried membrane was removed from the glass plate by immersed in deionized water at 60°C and finally dried *in vacuo* at 50°C for 24 h. The membrane thickness was measured as a range of 80–110 μm at dry state using a digital micrometer.

RESULTS AND DISCUSSION

Structure and Property Copolymer

The reaction scheme for the synthesis of the sP(BN/PhHN) copolymer is illustrated in Scheme 1. As we all know, vinyl-type PNBs have poor solubility in common organic solvents, mechanical brittleness and low adhesive property limit the applications of PhHN. Copolymers or vinyl-type PNB derivatives with suitable pendant groups could improve the solubility and adhesion properties. We designed the norbornene ether derivative (BN and PhHN) by introducing a flexible alkyl side chain into the rigid norbornene backbone via ether linkages. The rigid

pendant aromatic rings were attached to the main chain through a rope-like flexible $-\text{O}(\text{CH}_2)_6\text{O}-$, which making the packing of the polymer chain tighter, thus the water uptake will be kept at a quite low and stable level even at elevated temperature and ion clusters formed easily. The obtained copolymers readily dissolved in THF, chlorobenzene, methyl-2-pyrrolidone, CHCl_3 , and so on.

Ni(II)-based catalysts are of particular interest because they provide PNB with excellent processability.¹⁸ For this reason, the vinyl addition polymerization of the two functional norbornene monomers used homogeneous bis(β -ketonaphthylamino)nickel(II) as a precatalyst and $\text{B}(\text{C}_6\text{F}_5)_3$ as a cocatalyst. The successfully synthesized of P(BN/PhHN) and sP(BN/PhHN) copolymers were confirmed by $^1\text{H-NMR}$ and FTIR spectroscopy.

Figure 1 displays the FTIR spectra of PhHN, P(BN/PhHN), and sP(BN/PhHN). In the spectrum of PhHN, the signals at 1246 cm^{-1} assigned to Ph-O-C , the signal of double bond at 1649 cm^{-1} and 1100 cm^{-1} assigned to C-O-C were observed, which indicated a successful synthesis of PhHN. In the spectra of P(BN/PhHN), the signal of double bond was not observed, which implied that polymerizations were carried out successfully. In the spectra of P(BN/PhHN) and sP(BN/PhHN), the peak at about 1470 cm^{-1} corresponded to the characteristic absorption of aromatic rings.¹⁹ After sulfonation, the appearance of characteristic peaks due to symmetric stretching of SO_3 at 1035 cm^{-1} was observed in spectrum sP(BN/PhHN)-40.²⁰ These results implied that sulfonation reactions were carried out successfully.

Figure 2 shows the $^1\text{H-NMR}$ spectra of the PhHN. The monomer exhibit the proton signals of norbornene skeleton at 0.7–2.2 ppm²¹ and 5.7–5.9 ppm ($-\text{CH}_2=\text{CH}_2-$) and norbornene $-\text{CH}_2-\text{O}-\text{CH}_2-$ in BN units corresponding to C_b, C_i at about 3.4 ppm. In the $^1\text{H-NMR}$ spectrum of monomer, introducing benzene group to the monomer produced peaks in the regions of 6.9, and 7.2 ppm associated to the proton signals of C_6H_5- , meaning that the benzene group was introduced successfully. The key resonance peaks were assigned to the appropriate protons, as marked in Figure 2.

Figure 3 shows the $^1\text{H-NMR}$ spectra of the P(BN/PhHN) and sulfonated copolymer sP(BN/PhHN)-40. We calculate the PhHN units in the block copolymer represent 12.3 wt % by $^1\text{H-NMR}$. After

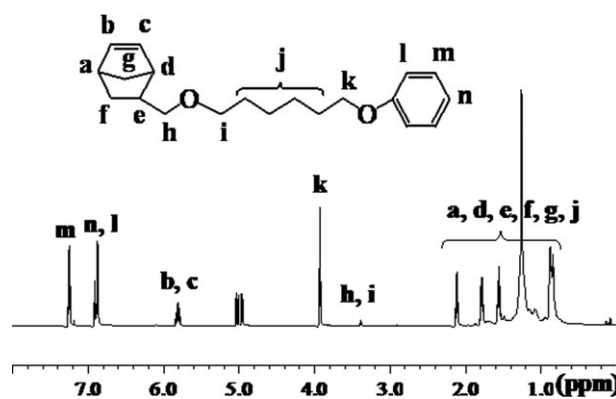


Figure 2. $^1\text{H-NMR}$ spectrum of PhHN.

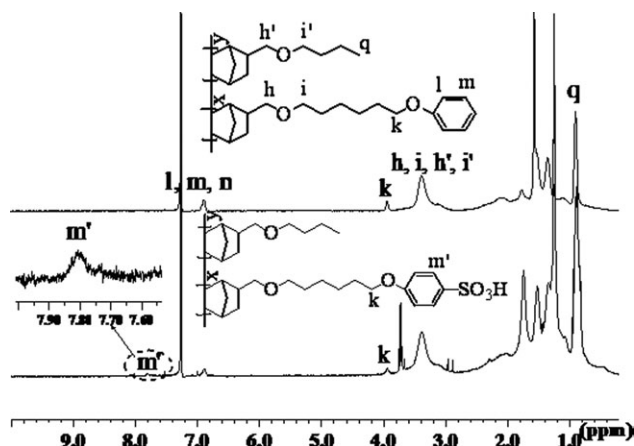


Figure 3. ¹H-NMR spectra of P(BN/PhHN) and sP(BN/PhHN)-40.

sulfonation, the presence of a peak at 7.8 ppm indicates that the sulfonic groups are successfully introduced onto the phenyl rings.

DS Values of sP(BN/PhHN)

The ¹H-NMR spectra of all sP(BN/PhHN) are exhibited in Figure 4. We can see the peak at 7.8 ppm increased as the content of sulfonation time. The DS of a sulfonated sP(BN/PhHN) was calculated from the area ratio between sulfonated and unsulfonated phenyl proton peaks in ¹H-NMR. The following equation is the DS of sP(BN/PhHN):

$$DS(\%) = \frac{m}{l} \times 100\% = \frac{C/2}{B/2} \times 100\%$$

where *m* and *l* are the number of repeat units sulfonated phenyl and unsulfonated phenyl; *C* and *B* represent the integrals of “*m*” and “*k*” peaks, respectively. These data are listed in Table I. The DS is observed to increase with reaction time.

WXRD of Copolymers

WAXD is widely used as a powerful tool for investigating the degree of crystallinity of a polymer and the structural changes in proton conducting membranes. The WAXD patterns for P(BN/PhHN) and sP(BN/PhHN) membranes with various DS are shown in Figure 5, where the intensity of the X-ray scattering is plotted against the diffraction angle. Two broad halos at

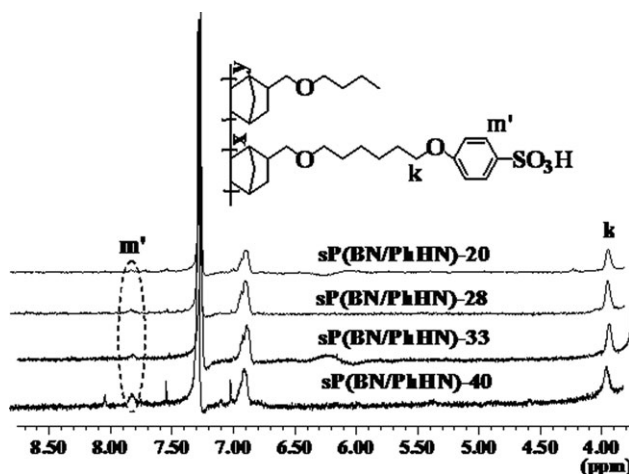


Figure 4. ¹H-NMR spectra of sP(BN/PhHN) with different DS.

2θ values of 6.7 and 19.1, which are characteristic for PNB homopolymer were observed. From the diffraction patterns, it was found that the intensity of both halos becomes weaker with the increase of DS. Perhaps due to the introduction of sulfonic acid groups, this may induce disorder of the polymer structure. This may suggest that the addition of sulfonic acid groups induced significant disorder into the P(BN/PhHN) polymer.

IEC, Water Uptake

IEC is an important measure of the proton conductivity and swelling properties of sulfonated copolymers and is related to the amount of H⁺ ions in a proton-conducting material. Typically, its theoretic value could be calculated by molecular formula and its experimental value was obtained by titration.^{22,23} The IEC values of the copolymer membranes measured by a titration method and calculated were listed in Table I. The IEC values of these copolymers determined experimentally by a titration method were in the range of 0.47–0.82 mequiv/g. These sP(BN/PhHN) membranes showed increased IEC value with the increasing of DS. All the experimental values basically coincide with the calculated ones. This further demonstrated that the sulfonate groups were successfully incorporated into the polymer backbones without any side reactions via copolymerization with sulfonated monomer.

Table I. DS, Water Uptake, IEC, Proton Conductivity and Methanol Permeability of sP(BN/PhHN) Membranes

Sample	DS (%)	Sulfonation time (h)	Proton conductivity at 70°C (×10 ⁻⁴ S cm ⁻¹)	Methanol permeability at 25°C (×10 ⁻⁸ cm ² s ⁻¹)	IEC ^a (mequiv/g)		Water uptake ^b (wt %)
					Calculated	titrated	
P(BN/PhHN)	0	0	–	2.06	0	0	0.52
sP(BN/PhHN)-20	20	8	1.16	2.60	0.40	0.47	3.6
sP(BN/PhHN)-28	28	12	3.04	3.36	0.56	0.55	3.9
sP(BN/PhHN)-33	33	16	9.72	33.0	0.66	0.71	5.2
sP(BN/PhHN)-40	40	20	33.5	65.8	0.80	0.82	9.4
Nafion 117	–	–	0.072 S cm ⁻¹	237	–	0.89	31.6

^aIEC measured with titration at room temperature, ^bMeasured at room temperature.

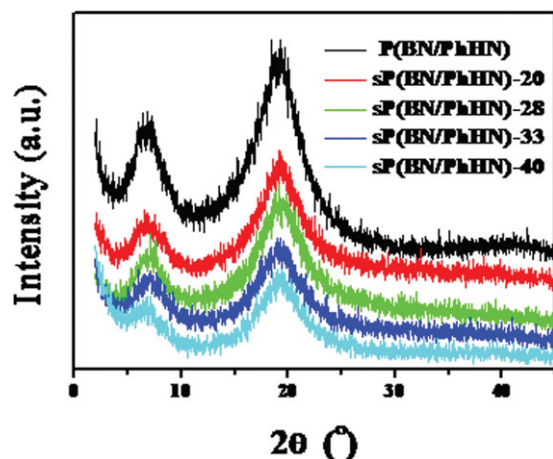


Figure 5. WAXS patterns for P(BN/PhHN) and sP(BN/PhHN) with different DS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

It is well known that water uptake is very important in PEMFC applications due to the dependence to water of proton conductivity and mechanical stability of PEMs. The proton exchange reaction requires a significant amount of water to coordinate with proton when the proton moves through the membrane. For this purpose, the membrane must be able to absorb enough water. However, overmuch water uptake and swelling will lead to the loss of mechanical strength, which will limit the practical application of the membrane in fuel cells. So selecting polymer membranes with appropriate levels of water uptake and swelling is very vital in PEMFCs.²⁴ The water uptake membranes were measured and the results are presented in Table I, the water uptake of membranes showed an increasing tendency with increasing of DS. The water uptake of the uncrosslinked materials increased when the IEC increased. This result suggests that the higher concentrations of sulfonic acid groups definitely induced the formation of aqueous clusters. Thus, increased incorporation of sulfonate groups generates higher hydrophilic-

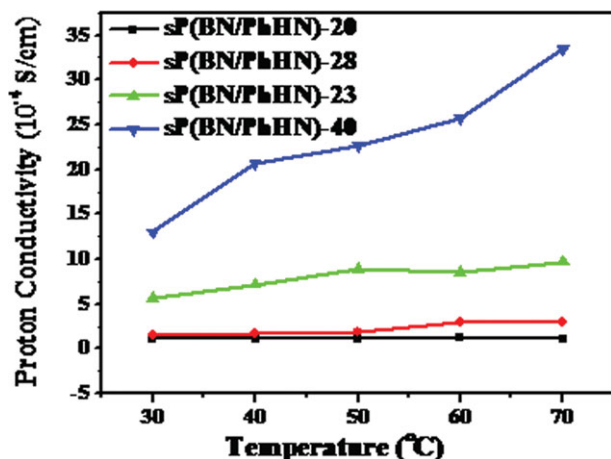


Figure 6. Proton conductivity of the sP(BN/PhHN) membranes with different DS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

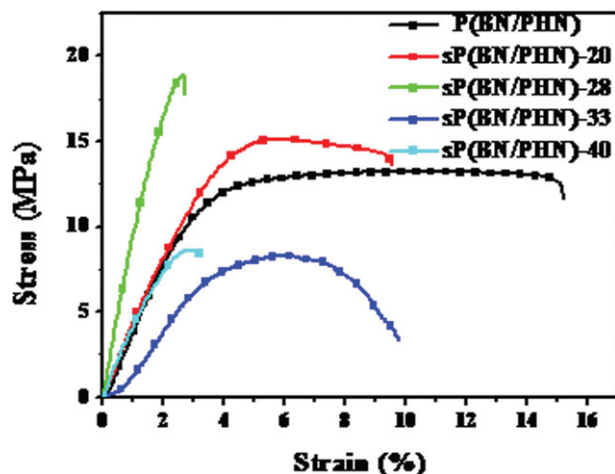


Figure 7. The tensile curves of P(BN/PhHN) and sP(BN/PhHN) membrane with different DS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ity and higher IECs. The distance between the organic polymer backbone and the acidic groups may also affect the water uptake, as shown from earlier studies.²⁵ At room temperature, all the membranes had water uptakes below 10%, the water uptake of these polymers were lower than that of other sulfonated polymers with similar IEC such as Nafion 117. The low water uptake property was owing to the lack of hydrophilic clusters and the long flexible aliphatic chain between the rigid main chain and pendant sulfonated aromatic groups which separated the hydrophobic main chain from the hydrophilic acid unit.

Proton Conductivity and Methanol Permeability

Proton conductivity is a key property of PEMs. To evaluate sP(BN/PhHN) membranes as candidates for PEMs, proton conductivity of sP(BN/PhHN) membranes was measured at different temperatures and shown in Figure 6. The values of proton conductivity increased as the increasing of temperatures, which suggested that the conductivity is a thermally activated process in these membranes. For the sP(BN/PhHN)-20 and sP(BN/PhHN)-28 membranes with low sulfonation degree, the proton conductivity increased very slowly in the entire temperature range studied. Proton conductivity of membranes was relatively lower than we expected. The sP(BN/PhHN)-40 with the maximum proton conductivity (3.35×10^{-3} S/cm) (IEC = 1.82

Table II. The Mechanical Properties of P(BN/PhHN) and sP(BN/PhHN) Membrane with Different DS

Sample	Tensile strength at break (MPa)	Elongation at break (%)	Elastic modulus (MPa)
P(BN/PhHN)	13.2	15.2	440.3
sP(BN/PhHN)-20	15.2	9.50	486.7
sP(BN/PhHN)-28	18.9	4.00	1020
sP(BN/PhHN)-33	8.30	9.80	253.8
sP(BN/PhHN)-40	4.30	3.30	476.0

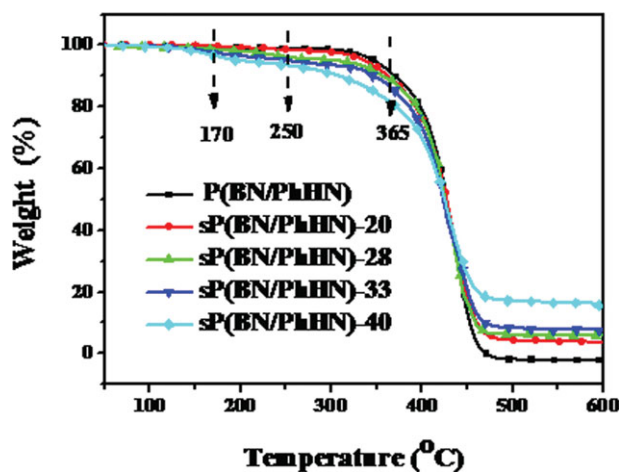


Figure 8. TGA of P(BN/PhHN) and sP(BN/PhHN) with different DS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mequiv/g), which is approximately one orders of magnitude lower than that of the commercial PEM material Nafion 117 (IEC = 1.89 mequiv/g). Table I shows the water uptake of these polymers was lower than that of other sulfonated polymers with similar IEC such as Nafion 117. It can be concluded that a lower water uptake plays a major role in controlling the proton conduction due to the decrease of proton carrier in the membrane. This conductivity, although not a significant breakthrough, is acceptable for small portable devices. We expect to improve the proton conductivity during future developments. Thus, the polymers described here remain potentially viable PEM materials.

Methanol permeability is a serious problem in fuel cells because it can result in fuel lost, efficiency reduction, and catalyst poison.²⁶ Especially, in DMFCs, methanol crossover is a major problem. Table I lists the methanol transport behavior of the sP(BN/PhHN) membranes in comparison with Nafion 117. The methanol permeability of these sP(BN/PhHN) membranes were in the range of $0.26\text{--}6.58 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, which were remark-

ably lower than the value $2.36 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ of the commercial PEM material Nafion[®] 117. All the sP(BN/PhHN) membranes possessed excellent methanol resistant property, which can be attributed to vinyl-type PNB as the main chain has good methanol resistant property. From the testing, it can be concluded that the prepared membranes would be met the request of methanol permeability for PEMFC applications.

Mechanical and Thermal Properties of the Membranes

The tensile curves of membrane with different DS are shown in Figure 7, and the mechanical properties are presented in Table II. As can be seen, the copolymer film shows better mechanical properties. The tensile strength increased firstly and then decreased with increasing DS values. This increase in the tensile strength for sP(BN/PhHN) membranes was because strong ionic interactions of sulfonic groups increased the interactions between molecular chains, restricted the stretch of backbone and hindered the strain during extension.²⁷ The decreasing in the tensile strength and elongation ratio for sP(BN/PhHN) may due to water absorption and since water in hydrated membranes acted as small molecular plasticizer, it makes the mechanical properties of the films damage.

The thermal stability of the copolymer and sulfonated copolymers were investigated by TGA in nitrogen, and the result is shown in Figure 8. The thermo gravimetric behavior of a polymer depends on its structure and the type of substituent in the main chain.²⁸ For all membranes with different DS values, a typical three-stage weight loss occurred. The first weight loss stage until about 170°C was attributed to the evaporation of absorbed water. The second stage (250–365°C) arose from the decomposition of pendant sulfonic acid groups, implying initial deterioration of membranes. Moreover, it could be inferred that higher DS, more sulfonic acid groups caused more weight loss when comparing the normalized weight loss of each membrane at second stage. The last stage at above 365°C was mainly due to main-chain decomposition. From the results above, it was concluded that the sP(BN/PhHN) was thermally stable to satisfy the requirement of thermal stability for the use in DMFC (>200°C).²⁹

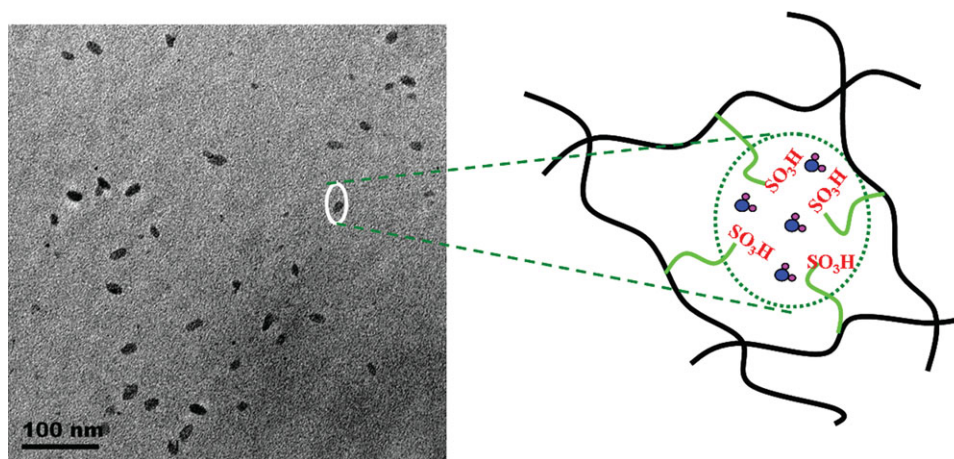


Figure 9. TEM image of sP(BN/PhHN)-40 membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Morphology of Membranes

The electrochemical behavior of sP(BN/PhHN) membranes should closely relate to their internal structures, especially, the spatial distribution of ionic site. The microstructure of the copolymer membranes was investigated with TEM. Figure 9 shows the morphology of the sP(BN/PhHN)-40 copolymer membranes. The membranes were stained with Ag⁺ ions; therefore, the dark areas represent hydrophilic (ionic) domains and the brighter areas represent hydrophobic domains. As it is clearly seen in Figure 9, sP(BN/PhHN)-40 membranes exhibited spherical ionic clusters, which contained aromatic biphenyl rings and sulfonic acid groups. The sulfonate groups aggregate and form clusters of hydrophilic nature to create pathways for ion transport. When this hydrophilic domain is hydrated, proton charge carriers dissociate from the SO₃²⁻ functional groups and proton conductance assisted by water dynamics occurs.³⁰

CONCLUSIONS

A kind of functionalized norbornene monomer 5-NB-2-CH₂O-C₆H₁₂O-C₆H₅ (PhHN) containing phenyl group on the pendant side chain was prepared and copolymerized with 2-BN successfully. The obtained copolymer was further sulfonated by concentrated sulfuric acid (98%) and the DS for membranes was controlled up to 20–40% by varying the sulfonating time from 8 to 20 h. FTIR, ¹H-NMR were involved to confirm the structure of achieved monomer, copolymer and sulfonated copolymer. The biggest DS calculated from the corresponding IEC value was 0.8, and corresponding water uptake was 9.4% much lower than that of Nafion[®] 117 of 31.6%, which lead to low proton conduction. The proton conductivity of sP(BN/PhHN) membranes increased with the increase of IEC values and temperature. The methanol permeability of the sP(BN/PhHN) membranes were in the range of 2.6 × 10⁻⁸ to 6.58 × 10⁻⁷ cm² s⁻¹ which were much lower than the value 2.37 × 10⁻⁶ cm² s⁻¹ of Nafion[®] 117. The tensile strength at break (from 18.9 to 4.3 MPa) and elongation at break (from 3.3 to 9.8%) for the sP(BN/PhHN) membranes indicated that the PEMs possessed good mechanical properties. In addition, the membranes also showed a high thermal decomposition temperature, at least up to 250°C. Microscopic phase separation occurred in sP(BN/PhHN) membrane and domains containing sulfonic acid groups were investigated by TEM.

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