

Vinyl-Addition Type Norbornene Copolymer Containing Sulfonated Biphenyl Pendant Groups for Proton Exchange Membranes

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ABSTRACT: The vinyl addition type copolymer poly(butoxymethylene norbornene-*co*-biphenyl oxyhexamethyleneoxymethylene norbornene) (P(BN/BphN)) was synthesized by using bis-(β -ketonaphthylimino)nickel(II)/B(C₆F₅)₃ catalytic system. P(BN/BphN) was sulfonated to give sulfonated P(BN/BphN) (SP(BN/BphN)) with concentrated sulfuric acid (98%) as sulfonating agent in a component solvent. The ion exchange capacity (IEC), degree of sulfonation (DS), water uptake, and methanol permeability of the SP(BN/BphN)s were increased with the sulfonated time. The methanol permeability of the SP(BN/BphN) membranes was in the range of 1.8×10^{-7} to 7.5×10^{-7} cm²/s, which were lower than the value 1.3×10^{-6} cm²/s of Nafion[®]115. The proton conductivity of SP(BN/BphN) membranes increased with the increase of IEC values, temperature, and water uptake. Water uptake of the SP(BN/BphN) membranes was lower than that of Nafion[®] 115 and leads to low proton conduction. Microscopic phase separation occurred in SP(BN/BphN) membrane and domains containing sulfonic acid groups were investigated by SEM and TEM. SP(BN/BphN) membranes had good mechanical properties, high thermal stability, and excellent oxidative stability. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Direct methanol fuel cells (DMFCs) have gained much attention as candidates for mobile power sources to portable electronic devices.^{1–5} Proton exchange membrane is a key component in the development of DMFCs, which directly transforming chemical energy into electrical energy without producing waste products and environmental problems.⁶ It has to meet several demanding requirements such as high proton conductivity, long-term stability in high levels of humidity and temperature, low permeability to fuel (methanol), simple manufacturing process, and low cost.

Besides the methanol crossover and the high cost, the state-of-the-art perfluorosulfonic acid membrane such as DuPont's Nafion[®] (Wilmington, Delaware) shows high proton conductivity and high chemical stability because of high phase-separated hydrophilic and hydrophobic domains, which makes it superior performance in fuel cell applications.⁷ One promising way to provide more distinct phase separation between hydrophilic and hydrophobic domains is locating the sulfonic acid groups on side chains.⁸

Currently, considerable efforts are being pursued to develop hydrocarbon-based polymers containing sulfonic acid groups on the side chains that can exhibit low cost and methanol cross-

over, high thermal stability, as well as easier processing for proton exchange membrane applications,^{9–14} including benzyisulfonated substituted poly(benzimidazole),¹⁵ polysulfone with sulfonated aromatic side chains, sulfonated derivatives of poly(*p*-phenylene).¹⁶

Vinyl addition polymerization of norbornene provides a completely saturated polymer with no rearranged norbornene units and remains double rings in the main chain, exhibits attractive physical properties such as good thermal stability, high optical transparency, low moisture absorption, and low dielectric constant. Shin et al.¹⁷ prepared a vinyl addition type polymer of *cis*-norbornene-*exo*-2,3-dicarboxylic acid dialkyl esters successfully. The polymer shows good solubility in common organic solvents and good thermal stability up to 330°C, and the process ability and the mechanical flexibility are significantly improved by the presence of polar side-chains in PNB. Therefore, PNB and PNB derivatives have been investigated on the proton-exchange membrane for DMFC applications.

In our previous study, a functional vinyl addition type polynorbornene graft copolymer membrane poly(butoxymethylenenorbornene-*co*-norbornenemethylene bromoisobutyrylate) grafted poly(hydroxy ethyl acrylate) [P(BN/NB)-*g*-PHEMA] has been

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synthesized.¹⁸ This graft copolymer is further crosslinked with 4,5-imidazole dicarboxylic acid (IDA) and then doped with phosphoric acid (H_3PO_4) to form imidazole- H_3PO_4 complexes in the membrane. The crosslinked membrane has good thermal stability, low methanol permeability and moderate proton conductivity at high temperature.

The objective of this article is to prepare a kind of functionalized norbornene containing biphenyl group on the pendant side chain via coupling reaction and etherification reaction and then copolymerized with a simple alkyl norbornene monomer by using bis(β -ketonaphthylimino)nickel(II)/ $\text{B}(\text{C}_6\text{F}_5)_3$ catalytic system. Using the concentrated sulfuric acid (98%) as the sulfonation reagent, degree of sulfonation (DS) was controlled by varying the reaction time. The achieved copolymer and sulfonated copolymer were confirmed through the analyses of FTIR and $^1\text{H-NMR}$. The water uptake, dimensional change, ion exchange capacity (IEC), degree of sulfonation (DS), methanol permeability, proton conductivity, mechanical strength, thermal behavior, morphology, oxidative stability, and cell performance of DMFC test are discussed and compared with Nafion[®] 115 membrane.

EXPERIMENTAL

Materials

5-Norbornene-2-methanol (86.4% endo, 13.7% exo) (Chongqing Hi-Tech chemical Co. Ltd, 98%, Chongqing, China) was used as obtained from the manufacturer. The catalyst bis(β -ketonaphthylimino)nickel(II) was synthesized according to the method reported in our previous work.¹⁹ Tris(pentafluorophenyl)borane ($\text{B}(\text{C}_6\text{F}_5)_3$, 95%) was purchased from J&K. 6-Bromo-1-hexanol (90%) was provided by Beijing Isomersyn Technology Co. Ltd (Beijing, China). *N*-butyl bromide (99%), 4-phenylphenol (98%), triphenylphosphine (TPP, 95%), diethyl azodicarboxylate (DEAD, 98%), and sodium hydride (NaH, 60%) was provided by Sigma-Aldrich (St. Louis, Missouri). Calcium hydride (CaH), sodium (Na), hydrochloride (HCl), and concentrated sulfuric acid (H_2SO_4 , 95–98%) were purchased from Sinopharm Chemical Reagent Co. Ltd (Beijing, China).

Synthesis of 4-(6-Bromohexamethyleneoxy)-biphenyl

A solution of *p*-phenylphenol (6.81 g, 40 mmol) and DEAD (17.4 g, 20 mmol, 18 wt % in toluene) in 40 mL of THF was added 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. After the addition was complete, the solution was stirred for 24 h. Then the solvent was evaporated, and the crude product was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate = 8 : 1, v/v). The product was obtained as colorless oily liquid. Yield: 7.79 g (78%) of product. $^1\text{H-NMR}$ (CDCl_3 , δ): 7.60–6.91 (m, 9H, $\text{C}_{12}\text{H}_9\text{-O-}$), 4.01 (t, 2H, $\text{-O-CH}_2\text{-}$), 3.44 (t, 2H, $\text{-CH}_2\text{-Br}$), 2.04–1.54 (m, 8H, $\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$).

Synthesis of Biphenyloxy Hexamethylene Oxymethylene Norbornene

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 tempera-

ture, and refluxing for 2 h, then 3.33g (0.01 mol) of 4-(6-bromohexamethyleneoxy)-biphenyl was added slowly (THF solution). The reaction was continued to stir for 24 h at 60°C. After being washed with deionized water, the organic layer was separated and dried with magnesium sulfate and concentrated by rotary evaporation. The product was purified by column chromatography (SiO_2 with eluent of petroleum ether: ethyl acetate (4/1 in v/v) and distilled at reduced pressure. Yield: 3.71 g (82%) of product. $^1\text{H-NMR}$ (CDCl_3 , δ): 7.62–6.86 (m, 9H, $\text{C}_{12}\text{H}_9\text{-O-}$), 6.05–5.88 (m, 2H, CH=CH), 3.96 (t, 2H, $\text{C}_{12}\text{H}_9\text{-O-CH}_2\text{-}$), 3.51–2.76 (m, 4H, $\text{-CH}_2\text{-O-CH}_2\text{-}$), 2.39–0.84 (m, 7H, norbornene-7H), 1.64–1.21 (m, 8H, $\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$).

Synthesis of Butoxymethylene Norbornene

The synthesis of butoxymethylene norbornene (BN) was followed by the method as described in the previous.¹⁸ Yield: 7.83 g (87%). $^1\text{H-NMR}$ (CDCl_3 , δ): 6.15–5.90 (m, 2H, CH=CH), 3.8–3.2 (m, 4H, $\text{-CH}_2\text{-O-CH}_2\text{-}$), 3.06–0.82 (m, 7H, norbornene-7H), 1.11 (t, 3H, -CH_3).

Copolymerization

The copolymerization of BN and biphenyloxy hexamethylene oxymethylene norbornene (BphN) was carried out in a 100 mL two-necked, round-bottom flask with a magnetic stirring bar and sufficiently purged with nitrogen by using the homogeneous bis(β -ketonaphthylimino)Ni(II) pre-catalyst with $\text{B}(\text{C}_6\text{F}_5)_3$ as co-catalysts. The mole feed ratio of BN and BPHN was 9 : 1, and the experiment process was followed by the method as described in the previous.¹⁸ The polymerization was terminated by venting off excess catalyst and addition with HCl/MeOH mixture (5/95, v/v). The resulting copolymer poly(butoxymethylene norbornene-*co*-biphenyl oxyhexamethyleneoxymethylene norbornene) (P(BN/BphN)) was separated off, washed with fresh methanol and deionized water, then dried in vacuum at 40°C until the weight remained constant.

Sulfonation of P(BN/BphN)

In a two-neck round-bottomed flask, 0.4 g of the copolymer P(BN/BphN) was dissolved in 20 mL of cyclohexane and 20 mL of ethyl acetate at 60°C and purged with nitrogen for 45 min. The concentrated sulfuric acid (98%) was added slowly to the polymer solution. The reaction flask was purged with nitrogen during the reaction. After the desired reaction time, 100 mL of methanol was slowly added to stop the reaction. The sulfonated P(BN/BphN) (SP(BN/BphN)) was filtered and washed with deionizer water until neutral pH. The final product was dried in vacuum at 40°C for 2 days.

Membrane Preparation

A 8 wt % solution of copolymer P(BN/BphN) and sulfonated copolymers SP(BN/BphN)s in THF were prepared and filtered. The solution was poured into a glass plate and stored at room temperature for 24 h. The residual solvent was evaporated in vacuum oven. The dried membrane was removed from the glass plate by immersed in deionized water at 60°C. The membrane thickness was measured at dry state using a digital micrometer. The thicknesses of fabricated membranes are in the range of 80–100 μm . Film forming properties of the polymers are related to their molecular weights, therefore, the molecular weights of

the P(BN/BphN) ($M_w = 1.07 \times 10^5$ g/mol) and SP(BN/BphN) of sulfonated 2 h ($M_w = 9.48 \times 10^4$ g/mol), 4 h ($M_w = 1.02 \times 10^5$ g/mol), 6 h ($M_w = 1.06 \times 10^5$ g/mol), and 8 h ($M_w = 9.16 \times 10^4$ g/mol) were tested.

Characterization

FTIR and $^1\text{H-NMR}$ Spectra. The FTIR spectrum spectroscopy was measured on a Shimadzu IRPrestige-21 FTIR spectrophotometer. NMR spectra were collected on a Bruker ARX 600 NMR with deuterated chloroform as the solvent and with tetramethylsilane ($\delta = 0$) as the internal standard.

Scanning Electron Microscopy and Transmission Electron Microscopy. 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 30 kV. 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 $-\text{H}$ of sulfonic acid groups with Ag ion, 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.

Thermal and Mechanical Analysis. The thermal gravimetric analysis (TGA) was performed using a Perkin-Elmer instrument TGA 7. Measurements were made by heating from room temperature to 670°C at a heating rate of $20^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed with a Shimadzu DSC-60 instrument calibrated with indium and tin under a high purity nitrogen flow. During the DSC experiment, the polymers were first heated to 400°C . The samples were then cooled to 50°C , followed by heating to 400°C . All heating and cooling rates were kept at $10^\circ\text{C}/\text{min}$. Tensile strength, elongation at break, and elastic modulus were measured with a CMT8502 Machine model GD203A (Shenzhen Sans Testing Machine Co. Ltd, China) at a speed of 5 mm/min.

Ion Exchange Capacity, Water Uptake, and Dimensional Change. Ion exchange capacity (IEC) of the membranes was measured by the classical titration method. The SP(BN/BphN) membranes were soaked in 1.5 M NaCl solution for at least 72 h before measuring IEC. The protons released due to the exchange reaction with Na ions were titrated with 0.005 M standardized NaOH solution, using phenolphthalein as an indicator. The IEC of the SP(BN/BphN) membranes was calculated from the following equation:

$$\text{IEC} = \frac{V(\text{NaOH}) \times C(\text{NaOH})}{M(\text{membrane})} \quad (1)$$

where $V(\text{NaOH})$ is the volume (mL) of NaOH solution consumed, $C(\text{NaOH})$ is the concentration of NaOH solution, and $M(\text{membrane})$ is the weight of the SP(BN/BPHN) membranes.

The membrane was dried at 80°C under vacuum over night until constant weight as dry material was obtained. It was immersed into deionizer water at room temperature for 48 h. Then the membranes were taken out, wiped with tissue paper, and quickly weighed on a microbalance. Water uptake of the membranes was calculated from

$$\text{Water uptake (\%)} = (W_s - W_d)/W_d \times 100\% \quad (2)$$

$$\text{Dimensional changes } \Delta T_c \text{ (\%)} = (T_s - T_d)/T_d \times 100\% \quad (3)$$

$$\Delta L_c \text{ (\%)} = (L_s - L_d)/L_d \times 100\% \quad (4)$$

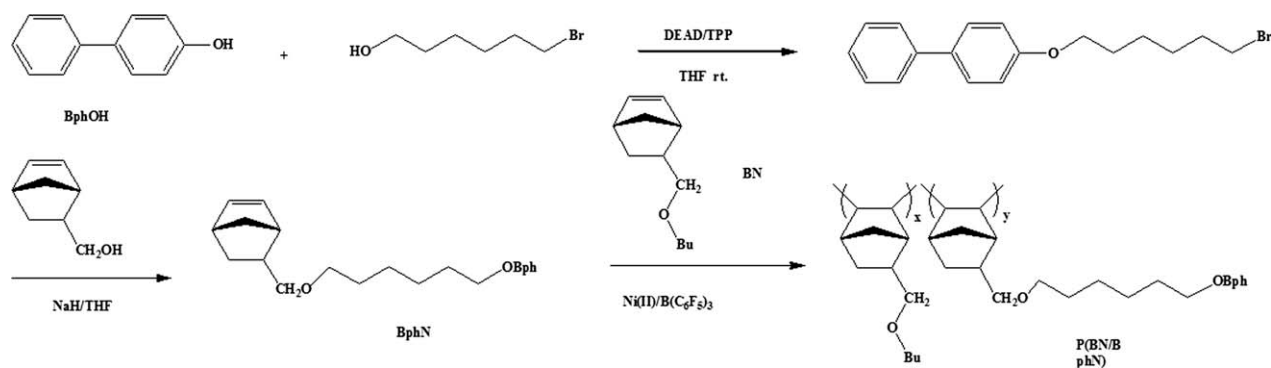
where W_d and W_s are the weights of dried and wet membranes, respectively. T_s , T_d , L_s , and L_d are the thickness and length of wet and dried membranes, respectively. Water uptake and dimensional changes of the samples were estimated from the average value of at least three measurements for each membrane.

Proton Conductivity and Methanol Permeability. 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 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 ($20\text{--}80^\circ\text{C}$) 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:

$$\delta = I/(RA) \quad (5)$$

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 1 M (C_1) methanol solution in distilled water. The other chamber (V_2) was filled with water. A sample (effective area 0.385 cm^2) 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



Scheme 1. Illustration of procedure for synthesis of P(BN/BphN).

versus time. The measurement temperature was room temperature. The membrane permeability (P) was calculated from the following equation:

$$P = S V_2 l / A C_1 \quad (6)$$

where A (cm^2) is the membrane area, l (cm) is the membrane thickness, C_1 is the methanol concentration, and V_2 is the volume of water.

Oxidative Stability. The oxidative stability of membrane was tested by soaking the film in Fenton's reagent (3% H_2O_2 aqueous solution containing 4 ppm of Fe^{2+}) at 80°C . The oxidative stability was evaluated by measuring the weight loss for the membrane after 10 days.

Performance Test of Single Cell. Cell performance was evaluated by using a DMFC unit cell in a commercial fuel cell test system (Arbin BT2000) at 70°C and membrane-electrode assemblies (MEA) was prepared by hot pressing. The Pt/Ru catalyst loading of the anode was $4 \text{ mg}/\text{cm}^2$ and the Pt catalyst loading of the cathode was $3 \text{ mg}/\text{cm}^2$. Two electrodes with effective area 6.25 cm^2 were hot-pressed onto a membrane for 3 min under pressure of $20 \text{ kg}/\text{cm}^2$ to form a MEA. The MEA was mounted in a single cell with stainless steel end plates and stainless steel mesh flow field as current collectors. Methanol (2M) was supplied to the anode with a micro-pump at $2.5 \text{ mL}/\text{min}$, while the cathode was supplied with dry air at a rate of $200 \text{ mL}/\text{min}$.

RESULTS AND DISCUSSION

Synthesis and Characterization of Copolymer

The reaction route for the synthesis of the P(BN/BphN) copolymer is illustrated in Scheme 1. The monomer BphN was prepared in an overall yield of 82% following the route shown in Scheme 1. This approach should be a general method for attaching aromatic systems to a norbornene.²⁰ Figure 1 shows the $^1\text{H-NMR}$ spectra of the copolymer obtained by bis-(β -ketonaphthylimino)nickel(II)/ $\text{B}(\text{C}_6\text{F}_5)_3$ catalytic system. The copolymer exhibit the proton signals of norbornene skeleton at 0.7–1.9 ppm²¹ and norbornene- $\text{CH}_2\text{—O—CH}_2\text{—}$ in BN and BphN units corresponding to C10, C11, C12, C13 at 3.0–3.5 ppm. In the $^1\text{H-NMR}$ spectrum of P(BN/BphN), introducing biphenyl group to the monomer produced peaks in the regions of 6.9, 7.1, 7.4, and 7.50 ppm associated to the proton signals of

$\text{C}_{12}\text{H}_9\text{—}$, meaning that the biphenyl group was introduced successfully. The composition of the copolymer was determined from the integral ratio of the signals originating from the PBN chains and the PBphN chains. From the $^1\text{H-NMR}$ spectra of the copolymer, it was found that the copolymer has a composition of 9 : 1 of PBN : PBphN, and the copolymer readily dissolved in the toluene, cycle hexane, THF, and chloroform, etc.

Sulfonation of Copolymer

The synthetic strategy for the synthesis of SP(BN/BphN) copolymer was depicted in Scheme 2. The sulfonic acid moiety was introduced to P(BN/BphN) copolymer via sulfonation. The criteria for selection of the best reagent for a specific polymer were based on its compatibility with polymer and film forming property besides the mechanical strength of the sulfonated polymer. Sulfonation was done with concentrated sulfuric acid (98%) as the procedure reported in the literature,²² but with slight modification. The FTIR spectra of copolymer P(BN/BphN) and sulfonated copolymer SP(BN/BphN) were shown in Figure 2. The peak at about $1470/\text{cm}$ corresponded to the characteristic absorption of aromatic rings.²³ After sulfonation, the new absorption band at $1054/\text{cm}$ was observed in the sulfonated copolymers SP(BN/BphN)s, which was assigned to the infrared absorption bands of S=O stretching vibration in sulfonic acid groups.²⁴ The results implied that sulfonation reactions were carried out successfully.

Characterization of Membranes

Water Uptake, Dimensional Change, IEC, and DS. The water in the membrane provides a carrier for the proton, and maintains high proton conductivity. However, excessive water uptake in a PEM will lead to unacceptable dimensional change or loss of dimensional shape, which could lead to weakness or a dimensional mismatch when incorporated into a membrane electrode assembly (MEA). Therefore, the preparation of sulfonated polymers with ideal water uptakes and dimensional stability are one of the critical demands for their application as PEMs.²⁵ The water uptake of P(BN/BphN) and SP(BN/BphN) membranes were determined by measuring the weight changes of membranes before and after absorption water. As shown in Table I, SP(BN/BphN) membranes exhibited water uptake in the range of 3.7–6.3%, depending on the sulfonation time. Furthermore, the water uptake value of SP(BN/BphN) was lower than that of Nafion[®] 115 of 32.6%, which may lead to lower proton conductivity of SP(BN/BphN) membrane than that of

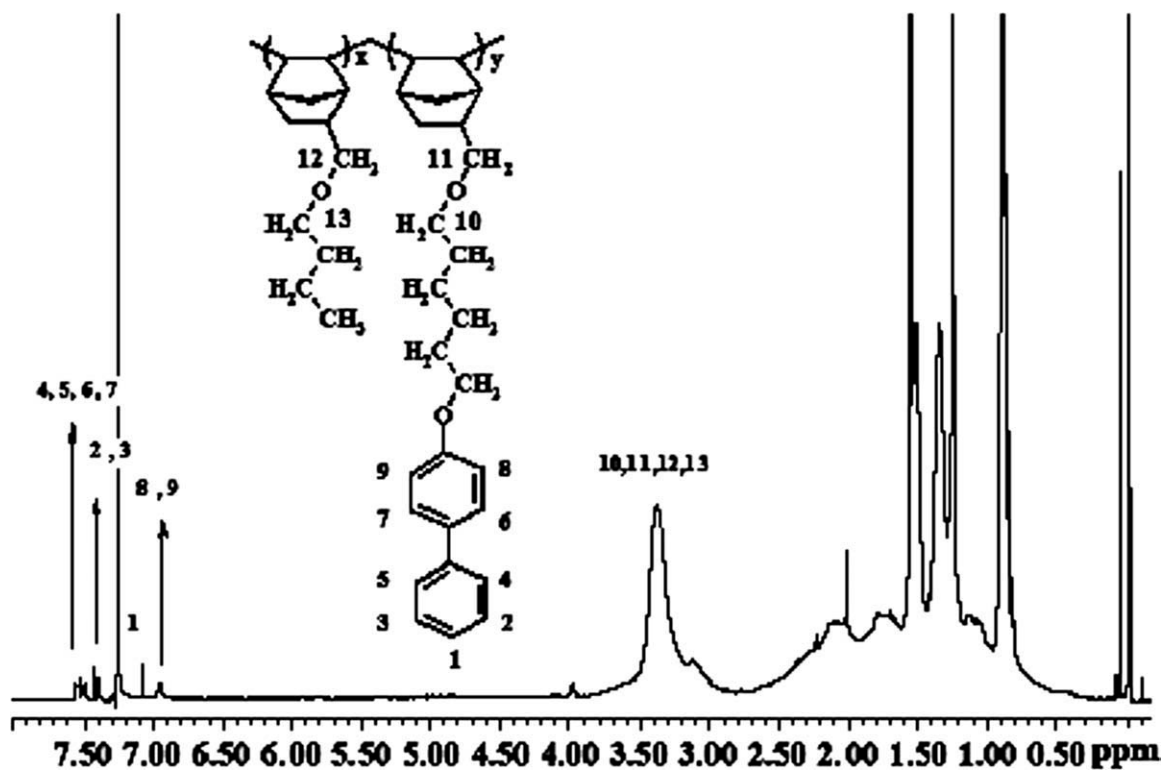


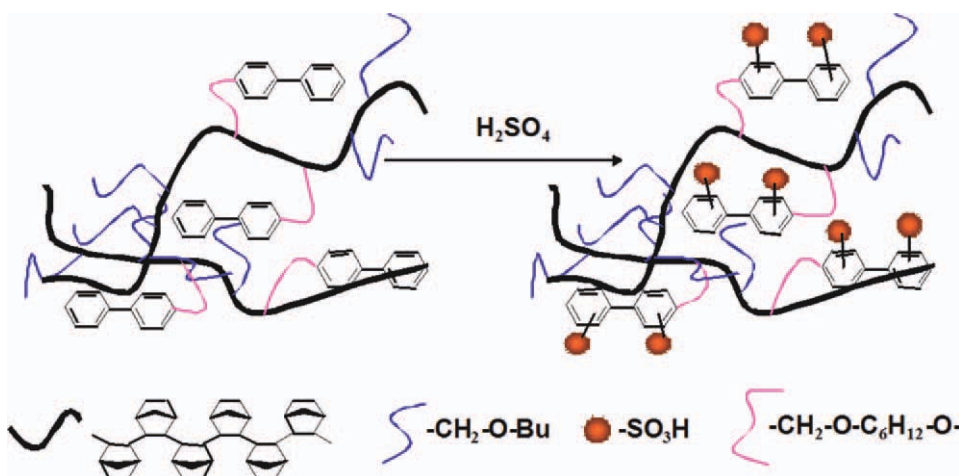
Figure 1. ¹H-NMR spectrum of the copolymer.

Nafion[®] 115. This needs further investigations in the upcoming studies. Because of the low water uptake, the P(BN/BphN) and SP(BN/BphN) membranes have a good dimensional stability.

As seen from Table I, due to the increase of sulfonic acid, the measured IEC values of the membranes increase from 0.68 to 1.11 mequiv/g with increase of sulfonated time varying from 2 to 8 h. The IEC value of SP(BN/BphN) membrane was higher than that of Nafion[®] 115 (0.88 mequiv/g) a little, which may lead to good proton conductivity of SP(BN/BphN) membrane.

The sulfonation level is commonly expressed using DS and IEC, where DS is defined as the average number of sulfonated groups per repeat unit and IEC (mequiv/g) indicates the number of milliequivalents of ions in 1 g of dry polymer. The DS can be calculated from the corresponding IEC value of SP(BN/BphN) membranes using the following equation:

$$DS = \frac{1976 \times IEC}{1000 - 81 \times IEC} \quad (7)$$



Scheme 2. Illustration of procedure for synthesis of SP(BN/BphN). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

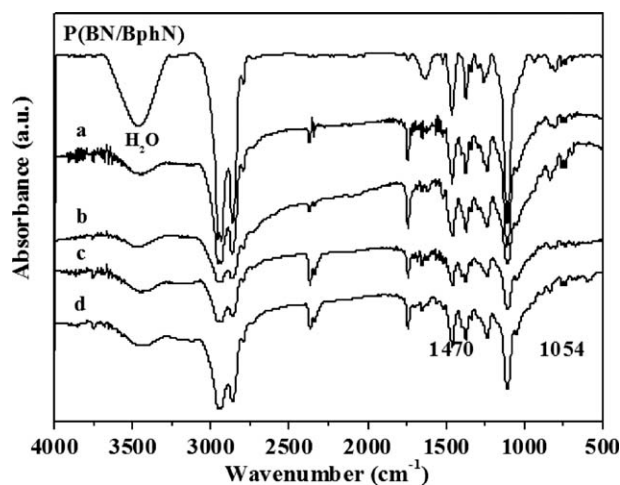


Figure 2. FTIR spectra of P(BN/BphN) and SP(BN/BphN) with different DS of (a) 1.42, (b) 1.62, (c) 1.77, and (d) 2.41.

The DS values are listed in Table I, increased as the sulfonation time increasing. It is suggested that the above equation could be used to the determination of the relative content of sulfonic groups introduced into the polymer chain.²⁶

Methanol Permeability and Proton Conductivity. As far as we know, the most significant shortcoming of Nafion[®] was its high methanol crossover in the DMFC application.²⁷ Table I indicated that SP(BN/BphN) membranes possessed excellent methanol resistant property. For SP(BN/BphN) membranes, and the methanol permeability were in the range of 1.8×10^{-7} to 7.5×10^{-7} cm²/s, which were remarkably lower than the value 1.3×10^{-6} cm²/s of Nafion[®] 115.

Figure 3 presents the relationship of methanol permeability and DS of SP(BN/BphN) membranes with sulfonation time. DS of SP(BN/BphN) membranes increased with sulfonation time increasing but the methanol permeability also increased with sulfonation time increasing. To obtain high proton conduction and low methanol permeability, DS must be controlled. When the sulfonation time was 8h, the DS was 2.14, the IEC value was 1.11 mequiv/g which was higher than that of Nafion[®] 115 and the methanol permeability of SP(BN/BphN) membranes was 7.5×10^{-7} cm²/s lower than that value 1.3×10^{-6} cm²/s of Nafion[®] 115.

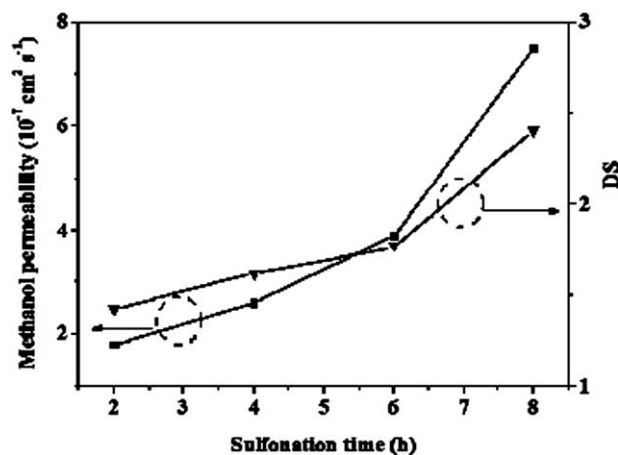


Figure 3. Methanol permeability and DS of SP(BN/BphN) membranes with sulfonation time.

In PEMFCs or DMFCs, proton conductivity of membranes is a crucial parameter because the cell performance strongly dependent on this property. The proton transport in membranes requires well-connected channels formed by ion clusters of hydrophilic sulfonic functional groups. The transport of ion and permeation of methanol highly depend on hydrophilic environment of highly polar sulfonic acid groups ($-\text{SO}_3\text{H}$) and hydrophobic environment of polymeric matrix, respectively.²⁸

Figure 4 presents the proton conductivity of the SP(BN/BphN) membranes as a function of work temperature. As expected, at a given temperature, the proton conductivity of SP(BN/BphN) membranes increased with the increase of IEC values. In addition, the values of proton conductivity increased as the temperatures increased.

It is well known that both water uptake and IEC have profound effects on membrane conductivity. Higher water uptake promotes the transportation of proton more effectively and higher IEC decreases the distance between anionic groups leading to faster proton conduction.²⁹ Figure 5 shows the proton conductivity of the SP(BN/BphN) membranes as function of IEC and water uptake (wt %) respectively. All the measured important properties related to proton exchange membrane were summarized in Table I. It can be concluded that a lower water uptake plays a major role in controlling the proton conduction due to

Table I. Water Uptake, IEC, Proton Conductivity, and Methanol Permeability of SP(BN/BphN) with Different DS

Membrane	Sulfonation time (h)	DS	IEC ^a (mequiv/g)	Water uptake ^b (wt %)	Proton conductivity at 70°C ($\times 10^{-4}$ S/cm)	Methanol permeability at 20°C ($\times 10^{-7}$ cm ² /s)
P(BN/BphN)	0	0	0	0.69	-	0.75
SP(BN/BphN)	2	1.42	0.68	3.7	0.82	1.8
	4	1.62	0.77	4.7	1.3	2.6
	6	1.77	0.83	5.2	3.5	3.9
	8	2.41	1.11	6.3	7.8	7.5
Nafion115 ^c	-	-	0.88	32.6	7.9×10^{-3}	13

^aIEC measured with titration at room temperature., ^bMeasured at room temperature., ^cMeasured under the same conditions as SP(BN/BphN) membranes.

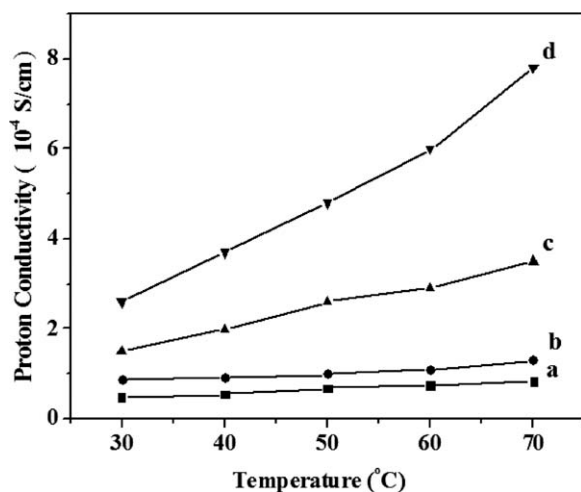


Figure 4. Proton conductivity of the SP(BN/BphN) membranes with different DS of (a) 1.42, (b) 1.62, (c) 1.77, and (d) 2.41 as a function of temperature.

the decrease of proton carrier in the membrane. The Nafion[®] 115 membranes exhibit the high value of proton conductivity due to the existence of large amount of water to promote the transportation of proton more effectively.

Mechanical and Thermal Properties of the Membranes. The tensile strength of P(BN/BphN) membrane and SP(BN/BphN) membranes with different DS is illustrated in Figure 6. The tensile strength of all SP(BN/BphN) membranes was higher than that of P(BN/BphN) membrane. This increase in the tensile strength for SP(BN/BphN) membranes maybe because that strong ionic interactions of sulfonic groups increased the interactions between molecular chains.³⁰ Big different film forming properties of membranes did not result from the molecular weight of copolymer and sul-copolymers.

The thermal stability of the copolymer and sulfonated copolymers were investigated by TGA in nitrogen, and the result is shown in Figure 7. The thermogravimetric behavior of a poly-

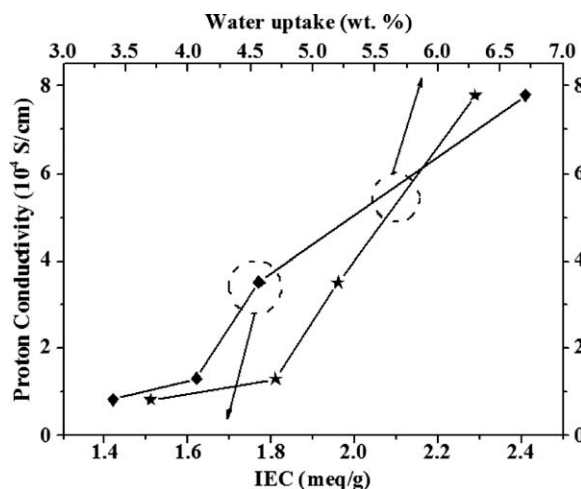


Figure 5. Proton conductivity of the SP(BN/BphN) membranes as function of IEC and water uptake (wt %).

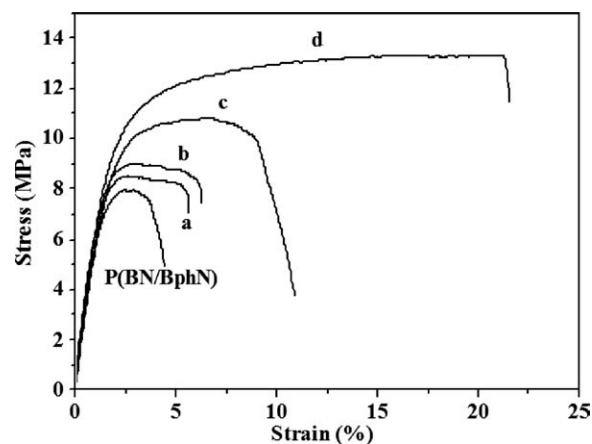


Figure 6. Mechanical properties of P(BN/BphN) membrane and SP(BN/BphN) membranes with different DS of (a) 1.42, (b) 1.62, (c) 1.77, and (d) 2.41.

mer depends on its structure and the type of substituent in the main chain.³¹ All sulfonated membranes exhibited a typical two-step degradation pattern. The initial weight loss of around 230 $^{\circ}$ C was attributed to the cleavage of the sulfonic acid and alkyl groups. The second weight loss around 380 $^{\circ}$ C is assigned to the decomposition of the polymer main chain. From the results above, it was concluded that the SP(BN/BphN) was thermally stable to satisfy the requirement of thermal stability for the use in DMFC (>200 $^{\circ}$ C).³² DSC curves and the T_g of the P(BN/BphN) and SP(BN/BphN) cannot be got because the copolymers had high T_g than their thermal decomposition temperature.

Oxidative Stability of Membranes. Chemical stability of proton exchange membranes is one of the most important factors that affect membrane durability. It is known that the formation of HO \cdot and HOO \cdot radicals by the catalytic process during PEMFC operation induces membrane degradation.^{33,34} Fenton test is an accelerated test, which is mostly used for the evaluation of oxidative stability of proton exchange membranes.³⁵

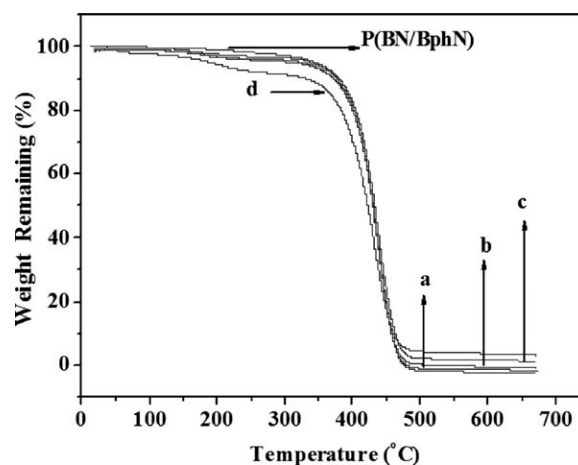


Figure 7. TGA curves for P(BN/BphN) and SP(BN/BphN) membranes with different DS of (a) 1.42, (b) 1.62, (c) 1.77, and (d) 2.41.

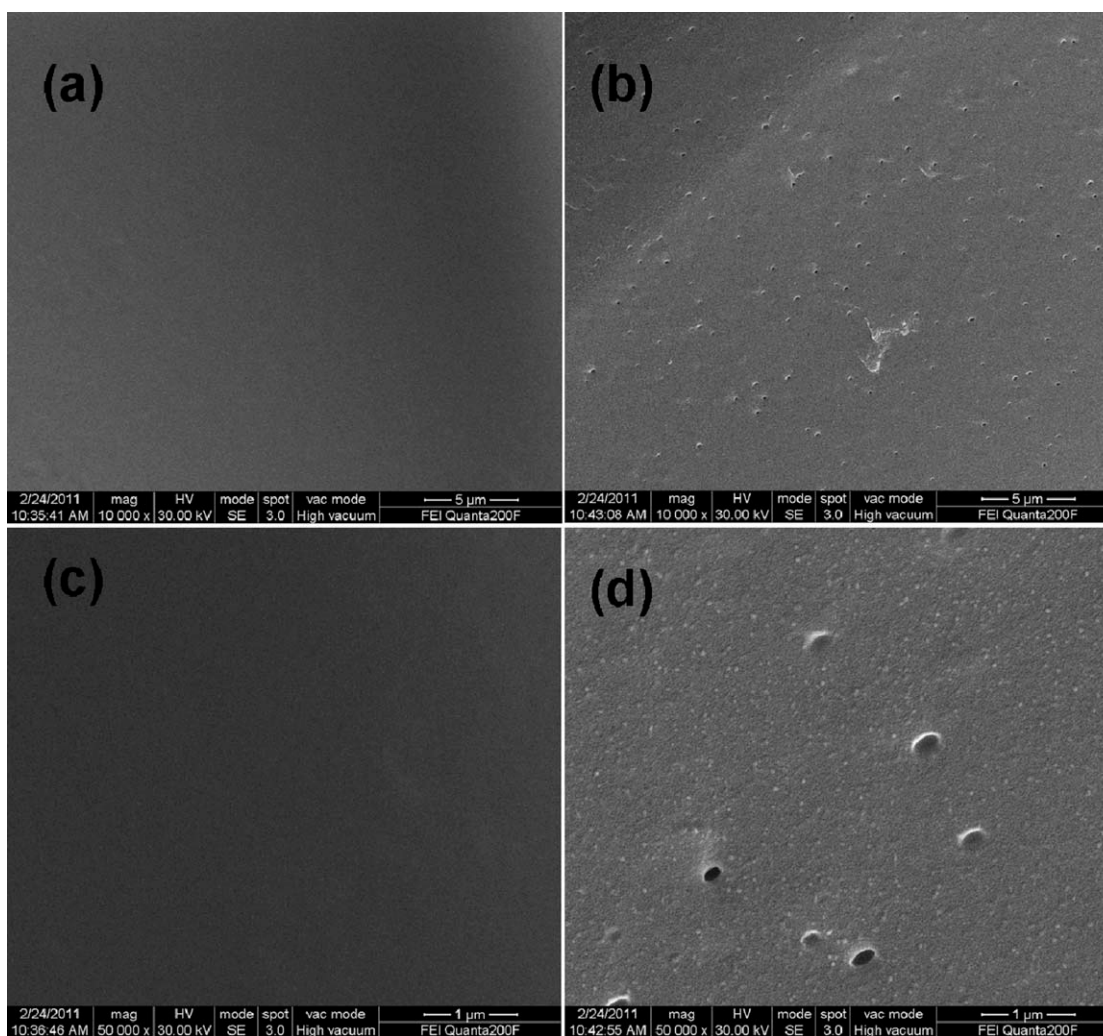


Figure 8. SEM cross-section of the membranes of (a) P(BN/BphN); (b) SP(BN/BphN) with DS of 2.41; (c) P(BN/BphN); and (d) SP(BN/BphN) with DS of 2.41.

After 10 days, the weight of all the membranes had no changes. It means that the P(BN/BphN) membrane and SP(BN/BphN) membranes showed excellent oxidative stability.

Morphology of Membranes. A cross-section image of the P(BN/BphN) and SP(BN/BphN) with DS of 2.41 membrane were obtained by SEM (Figure 8). From Figure 8(a,c), we can know that the P(BN/BphN) membrane has a very dense structure that was good for methanol resistance. After introducing $-\text{SO}_3\text{H}$ to the pendant side chain of SP(BN/BphN), the SP(BN/BphN) membrane showed some holes perpendicular to the direction of proton transfer which were caused by distinct microscopic phase separation occurred in PEM because of the coexistence of the hydrophobic and hydrophilic domains. Figure 8(d) shows that the small bright particles were homogeneously distributed inside the membrane. These small bright particles were the ion clusters containing aromatic biphenyl rings and sulfonic acid groups which conducted protons after hydration with the water.^{36,37}

To get a comprehensive understanding of the proton conductivity behavior of membranes, the membranes were examined by

transmission electron microscopy (TEM), which could provide some valuable insights as to the ordering and size of ionic domains in membranes. The sulfonic acid groups of sulfonation biphenyl pendant side chains stained with Ag^+ appeared as the dark region in the TEM micrographs, bright regions presented P(BN/BphN) chain domains.³⁸ Compared to Figure 9(b), there was almost no Ag^+ in the Figure 9(a) because that there was no sulfonic acid groups in the P(BN/BphN) membrane. The sulfonation biphenyl domains in SP(BN/BphN) with DS of 2.41 membrane were large and observed clearly. SP(BN/BphN) with DS of 2.41 membrane showed hydrophilic–hydrophobic micro-phase separation in Figure 9(b). This morphology may favor the easier transport of protons in the SP(BN/BphN) copolymer electrolyte membranes.^{39–41}

From the DS and morphology of membranes, we can see that the SP(BN/BphN) with DS of 2.41 membrane should have high proton conductivity. But in fact that the proton conductivity of SP(BN/BphN) was not high enough. The reason for low water uptake of the membranes should be that the main chain of the SP(BN/BphN) and the side chain of the PNB were too

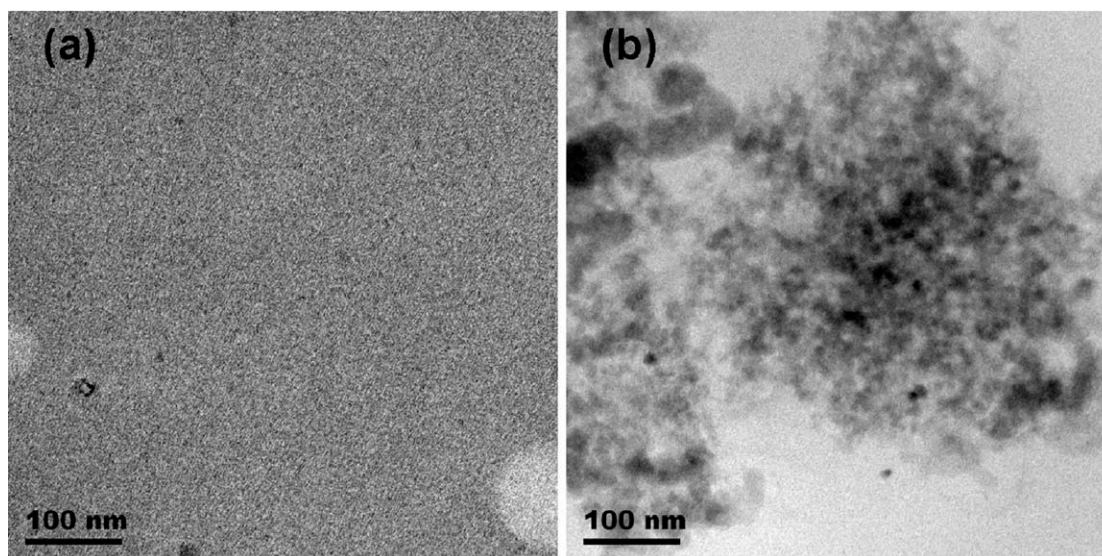


Figure 9. TEM images of Ag ion stained membranes (a) P(BN/BphN) and (b) SP(BN/BphN) with DS of 2.41.

hydrophobic to block water, which lead to not enough proton carrier to conduct the hydrated proton.

Cell Performance of DMFC Test. The single-cell performance of the SP(BN/BphN) with DS of 2.41 membrane and Nafion[®] 115 were prepared and tested at the temperature ranged from 30 to 80°C. The maximum power density was about 16 mW/cm² of Nafion[®] 115 and open circuit voltage was 0.559 V. This performance is a little lower than that of the commercial data⁴² due to the incomplete optimization of MEA preparation in the laboratory. The performance of SP(BN/BphN) with DS of 2.41 membrane was not better than that of Nafion[®] 115 under the conditions investigated in this study because of the low proton conductivity. The current density at the voltage of 0.06V was about 36 mA/cm², and the maximum power density was about 4.3 mW/cm² at the current density of around 144 mA/cm². These results indicate that the cell performance of SP(BN/BphN) membrane should be enhanced to have a potentiality as an electrolyte for DMFC.

CONCLUSIONS

The vinyl addition type copolymer poly(butoxymethylene norbornene-*co*-biphenyl oxyhexamethyleneoxymethylene norbornene) (P(BN/BphN)) was synthesized by using bis-(β -ketonaphthylimino)nickel(II)/B(C₆F₅)₃ catalytic system, followed by sulfonation to give sulfonated P(BN/BphN) (SP(BN/BphN)). The sulfonated time was controlled to be 8 h as the highest to obtain lower methanol permeability and the higher IEC. Microscopic phase separation and clusters were clearly observed by SEM and TEM. The biggest DS calculated from the corresponding IEC value was 2.41, and corresponding water uptake was 6.3% lower than that of Nafion[®] 115 of 32.6%, which lead to low proton conduction due to hydrophobic main chain of the SP(BN/BphN) and the side chain of the PNB. The proton conductivity of SP(BN/BphN) membranes increased with the increase of IEC values and temperature. The methanol permeability of the SP(BN/BphN) membranes were in the range of

1.8×10^{-7} to 7.5×10^{-7} cm²/s, which were lower than the value 1.3×10^{-6} cm²/s of Nafion[®] 115. SP(BN/BphN) membranes all had good mechanical properties, high thermal stability, and excellent oxidative stability.

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