

Novel Membranes Based on Poly(5-(methacrylamido)tetrazole) and Sulfonated Polysulfone for Proton Exchange Membrane Fuel Cells

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ABSTRACT: Proton-exchange membrane fuel cells (PEMFC)s are increasingly regarded as promising environmentally benign power sources. Heterocyclic molecules are commonly used in the proton conducting membranes as dopant or polymer side group due to their high proton transfer ability. In this study, 5-(methacrylamido)tetrazole monomer, prepared by the reaction of methacryloyl chloride with 5-aminotetrazole, was polymerized via conventional free radical mechanism to achieve poly(5-(methacrylamido)tetrazole) homopolymer. Novel composite membranes, SPSU-PMTetX, were successfully produced by incorporating sulfonated polysulfone (SPSU) into poly(5-(methacrylamido)tetrazole) (PMTet). The sulfonation of polysulfone was performed with trimethylsilyl chlorosulfonate and high degree of sulfonation (140%) was obtained. The homopolymers and composite membranes have been characterized by NMR, FTIR, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). ¹H-NMR and FTIR confirmed the sulfonation of PSU and the ionic interaction between sulfonic acid and poly(5-(methacrylamido)tetrazole) units. TGA showed that the polymer electrolyte membranes are thermally stable up to ~190°C. Scanning electron microscopy analysis indicated the homogeneity of the membranes. This result was also supported by the appearance of a single T_g in the DSC curves of the blends. Water uptake and proton conductivity measurements were, as well, carried out. Methanol permeability measurements showed that the composite membranes have similar methanol permeability values with Nafion 112. The maximum proton conductivity of anhydrous SPSU-PMTet0.5 at 150°C was determined as $2.2 \times 10^{-6} \text{ S cm}^{-1}$ while in humidified conditions at 20°C a value of $6 \times 10^{-3} \text{ S cm}^{-1}$ was found for SPSU-PMTet2. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40107.

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INTRODUCTION

Quite recently, fuel cells have been alternative energy sources, which convert the chemical energy directly into electrical energy. Among various types of fuel cells, particularly proton exchange membrane fuel cells (PEMFCs) have attracted a great deal of interest due to their high energy conversion efficiency and their ability to address the environmental concerns related to current energy production. Proton exchange membrane, as the proton conductive material is one of the key components of the PEMFC for transferring protons between anode and cathode.^{1,2}

Perfluorosulfonic acid membranes, the best known example of which is DuPont's Nafion, are most widely used in fuel cell research. Nafion has been commonly used as the polymer electrolyte membrane in PEMFCs because of its high proton conductivity, high chemical stability, and excellent mechanical

properties. However, due to the high price, low stability at high temperatures, low conductivity at low humidity or high temperature, and high methanol permeability of Nafion restrict the extent of its application and commercialization.¹

Therefore, efforts are made to develop alternative membranes based on novel polymeric materials, cheaper than Nafion and with higher or similar conductivities. These membranes have been prepared from thermostable aromatic polymers such as sulfonated polyethersulfones,³ sulfonated polyetheretherketones (SPEEK),⁴ sulfonated polyimide,⁵ sulfonated polybenzimidazole (PBI),⁶ sulfonated polyphosphazenes,⁷ and sulfonated polysulfones (SPSU).^{8–10}

Among the aforementioned polymers, the SPSU is a good candidate for producing proton exchange membranes because of its low cost and commercial availability. Furthermore, polysulfones

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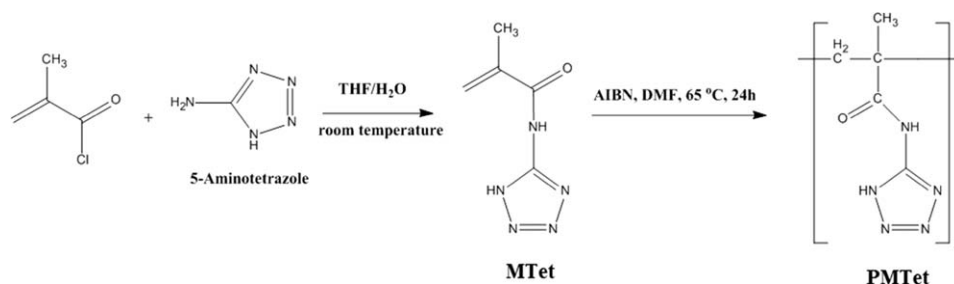


Figure 1. Synthesis and polymerization of tetrazole functional monomer.

(PSUs) show high thermal, chemical, and mechanical stability due to their phenyl rings on the polymer backbone. These aromatic polymers can be sulfonated by treatment with various sulfonating agents.^{9–11} The proton conductivity of the SPSU membranes depends on the sulfonation ratio and it can reach 10^{-2} S/cm at 80°C.¹⁰ In addition, the SPSU membranes have lower gas and liquid (water and methanol) permeability than the sulfonated perfluorinated ionomers.^{12,13} The studies about SPSU are mostly based on humidity control²; however, there are only few reports^{1,16,17} regarding its use in anhydrous proton conducting systems.

Polymers bearing tetrazole moieties have been the focus of a great deal of attention because of their powerful energetic usage, biological activity, and high thermal stability. Aliphatic chains improve their fabrication property whereas the tetrazole side groups may act as proton donors and acceptors, which give rise to proton transport.¹⁸

Blending two or more polymers is a simple approach to develop polymer electrolyte membranes with the advantage of combining superior features of each component.^{19–21} In particular, molecules or polymers bearing azole heterocycles with high proton conductivity can be suitably incorporated into stable polymers showing good mechanical and thermal properties such as sulfonated poly(ether ether ketone) (SPEEK),^{22,23} SPSU,^{1,11,17,24,25} Nafion,²⁶ PAA,²⁷ and PSSA,²⁸ respectively. Previously polyvinyl triazole was blended with several acid functional polymers such as poly(vinylphosphonic acid) (PVPA),²⁹ poly(styrenesulfonic acid) (PSSA),³⁰ and Nafion.³¹ The proton conductivity of PVPA based composites were analyzed both in humidified and anhydrous states and reported as 2.2×10^{-6} and 0.022 S/cm, respectively.^{29,30} Sen et al. blended another azole polymer, poly(2,5-benzimidazole) (ABPBI) with poly(vinylphosphonic acid)³² and obtained stable membranes.

In this study, SPSU was blended with poly(5-(methacrylamido)-tetrazole) (PMTet), which has high proton transfer capability with tetrazole group in each repeating unit. Here, 5-(methacrylamido)tetrazole monomer was prepared by the reaction of methacryloyl chloride with 5-aminotetrazole. It was subsequently polymerized via conventional free radical mechanism to obtain PMTet. In another pot, PSU was sulfonated using trimethylsilyl chlorosulfonate (TMSCS) in 1,2-dichloroethane (DCE). Homogeneous and semitransparent proton conducting composite membranes, SPSU-PMTetX, were successfully produced by blending SPSU with PMTet at several molar ratios. SPSU, having a hydrophobic aromatic backbone and hydrophilic side groups, can possibly play a role in the proton trans-

port mechanism in conjunction with PMTet through sulfonic acid and azole moieties. The membranes were characterized with FTIR, NMR, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). The proton conductivities of the membranes were explored using an impedance analyzer.

EXPERIMENTAL

Materials and Preparation

The commercial PSU (Sigma-Aldrich), TMSCS (Sigma-Aldrich), DCE (Merck), methanol (Sigma-Aldrich), 5-aminotetrazole (Alpha Aesar), 1,4-dioxane (Merck), and dimethylformamide (DMF; Merck) were used without further purification. Methacryloyl chloride was purchased from Alfa Aesar and distilled prior to use. Azobisisobutyronitrile (AIBN; Merck) was recrystallized in THF prior to use.

Tetrazole functional monomer, MTet, was synthesized according to a procedure as depicted in Figure 1.³³ Methacryloyl chloride (10.7 g, 10.0 mL, 102 mmol) was added dropwise to a suspension of 5-aminotetrazole monohydrate (10.0 g, 97.0 mmol) in THF (250 mL) and H₂O (12 mL) at room temperature. The solid dissolved during the addition of the first 3 mL of methacryloylchloride. After 15 min of stirring, the product began to precipitate, and the reaction mixture was diluted with water (250 mL), and was stored overnight in a refrigerator. The colorless solid was collected by filtration, washed with water (4×20 mL), and dried *in vacuo* at 20°C.

Then, azole functional methacrylic homopolymer was prepared using conventional free radical polymerization. A solution of 5-(methacrylamido)tetrazole (2.00 g, 13.1 mmol) and azobisisobutyronitrile (AIBN; 20 mg, 0.12 mmol) in DMF (20 mL) was degassed and stirred overnight at 65°C as depicted in Figure 1. The reaction mixture was then added dropwise to methanol (250 mL)/concentrated hydrochloric acid (5 mL). The colorless solid was collected by filtration, washed with methanol (4×20 mL), and dried *in vacuo* at 80°C.³³

SPSU (Figure 2) was prepared according to Ref. 14 The commercial PSU was dissolved in DCE at 25°C for 4 h under nitrogen atmosphere. TMSCS was added at room temperature as the sulfonation agent. PSU/TMSCS mole ratio was set as 1 : 2. During the reaction, N₂ was purged continuously through the reaction solution and HCl was constantly produced and released out of the reactor with N₂. After about 36 h, methanol was added to quench the reaction and to cleave the silyl sulfonate moieties yielding SPSU. Silicon containing compounds, methyl

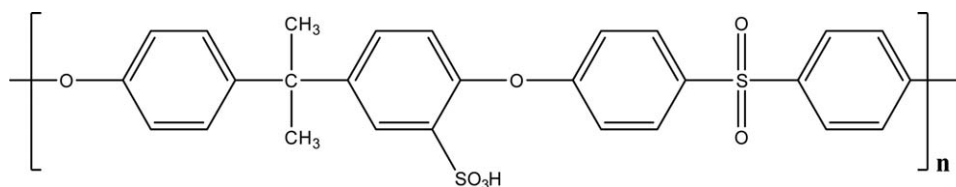


Figure 2. Structure of sulfonated polysulfone (SPSU).

sulfate, DCE, methanol, and water were removed through evaporation and then the polymer was dried *in vacuo* (400 mmHg) at 55°C.

The degree of sulfonation (DS) of SPSU was determined by acid–base titration with standard NaOH solution. Initially, the SPSU was dissolved in DMF. The solution of polymer was then titrated by an aqueous solution of 0.0147 N NaOH using phenolphthalein as the indicator. The titration gave a sulfonation ratio of 140% [(mol SO₃H/repeat unit) × 100], which was higher than those reported for this sulfonation method (127%).^{1,14}

Proton conducting composite membranes were prepared by doping of SPSU with PMTet. A stoichiometric amount of SPSU and PMTet was admixed in DMF with the following mol ratios: SPSU : PMTet : 1 : 0.5, 1 : 1, 1 : 2. The dissolution was completed with mechanical stirring at ambient temperature overnight. The membrane was prepared by casting of the SPSU–PMTet solution on a polished polytetrafluoroethylene dish, and the solvent was slowly evaporated at 50°C for 24 h. To ensure complete solvent removal, the membranes were placed under vacuum at 50°C. Homogeneous and semitransparent membranes were obtained (Figure 3).

Characterizations

FTIR spectra were recorded using a Bruker Alpha-P in ATR in the range of 4000–400 cm⁻¹. ¹H-NMR and ¹³C-NMR spectra were recorded using a 400 MHz Bruker Avance spectrometer. Chemical shifts are reported in ppm relative to TMS as internal standard.

Thermal stabilities of the polymer electrolytes were examined by a Perkin Elmer STA 6000 Thermal Analyzer. The samples (~10 mg) were heated from room temperature to 750°C under N₂ atmosphere at a scanning rate of 10°C/min.

Perkin Elmer JADE DSC was used to investigate the thermal transitions of the samples. The samples (~10 mg) were filled into aluminum pans and then heated to the desired temperature at a rate of 10°C/min under nitrogen atmosphere.

The proton conductivity studies of the samples were performed using a Novocontrol dielectric-impedance analyzer. The samples were sandwiched between platinum blocking electrodes and the conductivities were measured in the frequency range 1 Hz to 3 MHz at 10°C intervals. The temperature was controlled with a Novocontrol cryosystem, which is applicable between –150 and 250°C.

The surface morphology of blend membranes was investigated by SEM, JEOL-7001 FESEM (Tokyo, Japan). All of the samples

were coated with gold for 150 s in a sputtering device before SEM measurements.

Water uptake (WU) measurement was determined by the weight difference between the fully hydrated membranes and dried membranes. The dried membranes (W_{dry}) were weighed and then wetted until the weight remained constant. The wet or saturated weights of the membranes (W_{wet}) were measured quickly after removing or wiping out any remaining surface water with a paper. The WU was calculated according to the formula (2.1):

$$WU(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (2.1)$$

Methanol permeability was measured using our homemade diaphragm diffusion cell with a volume of 4 mL. The cell was filled with a pure methanol. Methanol vapor in equilibrium with the liquid diffused along the concentration gradient through the membrane, which was clamped between the mouth of glass and the cap. The cap has a hole with a 0.82 cm diameter so that the methanol diffused through the membrane could escape. The weight loss is recorded as a function of time and the data were used for permeability calculations.

The tapping mode AFM images of the blend membranes were acquired using a Park AFM (XE-100, Park AFM, Korea), supported on a Minus-K (25BM-6, Minus-K, Inglewood, CA) vibration isolation base. The AFM parameters to obtain the images were carefully set to minimize the pressure of tip on the composite membranes. 5 × 5 μm, 10 × 10 μm, and 20 × 20 μm images were acquired at a resolution of 512 × 512 points within the range of 0.5–0.8 Hz scan rate.



Figure 3. A picture of homogeneous and semitransparent SPSU–PMTet1 membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

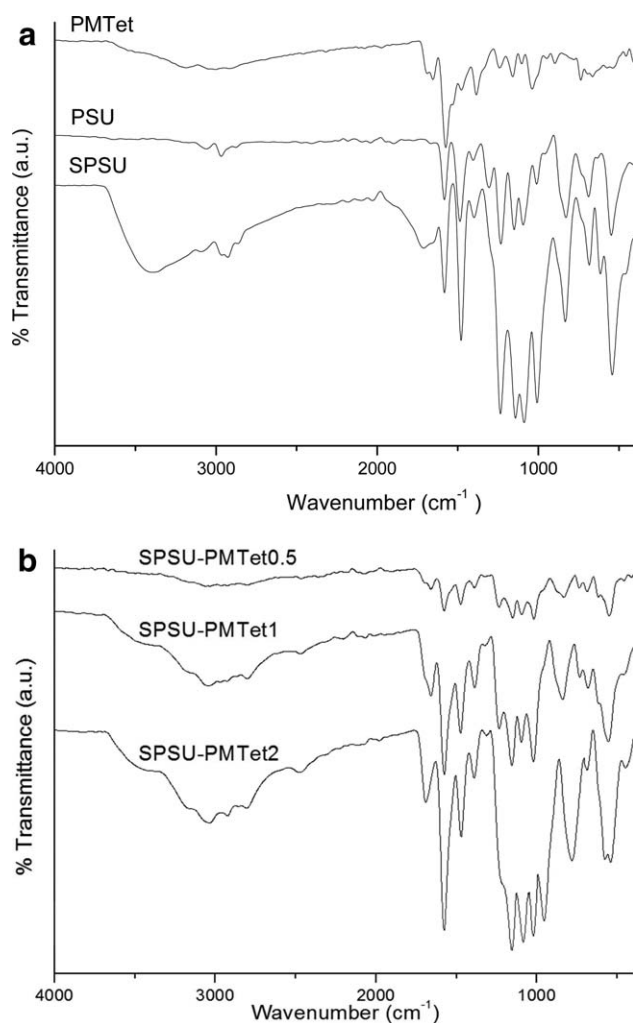


Figure 4. (a) FTIR spectra of polysulfone (PSU), sulfonated polysulfone (SPSU), and poly(5-(methacrylamido)tetrazole) (PMTet). (b) FTIR spectra of SPSU-PMTet0.5, SPSU-PMTet1, and SPSU-PMTet2.

RESULTS AND DISCUSSION

FTIR Studies

Figure 4(a) shows the FTIR spectra of pure PSU, SPSU, and PMTet. PMTet exhibited several medium or strong peaks between 1689 and 1475 cm⁻¹ due to amide bond and tetrazole ring vibrations, respectively.^{34,35} And also, PMTet has N=N stretching at 1245 cm⁻¹. The peaks at 735–1160 cm⁻¹ correspond to C–H stretching bands and the formation of a slightly broad peak at around 3200 cm⁻¹ shows the protonation of tetrazole rings. SPSU has peaks at 686, 1010, 1090, 1143, 1236, 1480, 2940, 3100, 3400 cm⁻¹, which correspond to C–S, SO₃, C–O, R–SO₂–R, C–O, C=C (aromatic), C–H (aliphatic), C–H (aromatic), and –OH stretching bonds, respectively. In FTIR of SPSU, the presence of OH peaks at 3400 cm⁻¹ and O=S=O stretching vibration of –SO₃ groups near 1010 cm⁻¹ confirms the sulfonation of PSU.^{1,12,14}

Figure 4(b) shows FTIR spectra of SPSU-PMTetX blends. The intensities of the bands corresponding to the azole ring stretchings at 1475 and 1650 cm⁻¹ have changed. SPSU-PMTetX exhibited a medium absorption at 1650 and 1475 cm⁻¹ due to

amide bond and tetrazole ring vibrations, respectively. SPSU-PMTetX blends have a peak at 3180 cm⁻¹ that corresponds to N–H stretching. Furthermore, between 3500 and 2000 cm⁻¹, a broadening of the band can be related to hydrogen bonding network formation N–H between heterocyclic PMTet homopolymer and SPSU (–SO₃H).

NMR Studies

Figure 5(a,b) show ¹H-NMR and ¹³C-NMR spectra of tetrazole functional monomer (MTet), respectively. The appearance of the peaks belonging to –NH proton of the tetrazole ring and amide bond proton at 15.90 and 11.97 ppm are a typical indication for the successful modification of methacryloylchloride monomer as depicted in Figure 5(a).³³ Also, the signals at 6.09 and 5.74 ppm are assigned to the methine proton (1H, –CH), which indicates in vinyl group. ¹H-NMR (400 MHz, DMSO-d₆, δ): 1.97 (s, 3H, CH₃), 5.74 (s, 1H, =CH), 6.09 (s, 1H, =CH), 11.97 (s, 1H, CONH), 15.90 (br s, 1H, tetrazole-NH). ¹³C-NMR (400 MHz, DMSO-d₆, δ): 18.2 (CH₃), 123.9 (CH₂), 137.6, 150.1, 166.7 (ipso-C, C=O).

Figure 6 illustrates the representative ¹H-NMR spectrum of PSU and SPSU. The proton resonance at around 7.70 ppm is assigned to the proton adjacent to the new pendant sulfonic acid.² Also, the aromatic –CH protons are depicted with numerical numbers. Consequently, FTIR and ¹H-NMR analysis

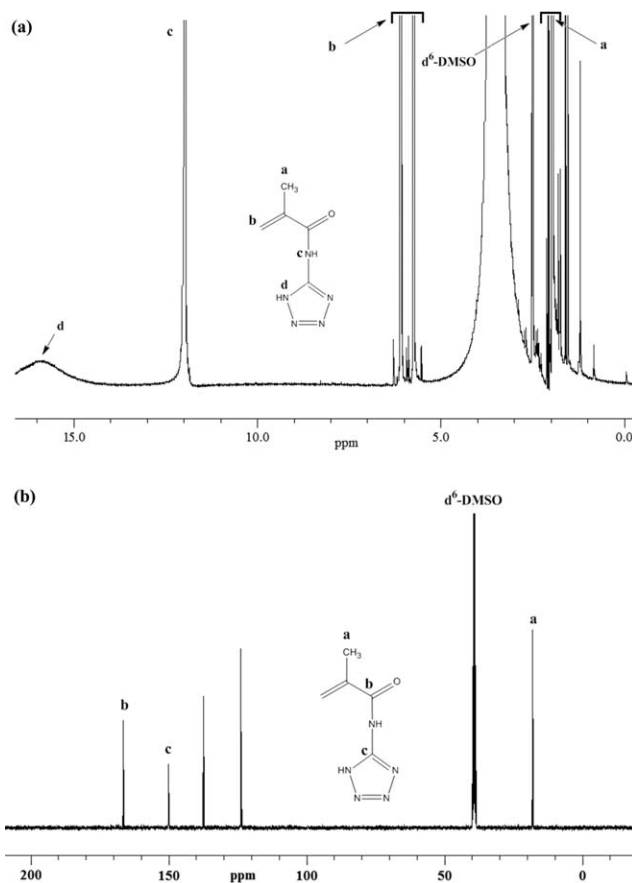


Figure 5. (a) ¹H-NMR spectra of MTet monomer recorded in DMSO-d₆. (b) ¹³C-NMR spectra of MTet monomer recorded in DMSO-d₆.

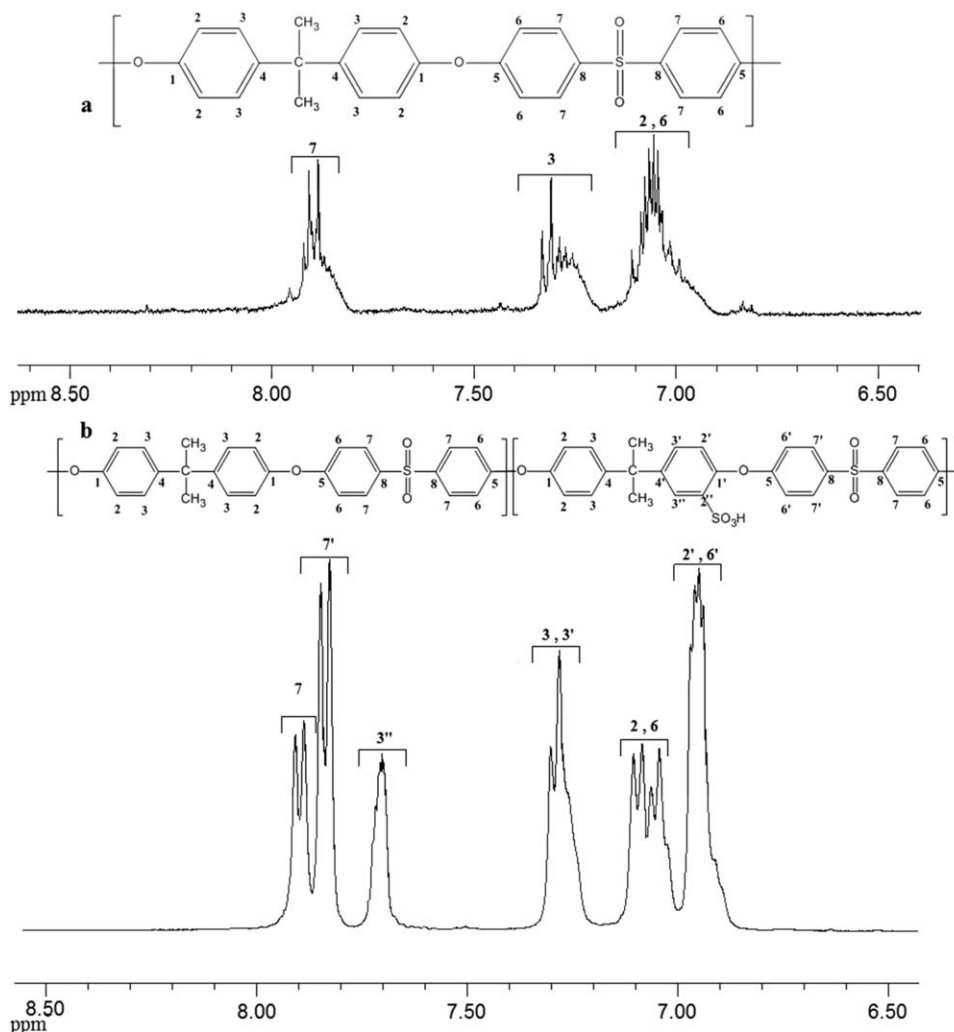


Figure 6. (a) ¹H-NMR spectra of polysulfone (PSU) recorded in DMSO-d₆. (b) ¹H-NMR spectra of sulfonated polysulfone (SPSU) recorded in DMSO-d₆.

confirmed the successful electrophilic substitution of TMSCS and chlorosulfonic onto PSU.²

Thermal Analysis

TGA of PMTet, PSU, SPSU, and SPSU-PMTetX ($X = 0.5, 1.0,$ and 2.0) membranes was reported in Figure 7. PMTet exhibited a thermal stability up to 220°C 40% of PMTet decomposes between 220 and 380°C because of degradation of tetrazole units and after 380°C, second weight loss region occurs because of decomposition of the polymer backbone.^{34,35}

Pure PSU is thermally stable up to around 500°C and there is only one weight loss step that is ascribed to the decomposition of the polymeric backbone.¹³ For the SPSU, there are three transitions of weight loss in three separate temperature ranges can be separated in the Figure 7. The first step around 100°C is related to the loss of the absorbed water. The second one, SPSU has weight loss region where 40% weight loss occurs between 200 and 370°C, can be assigned to the degradation of sulfonic acid groups. The third thermal degradation of SPSU after 460°C is attributed to the degradation of polymer backbone.^{2,15,36} This

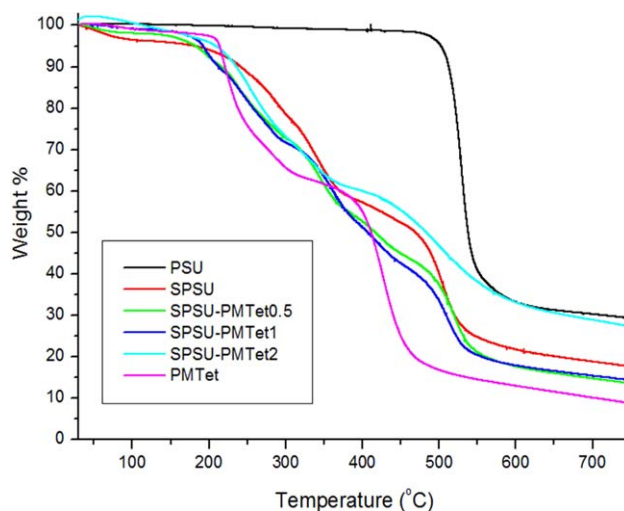


Figure 7. TGA curves of PMTet, PSU, SPSU, SPSU-PMTet0.5, SPSU-PMTet1, and SPSU-PMTet2 at a heating rate of 10°C min⁻¹. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. T_g of PSU, SPSU, PMTet, and Blend Membranes

Sample name	Polymer/polymer ratio	T_g (°C)
PSU	-	190°C
SPSU	-	128°C
PMTet	-	93°C
SPSU-PMTet0.5	1 : 0.5	183°C
SPSU-PMTet1	1 : 1	176°C
SPSU-PMTet2	1 : 2	185°C

distinct change in TGA curve also verifies the sulfonation of PSU. As SPSU was blended with PMTet, the degradation temperature decreased a little but all SPSU-PMTetX blends can be said to be thermally stable at least 190°C.

Table I shows the glass transition temperature, T_g , of PSU, SPSU, SPSU-PMTetX ($X = 0.5, 1,$ and 2) under inert atmosphere at a scan rate of 10°C/min, respectively. DSC curves of PSU, SPSU, PMTet, and SPSU-PMTetX ($X = 0.5, 1,$ and 2) composite membranes are given in Figure 8. In DSC measurements, the second heating curves were evaluated. The T_g of pure PSU was measured as 190°C. After sulfonation, the T_g decreased to 128°C. T_g of PMTet is measured at ~93°C. When PMTet is incorporated into the SPSU, the glass transition temperatures of blend membranes, SPSU-PMTet0.5, SPSU-PMTet1, and SPSU-PMTet2 were shifted to 183°C, 176°C, and 185°C, respectively (Figure 8). In the present blend membranes the presence of single T_g confirms the homogeneity of the materials. The composite membranes have higher T_g points than pure SPSU and PMTet, which also confirms the formation of ionic interaction between tetrazole and sulfonic acid groups.

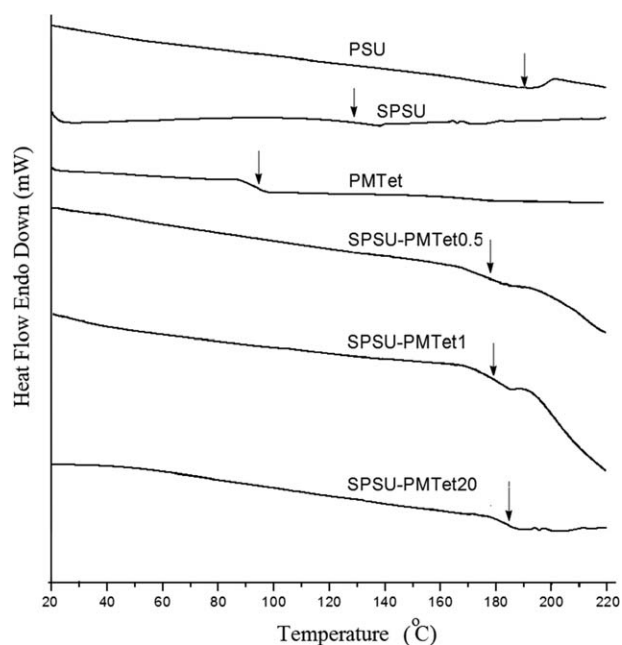
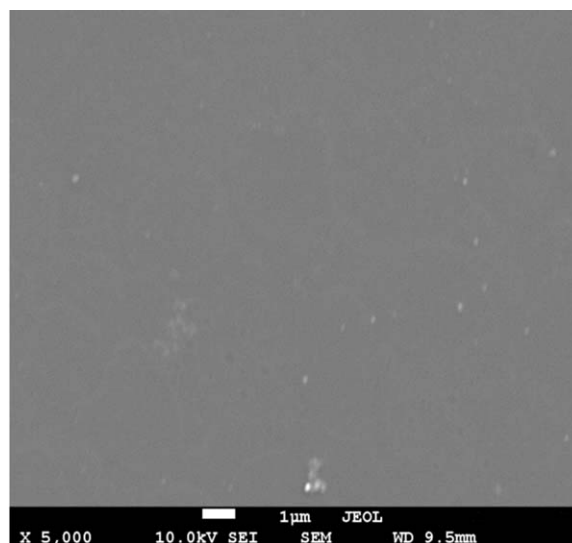
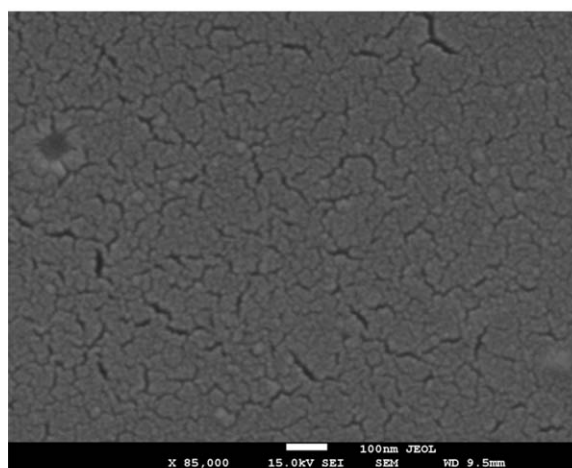


Figure 8. DSC thermograms of PSU, SPSU, PMTet, and SPSU-PMTetX ($X = 0.5, 1,$ and 2) composite membranes recorded under N_2 atmosphere at a heating rate of 10°C/min.



(a)



(b)

Figure 9. (a) SEM micrographs of the surface of SPSU-PMTet0.5. (b) SEM micrographs of the surface of SPSU-PMTet1.

Morphology

Surface morphologies of the blend membranes were investigated by SEM and depicted in Figure 9. For all the samples, the images show single phase formation due to strong interaction between the sulfonic acid groups of SPSU and the tetrazole units of PMTet and the membranes seem homogeneous. This shows that the heterocyclic dopant PMTet uniformly distributed into the PSU matrix, and there is no agglomeration or phase separation at nanoscale and micrometer-scale level.^{1,29}

Water Uptake

The WU of the membranes is a major parameter influencing proton conductivity, mechanical property, and stability. The WU measurements were made according to the Ref. 37. WUs of the SPSU-PMTetX ($X = 0.5, 1,$ and 2) membranes are shown in Figure 10. As can be seen, WU with increasing sulfonic acid content due to swelling of SPSU in the blend. This is due to the fact that the sulfonic acid groups are hydrophilic and hence in order to obtain the membranes, which have high DS

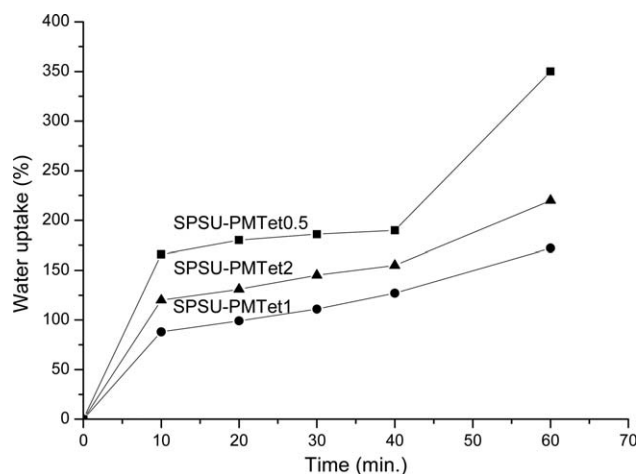


Figure 10. Water uptakes of SPSU-PM TetX ($X = 0.5, 1,$ and 2) at the time of 10–60 min in deionized water at 25°C .

polysulfone can absorb more water.³⁷ The swelling character of the samples reasonably decreased when there is equimolar of SPSU and tetrazole containing polymer. This finding is assigned to ionic interaction between SPSU and tetrazole containing polymer where the material becomes more rigid when $X = 1$. The sample with (1 : 0.5) composition has the highest WU value (350%).^{36,37} Clearly, the results showed that the increase in the sulfonic groups content in SPSU-PM TetX ($X = 0.5, 1,$ and 2) membranes improved the WU, and brought about better hydrophilicity.

Proton Conductivity

The AC conductivities, $\sigma_{ac}(\omega)$ of the polymers were measured at several temperatures using impedance spectroscopy. Frequency dependent AC conductivities [$\sigma_{ac}(\omega)$] were measured using the following eq. (3.1):

$$\sigma'(\omega) = \sigma_{ac}(\omega) = \varepsilon''(\omega)\omega\varepsilon_0 \quad (3.1)$$

where $\sigma'(\omega)$ is the real part of conductivity, $\omega = 2\pi f$ is the angular frequency, ε_0 is the vacuum permittivity ($\varepsilon_0 = 8.852 \times 10^{-14}$ F/cm), and ε'' is the imaginary part of complex dielectric permittivity (ε^*). The proton conductivities of anhydrous nano-composite polymer electrolytes were measured from 20 to 150°C .

Figure 11 shows the AC conductivity of SPSU-PM Tet1 versus log frequency at several temperatures. The conductivity increases with the temperature and the DC conductivity (σ_{dc}) of the samples was derived from the plateaus of σ_{ac} versus log frequency by linear fitting of the data (10^2 – 10^4 Hz at 110 – 150°C). The DC conductivities of SPSU-PM TetX ($x = 0.5, 1, 2$) were compared in Figure 12. It is clear that the DC conductivity strongly depends on the temperature and SPSU ratio. The maximum proton conductivity was obtained as 2.2×10^{-6} S/cm for all samples at 150°C .

SPSU has high thermal stability, good mechanical and film forming property and it was studied by several groups as proton conductive membrane. However, most of these works are in humidified condition.^{14,15} Firstly, SPUS/1H-1,2,3-triazole composite membranes were reported as anhydrous system but the

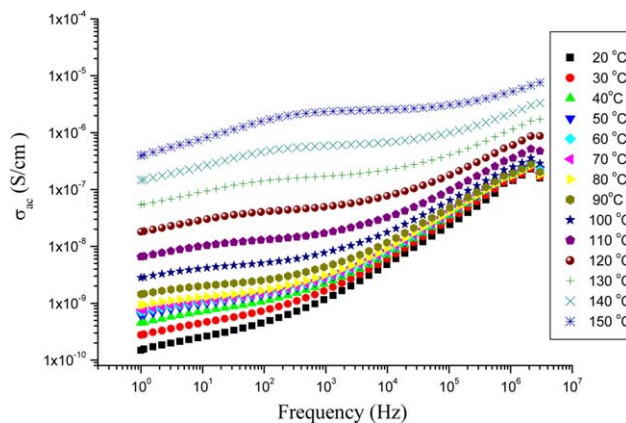


Figure 11. AC conductivity versus frequency of SPSU-PM Tet1 at several temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

system produced considerable proton conductivity at high dopant ratios.¹⁶ Manthiram and coworker attached 5-aminobenzotriazole to polysulfone backbone and after blending with sulfonated SPEEK they investigated the proton conductivity and reported values around 10^{-4} S/cm in anhydrous conditions.^{38,39} In another study phosphoantimonic acid was doped into SPSU and they investigated the proton conductivity in humidified state.⁴⁰ Previously, we studied SPSU/benzotriazole system, which resulted high proton conductivity at lower dopant ratios.¹ To be used in both humidified and anhydrous conditions, SPSU may be blended with azole containing polymer so that there is a proton transfer path between sulfonic acid and azole units. In addition, the absence of small molecules in the system prevents leaching and it is possible to use the membrane in low or high humidified states also.

5-Aminotetrazole is a heterocyclic molecule and previously used as proton source by immobilization into several polymer backbones.^{34,35} In these studies the tetrazole units provided high

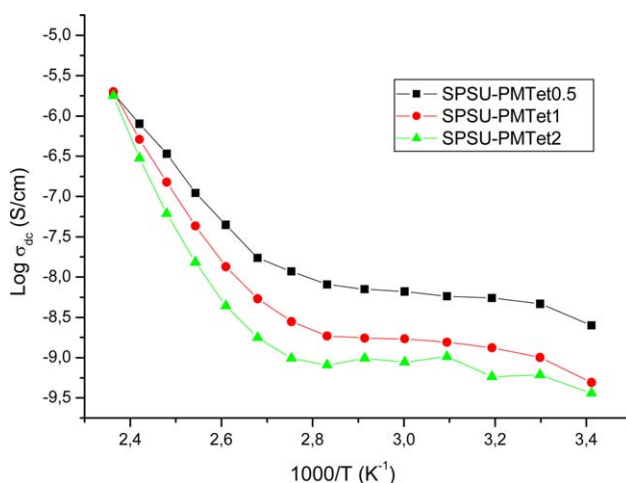


Figure 12. Variation of the DC proton conductivity of SPSU-PM Tet0.5, SPSU-PM Tet1, and SPSU-PM Tet2 as a function of reciprocal temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

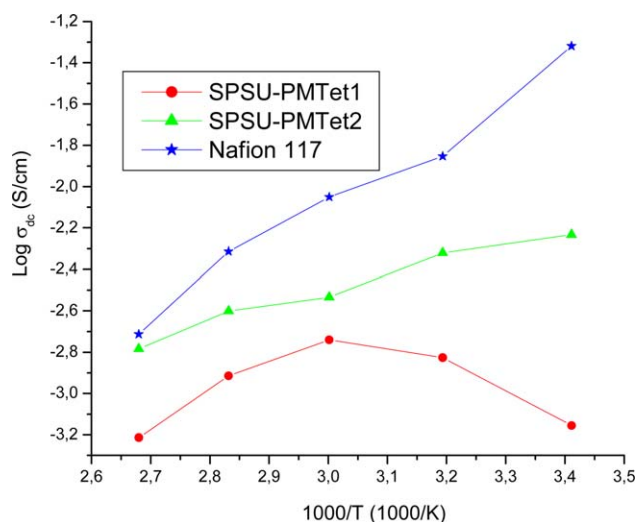


Figure 13. DC proton conductivity of fully humidified (100% humidity) SPSU-PMTet1, SPSU-PMTet2, and Nafion 117 as a function of reciprocal temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

proton conductivity after doping with triflic and phosphoric acids. However, these azole functional polymers have low film forming property and this makes them unsuitable for PEMFC applications.

In this work, 5-aminotetrazole was immobilized into methacryloyl chloride monomer and then PMTet homopolymer was produced via free radical polymerization. In addition, polysulfone was sulfonated with high ratio (140%) and blended with PMTet. Here PMTet is considered to make ionic interaction with sulfonic acid units of SPSU. As seen in SEM images the composite membranes are homogeneous but low proton conductivity may be due to ionic crosslink between PMTet and SPSU, which limits the proton transfer in the matrix.^{29,30} Therefore, the proton conductivity was investigated also in humidified condition and depicted in Figure 13. The proton conductivity values decrease with temperature due to the loss of water with temperature. As seen in the figure the proton conductivity of our samples are close to Nafion in the humidified condition. In addition, the membranes with higher SPSU ratio resulted higher proton conductivity values ($6 \times 10^{-3} \text{ S cm}^{-1}$).

Methanol Permeability

Methanol permeability is a possible problem in the application of the membranes in direct methanol fuel cells. At high methanol concentrations its permeability from anode side to the cathode side results polarization losses. In this work, methanol permeability of the composite membranes was measured by simple homemade diaphragm diffusion cell similar to the study of Gasa et al.^{41,42} The cell is filled with 2 mL methanol and the mass flow is recorded as a function of time (Figure 14). Molar methanol flux (J) through SPSU-PMTetX ($X = 0.5, 1, \text{ and } 2$) composite membranes was calculated using eq. (3.2). Methanol permeability of blend membranes may be calculated using molar flux (J) shown in eq. (3.3).^{26,43,44}

$$J = \frac{W}{M_W \times A \times t} \quad (3.2)$$

$$\frac{J_1 l_1}{J_2 l_2} = \frac{P_1}{P_2} \quad (3.3)$$

where J is the flux, M_W is the molecular weight, W is the weight loss (g), P is the permeability, l is the thickness (cm), A is the area (cm^2), and t is the time (s).

As seen in the equations the permeability is directly proportional to the molar flux. The molar flux of the SPSU-PMTetX ($X = 0.5, 1, \text{ and } 2$) composite membranes are shown in Figure 13. The values are $3.66 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$, $3.04 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$, and $1.91 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$ for SPSU-PMTet0.5, SPSU-PMTet1, and SPSU-PMTet2, respectively. Previously, we measured the methanol permeability of Nafion 112 in the same conditions and determined as $1.89 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$.²⁶ As seen in Figure 14 the methanol permeability of the composite membranes are very close to Nafion 112.

AFM

The selected AFM images of the SPSU-PMTetX ($X = 0.5, 1, \text{ and } 2$) membranes are illustrated in Figure 15. In this study, AFM was used for determination of phase morphology and homogeneity of the blend membranes. $5 \times 5 \mu\text{m}$, $10 \times 10 \mu\text{m}$, and $20 \times 20 \mu\text{m}$ images were taken at a resolution of 512×512 points within the range of 0.5–0.8 Hz scan rate and were subjected to first-order flattening. For all the samples in Figure 15, the images exhibit a single phase formation and the membranes seem homogeneous at nanometer-scale level. This shows that the heterocyclic PMTet homopolymer uniformly distributed into the SPSU matrix when the PMTet mol ratio was increased from 0.50 to 2.0. However, the surface image [in Figure 15(b,c)] shows regions, which are possibly due to salt formation between acid (sulfonic acid group)-base (azole groups) units. In Figure 15(a), the hole observed in nanometer scale might be related with the drying procedure for SPSU-PMTet0.5.

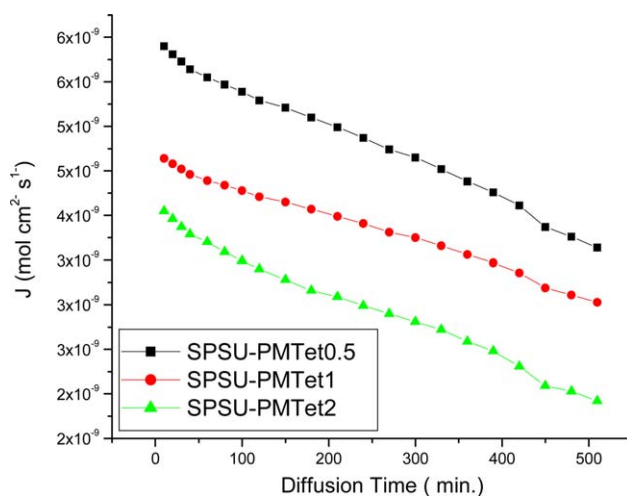


Figure 14. Methanol permeability of SPSU-PMTetX ($X = 0.5, 1, \text{ and } 2$) composite membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

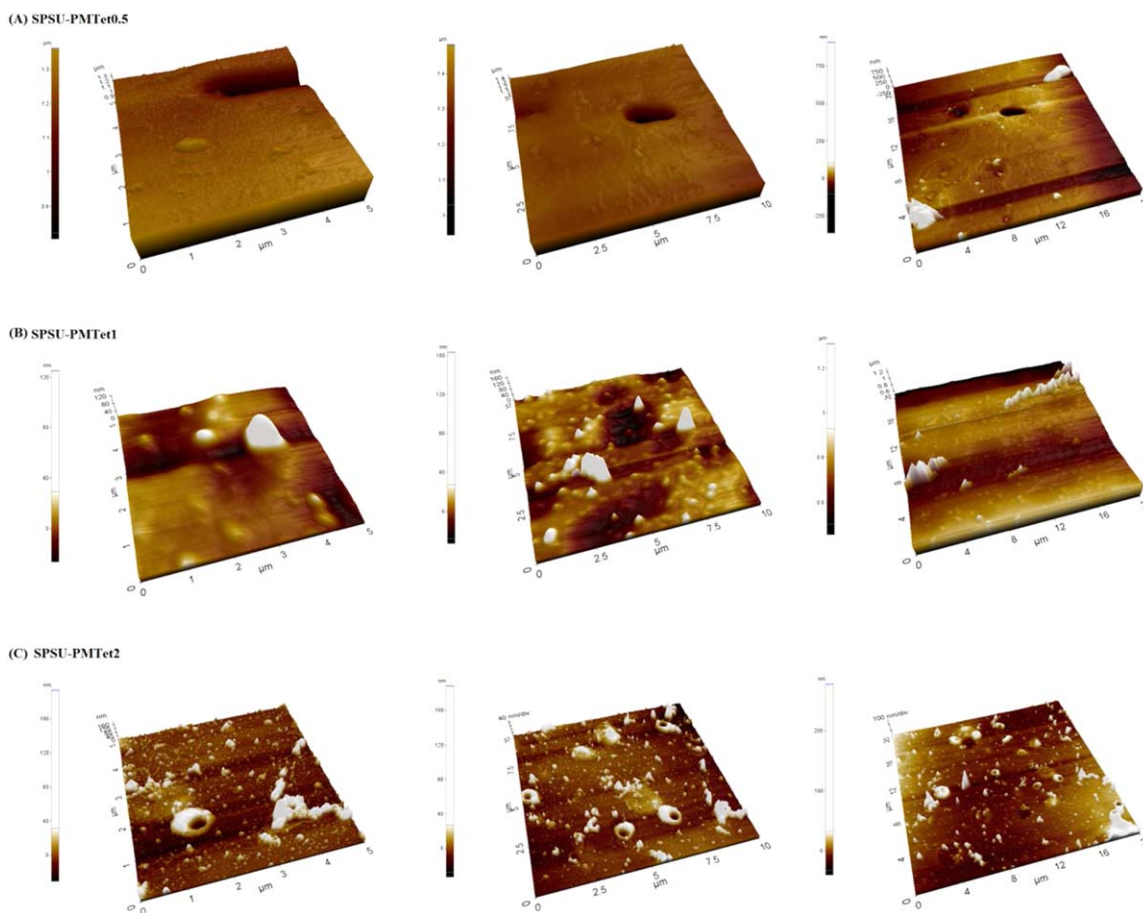


Figure 15. AFM pictures (3d) of SPSU-PMTeT X ($X=0.5, 1,$ and 2) composite membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

In this study, PMTeT monomer, prepared by the reaction of methacryloyl chloride with 5-aminotetrazole, was polymerized via conventional free radical mechanism to achieve PMTeT homopolymer. Novel composite membranes, SPSU-PMTeT X , were successfully produced by incorporating SPSU into PMTeT. The sulfonation of polysulfone was performed with TMSCS and high DS (140%) was obtained.

$^1\text{H-NMR}$ and FTIR confirmed the sulfonation of PSU and the ionic interaction between sulfonic acid and PMTeT units. TGA showed that the polymer electrolyte membranes are thermally stable up to $\sim 190^\circ\text{C}$. Methanol permeability experiments demonstrated that the composite membranes have similar methanol permeability values with Nafion 112. SEM analysis indicated the homogeneity of the membranes. This result was also supported by the appearance of a single T_g in the DSC curves of the blends. It is clear that the DC conductivity strongly depends on the temperature and SPSU ratio. The maximum proton conductivity of anhydrous SPSU-PMTeT0.5 at 150°C was determined as $2.2 \times 10^{-6} \text{ S cm}^{-1}$ while in humidified conditions a value of $6 \times 10^{-3} \text{ S cm}^{-1}$ at 20°C was found for SPSU-PMTeT2. In that study, tetrazole has high contribution to the proton conduction, and the sample with the highest tetrazole content (SPSU-

PMTeT2) has considerable conductivity in the humidified condition and low methanol permeability. This shows that it may be used as a membrane in the fuel cell applications.

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