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Imidazole-doped Poly(styrene sulfonic acid-co-vinyl imidazole)/Polyvinyl Alcohol Blends as Proton Conducting Membranes

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ABSTRACT

Proton-conducting membranes from imidazole-doped poly (styrene sulfonic acid-co-vinyl imidazole) (PSSA-co-PVIm)/polyvinyl alcohol (PVA) blends were reported. PSSA-co-PVIm with SSA:VIm of 5:1, 3:1, and 2:1 were synthesized via conventional free radical polymerization. Successful syntheses were confirmed by ¹H-nuclear magnetic resonance spectroscopy (NMR), elemental analysis, and Fourier transform infrared spectroscopy (FTIR). The copolymers were blended with PVA and imidazole. PVA/imidazole membrane was also prepared for comparison. Hygroscopic self-standing membranes were obtained from solution-cast method. All blend membranes showed thermal decomposition onsets of ~140 °C. Proton conductivity at room temperature depended highly on relative humidity. Proton conductivities of ~10⁻³ S/cm were obtained from membranes equilibrated with water vapor, while 2-4 orders of magnitude decreases were observed for dry membranes. Under non-humidified condition, conductivity was enhanced through the addition of PSSA-co-PVIm, and maximum conductivities of ~7.9 × 10⁻⁴ S/cm at 80-160 °C were achieved from (3:1) and (2:1) blend membranes.

Keywords: copolymerization, electrolyte, fuel cell, polymer blends

1. INTRODUCTION

Polymer electrolyte membrane fuel cells (PEMFCs) have been considered promising environmentally friendly energy sources for automotive and portable electronic devices due to their high efficiency. The key component in PEMFCs is polymer electrolyte membrane. Hydrated perfluorosulfonic acid membranes such as Nafion[®] have attracted a lot of interest because of their chemical and electrochemical stabilities; however, they can generally be operated at temperatures below 100 °C under high relative humidity due to the decrease in proton conductivity resulting from the water evaporation [1-2]. Poly (styrene sulfonic acid) (PSSA) is an encouraging alternative polymer because of its low cost and relatively high proton conductivity. A conductivity of 10^{-2} S/cm was observed at 80 °C for sulfonated poly(styrene-*co*-acrylonitrile) membrane under fully humidified condition [3]. In addition, blends comprising PSSA and polyvinyl alcohol (PVA) and interpenetrating networks of PSSA and PVA demonstrated proton conductivities of ~ 10^{-2} S/cm at 100 °C [4-5]. Despite the high conductivity of these PSSA-based polymers, their systems require external humidification as proton conduction relies strongly on water content.

Great attempts in developing polymer electrolyte membranes that can highly conduct under anhydrous condition and at high temperatures have been made. Operating at elevated temperatures offer several advantages including simplifying humidification system, improving CO tolerance of Pt catalyst at anode, and increasing reaction rates and fuel cell efficiency [6-8]. Nitrogen-based heterocycles, such as imidazole, benzimidazole, and pyrazole, were shown to have intrinsic conductivity through their hydrogen bonded networks similar to that of water [9-10]. These heterocycles have been either doped or immobilized to polymer chain to provide high conduction [11-16]. The use of imidazole as dopant has been reported in several proton conducting materials including sulfonated polyetherketone [17], cellulose [18], polyacrylic acid [19], poly(styrene sulfonic acid-co-maleic acid) [20], and sulfonated poly(styrene-co-acrylonitrile) [21]. Imidazoledoped poly(vinyl phosphonic acid) (PVPA) exhibited a proton conductivity of 7×10^{-3} S/cm at 150 °C under anhydrous condition [22]. The nitrogen atoms of imidazole may act as both proton donors and acceptors in proton transfer process, while PVPA functions

as a proton source.

PVA has several properties that make it an attractive material for PEMFCs including easy preparation, chemical and mechanical stabilities, hydrophilic properties, and low cost [23-24]. As PVA cannot conduct proton, it has been either chemically modified, blended with proton conducting materials or used to form hybrid structures [25-26]. Interestingly, PVA-sulfosuccinic acidglutaraldehyde electrolyte membranes provided proton conductivity of 5.3×10^{-3} S/cm at room temperature, higher than that of Nafion[®] [27].

In this work, poly(styrene sulfonic acid-co-vinyl imidazole) with various copolymer compositions were synthesized via conventional free radical polymerization. The obtained copolymers were blended with PVA and imidazole. PVA was used to provide good film forming property. Imidazole was introduced to the membranes as both dopant and tethering group to polymeric chain to facilitate proton transfer process. These blend membranes were prepared in an effort to obtain flexible membrane with high conductivity under low relative humidity or anhydrous condition where proton transport may occur through vehicular mechanism in the presence of water, and proton hopping mechanism in dry state. PVA/imidazole membrane was also prepared for comparison purpose. The effect of copolymer composition on thermal properties, and proton conductivity was investigated.

2. MATERIALS AND METHODS 2.1 Materials

Styrene sulfonic acid sodium salt (SSANa, \geq 90%), 1-vinylimidazole (VIm, 99%), and polyvinyl alcohol (PVA, $M_w =$ 130,000 g/mol, 99+% hydrolyzed) were purchased from Sigma-Aldrich. Imidazole

(99%), potassium persulfate $(K_2S_2O_8)$, and acetone (commercial grade) were supplied from Acros Organics, VWR, and Zenith Science (Thailand), respectively. Hydrochloric acid (37% w/w) was obtained from Merck. All chemicals were used as received. Dialysis tube with a molecular weight cutoff of 12,000-14,000 was purchased from Cellu Sep.

2.2 Characterization

¹H-NMR spectra were obtained on a Varian Mercury-400 NMR spectrometer using deuterium oxide as solvent. Elemental analysis was carried out using a 2400 series II CHNS/O elemental analyzer. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were obtained with a Bruker FTIR spectrometer (Tensor 27) with Opus 7.0 software. Thermogravimetricdifferential thermal analysis (TG-DTA) was conducted using STA7200 TG/DTA (Hitachi) system from 30-700 °C with a heating rate of 10 °C/min under nitrogen atmosphere. Glass transition temperature (T_{a}) was obtained by differential scanning calorimetry (DSC) using a PerkinElmer Pyris 6 DSC. Samples were analyzed from room temperature to 200 °C with a heating rate of 10 °C/min under nitrogen flow. The reported T_g values were half extrapolated heat capacity temperatures on the second heating cycle.

2.3 Synthesis of Poly(styrene sulfonic acid-co-vinyl imidazole) (PSSA-co-PVIm)

Poly(styrene sulfonic acid sodium salt-covinyl imidazole) copolymers (PSSANa-co-PVIm) with the feed ratios of SSANa: VIm = 2:1, 1:1 and 1:2 were synthesized via conventional free radical polymerization initiated with $K_2S_2O_8$ (2 mol%). All polymerizations were carried out in deionized (DI) water at 80 °C for 8 h. After polymerization, the solution was concentrated and precipitated in acetone. The obtained solid was further purified by reprecipitaion in acetone. The polymer was then stirred in 1.0 N HCl at room temperature for 24 h to exchange proton, and later dialyzed against DI water. The aqueous polymer solution was freeze-dried (LaboGene) overnight, and light yellow solid was obtained.

2.4 PVA/imidazole Membrane and PSSA-*co*-PVIm/PVA/imidazole Blend Membranes

PVA/imidazole membrane was prepared by dissolving PVA in DI water (5 wt%) at 80 °C for 8 h. The solution was cooled to room temperature, and imidazole was added at the weight ratio of PVA to imidazole of 1:1. In a preparation of PSSA-co-PVIm/PVA/imidazole blend membrane, aqueous solution of PSSA-co-PVIm was also added at the weight ratio of PSSA-co-PVIm to PVA to imidazole of 1:1:2. The resulting solution was stirred at room temperature for 24 h to ensure homogeneous mixing. The solution was then poured into a glass petridish, and dried at 50 °C for 24 h. The membrane was peeled off, and stored in a desiccator with dried silica gel.

2.5 Proton Conductivity

Proton conductivity was measured using impedance spectroscopy (KEYSIGHT E4990A Impedance Analyzer) by an application of 500 mV excitation voltage with a logarithmic frequency sweep from 40 to 1×10^{6} Hz. A template with a 0.60-cm diameter hole was placed onto the membrane surface prior to gold-coating using a Polaron SC500 sputter coating unit. The template was removed and the gold-coated membrane was placed between a sample holder for

conductivity measurement. Dry membranes and membranes equilibrated with water vapor for 24 h were measured at room temperature. In addition, the dry membranes were measured at elevated temperatures from 40-180 °C at 20 °C intervals under non-humidified condition. The proton conductivity was calculated from the observed resistance taken at the high-frequency intercept with the real impedance in the Nyquist plot, real impedance (Z') versus imaginary impedance (Z") plot [28], using

$$\sigma = \frac{1}{RA}$$

, where σ is the proton conductivity (in S/ cm), l is the membrane thickness (in cm), and A is the membrane sectional area (in cm²). The reported value was the mean of two measurements.

3. RESULTS AND DISCUSSION 3.1 Synthesis and Characterization of PSSA-co-PVIm

The synthesis of PSSA-co-PVIm involved free radical copolymerization of styrene

sulfonic acid sodium salt (SSANa) and vinylimidazole (VIm) with the molar feed ratios of 2:1, 1:1, and 1:2, followed by the exchange of Na^+ with H^+ (Scheme 1). After proton exchange, aqueous solutions of polymers were dialyzed against water, and later freeze-dried to yield light yellow solids. Successful synthesis was confirmed by ¹H-NMR. Refer to Figure 1, peaks between δ 1.0 and δ 2.3 ppm corresponded to -CH₂- and -CH- protons on polymeric backbone. Peaks relating to protons of the phenyl ring on PS and of imidazole ring were observed around δ 6.3-7.9 ppm. It was difficult to determine copolymer compositions by NMR due to the peak overlap; therefore, elemental analyses were conducted, and reported in Table 1. As expected, nitrogen content in the copolymer increased with increasing VIm feed. The molar ratios of SSA to VIm in the copolymers were calculated to be 5:1, 3:1, and 2:1 from the feed ratios of 2:1, 1:1, and 1:2, respectively. The copolymers were therefore referred to as PSSA-co-PVIm (5:1), (3:1), and (2:1) in further discussions.



m:n = 2:1, 1:1, 1:2

PSSA-co-PVIm

Scheme 1. Synthetic route to poly(styrene sulfonic acid-co-vinyl imidazole).



Figure 1. ¹H-NMR spectra of PSSA-co-PVIm with various ratios of SSA to VIm in the copolymers.

Table 1. Copolymer formulas and compositions calculated from elemental analysis.

| SSANa:VIm | Composition (wt.%) | | | Copolymer formula | SSA:VIm |
|-----------|--------------------|------|------|---------------------------|--------------|
| in feed | | | | | in copolymer |
| | % C | %Н | % N | | |
| 2:1 | 37.60 | 5.11 | 1.79 | $C_{24,1}H_{39,3}N_{1,0}$ | 5:1 |
| 1:1 | 39.23 | 5.33 | 3.14 | $C_{14.9}H_{24.2}N_{1.0}$ | 3:1 |
| 1:2 | 41.80 | 5.10 | 4.72 | $C_{10.2}H_{15.0}N_{1.0}$ | 2:1 |

ATR-FTIR spectra of as-synthesized PSSA-co-PVIm copolymers were shown in Figure 2. Bands attributing to asymmetric and symmetric stretching vibrations of S=O in sulfonic acid of PSSA were found at 1227 and 1037 [29]. The bands at 1170 and 1006 cm⁻¹ were assigned to the vibration of the phenyl ring substituted with a sulfonic group [30-31]. The wagging vibration of C-H in 1, 4-substituted benzene ring of PSSA was also shown at 829 cm⁻¹. Characteristic band of C=C stretching vibrations was shown at 1643 cm⁻¹ [32]. The C-N stretching band of imidazole ring was shown at 1574 cm⁻¹ [20]. In addition, band at 1497 cm⁻¹ could be related to C=N stretching vibrations of imidazole.



Figure 2. FTIR spectra of PSSA-*co*-PVIm copolymers.

3.2 Preparation and Characterization of Membranes

PSSA-*co*-PVIm copolymers were blended with PVA and imidazole at the weight ratio of 1:1:2, i.e. the amount of imidazole was equal to the sum of PSSA-*co*-PVIm and PVA. Hygroscopic self-standing membranes with thickness of ca. 0.3 mm were obtained from solution-cast method, shown in Figure 3. PVA/imidazole membrane was also prepared at the weight ratio of 1:1 for comparison. FTIR spectra of PSSA-*co*-PVIm (3:1), PVA, imidazole, and the resulting blend membrane were shown to be representative in Figure 4. The major bands were those from imidazole as imidazole was the largest component in the blend. In addition to bands corresponding to PSSA-*co*-PVIm, characteristic O-H stretching and bending bands of PVA were observed at 3289 and 1415 cm⁻¹, respectively [29, 33].



Figure 3. Photographs of PVA/imidazole membrane (a), and PSSA- ω -PVIm/PVA/imidazole blend membranes prepared from PSSA- ω -PVIm (5:1) (b), (3:1) (c), and (2:1) (d). ca. 1 × 1 cm².



Figure 4. FTIR spectra of PSSA-*co*-PVIm (3:1), PVA, imidazole, and the resulting blend membrane.

3.3 Thermal Properties

TGA thermograms of as-synthesized PSSA-*co*-PVIm copolymers, PVA, imidazole and blend membranes were illustrated in Figure 5. PSSA-*co*-PVIm copolymers showed two degradation stages. The first weight loss below 100 °C was related to the loss of absorbed water, indicating the hygroscopic nature. The second simultaneous weight loss between 350 to 550 °C was attributed to the losses of sulfonic acid groups, PSSA main chain and PVIm main and side chains [34-36]. At 700 °C, approximately 60% char yields were observed. Thermal stability and char yield were found to slightly increase with PSSA content.

PVA exhibited three degradation stages. The first weight loss below 130 °C was due to the evaporation of bound water. The second loss between 240-340 °C was attributed to the loss of PVA side chains, and the last degradation stage at around 360-500 °C corresponded to the cleavage of PVA backbones [37]. The char yield at 700 °C was about 4%. A similar weight change was observed for PVA/imidazole membrane with an additional decomposition step from approximately 100 to 200 °C due to the loss of imidazole molecules from the membrane [18]. PSSA-co-PVIm/PVA/ imidazole blends exhibited slightly lower thermal stabilities compared to

PVA/imidazole membrane. Thermal decomposition onsets, 5% of the weight after initial weight loss, of PVA/imidazole membrane, and (5:1), (3:1), and (2:1) blend membranes were 148 °C, 136 °C, 138 °C, and 143 °C, respectively.

Broad glass transition ranges of approximately 60 °C were observed in DSC for as-synthesized copolymers, and imidazole-doped membranes (data not shown). Glass transition temperatures (T_g) determined from half extrapolated heat capacity temperatures on the second heating cycle were listed in Table 2. T_g values of PSSA-*co*-PVIm copolymers slightly increased with increasing PSSA content. PVA/imidazole membrane showed a T_g of 147.5 °C, and T_g values of PSSA-*co*-PVIm/PVA/imidazole membranes were 4-20 °C lower as a result from the lower T_g 's of PSSA-*co*-PVIm copolymers.



Figure 5. TGA thermograms of assynthesized PSSA-*co*-PVIm copolymers (5:1 (a), 3:1 (b), and 2:1 (c)), PVA (d), imidazole (e), PVA/imidazole membrane (f), and PSSA-*co*-PVIm/PVA/imidazole blend membranes (from 5:1 (g), 3:1 (h), and 2:1 (i)).

Table 2. Glass transition temperatures obtained from DSC of as-synthesized PSSAco-PVIm copolymers, PVA/imidazole membrane and PSSA-co-PVIm/PVA/ imidazole membranes.

| Sample | $T_g (^{\circ}C)$ |
|-----------------------------|-------------------|
| PSSA-co-PVIm (5:1) (powder) | 127.1 |
| PSSA-co-PVIm (3:1) (powder) | 126.3 |
| PSSA-co-PVIm (2:1) (powder) | 112.9 |
| PVA/imidazole membrane | 147.5 |
| PSSA-co-PVIm (5:1)/PVA/ | 143.5 |
| imidazole membrane | |
| PSSA-co-PVIm (3:1)/PVA/ | 133.6 |
| imidazole membrane | |
| PSSA-co-PVIm (2:1)/PVA/ | 127.6 |
| imidazole membrane | |

3.4 Proton Conductivity

Proton conductivities at room temperature of dry membranes and membranes equilibrated with water vapor for 24 h were shown in Figure 6. Proton conductivity highly depended on relative humidity where 2-4 orders of magnitude differences in conductivity were observed between dry and equilibrated membranes. It should be noted that due to hygroscopic nature of PSSA-co-PVIm and imidazole, there was a small amount of absorbed water in our dry membranes as the conductivity measurement was conducted under atmospheric environment. Similar proton conductivities between 9.3×10^{-4} to 1.7×10^{-3} S/cm were observed from all equilibrated membranes. It is worth mentioning that these blend membranes were not suitable for long-term use under high relative humidity due to their low hydrolytic stability. For dry membranes,

proton conductivity was slightly enhanced through the introduction of PSSA-*co*-PVIm; however, the effect of the ratio of SSA to VIm in copolymer on proton conduction was not clearly seen.



Figure 6. Proton conductivities of dry membranes and membranes equilibrated with water vapor at room temperature.



Figure 7. Proton conductivities as a function of inverse temperature of dry membranes under non-humidified condition.

Proton conductivities of dry membranes were also measured from 40-180 °C under non-humidified condition. A plot of conductivity as a function of inverse temperature was demonstrated in Figure 7. Proton conductivity was found to increase

with increasing temperature in the temperature range of 40-80 °C due to the increase in segmental mobility. Large variations in conductivity at room temperature and 40 °C of PVA/imidazole membrane and (2:1) blend membrane could be explained by the presence of different contents of absorbed water on membranes. The variation was less pronounced at elevated temperatures as water evaporated. At higher temperatures (80-160 °C), the conductivity stayed almost the same for each membrane, and a small decrease was observed at 180 °C as a result from membrane degradation. In dry system where proton conducts through proton hopping or Grotthuss mechanism, Scheme 2, conductivity depends mainly on mobility and charge carrier density. At temperatures above the melting point of imidazole (90 °C) and the T's of blend membranes, there were no remarkable changes in mobility and proton density; therefore, conductivity remained relatively stable. It was clear that proton conductivity was enhanced by the addition of PSSA-co-PVIm to PVA/imidazole membrane. The enhancement could be attributed to the increase in proton source, that is -SO₂H in PSSA. Maximum proton conductivities of \sim 7.9 × 10⁻⁴ S/cm were achieved for (3:1) and (2:1) blend membranes at 80-160 °C. Although (5:1) blend possessed the largest sulfonic acid content among the three blends, the rigid and bulky group of PSSA might have interrupted proton transfer, leading to lower proton conductivity. The effect of the molar ratio of sulfonic acid to azole on proton conduction was also observed in PVA/poly (2-acrylamido-2-methylpropane sulfonic acid) (PAMPS)/1,2,4-triazole composite membranes, where the suitable ratio was found to be 3:1 [8].



Scheme 2. Possible proton transport pathway of imidazole-doped PSSA-*co*-PVIm/PVA blends via Grotthuss mechanism under dry condition.

4. CONCLUSIONS

The development of proton conducting membranes based on PSSA-co-PVIm/PVA/ imidazole blends was reported. PSSA-co-PVIm copolymers with various compositions were synthesized and confirmed by ¹H-NMR and FTIR. The molar ratios of SSA:VIm of 5:1, 3:1, and 2:1 were determined from elemental analysis. PSSA-co-PVIm/PVA/ imidazole blends demonstrated good flexibility with hygroscopic property. Thermal decomposition onsets of ~140 °C were observed for all membranes. Relative humidity was found to significantly affect proton conductivity at room temperature. Membranes equilibrated with water vapor showed proton conductivity of $\sim 10^{-3}$ S/cm at room temperature, and the effects of the presence of PSSA-co-PVIm and copolymer composition on proton conductivity were not clearly seen. For dry membranes, the addition of PSSA-co-PVIm provided higher conductivities at elevated temperatures under non-humidified condition, and maximum conductivities of ~7.9 \times 10⁻⁴ S/cm at 80-160 °C were obtained from (3:1) and (2:1) blend membranes.

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