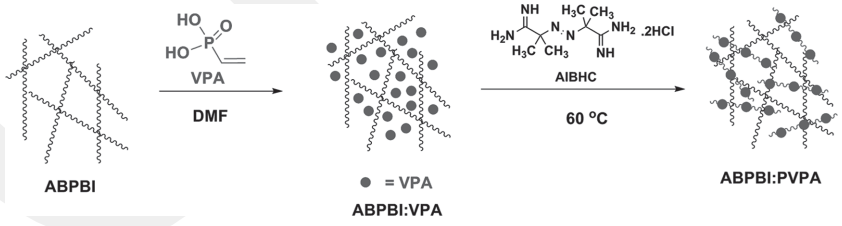
Enhancement of Anhydrous Proton Conductivity of Poly(vinylphosphonic acid)–Poly(2,5-benzimidazole) Membranes via In Situ Polymerization

Unal Sen,* Hakan Usta,* Oktay Acar, Murat Citir, Ali Canlier, Ayhan Bozkurt, Ali Ata

Polymer electrolyte membranes (PEMs) are synthesized via in situ polymerization of vinylphosphonic acid (VPA) within a poly(2,5-benzimidazole) (ABPBI) matrix. The characterization of the membranes is carried out by using Fourier transform infrared (FTIR) spectroscopy for the interpolymer interactions, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) for the thermal properties, and scanning electron microscopy (SEM) for the morphological properties. The physicochemical characterizations suggest the complexation between ABPBI and PVPA and the formation of homogeneous polymer blends. Proton conductivities in the anhydrous state (150 °C) measured by using impedance spectroscopy are considerable, at up to 0.001 and 0.002 S cm^{-1} for (1:1) and (1:2) molar ratios, respectively. These conductivities indicate significant improvements (>1000×) over the physically blended samples. The results shown here demonstrate the great potential of in situ preparation for the realization of new PEM materials in future high-temperature and non-humidified polymer electrolyte membrane fuel cell (PEMFC) applications.



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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are of extensive scientific and technological interest as alternative energy sources with high energy conversion efficiencies. These fuel cells are envisioned as one of the most promising power sources for cars, mobile vehicles, portable electronic devices, and on-site power-generators near houses, and business areas.[1–4] In a typical PEMFC, a polymer-based separator material (PEM) is used to allow the diffusion of protons (H^+) from anode to cathode, while preventing any undesired fuel diffusion between two electrochemical sites. Recently, there has been increasing attention to the development of high-temperature (100–200 °C) PEMFC systems since they offer several advantages

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such as high catalytic activity, low cost, elimination of CO poisoning, and ease of device cooling and water management.[5,6] Additionally, high temperature PEM fuel cells are very important to utilize fuels other than hydrogen, such as methanol, and to utilize nonprecious metal catalysts due to its high reactivity. For these fuel cell systems, it is crucial to have PEMs exhibiting high proton conductivities at relatively high temperatures. Some of the conventional perfluorinated polyelectrolytes such as Nafion have limited operation temperatures of below 100 °C since they exhibit high conductivities only via water-assisted proton conduction (vehicle mechanism). Therefore, the realization of new polyelectrolyte systems with high conductivity at the temperature range of 100–200 °C has been strongly desired.

To date, one of the most successful approaches to achieve high proton conductivity at low humidity or completely anhydrous conditions in PEMFCs relies on the construction of strong acid-based complexes between functionalities attached to the polymeric backbones.[7–12] In these structures, a homogeneous polymeric matrix forms via strong multipoint acid–base interactions and hydrogen bonding networks, and proton conductivity occurs through Bronsted acid–base pairs. Since both acid and base functionalities are attached to the polymeric backbones, dopant leaching-out problem does not affect the fuel cell performance over prolonged usage and higher ratios of acidic parts can be safely used to further improve the proton conductivities.

In previous work, we reported the development of new PEMs via solution-casting blends of poly(2,5-benzimidazole) (ABPBI) and poly(vinylphosphonic acid) (PVPA) at several stoichiometric ratios.[13] For these polymeric blend systems, spectroscopic measurements and water uptake studies indicated the proton-exchange reactions and complexations between ABPBI base and PVPA acid moieties, which inhibited dopant exclusion upon swelling in excess water. Considerable proton conductivities of 0.004 S cm^{-1} were measured for these ABPBI:PVPA films at 20 °C (RH = 50%) and 1:4 molar ratio. However, these films were found to exhibit very poor proton conductivities of 10^{-6}–10^{-7} S cm^{-1} at anhydrous conditions (150 °C). As a part of our effort to further explore this new polymeric system for anhydrous PEM applications, we envision that in situ preparation of PVPA chains within ABPBI matrix might result in enhanced segmental motions and more labile proton carrier sites if lower glass transition temperatures can be achieved. Additionally, better multipoint acid–base interactions can be obtained in the final blend via in situ polymerization since the ABPBI matrix imidazole units might serve as directing sites for VPA monomers. All these considerations prompted us to explore a new in situ preparation method for ABPBI:PVPA PEM films to achieve better proton conductivities at anhydrous conditions. The most important advantage here would be that high conductivity can be achieved without compromising the optimum acidic content, i.e., there is no need to go to very high acid concentrations.

In this study, we report novel PEM films based on ABPBI:PVPA polymer blends fabricated via in situ polymerization of vinylphosphonic acid (VPA) monomers in an ABPBI polymeric matrix (Figure 1). The blends were prepared under inert atmosphere at several different stoichometric ratios (2:1, 1:1, 1:2) with respect to monomer repeating units, i.e., molar ratio of benzimidazole to VPA. The physicochemical characterization of the membranes was carried out by using Fourier-transform infrared (FTIR) spectroscopy for interpolymer interactions, scanning electron microscope (SEM) for surface morphology and homogeneity, and thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC) for thermal properties. The effects of benzimidazole and VPA contents on the conductivity of final product were investigated. The synthesis, molecular interactions, thermal properties, and proton conductivity results were discussed and compared with physically blended membrane films. With these new PEM films, proton conductivities as high as 0.002 S cm^{-1} were achieved at relatively high temperatures (150 °C) for molar ratios of 1:2 (ABPBI:PVPA). This indicates a significant improvement (1000×) over the physically blended PEM films, which is attributed to mainly decreased T_gs. The observed lower Tgs of these blends ensure enhanced polymer segmental motions and more labile proton transporting active sites at high temperatures on the polymer backbones compared to the physically blended films. To the best of our knowledge, this is the first report employing in situ polymerized PVPA:ABPBI film as PEM to operate under non-humidified, high temperature condition with good proton conductivities.

2. Experimental Section

2.1. Materials

All the reagents were purchased from commercial sources and used without further purification unless otherwise noted. VPA (>95%; Fluka), α,α′-azodiisobutyramidine dihydrochloride (AIBHC) (>98%; Fluka), 3,4-diaminobenzoic acid (DABA) (97%; Alfa Aesar), polyphosphoric acid (PPA) (≈85%; Merck), dimethylformamide (DMF) (Merck), and trifluoroacetic acid (TFA) (Merck) are the chemicals that were used throughout this work.

2.2. Synthesis of ABPBI–VPA In Situ Polymer and Preparation of The Membranes

Poly(2,5-benzimidazole) was synthesized by condensation of DABA in PPA as reported in the literature: 3,4-diaminobenzoic acid (1.0 g, 6.6 mmol) was added to a reaction mixture containing P_2O_5 (1.5 g) and CH_3SO_3H (10 mL). The reaction mixture

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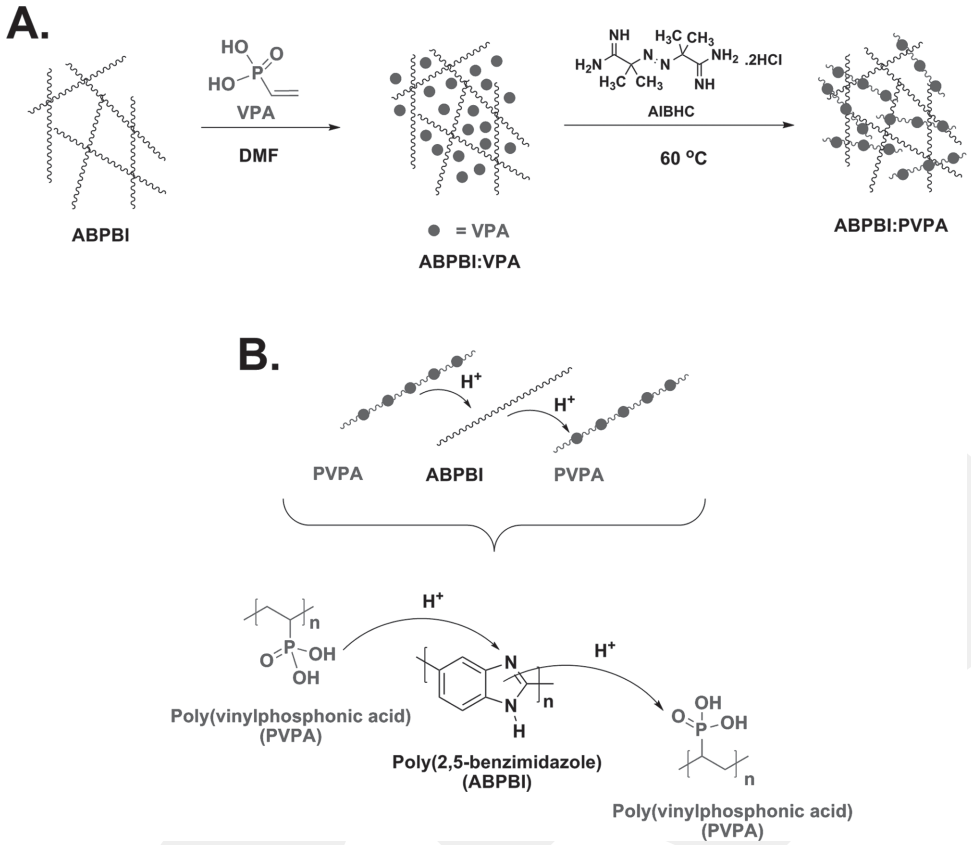

Figure 1. A) Schematic representation of the preparation of in situ polymerized ABPBI:PVPA blend membranes. B) Chemical structures of poly(2,5-benzimidazole) (ABPBI) and poly(vinylphosphonic acid) (PVPA) and schematic representation of the proton transfer process.

was heated at 150 °C under N_2 for 1 h and a homogeneous solution was obtained. During this period, a viscosity increase was observed. The hot polymer solution was slowly poured into water (300 mL) to get thin fiber-like polymers. The polymer fiber was collected and washed several times with water. The residual phosphoric acid in the polymer fibers was extracted with 10% ammonium hydroxide solution in a Soxhlet extractor to get 0.6 g of ABPBI.[14] Membranes were prepared by in situ polymerization of VPA in swollen ABPBI. ABPBI and VPA were mixed in order to get ABPBI–VPA molar ratios of (2:1), (1:1), and (1:2) with respect to the monomer repeating units, i.e., molar ratio of benzimidazole to VPA. Then, DMF was added into these mixtures (10 mL for 100 mg of ABPBI) and they were stirred for 1 d under nitrogen. During this step, while ABPBI polymer was being swollen with the solvent, VPA monomers are getting dispersed within the polymeric matrix. Then, the radical initiator AIBHC (2–3 mg) was added and in situ polymerization of VPA in ABPBI was performed in 1 h at 60 °C under nitrogen. The blend samples were dried under vacuum for 2 d at 80 °C, and then they were stored in the glove box as pellets. Unfortunately, since the polymer blends are found to be very insoluble in common solvents, gel permeation chromatography (GPC) analyses were not informative in terms of determining molecular weights. However, thin-layer chromatography (TLC) technique was used with silicagel-60/ethyl acetate system to identify any unreacted VPA monomer. After the polymerization reaction is done, a small polymer blend sample was taken and ethyl acetate was added, sonicated/heated to extract any unreacted monomer of VPA into the organic phase. After filtering this mixture, a small sample was spotted on a TLC plate and ran with ethyl acetate together with a reference VPA monomer. Since TLC is a very sensitive technique to observe any residual unreacted monomer, our test indicated that there was no monomer left after the polymerization protocol.

2.3. Characterizations

FTIR spectra of dry ABPBI–PVPA in situ polymer membranes were investigated over a wavelength range from 650 to 4000 cm^{-1} by the attenuated total reflection (ATR) module by using Perkin–Elmer FTIR spectrum BX. Prior to FTIR measurements, the samples were further dried under vacuum at 70 °C. Thermal stabilities of the polymer films were determined by using TGA with Perkin–Elmer STA 6000. The analysis was carried out heating the samples from room temperature to 900 °C at the rate of 10 °C min^{-1}. DSC measurements were done by using Perkin–Elmer DSC 4000 under nitrogen atmosphere heating from 0 to 200 °C at a rate of 10 °C min^{-1}. The glass transition temperature of a polymer sample was determined based on the intersection of two tangents (at the start and at the end of the endotherm) in the second heating curves.[15] The measurements of proton conductivity of membranes were performed by using Novocontrol

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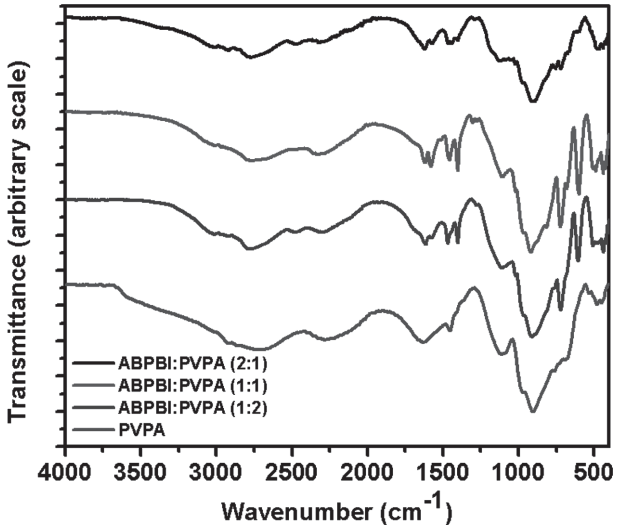

Figure 2. FTIR spectra of ABPBI:PVPA in situ polymerized membranes and the reference PVPA polymer at different molar ratios (2:1, 1:1, 1:2).

impedance analyzer over a frequency range of 0.1 Hz to 3 MHz with Novocontrol cryosystem controlled temperature, applicable between –100 °C and 250 °C. Membranes were placed between two platinum blocking electrodes. The variation of temperature was from 20 °C to 150 °C with 10 °C intervals.

3. Results and Discussion

3.1. FTIR Spectroscopy

The present in situ polymerized ABPBI–PVPA membranes were characterized by FTIR spectroscopy in order to gain insight into their molecular structures, nature of functional groups, and interchain interactions. The spectra are shown in Figure 2. The IR spectra of all the blends exhibit broad bands at 920–1010 and 1117 cm^{-1} corresponding to (P—O)H and P=O stretching, respectively.[16] The phosphonic acid (—$PO(OH)_2$) group gives an additional band in the region of 1620–1700 cm^{-1}. Due to —OH stretching of the same group, broad bands at 2800–3250 cm^{-1} are observed. On the other hand, the aromatic rings present in the ABPBI backbone exhibit several bands at 1621, 1571, and 1451 cm^{-1}, which can be attributed to the C=N and C=C stretching.[17] The small peaks observed near 3100 cm^{-1} is the result of N^+—H stretching, which indicates that some portion of benzimidazole nitrogens are protonated. Additionally, significant band broadenings were observed between 3000 and 2500 cm^{-1}, which are attributed to the formation of hydrogen bonding networks between polymer chains.[14] Therefore, based on the above considerations and literature reports on similar systems, we can conclude that the current ABPBI:PVPA blends form a polymeric acid:base matrix of deprotonated phosphonic acid side groups with benzimidazolium counterions. The FTIR characterization also

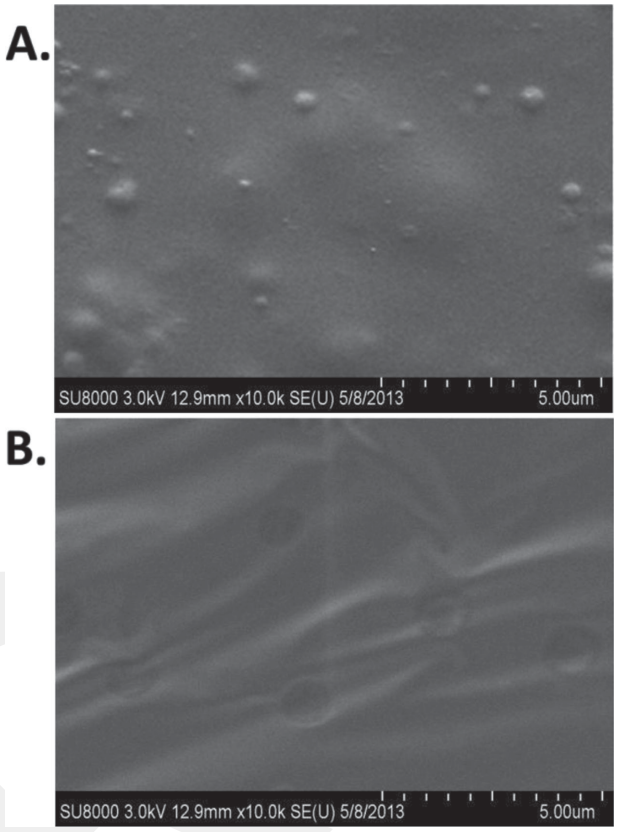

Figure 3. SEM micrographs of the surface of ABPBI:PVPA in situ polymerized membranes with 1:1(A) and 1:2(B) molar ratios.

indicates that the proton conduction in the present blend membranes occurs through jumping of protons between Bronsted acid–base pairs of benzimidazole and phosphonic acid groups.[18]

3.2. Morphology

Morphological analysis of the blend membranes was carried out by scanning electron microscopy (SEM), which is crucial for understanding the compatibility between two polymeric species. As shown in Figure 3, SEM images indicate the formation of homogeneous films with no discernible phase separation. This morphology indicates a very good compatibility between ABPBI polymer chains and in situ polymerized PVPA polymer chains as a result of strong inter-polymer interactions via acid-base complexations. The observed morphology should also be advantageous to form an efficient proton conducting network with a homogeneous blend of polymeric chains carrying acid and base functionalities.

3.3. Thermal Analysis

Thermal properties of ABPBI/PVPA blend membranes were analyzed by TGA and DSC. The membranes were dried for

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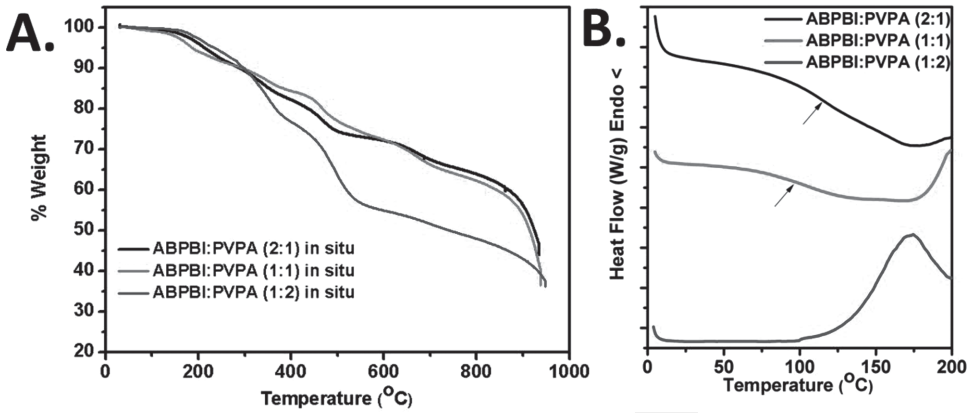

Figure 4. A. TG thermograms recorded at a heating rate of 10 °C min^{-1}. B. DSC graphs recorded in an inert atmosphere at a heating rate of 10 °C min^{-1} for ABPBI:PVPA in situ polymerized membranes at different molar ratios (2:1, 1:1, 1:2). Second heating curves were used for T_g detection.

2 d under vacuum at 80 °C prior to the thermal analysis. As shown in Figure 4A, all the membranes (1:2, 1:1, 1:2) exhibit good thermal stability with negligible weight losses up to 200 °C. The observed slight decreases in the weight for ABPBI:PVPA (1:2) membrane at around 150 °C and for ABPBI:PVPA (2:1 and 1:1) above 190 °C are possibly due to the condensation reaction of phosphonic acid (—$PO(OH)_2$) groups, which causes elimination of water molecules. The lower condensation onset temperature measured for 1:2 molar ratio is due to higher acidic functionality content of this polymer compared to the polymers with 1:1 and 2:1 molar ratios. All the polymer membranes exhibit significant decompositions above around 240 °C, and loses around 25% of its original weight until around 450–500 °C. Further weight losses observed above 450–500 °C indicates the decomposition of the ABPBI main chain, which leads to the formation of highly volatile phenol and benzene derivatives.

The DSC thermograms of the blend membranes are shown in Figure 4B. T_gs of the polymer blends were evaluated based on the second heating curves. T_g of the membranes was measured as 115 °C for ABPBI:PVPA (2:1) and 98 °C for ABPBI:PVPA (1:1). However, due to the existence of a large exothermic condensation peak observed for ABPBI:PVPA (1:2), its T_g value could not be determined clearly. This is consistent with the TGA data for this blend, which also indicates lower condensation onset temperature for higher acidic content. The existence of single glass transition for each sample indicates that the blend membranes are homogeneous without any phase segregation. The observed T_gs are much higher than that of pure PVPA polymer (T_g = –23 °C), which shows that the segmental motion of the polymer chains become more restricted via multi-point acid–base interactions, ionic attractions, and hydrogen networks resulting in increased T_gs.

As typically seen for acid–base polymer blends, the T_g of the present membranes decreases going from 2:1 (ABPBI:PVPA) to 1:1 (ABPBI:PVPA) molar ratio. This trend can be explained by PVPA content increase, which lowers the rigidity of the blend matrix and it is very similar to our previous observations with physically blended polymers.[13] For the in situ polymerized membrane with 1:1 molar ratio, significantly lower T_g (ΔT_g = –55 °C) was observed compared to its physically blend polymer counterpart, which may be attributed to the enhanced segmental motion of PVPA polymer chains in the matrix as a result of in situ polymerization, which possibly yielded lower $\bar{M}_n$ chains. This enhanced segmental motion compared to the physically blend polymers should contribute to the proton conductivity of the membranes at temperatures higher than the T_gs. The difference for 2:1 ratio was minimal, which indicates that for these lower acidic content samples, T_g is still governed by interchain interactions and polymer chain lengths does not play a significant role on it.

3.4. Proton Conductivity

The proton conductivities of the new in situ polymerized blend membranes were characterized by impedance methods in order to observe their suitability for high-temperature PEMFCs. Before the proton conductivity measurements, the samples were further dried under vacuum at 70 °C for 24 h. The frequency-dependent proton conductivities of the anhydrous ABPBI:PVPA blends with (2:1), (1:1), and (1:2) molar ratios were measured by AC impedance method over a range of frequency (0.1 Hz–3 MHz) at several temperatures (20–150 °C) under dry nitrogen flow. A representative graph for ABPBI:PVPA (1:1) is shown in Figure 5. AC conductivities (σ_{ac} (ω)) were calculated from the equation: $\sigma'(\omega) = \sigma_{ac}(\omega) = \varepsilon''(\omega)\omega\varepsilon_o$, where $\sigma'(\omega)$ is the real part of conductivity, $\omega = 2\pi f$ is the angular frequency, ε_o is the vacuum permittivity (ε_o = 8.852 × 10^{-14} F cm^{-1}), and ε'' is the imaginary part of complex dielectric permittivity (ε^*).

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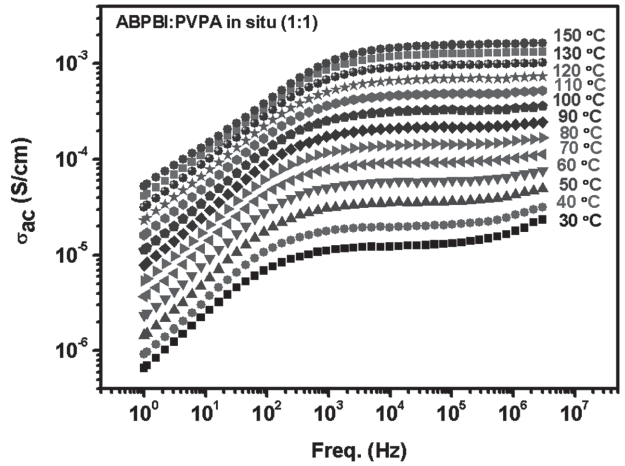

Figure 5. AC conductivity versus frequency of anhydrous in situ polymerized ABPBI:PVPA blend membrane (1:1) at several temperatures (30–150 °C).

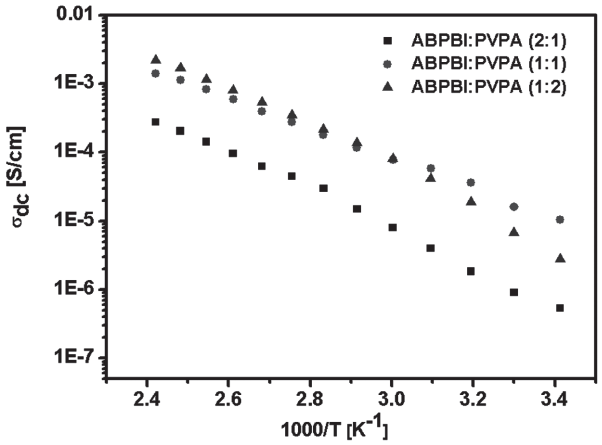

Figure 6. The DC conductivity versus reciprocal temperature for in situ polymerized ABPBI:PVPA blend membranes with different molar ratios (2:1, 1:1, 1:2).

All the curves at different temperatures include frequency dependent and independent areas, which is a typical behavior of ion conducting polymers. The frequency-independent plateau regions are well developed at low frequencies and low temperatures, and shift toward higher frequencies with increasing temperature. The observed conductivity increases at low frequencies (1–100 Hz) and at high frequencies (>10^5–10^6 Hz) are attributed to the electrode polarization of the blocking electrodes and dispersion formation in polymers, respectively. The plateau regions were observed over 2–3 decades at intermediate frequencies (10^3–10^4 Hz), and by extrapolation to zero frequency, the direct current (DC) conductivity (σ_{dc}) of the samples were calculated.

The temperature dependence of proton conductivities for anhydrous ABPBI:PVPA in situ polymerized membranes with 2:1, 1:1, and 1:2 molar ratios is shown in Figure 6. The conductivity of the present membrane systems is found to be highly dependent on the blend composition and temperature. In general, the proton conductivities of the samples were found to increase with temperature. Additionally, the amount of PVPA in the blend samples played an effective role on the proton conductivity. ABPBI:PVPA feeding ratio of at least 1:1 is required in order to obtain a respectable proton conductivity (≥10^{-3} S cm^{-1}) at high temperature. The ABPBI:PVPA blend with 2:1 molar ratio exhibited one order of magnitude lower conductivities compared to 1:1 and 1:2 blend systems. Considerably, the samples with (1:1) and (1:2) molar ratios exhibited the highest proton conductivities of 0.001 and 0.002 S cm^{-1} at 150 °C, respectively. These conductivities represent a three-to-four orders of magnitude increase in high-temperature conductivity compared to physically blended samples (10^{-6}–10^{-7} S cm^{-1} at 150 °C).[13]

On the other hand, the observed high-temperature conductivity is in the order of previously reported PVPA-doped PBI (polybenzimidazole) blend membranes (≈0.001 S cm^{-1} at 50% RH, 80 °C).[19]

In anhydrous polymer blend membranes, since water molecules do not exist protonic defect sites form throughout the polymer matrix and it provides strongly labile proton donor and acceptor functional sites. During a typical proton transfer, benzimidazole heterocycle of ABPBI and phosphonic acid group of PVPA act as donor and acceptor proton-carrier sites, and they undergo continuous protonation/deprotonation processes through their nitrogen and oxygen atoms, respectively.[20] Based on the FTIR spectra, polymer blend composition, and conductivity data, a Grotthuss-type conduction mechanism (structural diffusion) can be safely proposed for the present polymer blends, which includes ordered acid–base complexes throughout the polymeric matrix. This is also consistent with the previous studies that indicated rapid exchange of protons for PVPA homopolymer and copolymers via hydrogen bonding network by solid-state NMR under fast magic angle spinning.[18,21] It is very likely that in situ polymerization results in more favorable proton conducting network compared to the physically blended PEMs, since during polymerization, VPA monomers can be directed to appropriate local positions by imidazole units in the ABPBI backbone. On the other hand, it is noteworthy that the observed significant increases of proton conductivities at high temperatures compared to the physically blended samples might also indicate the contribution of enhanced segmental motion of the polymer (vehicular-type mechanism) to the proton conductivity. The reason is based on the lower T_gs of in situ polymerized blends, which are lower than the measurement

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temperature of 150 °C. However, in physically blended samples, the T_gs are higher than 150 °C for 1:1 and 1:2 molar ratios, which should restrict the segmental motions more. The contribution of proton hopping and segmental motion to the proton transport depends on the temperature and the PVPA content in the polymer blend.

4. Conclusion

Polymer electrolyte membranes (PEM) were successfully developed by in situ polymerization of VPA within a ABPBI matrix. The proton exchange reactions between ABPBI and PVPA were confirmed by FTIR spectra. DSC graphs indicated the formation of homogeneous polymer blends. Decomposition of the membranes starting at approximately 240 °C was shown by TGA. In the anhydrous state (150 °C), all the membranes showed appreciable proton conductivities (>10^{-4} S cm^{-1}) with the highest values being 0.001 and 0.002 S cm^{-1} for (1:1) and (1:2) molar ratios, respectively. These conductivities indicated significant improvements (10^3–10^4 times) over the physically blended samples and it can attributed to more favorable proton conductive patways/mechanism for lower T_g samples. To the best of our knowledge, this study shows the first example of an in situ polymerized PVPA:ABPBI PEM system with the great advantage of high conductivity at high temperature. We believe that this study will open a new door for the realization of new PEM materials via in situ preparation for next-generation high-temperature and non-humidified PEMFCs.

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