

# Proton Conducting Polymer Blends from Poly(2,5-Benzimidazole) and Poly(2-Acrylamido-2-methyl-1-propanesulfonic acid)

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**ABSTRACT:** Proton conducting polymer electrolyte membranes were produced by blending of poly(2,5-benzimidazole) (ABPBI) and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) at several stoichiometric ratios with respect to polymer repeating units. The membranes were characterized by using Fourier transform infrared spectroscopy for interpolymer interactions and scanning electron microscope for surface morphology. Thermal stability of the materials was investigated by thermogravimetric analysis. Glass transition temperatures of the samples were measured via differential scanning calorimetry. The spectroscopic measurements and water uptake studies indicate a complexation between ABPBI

and PAMPS that inhibited polymer exclusion up on swelling in excess water. Proton conductivities of the anhydrous and humidified samples were measured using impedance spectroscopy. The proton conductivity of the humidified ABPBI:PAMPS (1 : 2) blend showed a proton conductivity of 0.1 S/cm, which is very close to Nafion 117, at 20°C at 50% relative humidity. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1193–1198, 2011

**Key words:** poly(2,5-benzimidazole); poly(2-acrylamido-2-methyl-1-propanesulfonic acid); blend; proton conductivity; fuel cell

## INTRODUCTION

In the past few decades, there has been an increasing interest in the development of novel proton conducting polymer electrolytes to be used in polymer electrolyte membrane fuel cells (PEMFC).<sup>1–7</sup> Humidified perfluorosulfonic acid membranes have been emerged as the membrane materials for low temperature fuel cell application because of their high proton conductivity and excellent chemical stability.<sup>8</sup> Also, a number of proton conducting membranes have been successfully investigated such as the sulfonated aromatic polymers,<sup>9</sup> irradiation graft polymers,<sup>10,11</sup> crosslinked<sup>3,12</sup> and blending polymers.<sup>13–16</sup> Another approach is the phosphoric acid-doped polymers in which proton transport is mainly provided over bronsted acid-base pairs ( $\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-$ ) via structure diffusion.<sup>8,17–20</sup> Although high proton conductivity can only be reached at higher acid compositions, dopant leaching out is an important drawback during prolonged usage in fuel cells. Thus,

blending of high molecular weight acidic and basic polymers could be a solution for this problem.

Previously, proton conducting membranes based on Nafion and polybenzimidazole (PBI) were produced by solution casting.<sup>21</sup> A decrease in proton conductivity was reported as a consequence of the involvement of some fraction of the sulfonic acid groups in PBI crosslinking. In another work, proton conducting polymer electrolytes based on the sulfonated polysulfones (SPSF) and polybenzimidazole (PBI) were produced by doping with phosphoric acid. The water uptake of the blends increased with increasing PBI content. Because of increasing temperature and doping level, ionic conductivity of the membranes increased. However, almost no effect of relative humidity on the proton conductivity was observed.<sup>13</sup>

Pasupathi et al.<sup>22</sup> studied polymer blends based on sulfonated poly(ether ether ketone) (SPEEK) and poly(benzimidazole) (PBI). They compared thermal stability, water uptake, conductivity of the blend membrane to that of Nafion. The conductivity of Nafion was found to be better than SPEEK/PBI membrane, but the thickness of SPEEK/PBI membranes was reduced considerably.

Sulfonated poly(aryl ether ether ketone) (SPAEEK) and polybenzimidazole (PBI) composite membranes were investigated by Zhang et al.<sup>23</sup> It was shown that the proton conductivity of the composite membranes depends on the PBI content. The thermal

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stability and mechanical properties of the SPAEEK membranes increased with increasing PBI content. The water uptake of the membrane and proton conductivity decreased with increasing PBI content whereas increased with increasing temperature.

PBI is a commercially available polymer and high proton conducting membranes have been produced by impregnation of phosphoric acid.<sup>24</sup> Poly(2,5-benzimidazole) (ABPBI), one of the benzimidazole polymers has the simplest structure and could be polymerized from just only one commercial monomer without previous purification.<sup>25</sup> PAMPS is a sulfonic acid containing polyelectrolyte that has certain chemical stability and can be used as a blend component.<sup>26,27</sup>

In this study, novel blends based on ABPBI and PAMPS were synthesized (Fig. 1). The blends were prepared by solution casting from ABPBI solutions and PAMPS at several molar ratios. The effect of ABPBI and PAMPS contents on the conductivity of final product was investigated. The syntheses, molecular interactions, surface morphology, thermal properties, water uptake, and proton conductivity were reported.

## EXPERIMENTAL

### Materials

3,4-diaminobenzoic acid (97%) was obtained from Alfa Aesar. Polyphosphoric acid (~ 85%) and trifluoroacetic acid (TFA) were purchased from Merck. All the chemicals were used as received.

### Synthesis of PAMPS and ABPBI

PAMPS was synthesized by free radical polymerization of 2-acrylamido-2-methyl propane sulfonic acid according to the procedure described in the literature.<sup>28</sup> The molecular weight of PAMPS was measured around 18,000, and the glass transition was around 110°C. ABPBI was synthesized by condensation of 3,4-diaminobenzoic acid (DABA) in polyphosphoric acid (PPA) as reported in the literature.<sup>25</sup> Synthesized polymers showing the same properties with the literature were used for blend membrane preparation.

### Preparation of the membranes

1.5 g of ABPBI was dissolved in 60 mL of TFA by stirring overnight at 70°C. Then water was added dropwise into ABPBI/TFA system, and the mixture was stirred until a uniform solution was obtained. ABPBI/TFA and PAMPS/water solutions were admixed to get ABPBI:PAMPS membranes with (2 : 1), (1 : 1), (1 : 2), and (1 : 4) molar ratios regarding to monomer repeating units, i.e., molar ratio of benzimidazole to 2-acrylamido-2-methyl propane sulfonic acid. Solutions were cast on the petri dishes

and dried at 70°C, under normal atmospheric pressure. Then the films were further dried under vacuum at 80°C, and stored in the glove box. Film thicknesses were ranging between 150 and 250  $\mu\text{m}$ .

### Characterizations

Fourier-Transform IR spectra of dry ABPBI-PAMPS membranes was investigated over a wavelength range from 650 to 4000  $\text{cm}^{-1}$  by the attenuated total reflection (ATR) module by using Perkin-Elmer FTIR spectrum BX. Prior to FTIR measurements, the samples were dried under vacuum at 80°C.

The surface morphology of membranes was investigated by scanning electron microscopy (SEM, Philips XL30S-FEG). All of the samples were sputtered with gold for 150 s before SEM measurements.

Thermal stabilities of the polymer films were determined by using thermogravimetric analysis (TGA) with PerkinElmer STA 6000. The analysis was carried out heating the samples from room temperature to 900°C at a rate of 10°C/min.

Differential scanning calorimetry (DSC) measurements were performed using PerkinElmer DSC 4000 under nitrogen atmosphere heating from 0 to 180°C at a rate of 10°C/min. The glass transition temperatures of the membranes were assessed from the second heating curves.

Water uptake (WU) measurement was determined by the weight difference between the fully humidified membranes and dried membranes. The dried membranes ( $W_{\text{dry}}$ ) were weighed and then wetted until the weight remained constant. The wet or saturated weights of the membranes ( $W_{\text{wet}}$ ) were measured quickly after removing or wiping out any remaining surface water. The water uptake was calculated according to the formula (1):

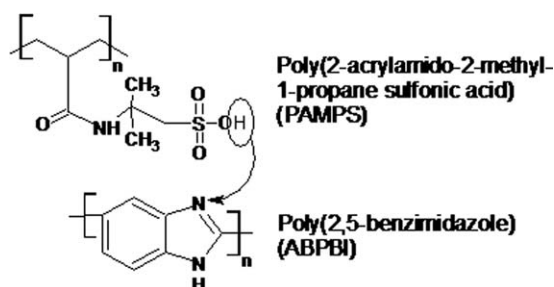
$$\text{Water uptake (WU)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (1)$$

The measurements of the proton conductivity of the membranes were performed by using Novocontrol impedance analyzer over a frequency range of 0.1 Hz to 3 MHz with Novocontrol cryosystem controlled temperature, applicable between -100 and 250°C. Membranes were placed between two platinum blocking electrodes. The variation of temperature was from 20 to 150°C with 10°C intervals for anhydrous membranes and from 20 to 100°C with 20°C intervals for humidified membranes.

## RESULTS AND DISCUSSION

### FTIR spectroscopy

The ABPBI-PAMPS interactions in the blend membranes were characterized by FTIR spectroscopy as

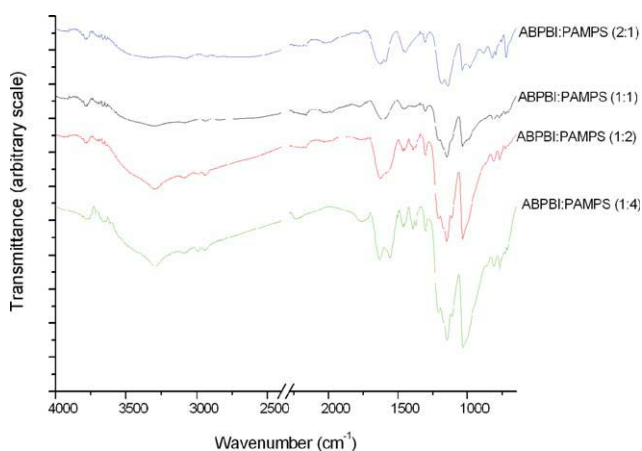


**Figure 1** Chemical structures and interaction between ABPBI and PAMPS polymers.

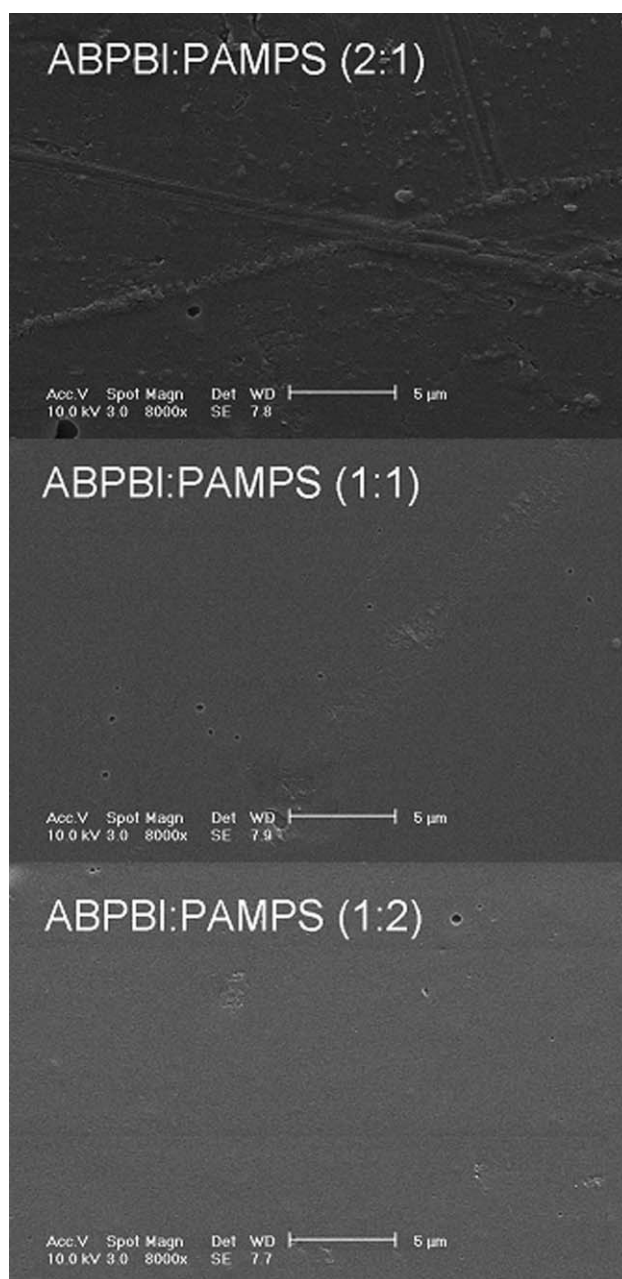
shown in Figure 2. The strong absorption bands at 1033 and 1212  $\text{cm}^{-1}$  are attributed to asymmetric and symmetric stretching vibration of O=S=O unit of  $-\text{SO}_3\text{H}$ , respectively.<sup>29</sup> The bands at 1628, 1560, and 1458  $\text{cm}^{-1}$  could be attributed to C=N and C=C stretching.<sup>25</sup> The region from 3500 to 2500  $\text{cm}^{-1}$  includes both CH and NH stretching modes and band broadening in this region is due to hydrogen bonding network formation. The band detected at 3375  $\text{cm}^{-1}$  is assigned to nonhydrogen bonded N-H stretching. At higher PAMPS contents, the intensity of this peak increases. In addition, the peak near 3100  $\text{cm}^{-1}$  is the result of  $\text{N}^+\text{-H}$  stretching that indicates the protonation of the ABPBI.<sup>30</sup> These results imply that the proton conduction may occur by transfer of protons from a protonated benzimidazole to a nonprotonated one and then to sulfonic acid functional groups of PAMPS.

### Morphology

The microtopography of ABPBI/PAMPS blend membranes was studied by SEM as shown in Figure 3. Because of strong acid-base interactions between sulfonic acid group of PAMPS and imidazole units of ABPBI, complexation occurred immediately after mixing and homogeneous films were produced. Fig-



**Figure 2** FTIR spectra of ABPBI:PAMPS blend membranes. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]



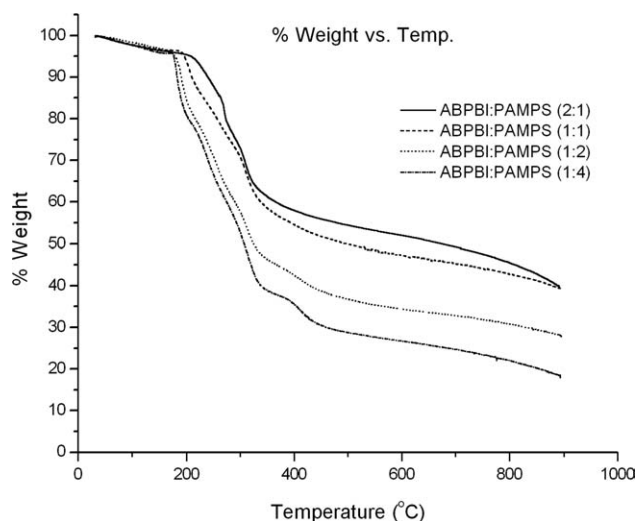
**Figure 3** SEM micrographs of the surface of ABPBI-PAMPS blend membranes at of (2 : 1), (1 : 1), and (1 : 2) molar ratios.

ure 3 indicates a very good compatibility between ABPBI and PAMPS.

### Thermal analysis

Polymer electrolyte membranes (PEM) that maintain stable proton conductivity at elevated temperatures are required for PEMFC applications. Thermal properties of ABPBI/PAMPS blend membranes were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

For all the ABPBI/PAMPS blend membranes, an elusive weight change was observed up to



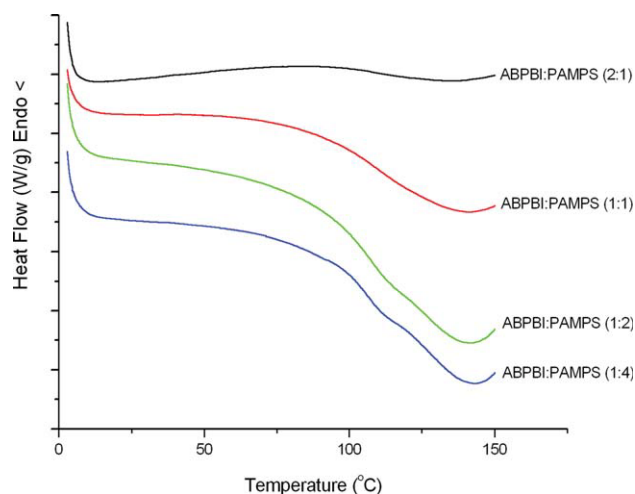
**Figure 4** TG thermograms of ABPBI:PAMPS blend membranes at a heating rate of 10°C/min.

approximately 180°C because of absorbed humidity (Fig. 4). The second weight loss, beginning at 190–210°C can be attributed to decomposition of the polymer, PAMPS.<sup>29</sup>

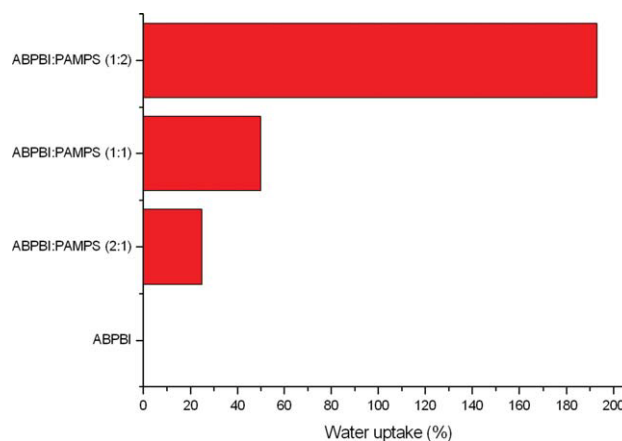
The DSC thermograms were obtained by heating-cooling cycles from 0 to 180°C, and  $T_g$  values of the blends were evaluated from the second heating curves (Fig. 5). The  $T_g$  of the samples, except for the sample ABPBI:PAMPS (2 : 1), slightly shifts to lower temperatures with increasing PAMPS content, i.e., the  $T_g$  of ABPBI:PAMPS (1 : 1) is 116°C and that of ABPBI:PAMPS (1 : 4) is 104°C.

### Water uptake

The water uptake of the membranes is a major parameter influencing proton conductivity, mechanical property, and stability. Water uptakes of the ABPBI



**Figure 5** DSC curves of ABPBI:PAMPS blend membranes at a heating rate of 10°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 6** Water uptakes of the blend membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and the membranes are shown in Figure 6. The samples ABPBI:PAMPS (2 : 1), ABPBI:PAMPS (1 : 1), and ABPBI:PAMPS (1 : 2) have the water uptakes 25, 50, and 193%, respectively. As it is seen, percent water uptake increasing with PAMPS content in the matrix. Although the mechanical strength of the swelled membrane decreased to a certain extent, almost no PAMPS dissolved in the solution. The result showed that the complexation of ABPBI with PAMPS prevented the loss of guest polymer (PAMPS) to the solution.

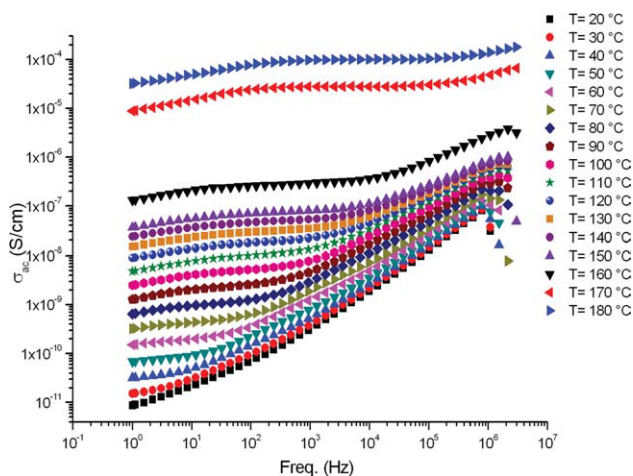
### Proton conductivity

Frequency dependent proton conductivity of the samples was measured by AC impedance method over 0.1 Hz to 3 MHz frequency range at various temperatures under dry nitrogen flow. AC conductivities,  $\sigma_{ac}(\omega)$  were measured using eq. (2):

$$\sigma'(\omega) = \sigma_{ac}(\omega) = \varepsilon''(\omega)\omega\varepsilon_0 \quad (2)$$

where  $\sigma'(\omega)$  is the real part of conductivity,  $\omega = 2\pi f$  is the angular frequency,  $\varepsilon_0$  is the vacuum permittivity ( $\varepsilon_0 = 8.852 \times 10^{-14}$  F cm<sup>-1</sup>), and  $\varepsilon''$  is the imaginary part of complex dielectric permittivity ( $\varepsilon^*$ ).

The samples were dried under vacuum at 80°C for 24 h prior to measurements. Alternating current (AC) conductivity,  $\sigma_{ac}$ , versus frequency curves are shown in Figure 7 for anhydrous ABPBI:PAMPS (1 : 4) blend membrane. The curves for all the samples involve the frequency dependent and independent regions which are typical in ion conducting polymers. A frequency independent region over two to three decades was observed at higher frequencies and higher temperatures. The direct current (DC) conductivity,  $\sigma_{dc}$ , of the samples was derived from those plateau regions by linear fitting.



**Figure 7** AC conductivity versus frequency of ABPBI:PAMPS (1 : 4) blend membrane at several temperatures. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The temperature dependence of proton conductivities for anhydrous ABPBI:PAMPS blends is shown in Figure 8. It seems that the proton conductivity of the ABPBI:PAMPS system depends on the composition and the temperature. Clearly, the proton conductivity of the samples changes with the PAMPS content. For example, ABPBI:PAMPS (1 : 4) membrane showed better conductivity within the temperature range of measurement. A sudden increase in conductivity above 160°C was observed which may be due to morphological changes in the membrane materials, prior to degradation. In the anhydrous state, ABPBI:PAMPS (1 : 4) showed a maximum proton conductivity of  $10^{-4}$  S  $\text{cm}^{-1}$  at 180°C. However, ABPBI:PAMPS (1 : 1) yielded lowest conductivity compared to others. The reason can be attributed to equimolar existence of acidic and basic units protonated the free nitrogens benzimidazole units of ABPBI, inhibiting long range proton diffusion. At higher temperature domain, the proton conductivities of the samples ABPBI:PAMPS (1 : 2) and ABPBI:PAMPS (2 : 1) are very close to each other. The former sample has higher PAMPS content where the proton conductivity can also occur over acidic units. However, in the latter sample, there are two benzimidazole units per sulfonic acid unit and structural diffusion can occur over azole units. As a matter of fact, the conduction of the proton can occur through the transition of proton from protonated guest molecules to a nonprotonated neighbor host molecule. As reported in the literature, anhydrous polymer systems facilitate the formation of protonic defects and provide strongly labile proton donor and acceptor functions. In addition, acidic molecules such as sulfonic acid could also act as proton donors and acceptors.<sup>31</sup> Protonated and nonprotonated nitrogen in heterocyclic group of ABPBI and sulfonate group of PAMPS may act as donors and acceptors in proton transfer reactions. Considering the

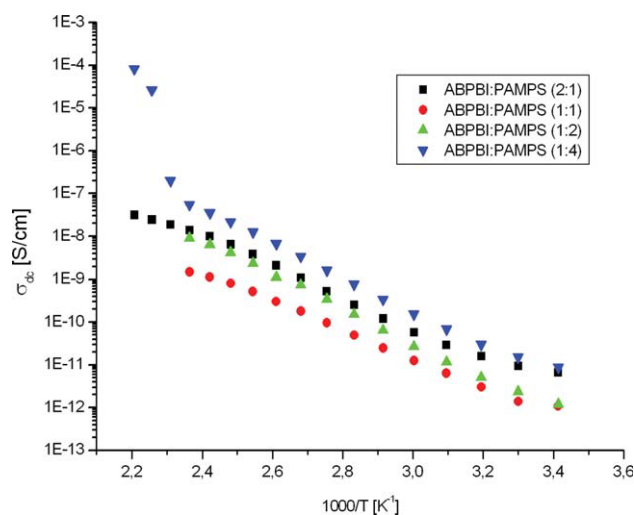
FTIR spectra of polymer blend composition as well as conductivity data, Grotthuss mechanisms (structural diffusion) causes a pathway for the total proton diffusion (Fig. 1).

The effect of relative humidity levels on proton conductivity of Nafion 117 was reported in earlier studies. The proton conductivity of fully humidified Nafion 117 membrane exceeds  $0.11$  S  $\text{cm}^{-1}$  at room temperature. The proton conductivity of Nafion 117 at 50% relative humidity is approximately  $0.03$  S  $\text{cm}^{-1}$  at 40°C.<sup>32–34</sup>

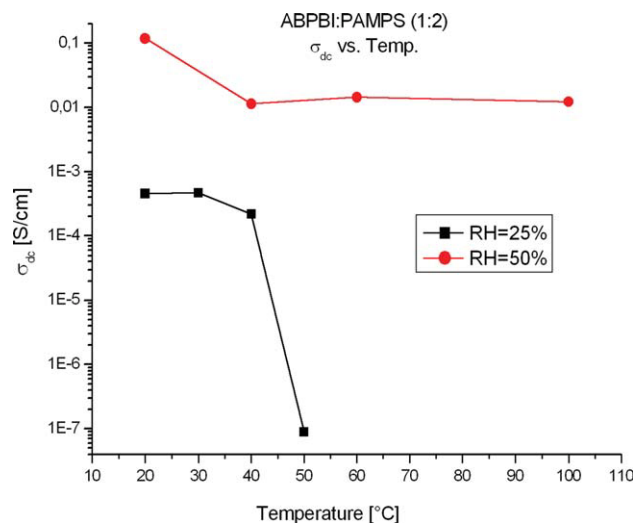
To see the effect of relative humidity on the proton conductivity of ABPBI:PAMPS (1 : 2) blend, this material was humidified with RH of 25 and 50%. The temperature dependence of proton conductivity of humidified ABPBI:PAMPS (1 : 2) blend is illustrated in Figure 9. Clearly, the proton conductivity increased in parallel with %RH that might be explained by increasing mobility of proton with increasing water content in the membrane. The sample ABPBI:PAMPS (1 : 4) loses its mechanical strength and stability even at low humidity levels and ABPBI:PAMPS (1 : 2) seems to be more promising membrane. The proton conductivity of ABPBI:PAMPS (1 : 2) with RH = 25% was measured as  $5 \times 10^{-4}$  S  $\text{cm}^{-1}$ . Furthermore, the highest conductivity of  $0.1$  S  $\text{cm}^{-1}$  was achieved for the same sample when RH = 50% at ambient temperature. This value is very close to Nafion 117, at room temperature with RH = 100%.

## CONCLUSIONS

PEM were successfully produced from the blends of ABPBI and poly(2-acrylamido-2-methyl-1-propane-sulfonic acid) (PAMPS) by solution casting. Proton exchange reaction between ABPBI and PAMPS was



**Figure 8** The DC conductivity versus reciprocal temperature for the anhydrous ABPBI:PAMPS blend membranes. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 9** DC conductivity versus temperature of humidified ABPBI:PAMPS (1 : 2) membranes (RH = 25% and RH = 50%) at several temperatures. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

confirmed by FTIR spectra. Formation of homogeneous polymer blends was proved from the SEM and DSC results. Thermogravimetric analysis showed that the materials are thermally stable up to 190°C. Water uptake and the proton conductivity of the samples increased with increasing PAMPS content. After humidification, the proton conductivity of the sample ABPBI:PAMPS (1 : 2) dramatically increased to 0.1 S cm<sup>-1</sup> (RH = 50%) which is very close to Nafion 117, at 20°C. The swelling experiment suggested the complexation between ABPBI and PAMPS that inhibited dopant exclusion up on swelling in excess water. As a conclusion, PBI/PAMPS blend membranes can form homogeneous free-standing thin films that have thermal and mechanical stability and illustrate sufficient proton conductivities under low humidity conditions to be used in PEM fuel cells.

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