

Proton Conduction in PVPA –Benzimidazole Hybrid Electrolytes

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Received 26.11.2004

Proton conducting properties of benzimidazole (BnIm) doped poly(vinylphosphonic acid) (PVPA) were studied. The doping ratio, x , which is the number of moles of BnIm per mole of polymer repeat unit, varied from 0.5 to 2. The samples were characterized by FT-IR spectroscopy, thermogravimetric analysis (TG), differential scanning calorimetry (DSC) and impedance spectroscopy. The IR study indicates the protonation of heterocyclic units from the "free nitrogen" side. The proton conductivity and thermal stability of the blends increase with x . Maximum conductivity of PVPA x BnIm blends is approximately 10^{-3} S/cm at 150 °C.

Key Words: Poly(vinylphosphonic acid), benzimidazole, proton, conductivity, thermal properties

Introduction

Heterocycles such as imidazole or pyrazole are known to be involved in proton transport across biological membranes. The proton mobilities in these proton solvents show behavior similar to that of water when compared at temperatures relative to their respective melting points¹. The replacement of water with heterocycles in host-guest systems may be of interest for the synthesis of one-phase polymer-imidazole membranes that can be applicable to various electrochemical devices such as fuel cells at higher temperatures ($T > 100$ °C). In this context, anhydrous proton conducting polymer electrolytes were prepared by blending imidazole with host polymers that contain acidic functional groups i.e. $-\text{CO}_2\text{H}$, $-\text{PO}_3\text{H}_2$, and $-\text{SO}_3\text{H}$ ²⁻⁴. Intercalation of imidazole into polymers was shown to produce transparent, homogeneous and high proton conducting materials that could be used at medium operation temperatures (~ 150 °C).

Benzimidazole ($T_m = 174$ °C) is another promising heterocycle and more temperature tolerant proton conducting polymer membranes can be obtained when it is blended with high temperature stable acidic host matrixes. Previously, the blends of polybenzimidazole (PBI) and phosphoric acid have been shown to be more temperature stable and to have high proton conductivity in the anhydrous state⁵⁻⁸. Recently, proton conduction in mono-dodecylphosphate (MDP) - benzimidazole mixed materials has been reported⁹.

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In the present study, anhydrous proton conducting polymer electrolytes on the basis of PVPA (I) and BnIm (II) are reported (Figure 1). The synthesis of these materials and their thermal and conductivity properties are discussed.

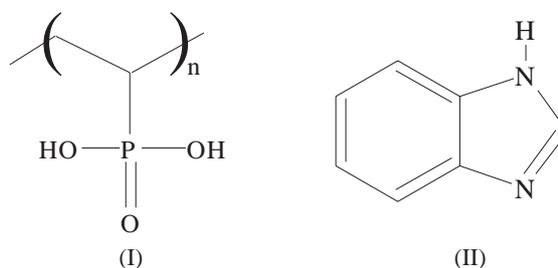


Figure 1. Chemical structures of PVPA and BnIm.

2. Experimental

Materials preparation

Poly(vinylphosphonic acid) (PVPA) provided by Polysciences has an average molecular weight of 20,000 g/mol. A stoichiometric amount of BnIm (Aldrich) and PVPA was mixed in H₂O/EtOH and the resulting mixture was stirred for several days to make it homogeneous. Solutions with x ranging from 0.5 to 2.0 were prepared where x is the number of moles of benzimidazole per mole of polymer repeat unit. From the solutions films were cast in polished polytetrafluoroethylene (PTFE) plates, and the solvent was carefully evaporated and further dried under vacuum at 60 °C for several days to remove residual water. Transparent and homogeneous films with thicknesses between 100 and 300 μm were obtained for all the blends. The films with x = 1 and x = 2 are flexible at room temperature and very hygroscopic.

Characterizations

FT-IR spectra of the samples were recorded using a Mattson Genesis I spectrophotometer. Thermal stabilities of the materials were investigated using a thermogravimetric analysis (TG) (Mettler-Toledo TG-50). Differential scanning calorimetry (DSC), a Mettler-Toledo DSC 30 instrument was used to determine the glass transition temperatures (T_g) of the PVPA and blends were loaded into aluminum pans (10-20 mg) and heated to the desired temperature at a rate of 10 °C/min under nitrogen flow. The second heating curves were evaluated. The alternating current (AC) conductivities of PVPA x BnIm samples were determined using a Novocontrol impedance spectrometer in the frequency range from 1 Hz to 1 MHz and in the temperature regime from 20 to 150 °C. The film samples were placed between platinum electrodes and their conductivities were measured at 10 K intervals.

Results and Discussion

Polymer–base interactions

FT-IR spectra of PVPA-x-BnIm (x = 1 and x = 2) blends are represented in Figure 2. The IR spectrum of the homopolymer shows strong bands at 1040-910 cm⁻¹ and 1150cm⁻¹ due to (P-O)H and P = O stretching

respectively. The phosphonic acid group gives an additional band in the region of $1700\text{--}1630\text{ cm}^{-1}$. The broad band at $3300\text{--}2850\text{ cm}^{-1}$ belongs to --OH stretching of the same group. After blending the polymer with benzimidazole, the intensity of (P-O)H stretching at 910 cm^{-1} decreases with increasing x . In addition, two new absorption bands appear near 1120 and 1050 cm^{-1} owing to stretching vibration bands of --HPO_3^- and PO_3^{2-} . These results indicate that P-OH groups of the polymer are deprotonated with BnIm and form P-O⁻ side groups. The absorption band near 3150 cm^{-1} corresponds to the N-H group and increases relatively with increasing x . Additionally, the weak absorption band at 1620 cm^{-1} has been related to the protonated heteroaromatic ring. Such phenomena have been reported in polybenzimidazole (PBI)/phosphoric acid or sulfuric acid complexes and in mono-dodecylphosphate (MDP)/ benzimidazole (BnIm) ^{8,9}. Therefore, the blend of PVPA- x -BnIm forms a new “polysalt” including deprotonated phosphonic side groups with benzimidazolium counterions.

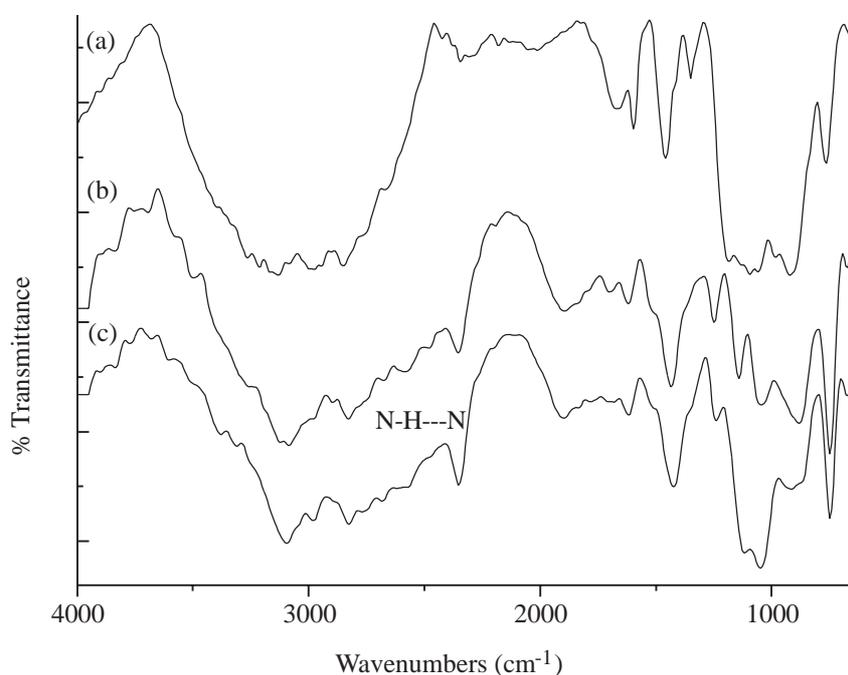


Figure 2. FT-IR spectra of pure PVPA (a) , PVPA 1 BnIm (b), and PVPA 2 BnIm (c).

Thermal analysis

The samples were dried for 2 days under vacuum at $60\text{ }^{\circ}\text{C}$ prior to TG measurements. It was previously reported that the homopolymer of PVPA is thermally stable up to at least $200\text{ }^{\circ}\text{C}$ under both nitrogen and air ¹⁰. Figure 3 shows the TG curves of $x = 1$ and $x = 2$. For the anhydrous PVPA 1 BnIm blend, the initial weight reduction starts near $140\text{ }^{\circ}\text{C}$. A small exponential decay above this temperature may be due to free water in this hygroscopic material and is followed by decomposition of the blend above $200\text{ }^{\circ}\text{C}$. The PVPA 2 BnIm blend is thermally stable up to $200\text{ }^{\circ}\text{C}$.

DSC thermograms of PVPA x BnIm are shown in Figure 4. The T_g of the homopolymer ($-23\text{ }^{\circ}\text{C}$) shifted to $-5\text{ }^{\circ}\text{C}$ for $x = 1$ and $-8\text{ }^{\circ}\text{C}$ for $x = 2$. The increase in T_g with benzimidazole contents is the effect of restriction of segmental motions, which may be due to ionic interactions and hydrogen bond network formation in the blends.

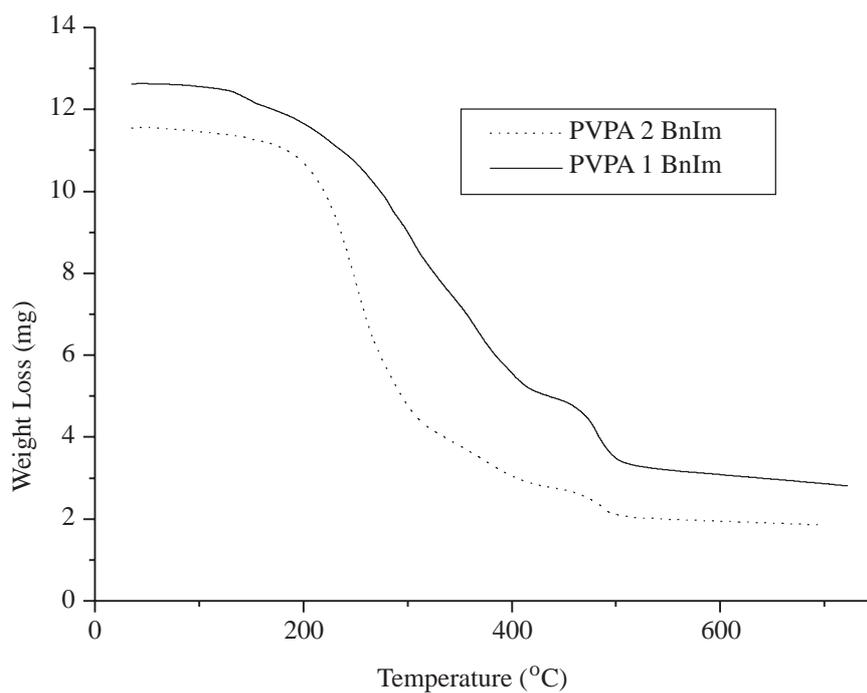


Figure 3. TG curves of PVPA 1 BnIm, and PVPA 2 BnIm recorded under N₂ atmosphere with a heating rate of 10 K/min.

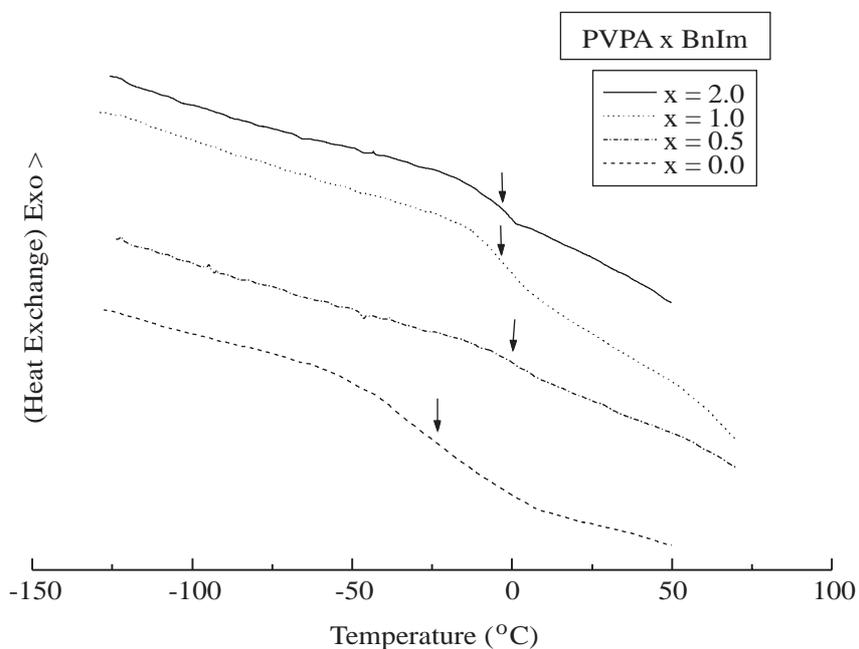


Figure 4. DSC curves of PVPA, PVPA 0.5 BnIm, PVPA 1.0 BnIm, and PVPA 2.0 BnIm recorded under N₂ atmosphere with a heating rate of 10 K/min.

Conductivity measurements

Figures 5 and 6 show the frequency dependence of the alternating current, AC conductivities (σ_{ac}) of PVPA 1 BnIm and PVPA 2 BnIm, respectively. Characteristic σ_{ac} versus log F curves consist of the frequency independent conductivity plateau regions, which are well developed at low frequencies and at low temperatures and expand and shift toward higher frequencies with increasing temperature. The irregularities on the low frequency side at higher temperatures, i.e. $T > 100\text{ }^{\circ}\text{C}$ for $x = 2.0$, are the effect of electrode polarization of the blocking electrodes. The direct current, DC conductivity (σ_{dc}) of the samples is estimated from the AC conductivity plateau by extrapolation to zero frequency. These plateau values coincide quite well with the σ_{dc} values obtained from the Z' minimum of impedance diagrams. The temperature dependence of the proton conductivity of PVPA x BnIm blends is compared in Figure 7. Clearly, there is no significant change in the conductivities of $x = 0.5$ and $x = 1.0$ with benzimidazole content. The conductivity of $x = 2$ is at least one order of magnitude higher than $x = 0.5$ and $x = 1.0$ at higher temperatures. The conductivity increase with x can be explained by the increase in defect number where the protons will transfer. In contrast to polymer-imidazole blends which show Vogel-Tamman-Fulcher (VTF) behavior for larger x , the conductivity isotherms of PVPA x BnIm follow Arrhenius law irrespective of BnIm content. The latter behavior can be explained by the restrictions of segmental relaxations of the polymer chains, which is also proved by DSC.

The intercalation of benzimidazole with a different doping ratio, x , into PVPA as Bronsted acid increased the conductivity PVPA x BnIm membranes and showed maximum conductivity of approximately 10^{-3}S/cm at $150\text{ }^{\circ}\text{C}$. The proton conductivity of anhydrous heterocycles has been investigated in a previous work^{11,12}. The protonic defect may cause local disorder by forming protonated and unprotonated benzimidazoles. In such materials the proton transport may occur through structure diffusion (Grotthuss-type mechanism) comprising proton transfer between benzimidazole and benzimidazolium ion.

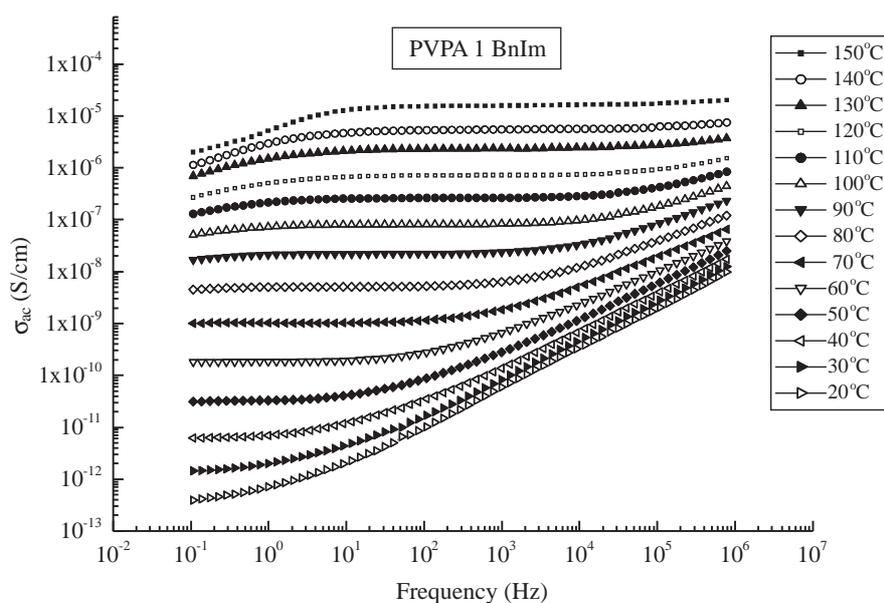


Figure 5. σ_{ac} vs. Frequency (Hz) for PVPA 1.0 BnIm at various temperatures.

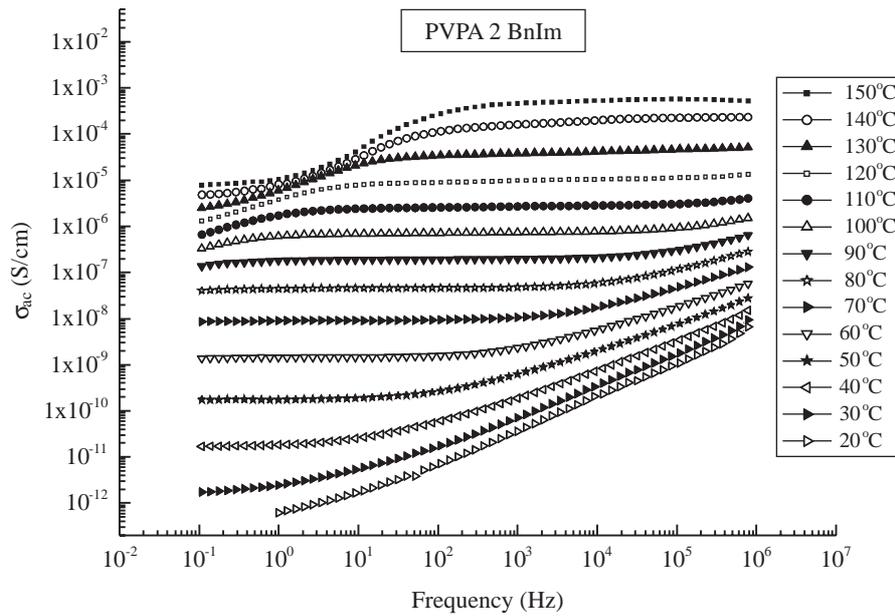


Figure 6. σ_{ac} vs. Frequency (Hz) for PVPA 2.0 BnIm at various temperatures.

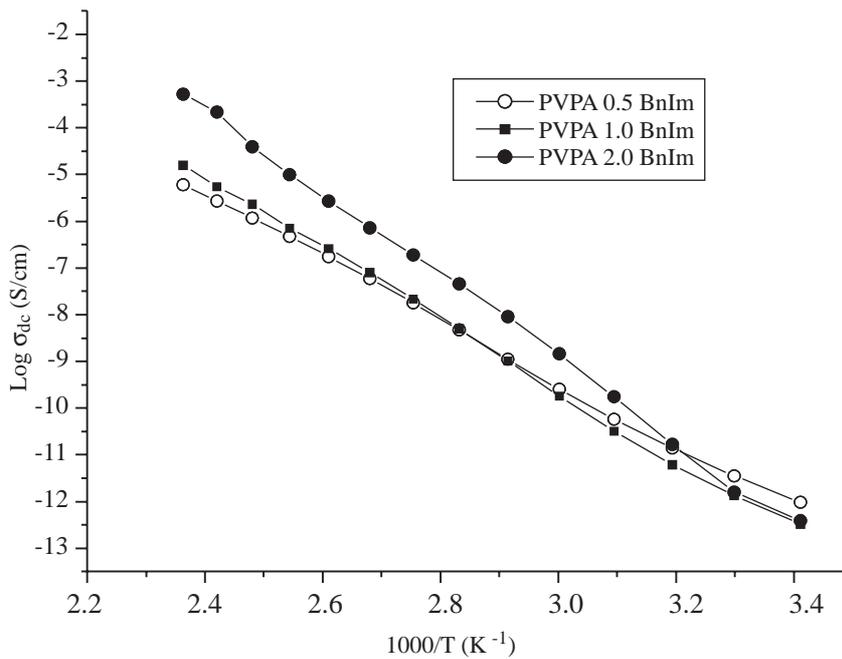


Figure 7. Temperature dependence σ_{dc} of PVPA x BnIm.

Conclusions

We prepared proton conductors by doping PVPA with BnIm to form PVPA x BnIm, which is amorphous and transparent. The IR study indicates the protonation of heterocyclic units from the "free nitrogen" side. Clearly, PVPA x BnIm membranes seem to be more temperature tolerant than their polymer-imidazole counterparts. The DC conductivity of the blends increases with benzimidazole content, reaching $\sim 10^{-3}$

S/cm for $x = 2$ at 150 °C. A cooperative proton migration may occur through the proton vacancies, which is a Grotthuss-type diffusion mechanism.

Acknowledgements

The authors thank C. Sieber and P. Rader in the Max-Planck Institute for Polymer Research, Mainz - Germany for technical assistance.

References

1. W. Münch, K.D. Kreuer, W. Silvestri, J. Maier and G. Seifert, **Solid State Ionics** **145**, 437 (2001).
2. A. Bozkurt, W.H. Meyer and G. Wegner, **J. Power Sources** **123**, 126-131 (2003).
3. H. Erdemi, A. Bozkurt and W.H. Meyer, **Synth. Met.** **143**, 133-138 (2004).
4. F. Sevil and A. Bozkurt, **J. Phys. Chem. Solids** **65(10)**, 1659-1662 (2004).
5. J.S. Wainright, J.T. Wang, D. Weng, R.F. Savinell and M. Litt, **J. Electrochem. Soc.** **142**, 121 (1995).
6. Q. Li, H.A. Hjuler and N.J. Bjerrum, **J. Appl. Electrochem.** **26**, 773 (2001).
7. A. Schechter and R.F. Savinell, **Solid State Ionics** **147**, (2002)181.
8. R. Bouchhet and E. Siebert, **Solid State Ionics**, **118**, 287 (1999).
9. M. Yamada and I. Honma, **Electrochim. Acta** **48**, 2411 (2003).
10. D.D. Jiang, Q. Yao, M.A. McKinney and C.A. Wilkie, **Polym. Degrad. Stabil.** **63**, 423-434 (1999).
11. K.D. Kreuer, A. Fuchs, M. Ise, M. Spaeth and J. Maier, **Electrochim. Acta** **43**, 1281 (1998).
12. M.F.H. Schuster and W.H. Meyer, **Annu. Rev. Mater. Res.** **33**, 233 (2003).