

Anhydrous Proton Conductive Polystyrene Sulfonic Acid Membranes

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A novel anhydrous proton conducting polymer electrolyte based on polystyrene sulfonic acid, PSSA and benzimidazole (BnIm) was synthesized. The PSSA-BnIm interactions were studied by FT-IR. The thermal properties of the blends were investigated by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). The proton conductivities of these materials were measured by AC impedance technique. The conductivities of these materials increase with increasing BnIm content and temperature and maximum conductivity was found to be approximately 5×10^{-4} S/cm at 150 °C.

Key Words: Polystyrene sulfonic acid, benzimidazole, thermal properties, proton conductivity.

Introduction

Polyelectrolytes are polymers that contain ionic centers as part of their constitutional repeating (monomeric) units and a counter ion securing for electroneutrality. The ion conductivity of polyelectrolytes is commonly low in the dry state due to extensive ion pairing and ion clustering¹⁻³. Polystyrene sulfonic acid (PSSA) is an often used model compound in polyelectrolyte chemistry and can be prepared from well defined, commercially available polystyrene samples⁴. Many investigations of PSSA have been utilized for ion-exchangers but applications of these materials as proton conducting membranes in various electrochemical devices are also interesting due to low product cost. In recent decades, hydrated perfluorosulfonic membranes such as Nafion have been used in proton exchange membrane fuel cells (PEMFC). However, in the anhydrous state, these membranes have poor conductivity, the conductivity increasing with an increasing degree of hydration (water content)⁵. Similarly, the use of hydrated polystyrene sulfonic acid (PSSA) and its composites in H₂/O₂ fuel cells has been investigated⁶. However, the application of these materials is problematic, especially at temperatures above 100 °C, where the membranes do not maintain a stable high conductivity.

In recent years, investigations of water-free polymer electrolyte systems with sufficient proton conductivity have been carried out. In this context, inorganic/organic hybrid proton conductors were obtained by the blending of basic polymers with strong acids, i.e. phosphoric acid⁷⁻⁹. Recently, nitrogen-containing heterocycles such as imidazole or benzimidazole have been reported to be promising protonic charge carriers in anhydrous state. This may be interesting for the synthesis of one-phase polymer-imidazole membranes

that can be applicable at higher temperatures. In that respect, we have described the synthesis, thermal and conductivity properties of polymer/imidazole blends^{10,11}.

The present study reports a novel anhydrous proton conducting polymer electrolyte system based on polystyrene sulfonic acid and benzimidazole (BnIm). The synthesis of these materials and their thermal and conductivity properties are discussed.

Experimental

Preparation of materials

Both polystyrene ($M_n = 140,000$) and BnIm were provided by Aldrich. Sulfuric acid (98%), phosphorus pentoxide and cyclohexane (all from Merck, reagent grade) were used as received. The sulfonated polystyrene was fabricated by a method similar to that described by Vink⁴. In the sulfonation step, 50 mL of sulfuric acid was transferred to a 500 mL round bottom flask and 10 g of P_2O_5 was slowly added with stirring. The reaction mixture was cooled to 40 °C. Then 1.5 g of polystyrene was dissolved in 25 mL of cyclohexane and added dropwise to the acid solution. After 30 min, the reaction was stopped and allowed to stand at 40 °C for about 1 h. Then the bottle was cooled and 25 g of crushed ice was slowly added with stirring. Polystyrene sulfonic acid was precipitated in the form of a pale-yellowish sticky mass. The mixture was separated and polyacid was put in 100 mL of water and dialyzed. The percent sulfonation of PSSA was 90%–95%, which is consistent with literature data⁴.

The polymer electrolytes were prepared by intercalation of a stoichiometric amount of BnIm into PSSA in ethanol/ H_2O and the resulting mixture was stirred overnight. Solutions with x ranging from 0.5 to 1.5 were prepared, where x is the mole ratio of BnIm to acidic unit. From these solutions, films were cast onto polished PTFE plates, and the solvent was carefully evaporated and further dried under vacuum at 70 °C. Transparent, hygroscopic films were obtained for all blends.

Characterizations

Infrared spectra of the samples ($4000\text{--}500\text{ cm}^{-1}$) were acquired using an Mattson Genesis II spectrophotometer by casting thin sample films onto silicon wafers.

Thermal degradation of the polymer electrolytes was examined by thermogravimetry analyses with a Mettler-Toledo TG-50. The samples (~ 10 mg) were heated from room temperature to 700 °C at a rate of 10 °C/min.

A Mettler-Toledo DSC 30 differential scanning calorimeter was used for thermal investigations. The samples were loaded into aluminum pans (10–20 mg) and heated to the desired temperature at a rate of 10 °C/min.

The proton conductivity measurements were performed with a Novocontrol impedance spectrometer in the Max-Planck Institute for Polymer Research, Mainz, Germany. The samples were placed between platinum electrodes and their conductivities were measured in the frequency range 10^{-1} to 10^6 Hz at 10 K intervals. The temperature was controlled with a Novocontrol cryosystem, which is applicable between -150 and 400 °C with a precision of 0.01 °C.

Results and Discussion

The protonic host matrix, PSSA, was obtained by direct sulfonation of polystyrene (PS). Then PSSA was doped by BnIm to get PSSA x BnIm polymer electrolytes. The solutions with different x values were cast onto a Teflon plate, where x varies from 0.5 to 1.5. After drying, brittle, transparent and hygroscopic films were obtained with thicknesses ranging from 100 to 300 μm .

Polymer – benzimidazole interactions

FT-IR spectra of the PSSA 0.5 BnIm and PSSA 1.5 BnIm are represented in Figure 1. A strong absorption band centered at 1200 cm^{-1} is the asymmetric stretching vibration of the O=S=O unit of PSSA. The peak at 1005 cm^{-1} results from the vibrations of the phenyl ring substituted with a sulfonic group¹². The broadening of this peak and overlapping with the phenyl ring attached sulfonic anion peak located at 1125 cm^{-1} indicates the deprotonation of the sulfonic acid peak. Additionally, the absorption band at 1620 cm^{-1} indicates the protonated BnIm from the free-nitrogen (unprotonated) side forming a benzimidazolium ion. Such phenomena have been reported in a polybenzimidazole (PBI)/phosphoric acid complex¹³. These results suggest that the $-\text{SO}_3\text{H}$ group deprotonates by doping with BnIm and forms $-\text{SO}_3^-$ group. Therefore, PSSA and BnIm produce the acid-base salt, including sulfonic anion side group and benzimidazolium counter ion.

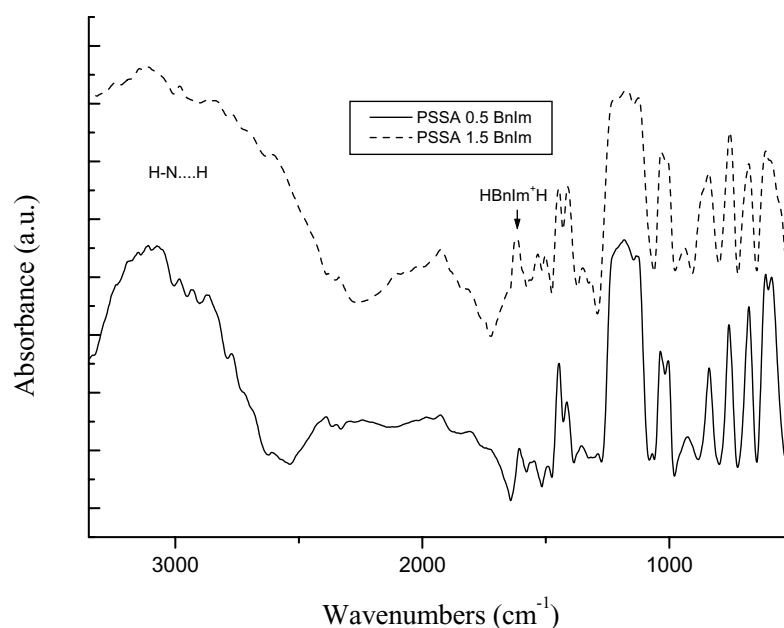


Figure 1. FT-IR spectra of PSSA 0.5 BnIm and PSSA 1.5 BnIm.

Thermal analysis

Previously the thermal degradation of poly(sodium 4-styrene sulfonate) was examined by Jiang et al.¹⁴. They indicated that the decomposition of polymer occurs in 2 steps within 200-500 $^{\circ}\text{C}$. The first step occurs from 100 to 280 $^{\circ}\text{C}$ and accounts for a 3-5% loss due to absorbed water in these hygroscopic materials. The second loss was observed over the temperature interval 300 to 400 $^{\circ}\text{C}$, which was attributed to degradation

of the polymer. The TG curve of PSSA 1.5 BnIm is shown in Figure 2. The overall decomposition pathway for PSSA x BnIm is remarkably similar to that observed for poly(sodium 4-styrene sulfonate).

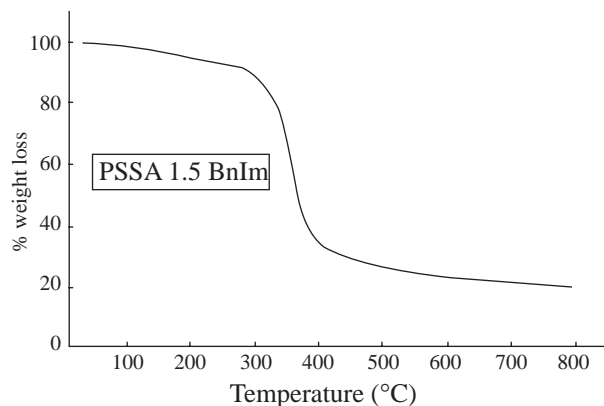


Figure 2. TG thermogram of PSSA 1.5 BnIm recorded at a heating rate of 10 K/min.

DSC curves of PSSA 0.5 BnIm and PSSA 1.5 BnIm are illustrated in Figure 3. The glass transition temperatures, T_g , of these blends are found to be 149 and 147 °C, respectively. The T_g of pristine PS is approximately 108 °C. After intercalation of BnIm, the T_g s of the blends shift to higher temperatures. This behavior can be expressed by the restriction of polymer segmental relaxations, which may be due to the formation of a hydrogen-bonding network. The presence of single glass transition is evidence of the homogeneity of these materials.

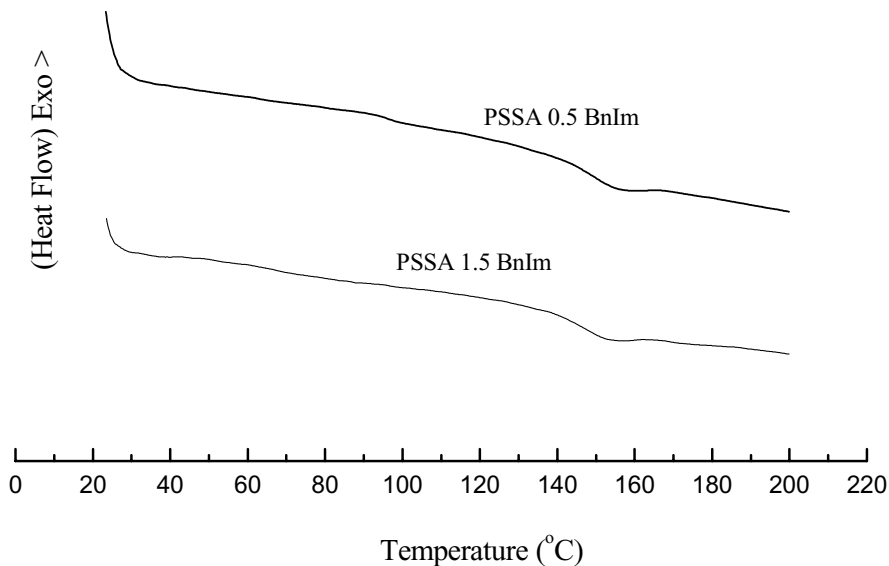


Figure 3. DSC of PSSA 0.5 BnIm and PSSA 1.5 BnIm. Temperature scanning rate is 10 K/min. Second heating curves are evaluated.

Conductivity measurement

Ion conductivities of the membranes were determined by impedance spectrometer at 10 K intervals within the frequency range 10^{-1} – 10^6 Hz. The alternating current (AC) conductivity, σ_{ac} , is obtained using Eq.

(1):

$$\sigma'(\omega) = \sigma_{ac}(\omega) = \varepsilon''(\omega)\omega\varepsilon_o \quad (1)$$

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

Figure 4 shows the σ_{ac} of PSSA 1.5 BnIm versus frequency at various temperatures. The curve consists of 2 well-defined regions; a low frequency zone at low temperatures is related to conduction processes in the bulk of samples. This region shifts to higher frequencies with increasing temperature. The irregularities at the low frequency side at higher temperatures are caused by electrode polarization due to the blocking effect of the platinum electrodes. The direct current (DC) conductivities of the samples are generated from the plateau regions by extrapolating to zero frequency.

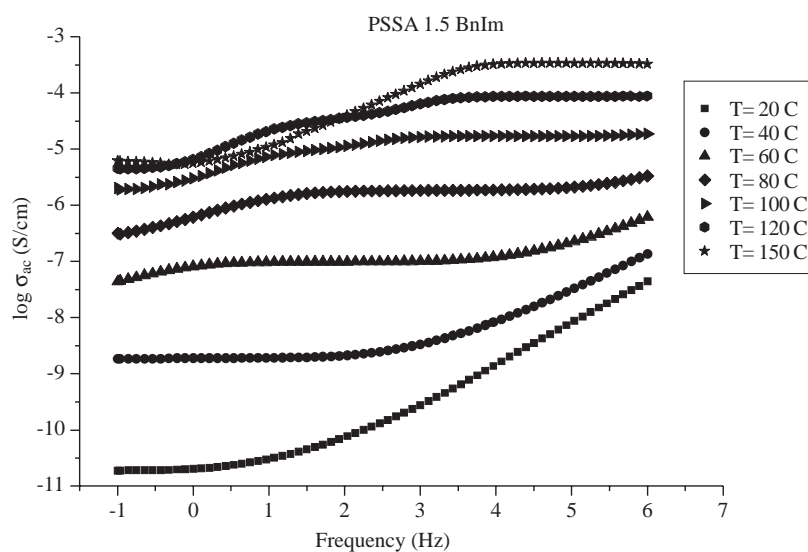


Figure 4. AC conductivity vs. frequency (Hz) for PSSA1.5 BnIm at various temperatures.

Figure 5 shows the DC conductivity as a function of inverse temperature for blends based on PSSA doped with BnIm at various mole ratios. The conductivity data were measured by heating and cooling cycles over a number of regions for a given sample, suggesting good homogeneity of polymer-heterocycle hybrid membranes. The temperature dependence of DC conductivity seems to follow the simple Arrhenius law at low doping ratios, i.e. $x = 0.5$ and $x = 1.0$, and the Vogel-Tamman-Fulcher (VTF) equation at a higher doping ratio ($x = 1.5$).

As illustrated, there is no significant proton conductivity for the samples with $x = 0.5$ or $x = 1.0$ within the measured temperature range. It can also be seen that the conductivities of these membranes are close to each other irrespective of their BnIm content. However, when the doping ratio is increased from 1 to 1.5, the ionic conductivity increases by at least 3 orders of magnitude. The conductivity, which is $\sim 10^{-7}$ S/cm at 130 °C for PSSA 1.0 BnIm, is $\sim 10^{-4}$ S/cm for PSSA 1.5 BnIm at the same temperature. The result is completely in agreement with our previously reported system, PAMPSA x Im¹¹. In the system studied, we confirmed that the low conductivity of PAMPSA 1 Im blend is due to complete protonation of imidazole from the “free” nitrogen site. Proton mobility relies on a Grotthuss type diffusion mechanism, that is transport of the proton from protonated guest molecules to a non-protonated neighboring molecule⁷.

Therefore, at higher doping ratios, a proton can be rapidly transferred to a neighboring molecule with a small activation energy, especially at higher temperatures. The PSSA x BnIm blends showed a maximum conductivity of 5×10^{-4} S/cm at 150 °C in the anhydrous state.

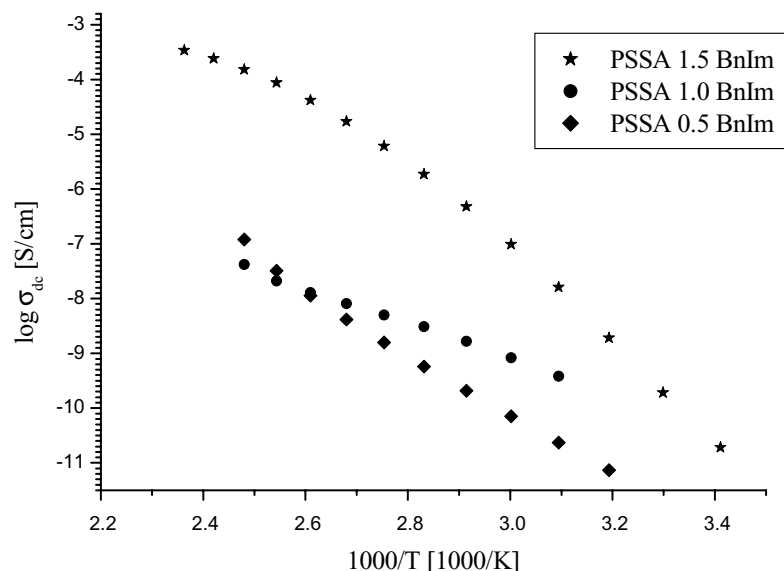


Figure 5. Temperature dependence of proton conductivities of the PSSA x BnIm blends.

Conclusion

Novel polymer/heterocycle hybrid proton conductive materials were prepared through the doping of PSSA with BnIm at various molar ratios. The thermal stability of the hybrid membrane is enhanced up to at least 200 °C. The homogeneity of the PSSA x BnIm blends was confirmed by DSC and conductivity measurements. From IR spectra and conductivity isotherms it can be concluded that proton conductivity occurs through structure diffusion. The proton conductivity of PSSA 1.5 BnIm reaches a maximum value of 5×10^{-4} S/cm at 150 °C.

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