Polym. Bull. (2011) 66:1099–1110
DOI 10.1007/s00289-010-0400-0

ORIGINAL PAPER

Proton conducting properties of ionically cross-linked poly(1-vinyl-1,2,4 triazole) and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) electrolytes

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Received: 13 July 2010 / Revised: 28 October 2010 / Accepted: 1 November 2010 /

Abstract The synthesis and thermal as well as proton conducting properties of complex polymer electrolytes based on poly(2-acrylamido-2-methyl-1-propanesulfonic acid) PAMPS and poly(1-vinyl-1,2,4-triazole) PVTri were investigated. The materials were produced by complexation of PAMPS with PVTri at various compositions to get PVTriP(AMPS)$_x$ where x is the molar ratio of the polymer repeating units and varied from 0.25 to 4. The structure of the materials was confirmed by FT-IR spectroscopy. The TGA results verified that the polymer electrolytes are thermally stable up to approximately 200 °C. The DSC and SEM results demonstrated the homogeneity of the materials. The electrochemical stability of the materials was studied by cyclic voltammeter (CV). Proton conductivity, activation energy, and water/methanol uptake of these membranes were also measured. After humidification ($RH = 50\%$), PVTriP(AMPS)$_2$ and PVTriP(AMPS)$_4$ showed proton conductivities of 0.30 and 0.06 S/cm at 100 °C, respectively.

Keywords Polymers · Chemical synthesis · Differential scanning calorimetry · Thermogravimetric analysis · Fourier transform infrared spectroscopy · Dielectric properties

Introduction

The proton conducting membranes have been recognized as one of the most important part of polymer electrolyte membrane fuel cells (PEMFCs) [1–3]. The performance of the PEMFC strongly depends on the proton conducting properties of

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the polymer electrolyte membranes having proton conductivity, better thermal and chemical as well as electrochemical stability [4–7]. At low temperature domains, perfluorinated sulfonic acid ionomers have been suggested as proton-conductive membrane for PEMFCs. Among these series, Nafion is the well-known polyelectrolyte which shows the high proton conductivity in its fully hydrated state [2, 8–10]. Also several polymer/acid blend membranes have been reported where the proton conduction can occur under completely anhydrous condition [11–13]. In addition, heterocyclic aromatic compounds such as imidazole and benzimidazole are known as strong proton solvents where the proton transport occurs between hydrogen-bonded neighboring heterocyclic units via structure diffusion [14–16]. Polymer/polymer blends have also been considered as more promising alternative materials due to their stability against dopant exclusion [17, 18]. In these systems, strong ionic interaction between polymer repeat units as well as hydrogen bonding network leads to homogeneous systems [15]. PVTri is an interesting host matrix where proton conducting materials with different physical properties can be produced via complexation with acidic polymers.

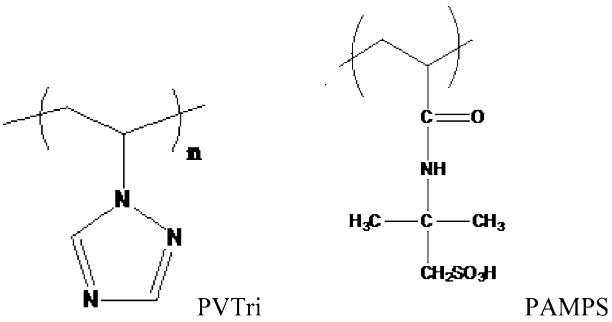
In this study, the synthesis of novel membranes based on the ionically crosslinked PVTri and PAMPS were discussed (Fig. 1). The materials were fabricated at several molar ratios to analyze the effect of VTri and AMPS contents on the proton conductivity of the samples. The polymer electrolytes PVTri-P(AMPS)$_x$ were characterized via FT-IR, TGA, DSC, CV, and SEM. Proton conducting properties of the copolymers were investigated by impedance analyzer, and the results were discussed accordingly.

Experimental

Materials

Synthesis of PVTri and PAMPS

1-Vinyl-1,2,4-triazole, VTri (>97%, Fluka), and 2-acrylamido-2-methyl-1-propanesulfonic acid were used as received. Azobisisobutyronitrile (AIBN; Merck) was



PVTri PAMPS

Fig. 1 Structure of PVTri and PAMPS

recrystallized from THF. Poly(1-vinyl-1,2,4-triazole), PVTri, was successfully produced via free radical polymerization of VTri in toluene with a high yield (>85%). PAMPS was produced by free radical polymerization of 2-acrylamido-2-methyl-1-propanesulfonic acid in 1,4-dioxane:deionized water (2:1) using potassium persulfate as initiator [19]. The reaction mixture was purged with nitrogen, and the polymerization reaction was performed at 70 °C for 36 h.

Membrane preparation

A stoichiometric amounts of PVTri and PAMPS were dissolved in water and then admixed to get PVTriP(AMPS)$_x$; $x = 0.25, 0.5, 1, 2, 4$) where x is the molar ratio of monomer repeating units (Table 1). The complex polymer electrolyte solutions were stirred under nitrogen atmosphere for 24 h, i.e., until getting a homogeneous milky solutions. The films were cast onto polished poly(tetrafluoroethylene) PTFE plates and dried under vacuum at 50 °C and then stored in a glove box. Transparent, hygroscopic, and free-standing films were obtained, and they were denoted as PVTriP(AMPS)$_x$ (Fig. 2).

Characterizations

Before FT-IR spectra measurements, samples were dried under vacuum and stored in a glove box. The IR spectra (4000–400 cm^{-1}, resolution 4 cm^{-1}) were recorded with a Bruker AlphaP-ATR system.

Thermal stabilities of the complex polymer electrolytes were examined by thermogravimetry (TG) analysis with a Perkin Elmer STA 6000. The samples (~10 mg) were heated from room temperature to 700 °C under N_2 atmosphere at a heating rate of 10 °C/min.

Differential scanning calorimetry (DSC) data were obtained using Perkin Elmer JADE DSC instrument. The measurements were carried out at a rate of 10 °C min^{-1} under a nitrogen flow.

Table 1 The proton conductivities and the glass transition temperatures (T_g) of the complex polymer electrolytes

Sample	Feed ratio (mol) VTri/AMPS (x:y)	Relative humidity (%)	T_g (°C)	Max. proton conductivity (S/cm)
PVTriP(AMPS)	1:1	0	147	8.6×10^{-9} at 150 °C
PVTriP(AMPS)$_2$	1:2	0	138	1.1×10^{-8} at 150 °C
PVTriP(AMPS)$_2$	1:2	50	–	0.3 at 100 °C
PVTriP(AMPS)$_4$	1:4	0	134	1.2×10^{-6} at 150 °C
PVTriP(AMPS)$_4$	1:4	50	–	0.06 at 100 °C
PVTriP(AMPS)$_{0.50}$	1:0.50	0	151	2.0×10^{-9} at 150 °C
PVTriP(AMPS)$_{0.25}$	1:0.25	0	178	7.8×10^{-10} at 150 °C

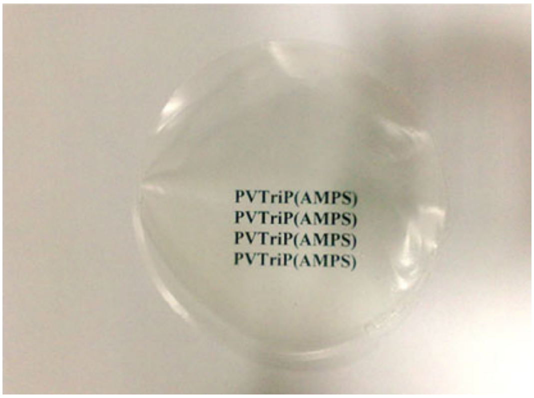


Fig. 2 Transparent and thin film of PVTriP(AMPS)

The surface morphology of blend 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.

The proton conductivity studies of the samples were performed using a Novocontrol dielectric impedance analyzer. The samples were sandwiched between platinum blocking electrodes, and the membranes were placed under water vapor until absorbing 50% (w/w) humidity for humidification measurements. Then, the conductivities were measured in the frequency range 0.1 Hz to 3 MHz at 10 °C intervals. The temperature was controlled with a Novocontrol cryosystem, which is applicable between −100 and 250 °C.

Results and discussions

Characterizations

The homopolymer of PVTri was obtained by free radical polymerization of 1-vinyl-1,2,4-triazole VTri in toluene. PAMPS was prepared by free radical polymerization of 2-acrylamido-2-methyl-1-propanesulfonic acid. Both PAMPS and PVTri are soluble in water, so they were dissolved in water, and then aqueous solutions were mixed to get PVTriP(AMPS)$_x$ polymer electrolytes.

Figure 3 shows the FT-IR spectra of PVTri and the complex polymer electrolytes. In PVTri, the triazole units show several medium or strong peaks in the 1430–1650 $\mathrm{cm^{-1}}$ range due to ring stretching (C–N, C=N) vibrations. The peak at 1270 $\mathrm{cm^{-1}}$ is due to the ring N–N stretching. At higher PVTri ratio, the peaks in the 1430–1650 $\mathrm{cm^{-1}}$ become stronger due to triazole units. This can be signified by the absorption at 1574 $\mathrm{cm^{-1}}$ that corresponds to the protonated triazole ring. A strong absorption peak at 1033 $\mathrm{cm^{-1}}$ belongs to asymmetric O=S=O stretching vibration, and the broad bond at 1218 $\mathrm{cm^{-1}}$ is due to the symmetric O=S=O stretching of the same group [20, 21]. The broad absorption in the region of 833–978 $\mathrm{cm^{-1}}$ is an additional evidence of the salt formation. The broad band between 3500–2500 $\mathrm{cm^{-1}}$ shows the hydrogen bonding network which is necessary for proton conduction [22].

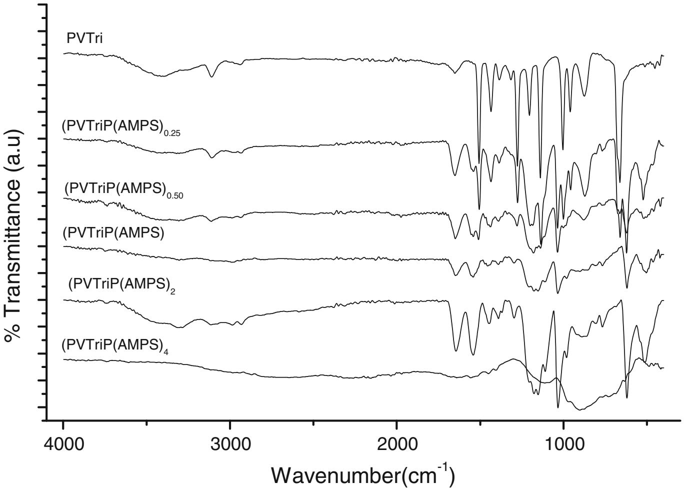


Fig. 3 FT-IR spectra of the PVTri, PVTriP(AMPS)$_{0.25}$, PVTriP(AMPS)$_{0.50}$, PVTriP(AMPS), PVTriP(AMPS)$_2$, and PVTriP(AMPS)$_4$

Thermal analysis

Glass transition temperatures of PVTriP(AMPS)$_{0.25}$, PVTriP(AMPS)$_{0.50}$, PVTriP(AMPS), PVTriP(AMPS)$_2$, and PVTriP(AMPS)$_4$ are summarized in Table 1. The glass transition temperature of the PVTri was reported as 160 °C [22]. The complex polymer electrolytes PVTriP(AMPS)$_{0.25}$, PVTriP(AMPS)$_{0.50}$, PVTriP(AMPS), PVTriP(AMPS)$_2$, and PVTriP(AMPS)$_4$ have definite glass transition temperatures at 178, 151, 147, 138, and 134 °C, respectively (Table 1). The results demonstrated that as the quantity of PVTri increased, the glass transition temperature of the samples shifted to higher temperatures.

Figure 4 shows the TG plots of PVTriP(AMPS)$_x$ samples. The homopolymers, PVTri and PAMPS were reported to be thermally stable up to 350 and 220 °C, respectively [21, 22]. As seen in TGA of the electrolytes, there is a slight weight change between 100 and 200 °C which may be due to evaporation of free water which could not be removed during drying process. Both of the complex polymer electrolytes PVTriP(AMPS) and PVTriP(AMPS)$_2$ can be said to be thermally stable up to at least 200 °C. First weight loss occurs up to 350 °C due to decomposition of PAMPS chain and than PVTri chains decomposes after 350 °C.

SEM micrographs

Surface morphologies of PVTriP(AMPS)$_4$ complex polymer electrolyte membrane was investigated by scanning electron microscopy (Fig. 5a, b). Due to strong interaction between sulfonic acid groups of PAMPS and the triazole units of PVTri, no phase separation occurred during solvent evaporation, hence homogeneous and transparent films formed. This result is also consistent with the DSC curves which showed no separate T_g temperatures.

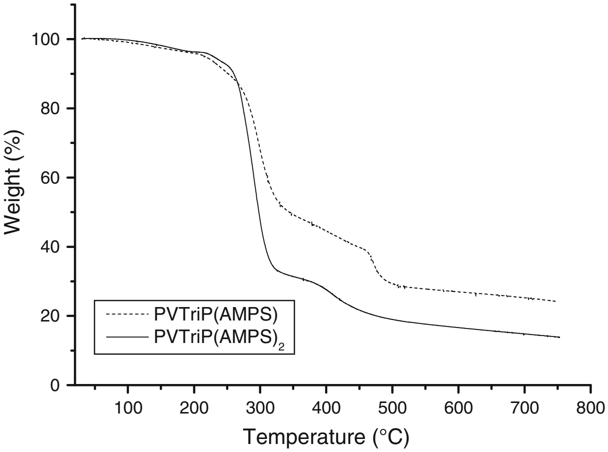


Fig. 4 TG thermograms of the PVTriP(AMPS) and PVTriP(AMPS)$_2$ at a heating rate of 10 °C/min

Water/methanol uptake

The solvent uptake measurements were made according to the literature [23, 24]. The pre-weighed dry films (W_{dry}) of the membranes were soaked into methanol/water (12 mol/L) solution. The external liquid of the swollen membranes was wiped out, and they were weighted (W_{wet}) after different time intervals. The solvent uptake values were obtained using the following equation.

$$\text{Uptake }(\%) = \left(W_{\mathrm{wet}} - W_{\mathrm{dry}}\right)/W_{\mathrm{dry}} \times 100 \qquad (1)$$

Figure 6 shows the methanol/water solution uptakes of PVTriP(AMPS)$_x$. All the materials absorb solvent within 10 min, and then a threshold is reached which might be due to saturation. Then further swelling of the samples occurs above 30 min. The swelling character of the polymer complex electrolytes reasonably decreased when there is equimolar of AMPS and VTri. This finding is primarily ascribed to ionic crosslinking where the material becomes more rigid when $x = 1$. The reason can be attributed to one to one complexation of triazole with sulfonic acid. At higher compositions of PVTri or PAMPS, the swelling character of the materials increased.

Conductivity measurement

Proton conductivity

The AC conductivities, $\sigma_{\mathrm{ac}}(\omega)$, of the polymers were measured at several temperatures using impedance spectroscopy. The AC conductivity of PVTriP(AMPS)$_2$ is shown in Fig. 7. Frequency dependent AC conductivities ($\sigma_{\mathrm{ac}}(\omega)$) were measured using Eq. 1;

$$\sigma'(\omega) = \sigma_{\mathrm{ac}}(\omega) = \varepsilon''(\omega)\,\omega\varepsilon_0 \qquad (1)$$

where $\sigma'(\omega)$ is the real part of conductivity, $\omega = 2\pi f$ is the angular frequency, ε_0 is the vacuum permittivity ($\varepsilon_0 = 8.852 \times 10^{-14}$ F/cm), and $\varepsilon''$is the imaginary part of

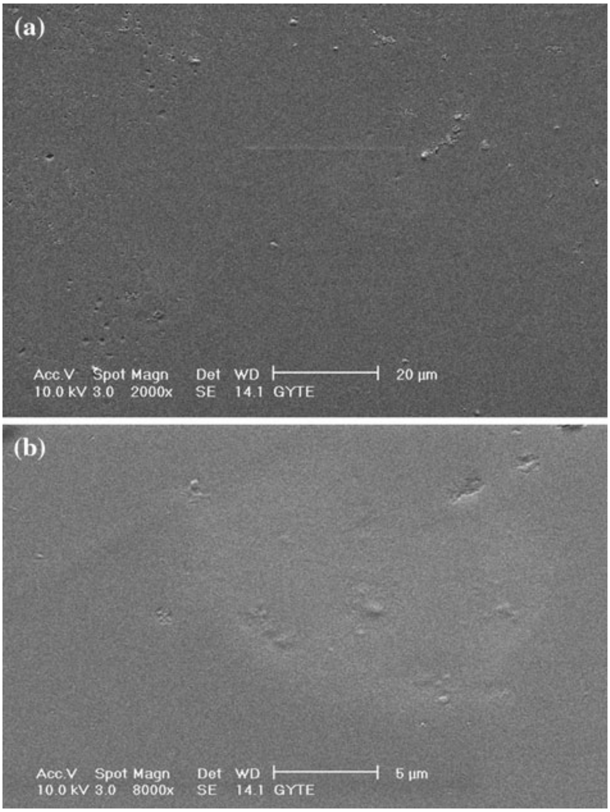


Fig. 5 SEM micrographs of the surface of PVTriP(AMPS)$_4$ **a** 20 µm and **b** 5 µm

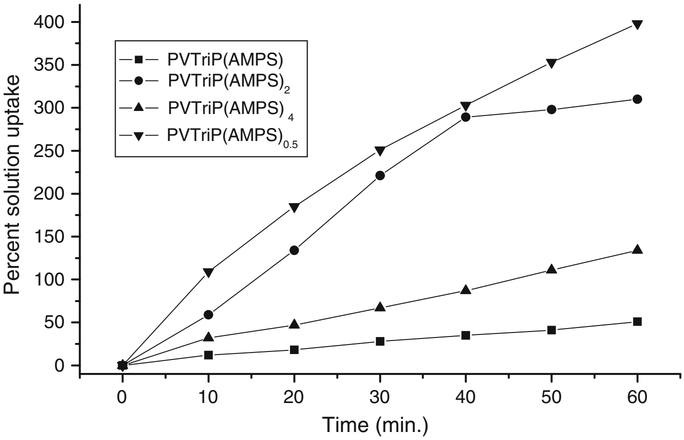


Fig. 6 Solvent uptakes of PVTriP(AMPS)$_x$ ($x = 1, 2, 4, 0.50$) at the time of 10–60 min in 12 mol/L methanol/water solution at 25 °C

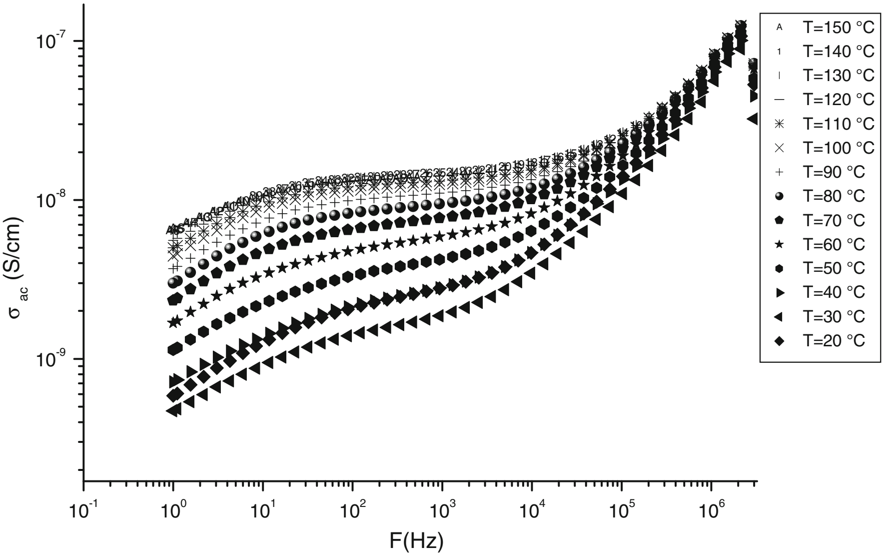


Fig. 7 Log σ_{ac} versus Log F (Hz) for PVTriP(AMPS)$_2$ at various temperatures

complex dielectric permittivity (ε^*). The proton conductivities of anhydrous complex polymer electrolytes were measured from 20 to 150 °C.

The proton conductivity of all anhydrous samples was compared in Fig. 8. The conductivity isotherm illustrates that the DC conductivity strongly depends on temperature as well as the ratio of PAMPS. For PVTriP(AMPS)$_{0.25}$, PVTriP(AMPS)$_{0.50}$, PVTriP(AMPS), PVTriP(AMPS)$_2$, and PVTriP(AMPS)$_4$ (Fig. 8), the conductivity isotherm can be fitted by Arrhenius equation (Eq. 2);

$$\ln\sigma = \ln\sigma_0 - E_a/kT \tag{2}$$

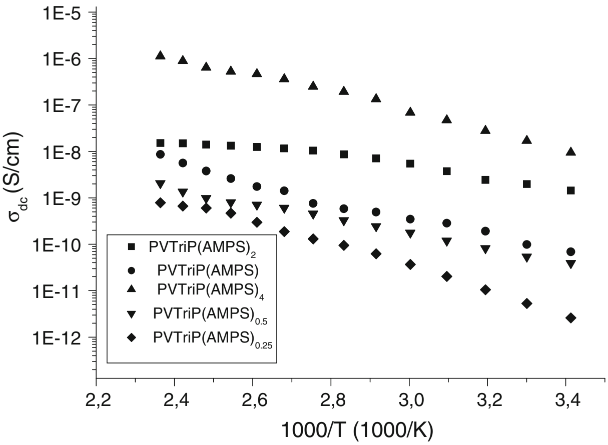


Fig. 8 The DC conductivity versus reciprocal temperature for the all complex polymer electrolytes

where σ_0 is the pre-exponential terms, E_a is the activation energy, and k is the Boltzmann constant. The activation energy of PVTriP(AMPS)$_4$ was found as $E_a = 0.41$ (eV).

The proton conductivity of these samples is improved with PAMPS content, and maximum proton conductivity was measured for PVTriP(AMPS)$_4$ and found as 1.1×10^{-6} at 150 °C in the dry state. The proton conductivity of PVTriP(AMPS)$_4$ is almost identical with PVTriP(AMPS)$_2$, except a slight deviation at higher temperatures. The optimum composition was evaluated as $x = 4$ for the complex polymer electrolytes. It is clearly seen that the PAMPS composition is highly effective on the proton conductivity of the samples. Although the major part of proton transport is provided over azole units, the conductivity decreases at higher PAMPS-containing samples. This behavior can be attributed to the threshold composition of PAMPS where most of the triazole units were expected to be protonated due to high acid ratio. Proton conduction in the PVTriP(AMPS) polymer electrolytes can occur through mobility of protonic defects over triazole units via structure diffusion the so called Grotthuss mechanism as in the case of other azole systems [16].

Effect of humidity on conductivity

The proton conductivities of humidified PVTriP(AMPS)$_2$ and PVTriP(AMPS)$_4$ (50% relative humidity) were compared in Fig. 9. The proton conductivity of hydrated PVTriP(AMPS)$_2$ was measured as 0.3 S/cm at 100 °C, which is higher than that of PVTriP(AMPS)$_4$. The proton conductivities of humidified PVTriP(AMPS)$_2$ and PVTriP(AMPS)$_4$ do not change with temperature within 20–100 °C. As seen in Fig. 9, PVTriP(AMPS)$_2$ has optimum composition in hydrated form, and it has slightly higher proton conductivity than PVTriP(AMPS)$_4$.

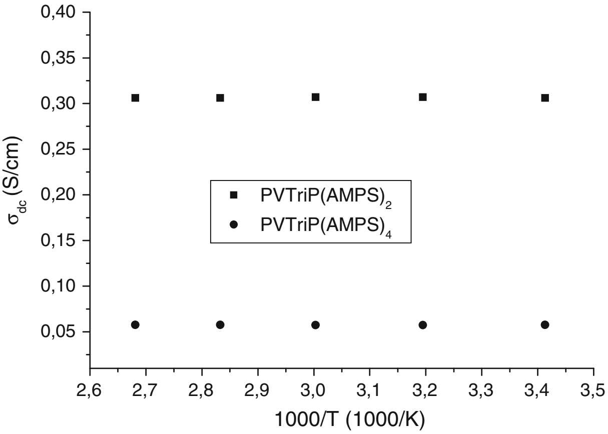


Fig. 9 Effect of RH (RH = % 50) on proton conductivities of PVTriP(AMPS)$_2$ and PVTriP(AMPS)$_4$

Cyclic voltammetry

The voltammograms of PVTriP(AMPS) which was obtained in a three-electrode system are shown in Fig. 10. It is clearly seen that the CV of $x = 1$ comprises no peak within in the anodic sweep (0.0–1.5 V potential range). In the cathodic sweep, formation of gaseous hydrogen is developed which localized near the electrode and is subsequently reoxidized toward the anodic cycle. It is clearly observed that the thin films at the electrodes diminish the intensities of the cathodic peak currents in subsequent cycling. This can be due to the redox ions (H^+) that are ejected from the electrolyte to the solution. Thus, the materials are electrochemically stable within 3 V domain.

Conclusions

In this study, poly(1-vinyl-1,2,4-triazole) and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) were produced by free radical polymerization of the corresponding monomers. The transparent thin films were produced by complexation of PAMPS with PVTri at various concentrations to get PVTriP(AMPS)$_x$. FT-IR spectroscopy confirmed the proton exchange reactions between PVTri and PAMPS forming ionic crosslinks. TG analysis showed that the samples are thermally stable up to at least 200 °C. DSC and SEM results illustrated the homogeneity of the materials. CV measurement results showed that the stability domain of PVTriP(AMPS) extends over 3 V. In the anhydrous state, the proton conductivity of PVTriP(AMPS)$_4$ was measured as 1.2×10^{-6} at 150 °C. Proton conductivity of PVTriP(AMPS)$_x$ increased with the humidity content and reached to

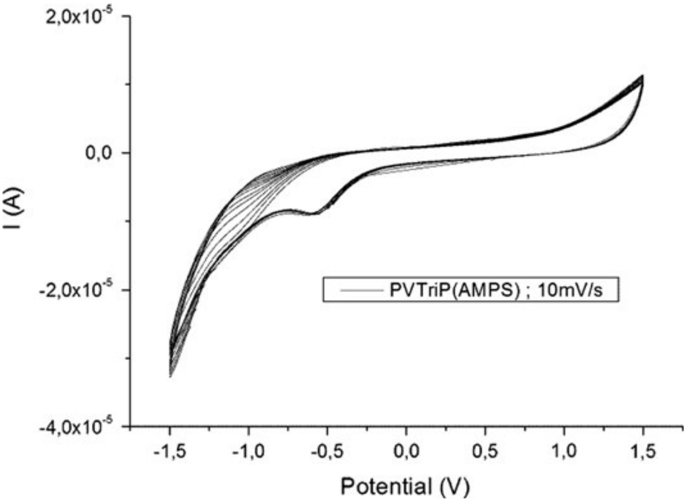


Fig. 10 Cyclic voltammograms of PVTriP(AMPS) in 0.1 M TBATFB/Acetonitrile. Curves with a scan rate 10 mV/s

0.3 S/cm for $x = 2$ and 0.06 S/cm for $x = 4$ at 100 °C. PVTri has a comparable thermal stability compared to PBI, and the complexes of PAMPS/PVTri can form free-standing films. After humidification, they can be suggested for application in PEMFCs.

Acknowledgments This study was supported by TÜBİTAK under the contract number TBAG-108T103.

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