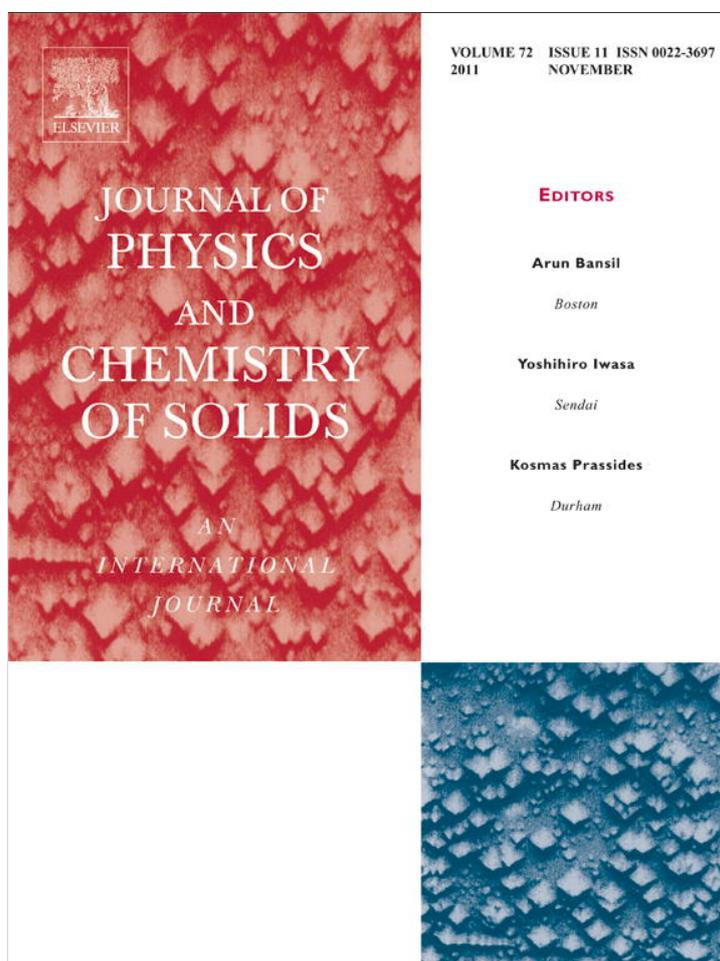


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## Proton conducting composite membranes based on poly(1-vinyl-1,2,4-triazole) and nitrilotri (methyl triphosphonic acid)

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### ARTICLE INFO

#### Article history:

Received 30 March 2011

Received in revised form

19 July 2011

Accepted 16 August 2011

Available online 26 August 2011

#### Keywords:

A. Polymers

B. Chemical synthesis

D. Electrochemical properties

### ABSTRACT

Polymer electrolyte composite membranes based on poly(1-vinyl-1,2,4-triazole) (PVTRI) and nitrilotri(methyl triphosphonic acid) (TPA) were investigated. PVTRI was produced by free radical polymerization of 1-vinyl-1,2,4-triazole. The polymer PVTRI was doped with TPA at various molar ratios  $x=0.125$ ,  $x=0.25$ , and  $x=0.5$ . The proton transfer from TPA to the triazole rings was proved with Fourier-transform infrared spectroscopy (FT-IR). Thermogravimetry (TG) analysis showed that the samples are thermally stable up to approximately 250 °C. DSC results illustrated the homogeneity of the materials as well as the softening effect of the dopant. Cyclic voltammetry results illustrated that the electrochemical stability domain of the dopant extends over 1.5 V. The maximum proton conductivity has been measured for PVTRITPA-0.25 as  $8.5 \times 10^{-4} \text{ S cm}^{-1}$  at 150 °C.

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### 1. Introduction

Polymer electrolyte membranes (PEM) have attracted much attention with the development of perfluorinated sulfonic membranes due to their application in various electrochemical devices such as fuel cells [1,2]. The commercialization of Nafion by DuPont in the late 1960s helped to demonstrate the potential interest in terrestrial applications [3,4]. In the last decade, research on PEM has focused on the developing polymer electrolyte anhydrous in order to maintain the existence of proton conductivity at high temperature. The operation of the fuel cell at high temperature can provide benefits such as improved CO tolerance of platinum catalyst, increasing the mass transport, improved reaction kinetics, and simplifying humidity [5,6]. A common technique used in the synthesis of anhydrous proton conducting material, namely the doping of proton solvent into the polymer matrix so that proton transport occurs almost entirely through the diffusion structure. The procedure is done through the blending of neutral/basic polymer such as with a phosphoric acid, and also by doping the acidic polymer with a heterocyclic molecule [7,8]. For a fast Grotthuss-type mechanism these must enable the formation of protonic defects and provide strongly fluctuating proton donor and acceptor functions in a polar environment [9].

The polymer membranes based on acid-doped triazole functional polymers would be interesting where high conductivity can

be obtained even at lower dopant ratios [10,11]. The presence of three nitrogens in the ring may enhance long range proton diffusion, which can be far better than imidazole based host polymer, i.e., poly(4(5)-vinyl-imidazole) [12]. In poly(4(5)-vinyl-imidazole), polymer-acid complexation blocked the imidazole ring nitrogens and inhibited the structure diffusion at higher acid contents. Poly(1-vinyl-1,2,4-triazole) is a heterocyclic polymer that has three nitrogen sites per monomeric unit and showed that proton transfer is a strong contribution to proton conduction in poly(1-vinyl-1,2,4-triazole)/acid composites [7,13].

In addition several copolymers were synthesized using vinyl triazole with acidic monomers such as vinyl phosphonic acid [14] and 2-acrylamido-2-methyl-1-propanesulfonic acid [15]. The homopolymer, PVTRI was also blended with acid functional polymers like polyvinyl phosphonic acid [16], polystyrene sulfonic acid [17] and Nafion [18]. Although high proton conductivity was obtained in copolymers, the blends did not result sufficient proton conductivity due to ionic crosslinking and elimination of segmental motions in the membrane.

Another dopant that can be used within wide temperature range is nitrilotri (methyl triphosphonic acid). Nitrilotri(methyl triphosphonic acid) is a powerful complexing agent and proton solvent with a melting point of 215 °C and boiling point of 746 °C. It has high thermal stability and a suitable solubility in water. It has three phosphonic acid groups and when used as dopant in a host polymer it may have a high contribution to proton conductivity.

In this work, novel proton conductive polymer blends were prepared using poly(1-vinyl-1,2,4-triazole) and nitrilotri(methyl triphosphonic acid) at several molar ratios. The polymer electrolytes

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were characterized via FT-IR, TGA, and DSC. Proton conducting properties were investigated by impedance analyzer.

## 2. Experimental

### 2.1. Materials and Preparation

1-Vinyl-1,2,4-triazole (>97%, Fluka), toluene (>99%, Merck), azobisisobutyronitrile (AIBN; Merck), and nitrilotri(methyl triphosphonic acid) (TPA) (Aldrich) were used as received. Poly(1-vinyl-1,2,4-triazole) (PVTRI) was produced by free radical polymerization of 1-vinyl-1,2,4-triazole in toluene using AIBN (1 mol%) as the initiator. The reaction mixture was purged with nitrogen and the polymerization reaction was performed at 85 °C for 2 h. The resulting polymer was precipitated as white powder and filtered and washed several times with toluene. PVTRI was dried in vacuum and stored in the glove box. A stoichiometric amount of nitrilotri(methyl triphosphonic acid) and poly(1-vinyl-1,2,4-triazole) (Fig. 1) was admixed in water and homogeneous solutions with  $x=0.5$ ,  $x=0.25$ , and  $x=0.125$  were prepared. The solutions were cast in polished poly(tetrafluoroethylene), PTFE plates and the solvent was carefully evaporated at 50 °C and they were stored in the glove box for characterizations.

### 2.2. Characterizations

FTIR spectra were recorded on a Bruker a-P in ATR in range of 4000–400  $\text{cm}^{-1}$ .

DSC measurements were carried out on a Perkin Elmer JADE DSC under nitrogen atmosphere and heating-cooling curves were recorded at a rate of 10 °C/min.

Thermal stabilities of the polymer electrolytes were examined by TG analyses with a Perkin Elmer STA 6000. The samples (~10 mg) were heated from room temperature to 700 °C under  $\text{N}_2$  atmosphere at a scanning rate of 10 °C/min.

Cyclic voltammograms were obtained with a potentiostat CHI instrument Model 842B. Voltammograms of TPA were recorded in a three electrode CV system, using a polymerelectrolyte modified Pt working electrode and a Pt counter electrode. The reference electrode was silver/silver chloride (Ag/AgCl) calibrated by a ferrocene/ferricinium redox system. Cyclic voltammetry studies were carried out in 0.1 M tetraethylammonium tetrafluoroborate (TBATFB)/acetonitrile.

The proton conductivity studies of the samples were performed using a Novocontrol dielectric-impedance analyzer. The films were sandwiched between gold blocking electrodes and the conductivities were measured in the frequency range 0.1 Hz to 1 MHz at 10 °C intervals. The temperature was controlled with a Novocontrol cryosystem, which is applicable between –100 and 250 °C.

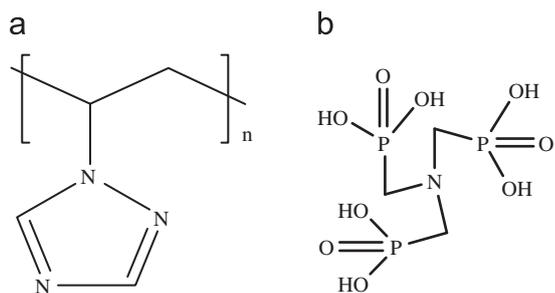


Fig. 1. The structures of (a) PVTRI and (b) TPA.

## 3. Results and discussion

### 3.1. FT-IR studies

Fig. 2a shows the FT-IR spectra of the homopolymer and the dopant. The homopolymer, PVTRI shows medium or strong peaks ring stretching (C–N, C=N) vibrations in the 1430–1650  $\text{cm}^{-1}$  range. The peak at 1270  $\text{cm}^{-1}$  is attributed to the N–N stretching of the triazole ring. The IR spectrum of TPA shows strong bands at 1040–910  $\text{cm}^{-1}$  that belong to asymmetric stretching vibrations of the P–OH group, at 1150  $\text{cm}^{-1}$  that corresponds to P=O stretching, and a weak peak around 3500  $\text{cm}^{-1}$  was attributed to O–H stretching [8]. Fig. 2b shows FT-IR spectra of the blends and after doping the intensities of the bands corresponding to the ring between 1430 and 1650  $\text{cm}^{-1}$  have changed. PVTRITPA shows a strong peak at 3100  $\text{cm}^{-1}$ , which may be associated with N–H absorption in the protonated triazole ring. Between 3500 and 2000  $\text{cm}^{-1}$  a broadening of the band can be related to hydrogen bonding network formation. Within 1800–900  $\text{cm}^{-1}$  region, the peaks near 1100  $\text{cm}^{-1}$  and 979  $\text{cm}^{-1}$  are attributed to characteristic absorptions of the formation anion TPA as a consequence of interaction of N–H [7].

### 3.2. Thermal analysis

The homopolymer, PVTRI was reported to have a glass transition at around 165 °C [7].  $T_g$  points of PVTRITPA blends ( $x=0.125$ ,

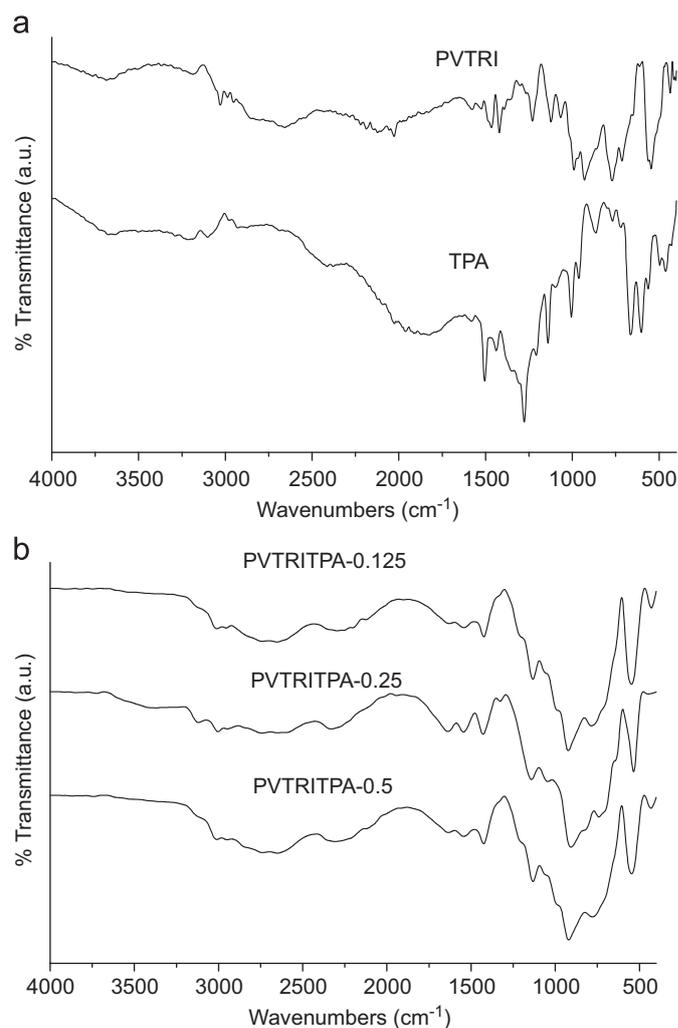
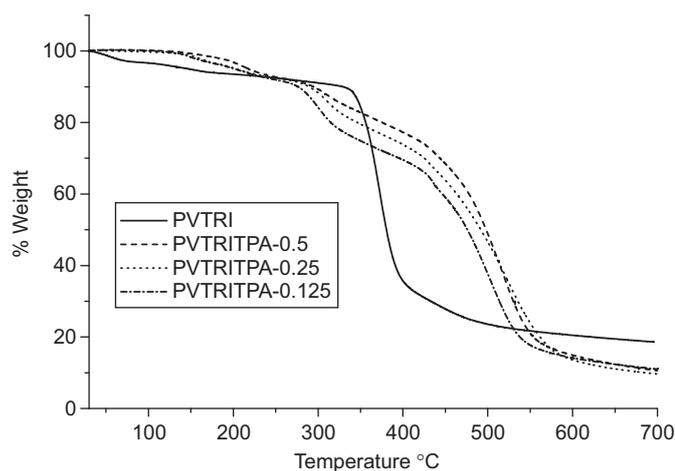


Fig. 2. (a). FT-IR spectra of the homopolymer PVTRI and the dopant TPA. (b). FT-IR spectra of the blends PVTRITPA-0.125, PVTRITPA-0.25, and PVTRITPA-0.5.

**Table 1**  
Glass transition temperature  $T_g$  (°C) and maximum proton conductivity of polymer electrolyte composite membranes.

Samples	PVTRI: TPA (mole)	$T_g$ (°C)	Max. proton conductivity ( $S\text{ cm}^{-1}$ )
PVTRI		165	$5.00 \times 10^{-9}$ at 190 °C
PVTRITPA-0.125	1: 0.125	53	$1.02 \times 10^{-4}$ at 140 °C
PVTRITPA-0.25	1: 0.25	44	$8.52 \times 10^{-4}$ at 150 °C
PVTRITPA-0.5	1: 0.5	37	$7.78 \times 10^{-5}$ at 150 °C



**Fig. 3.** Thermograms of the PVTRI, PVTRITPA-0.5, PVTRITPA-0.25, and PVTRITPA-0.125 at a heating rate of  $10\text{ °C min}^{-1}$ .

$x=0.25$ , and  $x=0.5$ ) were measured by DSC and exhibited in Table 1. For blends, the glass transition temperature,  $T_g$  shifts to lower temperatures where it is located at  $53\text{ °C}$  for  $x=0.125$ ,  $44\text{ °C}$  for  $x=0.25$ , and  $37\text{ °C}$  for  $x=0.5$ . This decrease can be explained as a softening effect of the proton solvent, nitrilotri(methyl triphosphonic acid) on the composite materials [12].

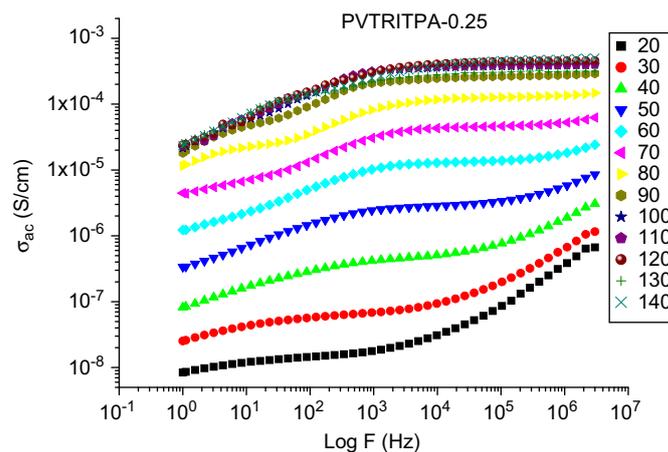
Fig. 3 shows the thermogravimetric analysis of PVTRI and polymer blends. Pure PVTRI is thermally stable up to  $330\text{ °C}$ . Little weight loss up to this temperature can be attributed to absorbed humidity. After doping the polymer with TPA the thermal stability decreased to approximately  $250\text{ °C}$ . The slight weight change between  $150$  and  $250\text{ °C}$  can be due to water loss by self-condensation of phosphonic acid units in nitrilotri(methyl triphosphonic acid). Above  $300\text{ °C}$  the major weight loss derives from the thermal decomposition of the triazole groups and polymer main chain. Although PVTRI decomposes with single step at  $330\text{--}400\text{ °C}$ , this region shifted to higher temperatures ( $550\text{ °C}$ ) for the polymer electrolytes, which may be attributed to strong hydrogen bonding interactions between the azole groups and the triazole units.

### 3.3. Conductivity measurement

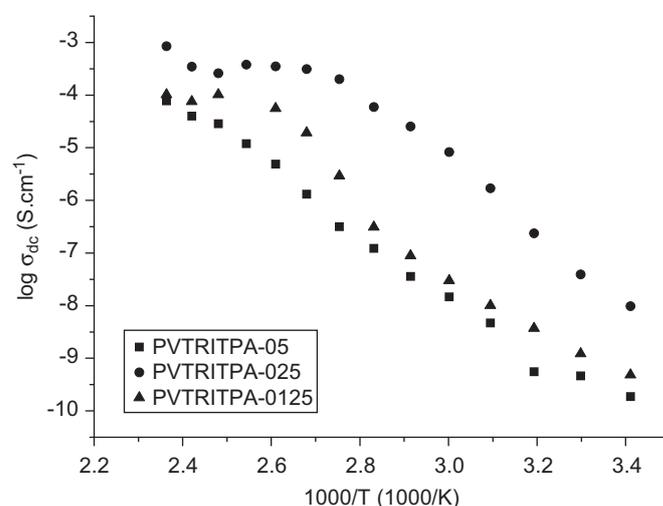
The frequency dependent AC conductivities,  $\sigma_{ac}(\omega)$  of the polymer blends were measured at several temperatures using Eq ;  $\sigma'(\omega) = \sigma_{ac}(\omega) = \epsilon''(\omega)\omega\epsilon_0$

where  $\sigma'(\omega)$  is the real part of conductivity,  $\omega=2\pi f$  is the angular frequency,  $\epsilon_0$  is the vacuum permittivity ( $\epsilon_0=8.852 \times 10^{-14}\text{ F/cm}$ ), and  $\epsilon''$  is the imaginary part of complex dielectric permittivity ( $\epsilon^*$ ). The proton conductivities of anhydrous complex polymer electrolytes were measured from  $20$  to  $150\text{ °C}$ .

Fig. 4 shows the AC conductivity of PVTRITPA-0.25 versus log frequency at several temperatures. The curve bears several regions,



**Fig. 4.** AC conductivity versus frequency (Hz) of PVTRITPA-0.25 at various temperatures.



**Fig. 5.** DC conductivities of PVTRITPA-0.5, PVTRITPA-0.25, and PVTRITPA-0.125 as a function of reciprocal temperature.

which are typical for ion conducting polymers. At lower frequency regions, the conductivity increases with log frequency then leveled off, which is due to electrode polarizations. The plateau domains that depend on the temperature, i.e.,  $10^0\text{--}10^1\text{ Hz}$  at  $20\text{ °C}$  and  $10^1\text{--}10^2\text{ Hz}$  at  $30\text{ °C}$ , shift to higher frequencies at higher temperatures. The irregularities at the low frequency side correspond to polarization blocking the electrode–electrolyte interface, and the conductivity increase at low temperature and high frequencies results from the regular dispersion in polymer electrolytes.

The DC conductivity ( $\sigma_{dc}$ ) of the samples was derived from the plateaus of  $\sigma_{ac}$  versus log frequency by linear fitting of the data. The DC conductivities of the composite membranes were compared in Fig. 5. PVTRITPA-0.125, PVTRITPA-0.25, and PVTRITPA-0.5 have resulted in the proton conductivity of  $1.02 \times 10^{-4}$  at  $140\text{ °C}$ ,  $8.52 \times 10^{-4}$  at  $150\text{ °C}$ , and  $7.78 \times 10^{-5}$  at  $150\text{ °C}$ , respectively. It is unexpected that the conductivity of PVTRITPA-0.25 becomes higher than of PVTRITPA-0.5. The proton conductivity of these samples increased with the content of dopant for PVTRITPA-0.125 and PVTRITPA-0.25, then declined for PVTRITPA-0.5. The conductivity decrease at higher TPA content can be attributed to the threshold ratio of TPA where excess acid blocks the free nitrogens in PVTRI and thus migration of protons through hydrogen bonding network is blocked. This situation is reported in many similar acid–base composite membranes [19,20].

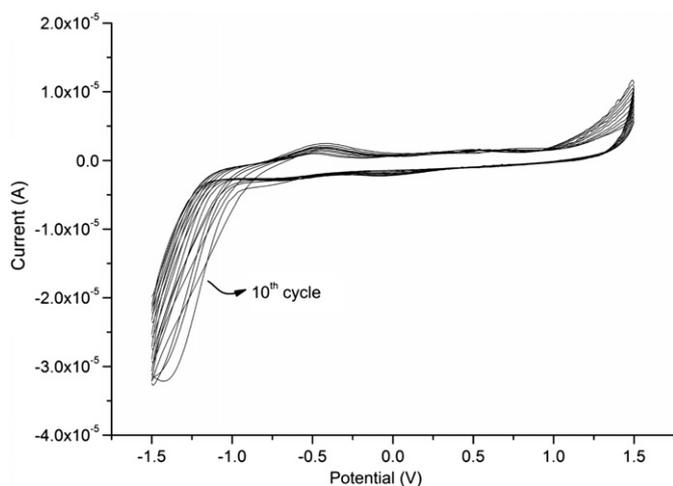


Fig. 6. Cyclic voltammograms of TPA in 0.1 M TBATFB/acetonitrile. Curves with a scan rate of 50 mV/s.

Furthermore, there are two different transport mechanisms that contribute to the proton conductivity in acid-doped polymer electrolytes. The first is the structural diffusion (Grotthuss mechanism) in which the conductivity is mainly controlled by proton transport through acidic ions, i.e.  $\text{PO}_3^-$  and the triazole ring (Grotthuss proton transport). The second is the vehicle mechanism where the protons travel through the material on a neutral or charged “vehicle” [21].

In the current system, the presence of  $\text{PO}_3^-$  anions and protonated triazole groups implies that the proton diffusion occurs mainly by Grotthuss mechanism. It seems that the proton hopping from one N–H site to a free nitrogen contributes to the conductivity of PVTRITPA as in the case of imidazole where the long-range proton transfer occurs throughout the protonic defects, i.e. protons transport between protonated and unprotonated heterocyclic units [9]. In addition, proton hopping from one N–H site to phosphonate ions may also contribute to the conductivity.

The system has low  $T_g$  values, which may show that the proton transport is mediated by segmental motion and also proton hopping between phosphonate moieties and triazole units via hydrogen bonds, and self-diffusion of phosphonate moieties can all contribute to the proton conductivity.

Previously, to produce an anhydrous proton conducting system poly((4) 5-vinyl-imidazole) was doped with phosphoric acid and a maximum proton conductivity of  $\sim 10^{-4}$  S/cm at ambient temperature was obtained [12]. Similarly, anhydrous proton conducting copolymer electrolytes based on 1-vinyl-1,2,4-triazole and 2-acrylamido-2-methyl-1-propanesulfonic acid were reported [15]. The proton conductivity of these copolymer electrolytes was improved with 1H-1-vinyl-1,2,4-triazole content and reached to  $9.3 \times 10^{-4}$  S/cm at 140 °C [15].

The interaction of phosphoric acid units with poly(1-vinyl-1,2,4-triazole) was also investigated previously. They reported a maximum proton conductivity of  $5.0 \times 10^{-3}$  S/cm at 150 °C [7].

In this study a novel compound with three phosphonic acid units and a high melting point was blended with poly(1-vinyl-1,2,4-triazole) and homogeneous free standing films were obtained. The material with  $x=0.25$  is considered as optimal composition to produce anhydrous polymer electrolyte.

### 3.4. Cyclic voltammetry

The voltammograms of the pure dopant, TPA are obtained in a three electrode system as shown in Fig. 6. It is clearly observed that the CV of the compound comprises no peak within in the anodic sweep (–0.5 to 1.0 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. Thus the electrochemical stability window is about 1.5 V.

## 4. Conclusions

In the present work, poly(1-vinyl-1,2,4-triazole) was produced by free radical polymerization of 1-vinyl-1,2,4-triazole. The polymer was doped with nitrilotri (methyl triphosphonic acid) with molar ratios  $x=0.125$ ,  $x=0.25$ , and  $x=0.5$ . The interaction of the triazole rings with nitrilotri (methyl triphosphonic acid) units was proved with FT-IR. TG analysis showed that the samples are thermally stable up to approximately 250 °C. DSC results illustrated the homogeneity of the materials as well as softening effect of the dopant. Proton conductivity increased with the temperature and the dopant ratio. The material with  $x=0.25$  is considered as an optimal composition with a proton conductivity of  $8.52 \times 10^{-4}$  at 150 °C.

## Acknowledgments

This work was supported by Fatih University Research Projects Foundation under contract number P50021003\_2.

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