Development and characterization of polymer electrolyte membranes based on ionical cross-linked poly(1-vinyl-1,2,4 triazole) and poly(vinylphosphonic acid)

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ABSTRACT

The fabrication, thermal and proton conducting properties of complex polymer electrolytes based on poly(vinylphosphonic acid) (VPA) and poly(1-vinyl-1,2,4-triazole) (PVTri) were investigated throughout this work. The membrane materials were produced by complexation of PVPA with PVTri at various concentrations to get PVTriP(VPA)$_x$ where x designates the molar ratio of the polymer repeating units and varied from 0.25 to 4. The complexed structure of the polymers was confirmed by FT-IR spectroscopy. The TGA results verified that the presence of PVTri in the complex polymer electrolytes suppressed the formation of phosphonic acid anhydrides up to 150 °C. The DSC and SEM results demonstrated the homogeneity of the materials. Proton conductivity, activation energy and water/methanol uptake of these membranes were also measured. PVTriP(VPA)$_2$ showed a proton conductivity of 2.5×10^{-5} S cm^{-1} at 180 °C in the anhydrous state. After humidification (RH = 50%), PVTri-P(VPA)$_4$ and PVTri-P(VPA)$_2$ showed respective proton conductivities of 0.008 and 0.022 S cm^{-1} at 100 °C, where the conductivity of the latter is close to Nafion 117 at the same humidity level.

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1. Introduction

The thin polymeric membrane is the main component of the membrane electrode assembly (MEA) which is sandwiched between catalytic composite electrodes to construct polymer electrolyte membrane fuel cells (PEMFC) [1]. During the last decade, research trend has been focused on the development of anhydrous or low humidity polymer electrolytes to maintain adequate proton conductivity at higher temperatures [1–4]. The operation of fuel cells at higher temperatures, i.e., in excess of 100 °C, provides additional advantages such as, improvement of CO tolerance of platinum catalyst, improve mass transportation, increase reaction kinetics and simplify the water management and gas humidification [1,2]. Previously, acid–base complexes have been considered as an alternative route for anhydrous proton conductors [2,5–7], where homogeneous systems were formed by means of strong acid/polymer interaction through hydrogen bonding [1].

The research on development of anhydrous neutral or basic proton conducting materials is also under-progress with particular interest in heterocyclic compounds. Recent attempt was the preparation of hybrid electrolytes by incorporation of imidazole or benzimidazole in polymer matrices [8–11]. The proton conduction may occur through non-vehicular mechanism where proton transferred from site-to-site by hydrogen bond breaking and forming processes [12].

Recently, Tri was used as blend components in acidic polyelectrolytes to get high-temperature resistive and electrochemically stable free-standing films [13]. Since polymer electrolyte membranes consisting of acidic polymer host and Tri allowed long range proton transport via structure diffusion [14,15]. One of the most important problems of the host/guest systems is the proton solvent leaching out which may be faced during cell operation [16]. Thus, immobilization of the proton solvents can be carried out via copolymerization of acidic monomer with heterocyclic comonomer. It was previously reported that copolymers of 4(5) vinylimidazole resulted in ionic complexation which blocked the free nitrogens, inhibiting the long range proton diffusion [17]. To solve blocking of free nitrogens in the heterocyclic ring, the use of triazole based polymer as a matrix would be interesting and may solve the blocking as well as dopant leaching out problems.

Previously several polymer–polymer blends such as sulfonated polysulfones (SPSF) and polybenzimidazole (PBI) doped with phosphoric acid were developed as potential high-temperature polymer electrolytes for fuel cells and other electrochemical applications. The water uptake and acid doping of these polymeric membranes were investigated. Ionic conductivity of the membranes was measured in relation to temperature, acid doping level, sulfonation degree of SPSF, relative humidity, and blend composition. The proton conductivity of blends increased in the presence of excess phosphoric acid [18].

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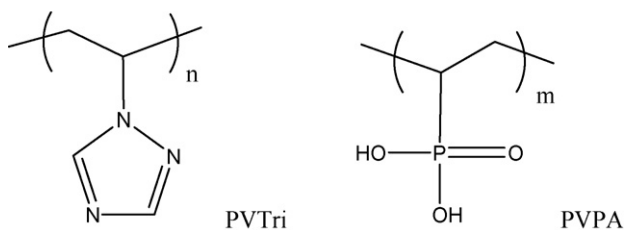 E-mail address: bozkurt@fatih.edu.tr (A. Bozkurt).

Fig. 1. Structure of PVTri and PVPA.

Another approach was the proton conducting membranes from blends of Nafion and polybenzimidazole (PBI) by solution casting [19]. The proton conductivity as well as methanol permeability of the blends decreased with increasing PBI content.

In addition the acid–base composite membranes were also prepared using highly sulfonated poly(aryl ether ether ketone) (SPEEK) and polybenzimidazole. The proton conductivity of the composite membranes was dependent on the content of PBI. The thermal stabilities and mechanical properties of the SPEEK membranes were improved. The composite membranes exhibited high proton conductivity, moderated swelling properties and ion exchange capacities [20].

In this work, the synthesis of novel membranes based on the ionically cross-linked PVTri and PVPA was discussed (Fig. 1). The materials were fabricated at several molar ratios to analyze the effect of VTri and VPA contents on the conductivity of final product. The polymer electrolytes PVTriP(VPA)$_x$ were characterized via FT-IR, TG, DSC and SEM. Proton conducting properties of the copolymers were investigated by impedance analyzer and the results are discussed and compared with previously reported systems.

2. Experimental

2.1. Materials and preparation

1-Vinyl-1,2,4-triazole (>97%, Fluka), vinylphosphonic acid (>95%, Fluka) and DMF (>99%, Fluka) were used as received. Azobisisobutyronitrile (AIBN; Merck) was recrystallized from THF. The PVTri, VTri was successfully produced via free-radical polymerization in toluene with a high yield (>85%). Poly(vinyl phosphonic acid) was produced by free-radical polymerization of vinyl phosphonic acid [10].

The stoichiometric amounts of PVTri and PVPA solutions were dissolved to get PVTriP(VPA)$_x$; $x = 0.25, 0.5, 1, 2, 4$ where x is the molar ratio of the vinyl triazole (in PVTri) and vinylphosphonic acid (in PVPA) repeating units (Table 1). The complex polymer electrolytes were isolated in the solution as light yellowish gel. Then the solutions were further stirred under nitrogen atmosphere for 24 h, i.e., until getting a homogeneous milky solution. The films were cast onto polished poly(tetrafluoroethylene) (PTFE) plates and dried under vacuum at 50 °C and then stored in a glove box. After removal of the solvent, transparent, hygroscopic and free-standing

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

films were obtained and the samples denoted as PVTriP(VPA)$_x$ (Fig. 2).

2.2. Characterizations

Prior to 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 Alpha-P in 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^{-1}.

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.

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 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.

3. Results and discussion

The homopolymer of poly(1-vinyl-1,2,4-triazole) (PVTri) was obtained by free-radical polymerization of 1-vinyl-1,2,4-triazole (VTri) in toluene. PVPA was prepared by free-radical polymerization of vinylphosphonic acid. Both PVPA and PVTri are good soluble in water and hence sample preparation was performed in aqueous solution.

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

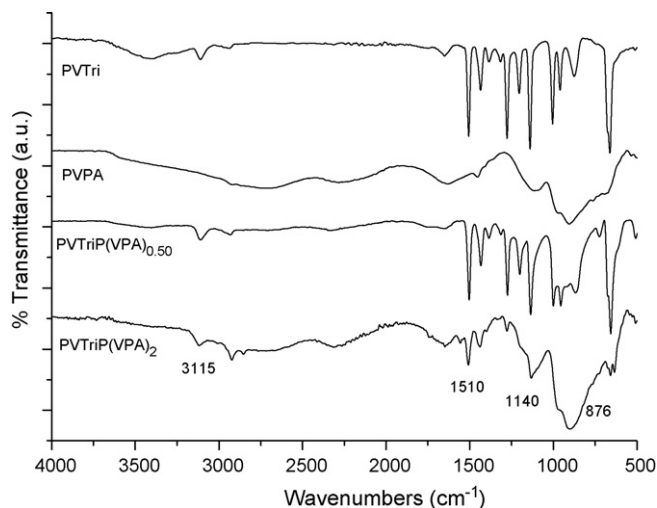| Sample	Feed ratio (mol) VTri/VPA (x:y)	Relative humidity (%)	T_g (°C)	Max. proton conductivity (S cm^{-1})
PVTriP(VPA)	1:1	0	158	2.24×10^{-7} at 180 °C
PVTriP(VPA)$_2$	1:2	0	140	2.141×10^{-6} at 180 °C
PVTriP(VPA)$_2$	1:2	50	–	0.022 at 100 °C
PVTriP(VPA)$_4$	1:4	0	126	1.22×10^{-6} at 180 °C
PVTriP(VPA)$_4$	1:4	50	–	0.008 at 100 °C
PVTriP(VPA)$_{0.50}$	1:0.50	0	163	1.18×10^{-7} at 180 °C
PVTriP(VPA)$_{0.25}$	1:0.25	0	145	2.57×10^{-7} at 180 °C

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

3.1. FT-IR study

Fig. 3 shows the FT-IR spectra of poly(1-vinyl-1,2,4-triazole) (PVTri), polyvinylphosphonic acid (PVPA) and the complex polymer electrolytes, PVTriP(VPA)$_x$. In PVTri, the triazole units show several medium or strong peaks in the 1430–1650 cm^{-1} range due to ring stretching (C–N, C=N) vibrations. The peak at 1270 cm^{-1} is due to the ring N–N stretching. The IR spectrum of PVPA shows strong bands at 1040–910 cm^{-1} that belong to asymmetric stretching vibrations of the P–OH group and at 1150 cm^{-1} that corresponds to P=O stretching [5]. At higher PVPA ratio the P–O–H vibration at 930 cm^{-1} becomes stronger, indicating the existence of excess acidic protons. Additionally, phosphonic acid units give rise to broad bands with medium intensity at 1700–1590 and 2850–2750 cm^{-1}. The protonation of the 'free' nitrogens of the triazole rings can be observed with the change of the intensity of the peaks within 1200–1520 cm^{-1}. The broad band between 3500 and 2500 cm^{-1} is the hydrogen bonding network which is necessary for proton conduction [21].

3.2. Thermal analysis

Characteristic DSC curves of PVTriP(VPA)$_{0.50}$, PVTriP(VPA) and PVTriP(VPA)$_2$ are shown in Fig. 4. The glass transition temperature
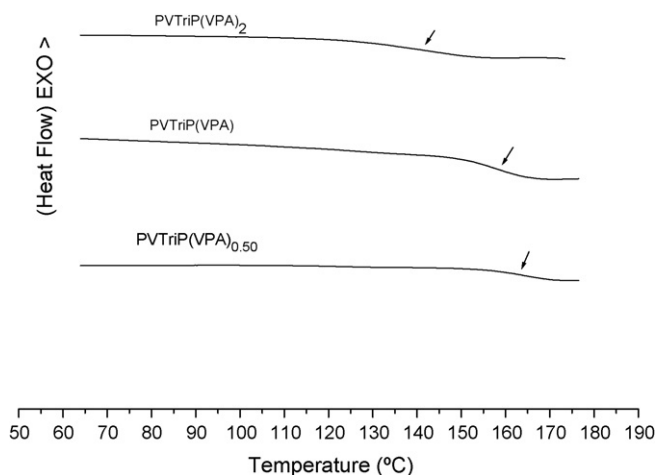

Fig. 4. DSC curves of the samples recorded under inert atmosphere at a heating rate of 10 °C min^{-1}.
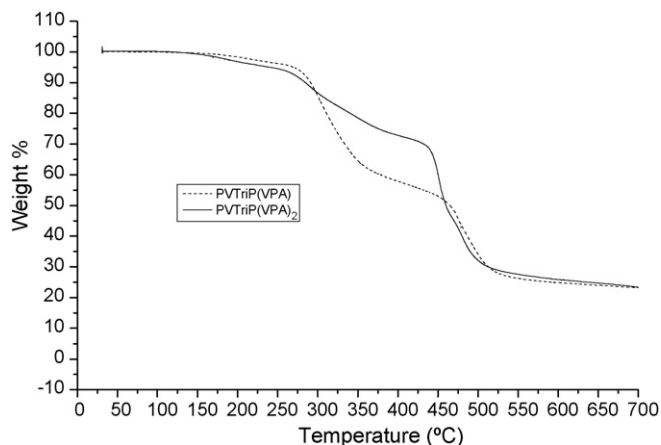

Fig. 5. TG thermograms of the PVTriP(VPA) and PVTriP(VPA)$_2$ at a heating rate of 10 °C min^{-1}.

of the PVTri was reported at around 160 °C. PVPA exhibits a glass transition at around −23 °C [21]. The complex polymer electrolytes PVTriP(VPA)$_{0.25}$, PVTriP(VPA)$_{0.50}$ PVTriP(VPA), PVTriP(VPA)$_2$ and PVTriP(VPA)$_4$ have definite glass transition temperatures at 163, 145, 158, 140 and 126 °C, respectively (Table 1). The results demonstrated that as the quantity of PVPA increased, the glass transition temperature of the samples shifted to lower temperatures.

Fig. 5 shows the thermogravimetry results of the homopolymer; PVTri has a considerable thermal stability under inert conditions. An exponential weight decay for the PVTri until 200 °C can be attributed to loss of absorbed humidity. Above 350 °C, a remarkable weight loss derives from the thermal decomposition of triazole groups and the polymer main chain. Both the complex polymer electrolyte PVTriP(VPA) and PVTriP(VPA)$_2$ illustrate no weight change up to approximately 150 °C. Then an elusive weight loss up to 250 °C can be attributed to anhydride formation [21]. Clearly, the dried PVTriP(VPA)$_x$ materials are thermally stable up to 250 °C and then they decompose.

3.3. SEM micrographs

Surface morphologies PVTriP(VPA) and PVTriP(VPA)$_4$ the complex polymer electrolytes membranes were investigated by scanning electron microscopy (Fig. 6a and b). Due to strong interaction between of phosphonic acid groups of PVPA 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 of blend membranes that no separate T_g transition of impregnated PVTri was observed.

3.4. Water/methanol uptake

The solvent uptake measurements were made according to the literature [22,23]. The pre-weighed dry films (W_{dry}) of the membranes were soaked into methanol/water (12 mol L^{-1}) 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:

$$\text{Uptake}(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \qquad (1)$$

Fig. 7 shows the methanol/water solution uptakes of PVTriP(VPA)$_x$. All the materials absorb solvent within 10 min 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
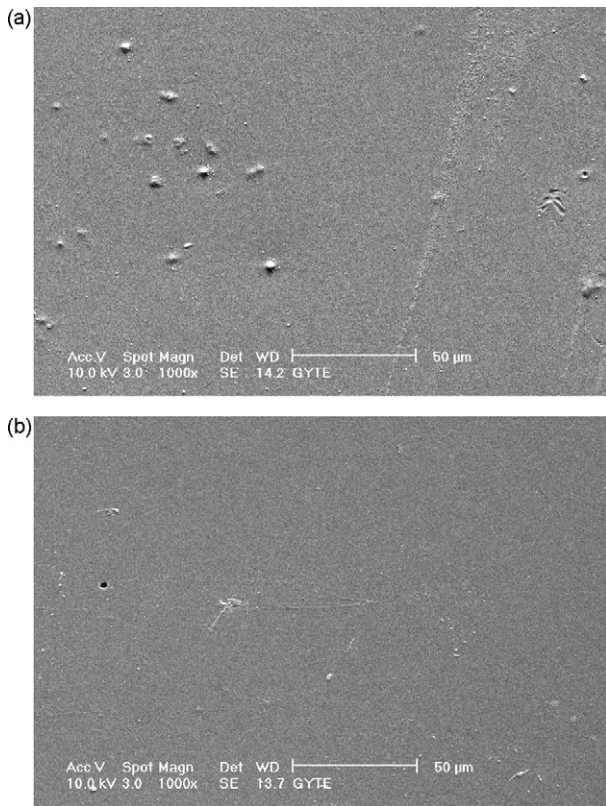
(a)

(b)

Fig. 6. SEM micrographs of the surface of (a) PVTriP(VPA) and (b) PVTriP(VPA)$_{0.25}$.

decreased when there is equimolar of VPA and VTri. This finding is primarily ascribed to ionic cross-linking where the material becomes more rigid when $x = 1$. The reason can be attributed to one-to-one complexation of triazole with phosphonic acid. At higher compositions of PVTri or PVPA the swelling character of the materials increased.

3.5. Conductivity measurement

The alternating current (AC) conductivities, $\sigma_{ac}(\omega)$ of the polymers were measured at several temperatures using impedance spectroscopy. The AC conductivity of PVTriP(VPA)$_4$ is shown in Fig. 8. Frequency dependent AC conductivities ($\sigma_{ac}(\omega)$) were mea-
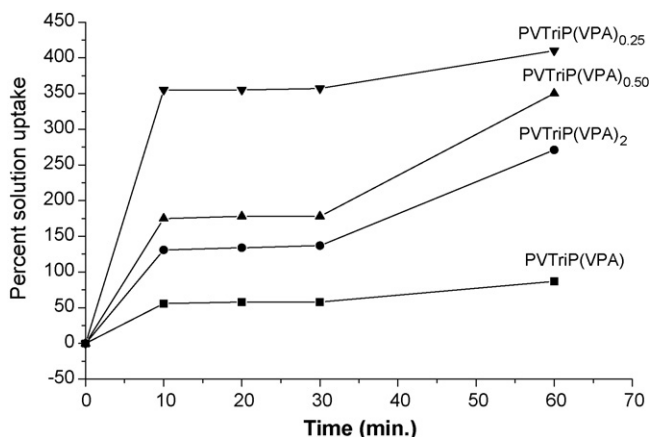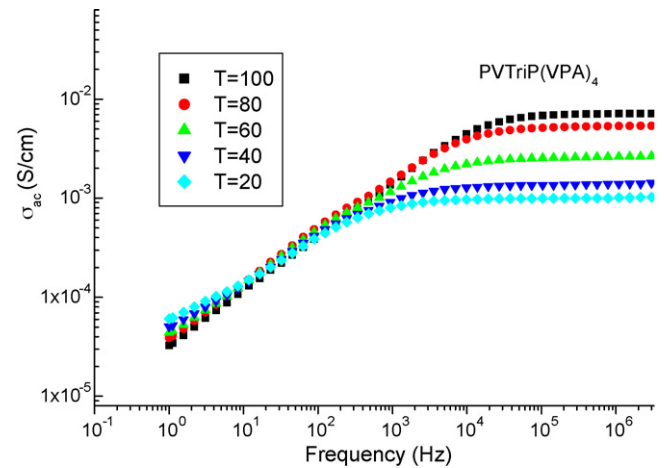

Fig. 8. $\log \sigma_{ac}$ versus $\log F$ (Hz) (RH = 50%) for PVTriP(VPA)$_4$ at various temperatures.

sured using Eq. (2):

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

where $\sigma'(\omega)$ is the real part of conductivity, $\omega = 2\pi f$ is the angular frequency, ε_0 is the vacuum permittivity ($\varepsilon_0 = 8.852 \times 10^{-14}\,\mathrm{F\,cm^{-1}}$), and ε'' is the imaginary part of complex dielectric permittivity (ε^*). The proton conductivities of anhydrous complex polymer electrolytes were measured from 20 to 180 °C.

The proton conductivity of all anhydrous samples is compared in Fig. 9. The conductivity isotherm illustrates that the DC conductivity strongly depends on temperature as well as the ratio of PVPA. For PVTriP(VPA)$_{0.25}$, PVTriP(VPA)$_{0.50}$ PVTriP(VPA), and PVTriP(VPA)$_2$ and PVTriP(VPA)$_4$ (Fig. 7), the conductivity isotherm can be fitted by Arrhenius equation (Eq. (3)):

$$\ln \sigma = \ln \sigma_0 - \frac{E_a}{kT} \tag{3}$$

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(VPA)$_2$ was found to be $E_a = 0.41$ eV.

The proton conductivity of these samples is improved with PVPA content and maximum proton conductivity was measured for PVTriP(VPA)$_2$ and found to be 2.2×10^{-6} at 180 °C in the dry state. The proton conductivity of PVTriP(VPA)$_2$ is almost identical with PVTriP(VPA)$_4$, except a slight deviation at higher temperatures. The material with $x = 2$ was considered to be the optimum composition
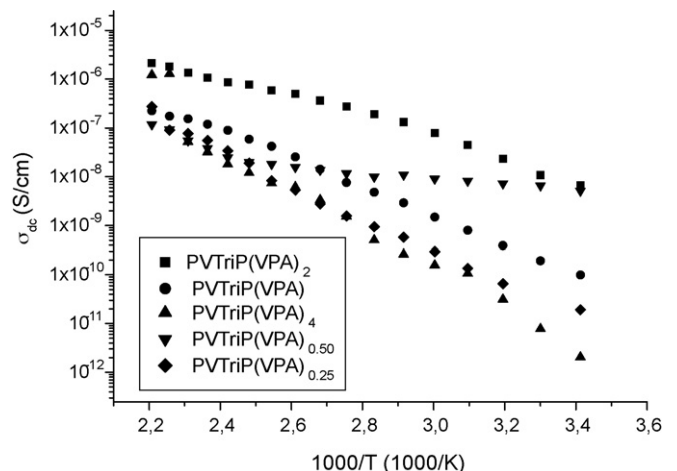

Fig. 7. Solvent uptakes of PVTriP(VPA)$_x$ (x = 1, 2, 0.25, 0.50) at the time of 10–60 min in 12 mol L^{-1} methanol/water solution at 25 °C.

Fig. 9. The DC conductivity versus reciprocal temperature for all complex polymer electrolytes.
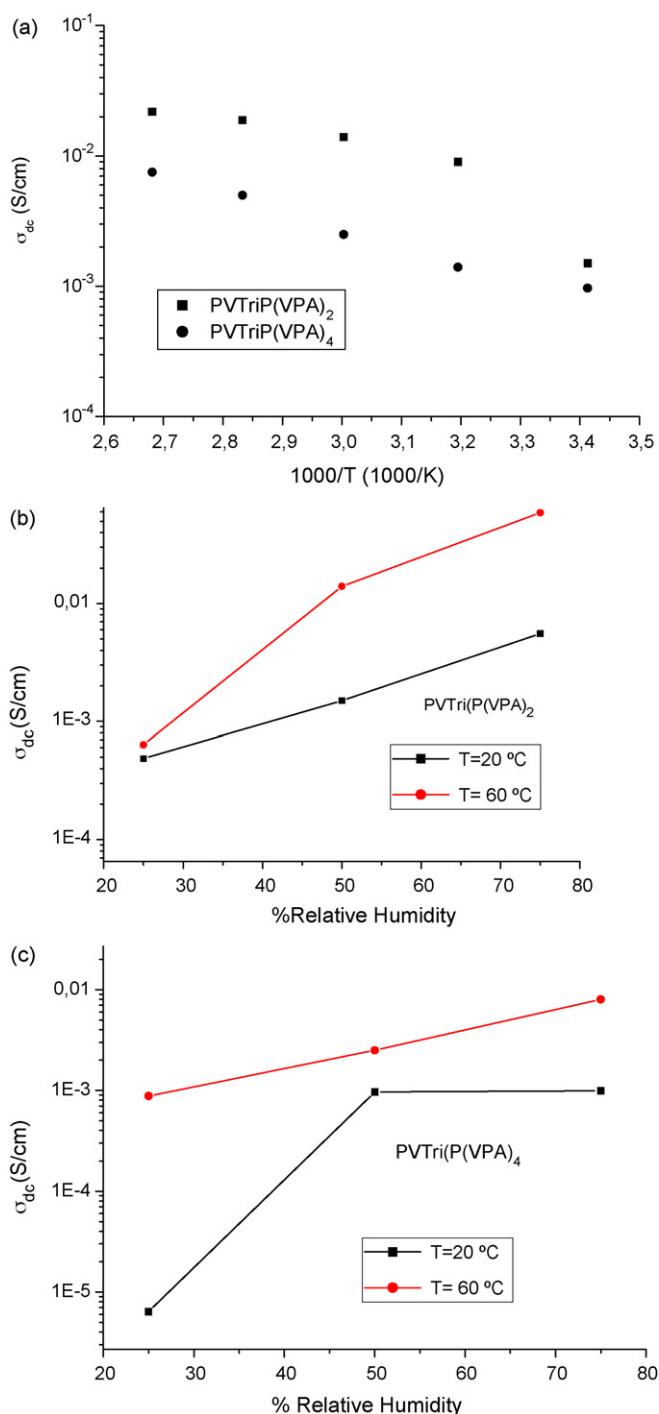
Fig. 10. (a) Effect of RH (% RH = 50) on proton conductivities of PVTriP(VPA)$_2$ and PVTriP(VPA)$_4$ as a function of temperature. (b) Effect of RH content on proton conductivity of PVTrip(VPA)$_2$. (c) Effect of RH content on proton conductivity of PVTrip(VPA)$_4$.

as the complex polymer electrolyte. Conductivity results showed that in the PVTriP(VPA) systems, the PVPA composition is highly effective on the proton conductivity of the samples. Although the major part of proton transport is provided over both phosphonic acid that are coordinated with azoles, the conductivity decrease at higher PVPA containing samples can be attributed to threshold composition of PVPA. Previously, the structure and the local proton mobility of the homopolymer, PVPA were studied by solid-state NMR under fast magic angle spinning [24]. The study concluded that the proton migration of PVPA is mediated by acidic protons

through hydrogen bonding network and condensation of acidic units blocked the proton transport resulting in a decrease in the proton conductivity [21].

3.6. Effect of humidity on conductivity

The relation between water uptake, self-condensation and proton conductivity of P(VPA) was investigated by Kaltbeitzel et al. [25]. They suggested that even after annealing and drying the material, water takes part in the conductivity mechanism. Maximum proton conductivity of pure PVPA 10^{-3} S cm^{-1} was reached under 1 bar H$_2$O atmosphere.

In addition the temperature dependence of proton conductivity of Nafion 117 at several humidity levels was reported in earlier studies [26,27]. The proton conductivity of Nafion 117 membrane was exceeding 0.11 S cm^{-1} at room temperature when the membrane is fully humidified [28–30]. The proton conductivity of Nafion 117 at 50% relative humidity was approximately 0.03 S cm^{-1} at 40 °C [26].

The temperature dependence of proton conductivity of humidified PVTriP(VPA)$_2$ and PVTriP(VPA)$_4$ (50% relative humidity) is compared in Fig. 10a. The proton conductivity of the humidified PVTriP(VPA)$_2$ was measured to be 0.022 S cm^{-1} at 100 °C, which is higher than that of PVTriP(VPA)$_4$. It seems that PVTriP(VPA)$_2$ optimum composition and both in humidified and anhydrous forms have slightly higher proton conductivities than PVTriP(VPA)$_4$.

Fig. 10b and c shows the plots of conductivity (in log scale) versus percent relative humidity (RH). Cleary, the conductivity depends on the humidity and increased with increasing water content. For example, the proton conductivity value of both samples with 25% of RH was approximately 1/100 that of 75% of RH at 60 °C. PVTriP(VPA)$_2$ with 75% RH showed the highest conductivity of about 0.077 S cm^{-1} at 80 °C. Also the humidified sample has better conductivity then pristine PVPA (under 1 bar H$_2$O atmosphere) which may be due to additional contribution of azoles to the proton conductivity of complex polymer electrolytes via structure diffusion.

4. Conclusions

In the present work, poly(1-vinyl-1,2,4-triazole) and poly(vinyl phosphonic acid) were produced by free-radical polymerization of the corresponding monomers. The transparent thin films were produced by complexation of PVPA with PVTri at various concentrations to get PVTriP(VPA)$_x$. FT-IR spectroscopy confirmed the proton exchange reactions between PVTri and PVPA forming ionic crosslinks. TG analysis showed that the samples are thermally stable up to at least 250 °C. DSC and SEM results illustrated the homogeneity of the materials. In the anhydrous state, the proton conductivity of PVTriP(VPA)$_2$ was 2.2×10^{-6} at 180 °C. The proton conductivity of PVTriP(VPA)$_x$ was increased at 50% relative humidity and reached to 0.022 S cm^{-1} for $x = 2$ and 0.008 S cm^{-1} for $x = 4$ at 100 °C. The proton conductivity of PVTriP(VPA)$_2$ is close to that of Nafion 117 membrane at the same humidification level. In this system, the proton diffusion is expected to occur by the transport of the protons through phosphonic acid units up to certain threshold composition of PVPA. PVTri has a comparable thermal stability compared to PBI and complexes of PVPA/PVTri can form free-standing films. After humidification they can be suggested for application in polymer electrolyte membrane fuel cells.

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