Intrinsically conducting polymers and copolymers containing triazole moieties

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Abstract

Random copolymer and terpolymers of 1,2,3-triazole-containing acrylates and poly(ethylene glycol)methyl ether acrylate (PEGMEA) have been synthesized and characterized. Proton conductivity measurements were made using impedance spectroscopy. The range of conductivity values from 80 °C to 200 °C spans only 1.5 orders of magnitude, demonstrating reduced temperature dependence over previously reported heterocycle based anhydrous proton conducting membranes. Introduction of PEG graft chains increased conductivity on both an absolute and $T-T_g$ normalized scale up to 30 mol% PEGMEA. Further increases in conductivity were achieved through addition of trifluoroacetic acid where increases of 0.5 to 1.5 orders of magnitude were observed depending on doping level.
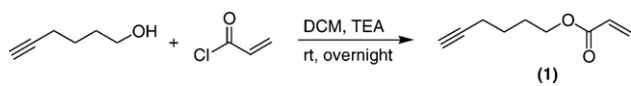© 2007 Published by Elsevier B.V.

1. Introduction

The commercialization of polymer electrolyte membrane fuel cells (PEMFCs) is becoming an increasingly important goal as the demand for clean, efficient, and portable energy rises. One of the main hurdles for the widespread utilization of PEMFCs power sources is the need for better performing, more cost effective materials [1–3]. Most current research efforts have focused on systems relying on water as the medium for proton transport whose use temperature is intrinsically limited to ∼ 100 °C [2–4]. However, there are many advantages in developing PEMFC′s capable of operating at temperatures close to 200 °C. Systems operating at such temperatures increase the efficiency of the fuel cell, reduce the overall cost by decreasing the required platinum loading, and simplify the overall heat management of the device [5].

Aside from the polybenzimidazole/H$_3$PO$_4$ membranes [6], there have been few reports of proton conducting systems capable

of operating efficiently at temperatures above 100 °C. An attractive alternative approach, using amphoteric nitrogen containing heterocycles as the proton conducting species, has been proposed by Kreuer [7,8]. The proton conductivity of membranes using heterocyclic motifs, either as dopants or as pendant groups, in does not depend on relative humidity and could thus enable the use of PEMFCs without the need for external humidification and at temperatures well above 100 °C. Further studies using imidazole and benzimidazole as proton conducting groups have revealed that proton conductivity depends on the local mobility of the heterocycles and the effective concentration of mobile protons within the polymer matrix [9–13]. Basicity of the heterocycle groups limits the mobile protons available for conduction. The mobile proton concentration can be increased by adding varying amounts of acid to protonate the heterocyclic nitrogens [11]. Liu and coworkers have observed a pronounced increase in the conductivity of vinyl heterocycle polymers when the heterocyclic group is changed from imidazole to triazole [14]. This is attributed to both a reduction in the pK$_a$ and reduced conformational changes needed for conduction in triazoles compared to imidazoles [15]. A recent report by Subbaraman et al. further

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Scheme 1. Synthesis of 5-hexyn-1-acrylate.

supports the importance of proton affinity (pK$_a$) in facilitating proton conduction in amphoteric heterocyclic systems [16].

Previous work in our group systematically studied the effect of polymer backbone mobility on proton conductivity [17]. The results from that study confirmed that proton conductivity increases as the backbone's glass transition decreases. A natural extension of this work is the combination of a low T$_g$ backbone with a smaller, more mobile, weakly basic heterocyclic motif, such as 1,2,3-triazole to increase the proton mobility within the resulting polymer membrane. Furthermore, the optimum combination of plasticizing and charge carrier groups that maximize backbone mobility and proton transport remains an open question. A series of copolymers with an increasing proportion of plasticizing side chains would probe the influence of inert flexible groups on proton conductivity while confirming the positive effect of substituting benzimidazole by 1,2,3-triazole as the proton carrier.

In the present work, we report the synthesis and characterization of polyacrylates with tethered 1,2,3-triazole motifs and varying degrees of poly(ethylene glycol)methyl ether acrylate (PEGMEA) incorporation to tune the glass transition temperature of the resulting materials. Doping the 1,2,3-triazole-based polymers with a strong acid as trifluoroacetic acid (TFA) increased the conductivity of the membranes by up to 1.5 orders of magnitude when 100 mol% TFA was added to the polymers. Polyacrylates were chosen as a model system in this study because of the ability to quickly and simply modify the structure of the copolymers to examine structural factors and to provide direct analogs to benzimidazole materials previously investigated in our laboratory [17].

2. Experimental

2.1. Materials

5-hexyn-1-ol, acryloyl chloride, triethylamine, copper(II) sulfate (CuSO$_4$·5H$_2$O), sodium ascorbate, t-butanol (t-BuOH), poly(ethylene glycol) methyl ether acrylate (PEGMEA) (M$_n$ ~ 454 g/mol), and trifluoroacetic acid (TFA) were purchased from Sigma-Aldrich and used as received. 2,2′-Azobis(2-methylpropionitrile) (AIBN) was purchased from Sigma-Aldrich and was recrystallized from methanol before use. Azidomethyl pivalate was prepared as reported in the literature [18].
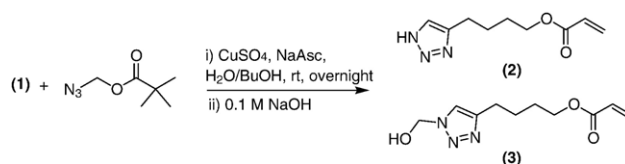
2.2. Instrumentation

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were obtained on a Bruker DPX-300 NMR Spectrometer with the samples dissolved in either chloroform-d or dimethyl sulfoxide-d$_6$ (DMSO-d$_6$). Molecular weight and polydispersity index were measured by gel permeation chromatography (GPC) in
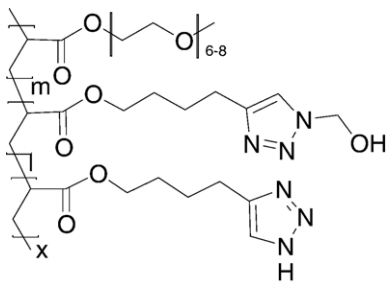
DMF at 50 °C with a flow rate of 1 mL/min on systems equipped with two-column sets (from Polymer Laboratories), and refractive index detectors (HP 1047A). Poly(methyl methacrylate) standards were used for molecular weight calibration. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/SDTA851e thermogravimetric analyzer with a heating rate of 10 °C/min from room temperature to 700 °C under air purge. Glass transition temperatures were obtained by differential scanning calorimetry (DSC) using a Perkin-Elmer Dupont DSC 2910. Samples, approximately 3–5 mg, were used with a heating rate of 10 °C/min from − 100 °C to 180 °C under a flow of nitrogen (50 mL/min). Electrochemical impedance data was obtained using a Solartron 1287 potentiostat/1252A frequency response analyzer in the 0.1 Hz–300 kHz range. The polymers were pressed between two gold coated blocking electrodes followed by an application of 100 mV excitation voltage with a logarithmic frequency sweep from 3×10^5 Hz to 1×10^{-1} Hz. Resistance values were taken at the minimum imaginary response in a Z' vs. Z'' plot to determine conductivity in the low frequency limit.

2.3. Monomer synthesis

The synthesis of the new monomers (Schemes 1 and 2) was achieved in three steps. Acryloyl chloride was reacted with 5-hexyn-1-ol in dichloromethane to yield 5-hexyn-1-acrylate (1). The [3+2] cycloaddition of acrylate (1) with azidomethyl pivalate was carried out under common "click" conditions (Cu (II) sulfate and sodium ascorbate in water/alcohol mixtures) to afford the pivaloyloxymethyl (POM)-protected triazole [18]. Removal of POM was accomplished with 0.1 M NaOH/MeOH to yield a mixture of compounds (2) and (3). The methanol substituted triazole is thought to be a result of the reaction between the cleaved triazoyl anion and formaldehyde (both formed during deprotection). Given the similarity in retention factor between the two products, (3) could not be separated by column chromatography. The presence of the free NH triazole was confirmed using ^{1}H NMR spectroscopy by the disappearance of signals at δ 1.11 and δ 6.26 ppm, corresponding to the protons in POM, a shift of the proton on the heterocycle ring from δ 7.99 ppm to δ 7.60 ppm, and the appearance of a new peak at δ 14.60 ppm corresponding to the triazole NH. Initially, the deprotection was performed on a small scale (0.7 g) yielding only 4 mol% of byproduct (3); however, upon scale-up it became exceedingly difficult to produce monomer with less than 27 mol% of (3). Therefore, model polymers were made using a monomer mixture containing 27 mol% of (3) for the PEGMEA incorporation study and with 30 mol% of (3) for the acid doping study.

Scheme 2. Synthetic route to 1,2,3-triazole functional acrylate monomers.

Scheme 3. Structure of prepared co- and terpolymers.

2.4. Polymer synthesis

Random copolymer and terpolymers with compositions varying from 0 to 52% of PEGMEA were prepared (Scheme 3). All polymerizations were carried out for 30 min at 60 °C in DMSO at a total monomer concentration of 1.0 M, initiated with AIBN (2 mol%) and purified by precipitation in ethyl acetate/hexane. Given the complexity of the repeat units a general nomenclature will be used to distinguish polymer structure. The polymers are designated as T5A-l-mPEG-nD, where l is mole percent of (3) in the monomer mixture of (2) and (3), m is mole percent of PEGMEA incorporation, and n is mole percent of TFA added compared to the mole fraction of free triazole in the backbone. It was found that after fully drying the resulting polymers, dissolution in any solvent became difficult; therefore, the compositions of wet polymers were determined by ^{1}H NMR, neither ethyl acetate nor hexane chemical shifts interfered with the analysis. Molecular weight determination of T5A-27-30PEG was attempted by GPC; however, the polymer was adsorbed to the column complicating a reliable comparison with the calibration data.

2.5. Acid doped polymer preparation

Due to the aforementioned difficulty to dissolve fully dried polymers, "wet" polymers were used in the acid doping study.

The weight percent of polymer in a stock solution was determined by both ^{1}H NMR and gravimetric methods. The values obtained were within 5% and the ^{1}H NMR data was used to calculate the required quantities of trifluoroacetic acid. A varying mol% of TFA ranging from 20 to 130% compared to moles of 1H-1,2,3-triazole content was added to a solution of 30% PEGMEA terpolymer (contains 30 wt.% of EtOAc) in MeOH($\sim$ 50 mg/mL). The solution was stirred at room temperature for 10 min, and then dried under vacuum at 45 °C overnight.

3. Results and discussion

3.1. Thermal analysis

Thermogravimetric analysis results can be seen in Fig. 1, all polymers were thermally stable up to approximately 220 °C, and thermal decomposition onset temperature increased with the degree of incorporation of PEGMEA. The decomposition of the copolymer proceeded in two steps, while that of the terpolymers proceeded in three steps. The second weight loss of the terpolymers was attributed to the loss of PEGMEA segments.

The glass transition temperatures (T_g) as determined by DSC are reported in Table 1. As expected, T_g decreases with addition of PEGMEA. The traces showed that polymers T5A-27, T5A-27-13PEG, T5A-27-22PEG, and T5A-27-30PEG were fully amorphous and displayed a single T_g, whereas polymer T5A-27-52PEG was semicrystalline and displayed a melting peak at 9 °C with ΔH_m of 3.9 J/g.

3.2. Proton conductivity as a function of polymer composition

The composition of the triazole containing polymers was varied in order to study the effects of charge carrier density, polymer matrix mobility and heterocycle nature on the proton conductivity of the resulting materials. The different compositions were designed to isolate each effect from the other structural factors. General trends and interesting observations can be extracted through methodical examination of our results.
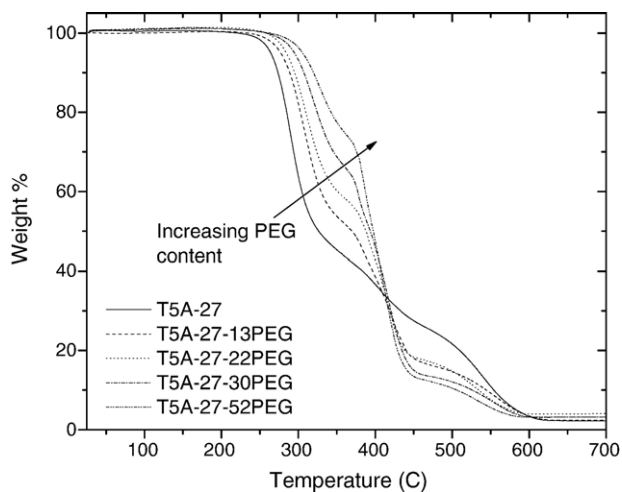

Fig. 1. TGA traces of polymers with increasing amounts of PEG.

Table 1
T_g values for all polymers and acid doped polymers

Material	T_g (°C)
T5A-27	16
T5A-27-13PEG	− 3
T5A-27-22PEG	− 19
T5A-27-30PEG	− 29
T5A-27-52PEG	− 43
T5A-4-30PEG	− 24
T5A-20-30PEG	− 28
T5A-30-28PEG	− 25
T5A-30-28PEG-20D	− 26
T5A-30-28PEG-50D	− 25
T5A-30-28PEG-80D	− 25
T5A-30-28PEG-100D	− 21
T5A-30-28PEG-130D	− 27
B5A-35PEG	2

3.2.1. Charge carrier density

The effect of charge carrier density on proton conductivity was examined originally via two avenues, doping of triazole rings with a strong acid and substitution of triazole motifs by low molecular weight poly(ethylene glycol). However, an additional approach was derived from our synthetic strategy which generated varying amounts of N-methyl hydroxyl substituted triazole as a co-product.

3.2.1.1. Influence of N-methyl hydroxyl substituted triazole. The effect of *N*-methyl hydroxy substituted triazole on the proton conductivity (σ) is illustrated in a log(σ) vs. 1000/K plot (Fig. 2). The conductivity increases approximately an order of magnitude throughout the studied temperature range when the fraction of *N*-methyl hydroxyl substituents decreased from 27 mol% to 4 mol%. Values for T5A-4-30PEG are 0.62 µS/cm at 80 °C and 17.8 µS/cm at 200 °C, spanning 1.5 orders of magnitude. The conductivity should increase upon complete removal of the co-product (3), however, given the time consuming nature of the multiple small scale syntheses required, this was not pursued any further. We expect that the observed trends outlined in this work will remain qualitatively the same if co-product (3) was completely eliminated. Insight into the effect of substituting the more basic benzimidazole by 1,2,3-triazole as the proton carrier can be obtained by comparing the conductivity of T5A-4-30PEG with that of B5A-35PEG, an analogous benzimidazole polyacrylate previously reported by this group [17]. The conductivity of T5A-4-30PEG is approximately 0.5 to 1.5 orders of magnitude higher than B5A-35PEG at 200 °C and 80 °C respectively. The improved conductivity may be attributed to several factors, the lower T_g of T5A-4-30PEG (-24 °C vs. 2 °C for B5A-35PEG), the decreased basicity of the protonic charge carrier (pK_a of 1,2,3-triazole = 9.26, pK_a of benzimidazole = 12.17),[14,19] and a lower number of conformational changes necessary for proton hopping in 1,2,3-triazole vs benzimidazole [15]. These factors are so intimately coupled that altering only one can have pronounced effects on the
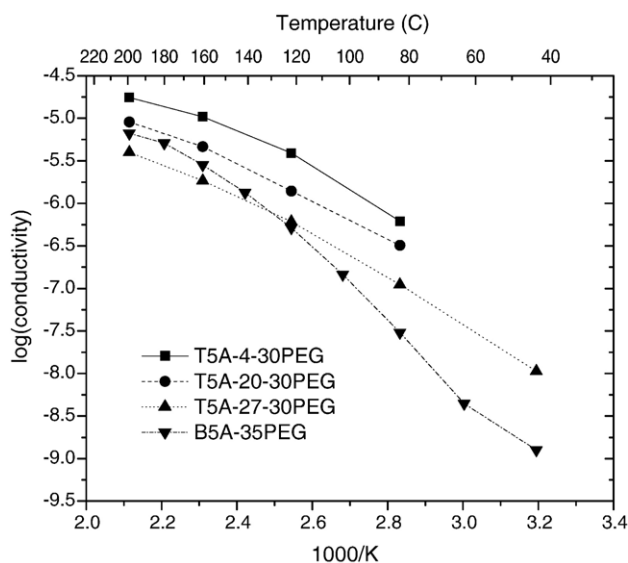

Fig. 2. Conductivity of T5A-PEGMEA terpolymers with increasing free triazole content.
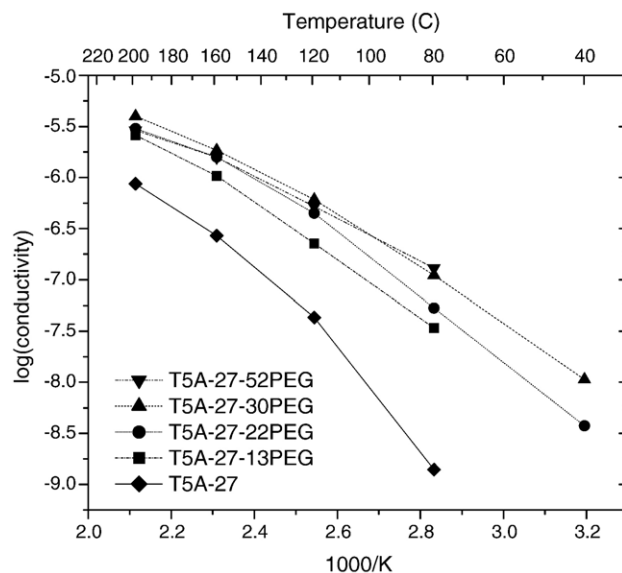

Fig. 3. Conductivity of polymers with increasing PEG content.

others; consequently, investigating each factor in a decoupled fashion becomes be a formidable task. However, to investigate general trends in a parallel manner to our reported benzimidazole containing polyacrylates, the effect of systematic increases in PEG content as a means to lower the polymer glass transition temperature and vary the charge carrier density are detailed below.

3.2.1.2. Influence of poly(ethylene glycol) methyl ether acrylate side groups. A plot of log(σ) vs. 1000/K is shown in Fig. 3 for T5A-27 and the four PEGMEA terpolymers prepared. The T5A-27 conductivity trace spans 3 orders of magnitude from 80 to 200 °C, with a maximum conductivity of 0.87 µS/cm. The initial PEG incorporation of 13 mol% provides a large initial decrease in the conductivity temperature dependence and an associated conductivity increase over the entire temperature range with a jump of nearly 1.5 orders of magnitude at 80 °C and ~ 0.75 orders of magnitude at 200 °C. Further increases in the amount of PEG resulted in small incremental improvements up to 30% PEG where conductivity of 3.98 µS/cm and 0.11 µS/cm were observed at 200 °C and 80 °C respectively. The drop in conductivity upon reaching 52% PEG is most likely due to the lower charge carrier density resulting from the high PEG loading.

The convex shape of the curves suggests non-Arrhenius behavior, where, in general, the bulk conductivity depends on the mobility, the number of charge carriers, and the charge of the carriers [20]. In polymer systems where the charge carrier and the density remain constant, conductivity is solely a function of the free volume conformational changes [11] with the temperature dependence being described by the Vogel–Tamman–Fulcher (VTF) equation describing polymer motion [21].

$$\sigma = \sigma_0 \exp[-B/(T - T_0)]. \tag{1}$$

Since the conductivity is, in part, governed by the free volume conformational changes[11] it is expected that log(σ)
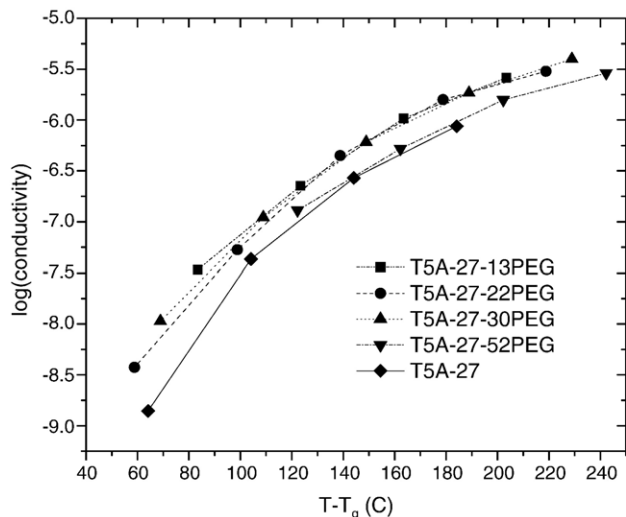
Fig. 4. Normalized conductivity vs. T–T_g plot of polymers with increasing PEG content.

vs. T–T_g curves would converge given a constant protonic charge carrier density. A plot of log(σ) vs. T–T_g for T5A and T5A-PEGMEA terpolymers (see Fig. 4) provides qualitative insight into the effect of charge carrier reduction as a result of increased PEG loading. The curves for T5A-27-13PEG, -22PEG, and, -30PEG converge around one curve and T5A-27 and T5A-27-52PEG converge around a second curve with slightly lower values. Incorporation of PEG affects two competing factors that determine conductivity, T_g and charge carrier density, such that a decrease in T_g is accompanied by a decrease in charge carrier density. In studies where benzimidazole is the protonic charge carrier (reported by us[17], and by Persson and Jannasch [22]), T_g reduction by incorporation of PEG results in increased conductivity below 160 °C on an absolute scale, however, in a normalized T–T_g plot the reduction in charge carrier density is evident from a stepwise reduction in conductivity given a constant T–T_g value [17,22]. In this case, where the heterocycle is 1,2,3-triazole, introduction of PEG resulted in conductivity increases on both an absolute scale and a normalized T–T_g scale. This implies that there may be a synergistic effect between PEG and triazole strong enough to improve conductivity despite the reduction of the number of charge carriers. These observations suggest that the chemical composition of the polymer matrix may have an appreciable effect on proton transport. A similar effect has been observed for lithium conducting polymer systems where the conductivity increases as the dielectric constant of the polymer matrix increases [23]. While the nature of the observed effect is not well understood at this time, it may be that incorporating a high dielectric constant material (PEG) has a positive influence on conductivity. Further exploration of this effect is in progress.

3.2.1.3. Trifluoroacetic acid doped materials.

Doping polymer T5A-30-28PEG with TFA shows a significant increase in conductivity with up to 1.5 orders of magnitude improvement depending on doping level (Fig. 5). The introduction of acid to

di-nitrogen heterocyclic proton conducting polymers is well known to result in conductivity improvements, however, the maximum effect in imidazole based systems is generally found at ~ 15 mol% acid [11]. In our case continued conductivity improvements were observed up to 100 mol% TFA, this may be explained by the nature of the heterocycle. The addition of a third nitrogen provides an additional proton acceptor site in the heterocycle, therefore even when the triazole is fully protonated, there are two proton donor sites and one proton acceptor allowing for a proton pathway. Further addition of TFA (130 mol%) to the system resulted in reduced conductivity.

3.2.2. Nature of heterocycle and polymer matrix mobility

Although we were not able to isolate the effect of decreased heterocycle basicity on proton conduction, direct replacement of 1,2,3-triazole for benzimidazole onto an acrylate backbone lead to significant increases in chain mobility due to reduced T_g (Table 1). This may be attributed to the large difference in melting point of benzimidazole (177 °C) and 1,2,3-triazole (25 °C). The indication is that utilization of 1,2,3-triazole as the protonic charge carrier will produce inherently more mobile polymeric systems, resulting in systems with reduced temperature dependence. Further investigation into the influence of alternate heterocycles on polymer mobility as well as isolating the effect of the heterocycle basicity is currently under investigation.

A systematic increase in the mole fraction of NH-triazole results in steady conductivity increases (Fig. 2), however, it is striking that there is a minimal associated increase in T_g as the charge carrier density increases, this is in contrast to the trend observed in benzimidazole containing polymers [22]. An interesting extension would be to investigate the effect of tether length on conductivity in 1,2,3-triazole containing polymers, by reducing tether length the volume fraction of charge carriers can be increased. In the case of benzimidazole[20] and imidazole [24] tether length reduction results in increased T_g and the conductivity displays an increase in temperature dependence.
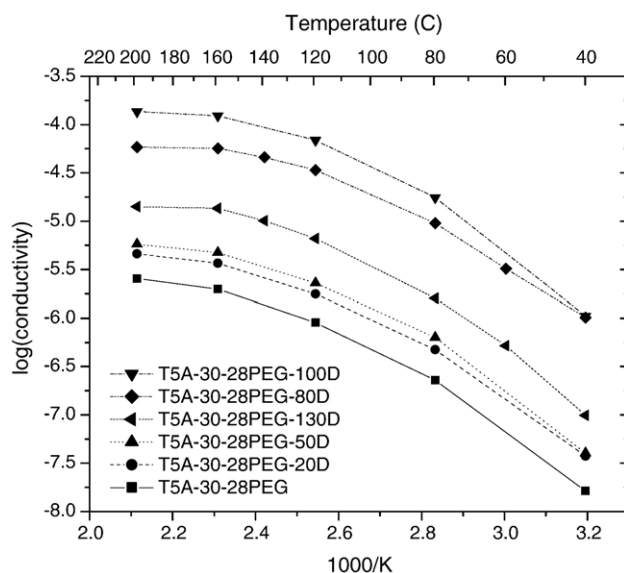

Fig. 5. Conductivity of TFA doped terpolymers.

Given the observed low T_g with tethered 1,2,3-triazole, it may be possible to increase the volume fraction of charge carriers without adversely affecting the temperature dependence of the conductivity.

4. Summary

Random copolymers and terpolymers of 1,2,3-triazole-containing acrylate and PEGMEA have been synthesized and characterized. A comparison of the conductivity of the 1,2,3-triazole based polyacrylate with 30% PEGMEA with the benzimidazole analog allowed us to probe the effect of using the more weakly basic 1,2,3-triazole as the proton carrier. The triazole containing polyacrylate showed higher proton conductivity and a less pronounced conductivity temperature dependence than the corresponding benzimidazole polyacrylate. This can be attributed in part to the lower pK_a of 1,2,3-triazole, but may also be due to the smaller size and low melting point of the hererocycle itself, resulting in a lower T_g material when attached to a polymer backbone. A more detailed study focused on decoupling basicity from the chemical structure is currently under way. The conductivity increases as a function of absolute and a normalized temperature as PEGMEA incorporation increases until reaching a limit at 30 mol%. This finding indicates that T_g reduction with PEG in 1,2,3-triazole systems can counteract the associated reduction in charge carrier density. The lower conductivity observed for terpolymers with higher PEGMEA fractions suggests that at those compositions the decrease in charge carrier concentration becomes the limiting factor for proton transport over the backbone mobility. Doping the polymers with TFA resulted in further conductivity increases ranging from 0.5 to 1.5 orders of magnitude compared to the undoped membranes. Though these polyacrylates can only be regarded as model systems, the trends observed in this study should translate to better defined, chemically stable backbones. In order to reconcile the need for a low T_g to achieve high proton mobility with a mechanically stable membrane for MEA fabrication, the use of polymer filled nanoporous inorganic membranes, thermally crosslinked films and diblock copolymers are currently being explored.

Acknowledgements

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