

# Proton Conducting Polymers Containing 1*H*-1,2,3-Triazole Moieties

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**ABSTRACT:** Polyacrylates containing a different number of 1*H*-1,2,3-triazole groups per repeat unit have been synthesized via conventional free radical polymerization. These polymers were characterized by nuclear magnetic resonance spectroscopy (NMR), gel permeation chromatography (GPC), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). Proton conductivity measurements were made using impedance spectroscopy. Introduction of more than one triazole per repeat unit did not result in an increase in conductivity as there was an accompanying increase in glass transition temperature ( $T_g$ ). A maximum conductivity of 17.5  $\mu\text{S}/\text{cm}$  was obtained at 200 °C under anhydrous condition. © 2008 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 47: 188–196, 2009

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## INTRODUCTION

Polymer electrolyte membrane fuel cells (PEMFCs) have been considered promising power sources for vehicles and electronic devices due to their high efficiency and nonpolluting properties.<sup>1–3</sup> Perfluorosulfonic acid membranes, such as Nafion<sup>®</sup>, have been extensively studied because of their chemical and electrochemical stability; however, their development and commercialization are limited to operating temperatures well below 100 °C because the proton transport mechanism relies on the presence of water.<sup>4,5</sup> Higher operating temperatures are desirable as this would increase the efficiency

of the fuel cell, decrease the required platinum catalyst loading, thus reducing the cost, and simplify the overall heat management of the device.<sup>6</sup>

As amphoteric nitrogen-based heterocycles, such as imidazole, pyrazole and benzimidazole, showed dynamic hydrogen bonding and proton transport mechanisms similar to water,<sup>7,8</sup> they were studied as proton solvents in PEMFCs.<sup>9,10</sup> Although these heterocycles have been shown to provide comparable proton conductivities to that of hydrated polymers, they will gradually leach out, resulting in continuous decrease in proton conductivity. To overcome this problem, these heterocycles have been immobilized to oligomers, such as ethylene oxide oligomers as reported by Schuster et al.<sup>11</sup> and Persson and Jannasch.<sup>12</sup> These oligomers show slightly lower conductivities compared to the parent compounds, which can be attributed to lower mobility of the protogenic groups.

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1*H*-1,2,3-triazole has recently drawn interest as an alternative heterocycle for use in PEMFCs due to its electrochemical stability and high proton conductivity. A study by Zhou et al. apparently demonstrated that a pronounced increase in conductivity was observed in vinyl-based polymers when the heterocyclic group was changed from an imidazole moiety to a triazole moiety.<sup>13</sup> Similar to the work on imidazole<sup>14</sup> and benzimidazole,<sup>15,16</sup> 1*H*-1,2,3-triazole has been tethered to several flexible polymeric backbones including polyacrylate,<sup>17</sup> polysiloxane,<sup>18</sup> and polyphosphazene.<sup>19</sup> Proton conductivities of these polymers depend strongly on mobility and charge carrier density.

In this work, we report the synthesis and characterization of polyacrylates containing a different number of 1*H*-1,2,3-triazoles per repeat unit. The various monomers used in this study were obtained as a direct consequence of the copper catalyzed alkyne-azide coupling, so-called "Click Chemistry,"<sup>20–22</sup> using pivaloyloxymethyl (POM) substituted azide.<sup>23,24</sup> These polymers were designed to investigate the effect of charge carrier density on proton conductivity by introducing more than one triazole per repeat unit. Conductivities of the polymers using impedance spectroscopy are compared and reported.

## EXPERIMENTAL

### Materials

1,3-Propanediol, 1,1,1-tris(hydroxymethyl)ethane, pentaerythritol, 3-butyn-1-ol, sodium hydride (NaH), sodium hydroxide (NaOH), propargyl bromide, acryloyl chloride, triethylamine (TEA), copper(II) sulfate (CuSO<sub>4</sub>·5H<sub>2</sub>O), sodium ascorbate, *t*-butanol (*t*-BuOH), and dimethyl sulfoxide (DMSO) were purchased either from Sigma-Aldrich or VWR and used as received. Regenerated cellulose dialysis tubing with a molecular weight cutoff of 3500 Da was purchased from Fisher Scientific. 2,2'-Azobis(2-methylpropionitrile) (AIBN) was purchased from Sigma-Aldrich, and recrystallized from methanol before use. 3-(Prop-2-yn-1-yloxy)propan-1-ol, **2a**,<sup>25</sup> 3-(prop-2-ynyloxy)-2,2-bis[(prop-2-ynyloxy)methyl]propan-1-ol, **2c**,<sup>26</sup> and azidomethyl pivalate (AMP)<sup>23</sup> were prepared as reported in the literature.

### Characterization

<sup>1</sup>H-NMR (300 MHz) and <sup>13</sup>C-NMR (75 MHz) spectra were obtained on a Bruker DPX-300

NMR Spectrometer with the samples dissolved in either chloroform-*d* (CDCl<sub>3</sub>) or methanol-*d*<sub>4</sub> (CD<sub>3</sub>OD). Molecular weight and polydispersity index (PDI) were measured by gel permeation chromatography (GPC) in DMF at 50 °C with a flow rate of 0.75 mL/min on systems equipped with two-column sets (from Polymer Laboratories), and refractive index detectors (HP 1047A). Poly(methyl methacrylate) (PMMA) standards were used for molecular weight calibration. Thermogravimetric analysis (TGA) was carried out using a TA Instruments TGA 2950 thermogravimetric analyzer with a heating rate of 10 °C/min from room temperature to 500 °C under nitrogen. Glass transition temperatures were obtained by differential scanning calorimetry (DSC) using a TA instruments Dupont DSC 2910. Samples were analyzed with a heating rate of 10 °C/min from –100 °C to 150 °C under a flow of nitrogen (50 mL/min). To prepare the polymer for impedance measurement it was cast from a methanol solution in a small cylinder formed by punching a 0.3175-cm diameter hole through a 0.0125-cm thick piece of Kapton<sup>®</sup>. The sample is then inserted between two 1.25-cm diameter gold-coated blocking electrodes and dried at 30 °C under vacuum for 8 h to evaporate the methanol. The cell geometry of the complete assembly closely approximates a parallel-plate capacitor in which the polymer is the dielectric medium. To ensure an anhydrous and inert environment, the measurement was conducted under vacuum. At temperatures between 40 and 200 °C, the impedance response was sampled logarithmically from 0.1 Hz to 300 kHz with a constant excitation voltage of 0.1 Vrms using a Solartron 1287 potentiostat and 1252A frequency response analyzer. We determined the approximate proton resistance by geometrically fitting<sup>27</sup> the impedance response that corresponds to proton conduction in the DC limit. From the resistance the conductivity was calculated by accounting for the well-defined cell geometry.

### Synthesis of 2-methyl-3-(prop-2-ynyloxy)-2-[(prop-2-ynyloxy)methyl]propan-1-ol, **2b**

In a modification of literature preparations for **2a**<sup>25</sup> and **2c**,<sup>26</sup> to a solution of 1,1,1-tris(hydroxymethyl)ethane (5.98 g, 49.8 mmol, 1 equiv.) in DMSO (60 mL), 20 mL of sodium hydroxide aqueous solution (6.58 g, 164.3 mmol, 3.3 equiv.) was added. The solution was stirred at room

temperature under N<sub>2</sub> for 1 h. Propargyl bromide (16.5 g, 110.9 mmol, 2.2 equiv.) was added slowly with stirring at 0 °C. The reaction was stirred at room temperature for 22 h. The product was extracted with ethyl acetate followed by washing with deionized water several times. The organic portion was dried over MgSO<sub>4</sub> and the volatiles were removed *in vacuo*. The crude product was further purified by column chromatography, using hexane:ethyl acetate (3:7) as an eluent, to give 5.0 g of **2b**.

Yield: 60%. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ: 0.90 (s, 3H), 2.43 (s, 2H), 2.45 (b, 1H), 3.50 (s, 4H), 3.56 (s, 2H), 4.15 (s, 4H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ: 17.34, 40.45, 58.73, 68.21, 73.96, 74.49, 79.71. FAB-HRMS (*m/z*): calculated 197.1099 [M + 1], found 197.1169.

#### Synthesis of 3-(prop-2-yn-1-yloxy)propyl Acrylate, **3a**

To a solution of compound **2a** (0.80 g, 7.0 mmol, 1 equiv.) and triethylamine (1.3 mL, 9.1 mmol, 1.2 equiv.) in anhydrous THF (20 mL), acryloyl chloride (0.68 mL, 8.4 mmol, 1.2 equiv.) was added slowly with stirring at 0 °C. A white precipitate of triethylammonium hydrochloride formed, and the reaction was stirred for 16 h at room temperature. The precipitate was removed by filtration. The product was extracted with ethyl acetate followed by washing with deionized water several times. The organic portion was dried over MgSO<sub>4</sub> and the volatiles were removed *in vacuo*. The crude product was further purified by column chromatography, using hexane:ethyl acetate (1:4) as an eluent, to give 0.82 g of the product.

Yield: 70%. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ: 1.97 (m, 2H), 2.42 (s, 1H), 3.62 (t, 2H), 4.15 (s, 2H), 4.26 (t, 2H), 5.80–6.38 (m, 3H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ: 28.85, 58.19, 61.58, 66.43, 74.38, 79.87, 128.46, 130.70, 166.18. EI-HRMS (*m/z*): calculated 169.1898 [M + 1], found 169.0876.

#### Synthesis of 2-methyl-3-(prop-2-yn-1-yloxy)-2-[(prop-2-yn-1-yloxy)methyl]propyl Acrylate, **3b**

Compound **3b** was prepared as described for **3a**.

Yield: 44%. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ: 1.00 (s, 3H), 2.40 (s, 2H), 3.42 (s, 4H), 4.12 (m, 6H), 5.80–6.43 (m, 3H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ: 17.24, 39.77, 58.64, 66.61, 72.19, 74.24, 79.82,

128.50, 130.58, 166.03. EI-HRMS (*m/z*): calculated 251.2903 [M + 1], found 251.1288.

#### Synthesis of 3-(prop-2-yn-1-yloxy)-2,2-bis[(prop-2-yn-1-yloxy)methyl]propyl Acrylate, **3c**

Compound **3c** was prepared as described for **3a**.

Yield: 51%. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ: 2.39 (s, 3H), 3.55 (s, 6H), 4.11 (s, 6H), 4.21 (s, 2H), 5.80–6.42 (m, 3H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ: 44.10, 58.69, 63.43, 68.60, 74.30, 79.76, 128.50, 130.58, 165.87. EI-HRMS (*m/z*): calculated 305.3377 [M + 1], found 305.1380.

#### Synthesis of 3-[(1-[(2,2-dimethylpropanoyl)oxy]methyl)-1H-1,2,3-triazol-4-yl]methoxy]propyl Acrylate, **4a**

To a solution of compound **3a** (0.82 g, 4.88 mmol, 1 equiv.) in 20 mL *t*-BuOH/H<sub>2</sub>O (2/1), azidomethyl pivalate (AMP, 0.92 g, 5.86 mmol, 1.2 equiv.), CuSO<sub>4</sub>·5H<sub>2</sub>O (0.06 g, 0.24 mmol, 0.05 equiv.), and sodium ascorbate (0.29 g, 1.46 mmol, 0.3 equiv.) were added. The solution was stirred at room temperature for 21 h. The product was extracted with ethyl acetate and washed with ammonium hydroxide aqueous solution and brine. The combined organic portion was dried over MgSO<sub>4</sub> and the volatiles were removed *in vacuo*. The crude product was further purified by column chromatography, using hexane:ethyl acetate (1:4) as an eluent, to give 0.8 g of product.

Yield: 50%. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ: 1.18 (s, 9H), 1.96 (m, 2H), 3.62 (t, 2H), 4.24 (t, 2H), 4.63 (s, 2H), 5.84–6.36 (m, 3H), 6.22 (s, 2H), 7.79 (s, 1H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ: 26.80, 28.91, 38.77, 61.53, 64.23, 67.10, 69.66, 123.91, 128.40, 130.74, 145.73, 166.14, 177.74. FAB-HRMS (*m/z*): calculated 326.1638 [M + 1], found 326.1738.

#### Synthesis of 3-[1-(2,2-dimethyl-propionyloxy-methyl)-1H-[1,2,3]triazol-4-yloxy]-2-[1-(2,2-dimethyl-propionyloxymethyl)-1H-[1,2,3]triazol-4-yloxymethyl]-2-methyl-propyl Acrylate, **4b**

Compound **4b** was prepared as described for **4a**.

Yield: 83%. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ: 0.94 (s, 3H), 1.18 (s, 18H), 3.39 (s, 4H), 4.05 (s, 2H), 4.59 (s, 4H), 5.80–6.40 (m, 3H), 6.23 (s, 4H), 7.78 (s, 2H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ: 17.27, 26.81, 38.78, 40.01, 64.73, 66.61, 69.71, 72.58, 123.89, 128.36, 130.74, 145.83, 165.98, 177.73.

FAB-HRMS ( $m/z$ ): calculated 565.2908 [M + 1], found 565.2922.

**Synthesis of 3-[1-(2,2-dimethyl-propionyloxy-methyl)-1H-[1,2,3]triazol-4-ylmethoxy]-2,2-bis[1-(2,2-dimethyl-propionyloxymethyl)-1H-[1,2,3]triazol-4-ylmethoxymethyl]-propyl Acrylate, 4c**

Compound **4c** was prepared as described for **4a**.

Yield: 61%.  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.16 (s, 27H), 3.46 (s, 6H), 4.11 (s, 2H), 4.55 (s, 6H), 5.80–6.42 (m, 3H), 6.22 (s, 6H), 7.78 (s, 3H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 26.82, 38.79, 44.46, 63.26, 64.73, 68.87, 69.78, 123.98, 128.31, 130.75, 145.63, 165.76, 177.69. FAB-HRMS ( $m/z$ ): calculated 776.3865 [M + 1], found 776.3991.

**Synthesis of POM-Protected Polyacrylate 5a**

The homopolymerization in THF (~1 M) with AIBN (2 mol %) was carried out in an air-free tube. After three cycles of freeze-pump-thaw, the solution was stirred at 60 °C for 23 h. The solution was precipitated in hexane to yield POM-protected polymer in a quantitative yield.

$^1\text{H-NMR}$  (300 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : 1.16 (s, 9H), 1.50–2.50 (m, 3H), 1.87 (s, 2H), 3.57 (s, 2H), 4.12 (s, 2H), 4.56 (s, 2H), 6.32 (s, 2H), 8.13 (s, 1H).

**Synthesis of POM-Protected Polyacrylate 5b**

The polymer was prepared as described for POM-protected polyacrylate **5a**.

$^1\text{H-NMR}$  (300 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : 0.88 (s, 3H), 1.15 (s, 18H), 1.50–2.50 (m, 3H), 3.35 (s, 4H), 3.95 (s, 2H), 4.54 (s, 4H), 6.32 (s, 4H), 8.11 (s, 2H).

**Synthesis of POM-Protected Polyacrylate 5c**

The polymer was prepared as described for POM-protected polyacrylate **5a**.

$^1\text{H-NMR}$  (300 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : 1.15 (s, 27H), 1.50–2.50 (m, 3H), 3.45 (s, 6H), 4.04 (s, 2H), 4.51 (s, 6H), 6.32 (s, 6H), 8.10 (s, 3H).

**Synthesis of Polyacrylate 5a**

Polyacrylate containing POM-protected triazole (0.29 g, 0.91 mmol, 1 equiv.) was treated with 0.1 M NaOH/MeOH (10 mL, 1.0 mmol, 1.1 equiv.) at room temperature under  $\text{N}_2$  for 1 h. The solution was neutralized with 1 M HCl aq. solution to pH 8. The solution was concentrated *in vacuo* fol-

lowed by dialysis against water and then methanol to yield polyacrylate **5a**.

$^1\text{H-NMR}$  (300 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : 1.50–2.50 (m, 3H), 1.86 (s, 2H), 3.53 (s, 2H), 4.11 (s, 2H), 4.60 (s, 2H), 7.75 (s, 1H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : 28.62, 34.85, 41.54, 61.84, 63.09, 66.55, 128.55, 142.38, 174.70.

**Synthesis of Polyacrylate 5b**

The polymer was prepared as described for polyacrylate **5a**.

$^1\text{H-NMR}$  (300 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : 0.83 (s, 3H), 1.50–2.50 (m, 3H), 3.35 (s, 4H), 3.91 (s, 2H), 4.51 (s, 4H), 7.72 (s, 2H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : 16.72, 25.88, 30.86, 39.70, 63.56, 66.95, 72.29, 128.41, 142.42, 174.29.

**Synthesis of Polyacrylate 5c**

The polymer was prepared as described for polyacrylate **5a**.

$^1\text{H-NMR}$  (300 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : 1.50–2.50 (m, 3H), 3.42 (s, 6H), 4.04 (s, 2H), 4.51 (s, 6H), 7.70 (s, 3H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : 25.84, 30.82, 44.17, 64.02, 65.91, 68.54, 128.30, 142.31, 174.27.

**Synthesis of but-3-yn-1-yl Acrylate, 7**

Compound **7** was prepared as described for **3a**.

Yield: 75%.  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.02 (s, 1H), 2.57 (m, 2H), 4.27 (m, 2H), 5.80–6.43 (m, 3H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 18.97, 62.21, 69.94, 79.97, 128.09, 131.26, 165.91. EI-HRMS ( $m/z$ ): calculated 125.1372 [M + 1], found 125.0599.

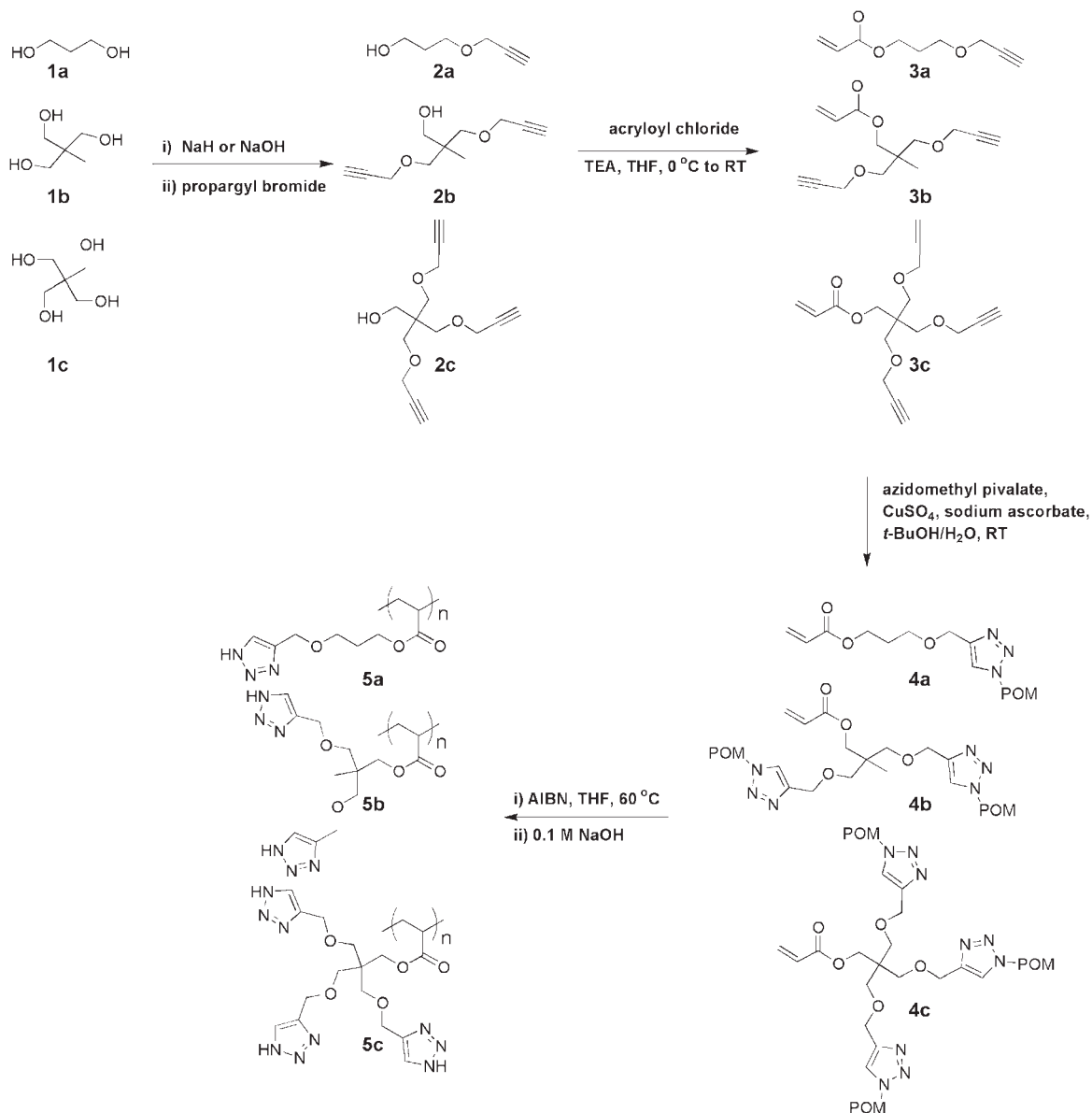
**Synthesis of 2-(1-[(2,2-dimethylpropanoyl)oxy]methyl)-1H-1,2,3-triazol-4-yl)ethyl Acrylate, 8**

Compound **8** was prepared as described for **4a**.

Yield: 68%.  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.18 (s, 9H), 3.13 (m, 2H), 4.44 (m, 2H), 5.81–6.42 (m, 3H), 6.21 (s, 2H), 7.63 (s, 1H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 25.29, 26.72, 38.71, 62.97, 69.58, 123.04, 128.12, 131.02, 144.59, 165.87, 177.71. FAB-HRMS ( $m/z$ ): calculated 282.1376 [M + 1], found 282.1482.

**Synthesis of POM-Protected Polyacrylate 9**

The polymer was prepared as described for POM-protected polyacrylate **5a**.



**Scheme 1.** Synthetic route to polyacrylates containing 1H-1,2,3-triazole moieties.

$^1\text{H-NMR}$  (300 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : 1.15 (s, 9H), 1.50–2.50 (m, 3H), 3.05 (s, 2H), 4.31 (s, 2H), 6.31 (s, 2H), 8.04 (s, 1H).

#### Synthesis of Polyacrylate 9

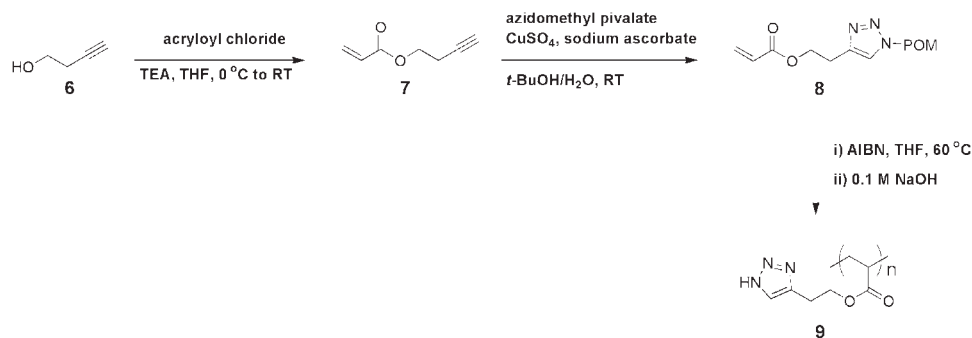
The polymer was prepared as described for polyacrylate **5a**.

$^1\text{H-NMR}$  (300 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : 1.50–2.50 (m, 3H), 3.00 (s, 2H), 4.25 (s, 2H), 7.64 (s, 1H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$ : 24.12, 34.43, 41.24, 63.18, 128.27, 141.68, 174.58.

## RESULTS AND DISCUSSION

### Synthesis

The synthetic route to polyacrylates containing a different number of 1H-1,2,3-triazoles per repeat unit, all having the same spacer length from the polymer backbone, is shown in Scheme 1. The starting alcohols (**1a–1c**) were first deprotonated with either NaH or NaOH, and then allowed to react with propargyl bromide. The resulting products (**2a–2c**) were then allowed to react with acryloyl chloride in the presence of triethylamine



**Scheme 2.** Synthetic route to polyacrylate **9**.

to give the acrylate monomers **3a–3c**. The overall yields ranged from 44 to 70%. The [3 + 2] cycloaddition of the acrylates with AMP was carried out under common click conditions (Cu(II) sulfate and sodium ascorbate in *t*-BuOH/water mixtures) to afford monomers containing pivaloyloxymethyl (POM)-protected triazoles (**4a–4c**). AMP was selected due to the ease of cleavage of the POM protecting group, mild base, with the result being a 1*H*-1,2,3-triazole having the requisite labile proton for proton conduction. Monomer **8** was synthesized using a similar procedure to that described above starting from 3-butyn-1-ol, **6** (Scheme 2).

Polyacrylates containing POM-protected triazoles were obtained from polymerization of **4a–4c** or **8** initiated with AIBN at 60 °C for 23 h. Molecular weights of POM-protected polymers obtained from GPC are in the range of 7–9 kg/mol (Table 1). The removal of the POM protecting group with NaOH/MeOH followed by dialysis against water and methanol, respectively, yielded four different polyacrylates (**5a–5c** and **9**). The <sup>1</sup>H-NMR spectra in Figure 1 show a shift of the peak of proton on the triazole ring from  $\delta$  8.13 to  $\delta$  7.75 ppm, and the disappearance of the methylene and methyl resonance at  $\delta$  6.32 and  $\delta$  1.16 ppm indicates that

the POM protecting group has been successfully removed. As determined by <sup>1</sup>H-NMR, more than 99% of the POM group has been removed for all polymers.

### Thermal Analysis

The onset of decomposition, reported as the temperature corresponding to 5% weight loss as determined by TGA, and glass transition temperatures ( $T_g$ ), determined by DSC, for the polymers are reported in Table 1. These polyacrylates are thermally stable up to approximately 200 °C. All polymers are amorphous, and the  $T_g$  value increased from 12 to 52 °C when the triazole content was increased from 32 to 47 wt %. The weight % of triazole contained in each polymer was calculated by dividing the equivalent weight of triazole unit(s) (68 g/mol) by the equivalent weight of the polymer repeat unit. The incremental increase in  $T_g$  is presumably a result from a more highly hydrogen bonded network. Similar increases in  $T_g$  as a function of increasing heterocycle content have been reported for benzimidazole based polymers.<sup>16</sup>

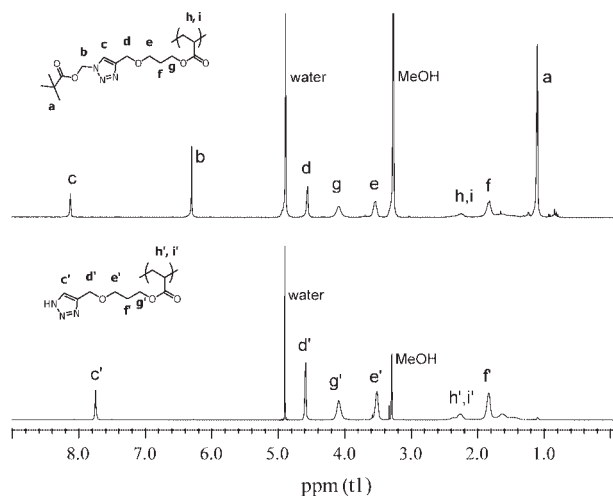
**Table 1.** Physical and Thermal Properties of the Polymers Studied

Polymer	wt % Triazole	$M_n$ (g/mol) <sup>a</sup>	PDI <sup>a</sup>	Decomp. onset (°C) <sup>b</sup>	$T_g$ (°C) <sup>c</sup>
Polyacrylate <b>5a</b>	32	7800	1.69	214	12
Polyacrylate <b>5b</b>	40	7500	1.24	222	44
Polyacrylate <b>5c</b>	47	9400	1.25	263	52
Polyacrylate <b>9</b>	40	7900	1.62	230	46

<sup>a</sup> Determined by GPC on the POM-protected polymers using DMF as an eluent and calibrated against PMMA standards.

<sup>b</sup> 5% weight loss as determined by TGA with a heating rate of 10 °C/min from RT to 500 °C under N<sub>2</sub>.

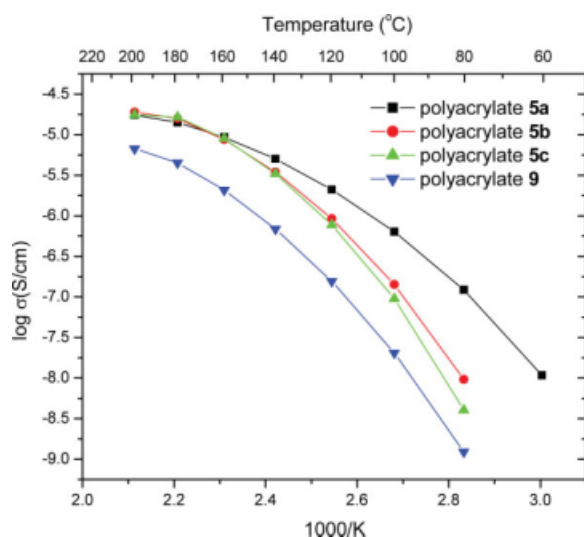
<sup>c</sup> Obtained from DSC on the second heating cycle.



**Figure 1.**  $^1\text{H-NMR}$  spectra of POM-protected polyacrylate **5a** (top) and polyacrylate **5a** (bottom) in  $\text{CD}_3\text{OD}$ .

### Proton Conductivity

In general, bulk conductivity depends on a number of factors including segmental mobility and charge carrier density.<sup>12</sup> As shown in Figure 2, proton conductivity of polyacrylate **5a** was higher than that of polyacrylates **5b** and **5c** throughout the temperature range studied with a maximum conductivity of  $17.5 \mu\text{S/cm}$ . This can be attributed to the lower  $T_g$  of **5a** relative to the other samples. At lower temperatures, where conductivity is more influenced by mobility, a larger difference in conductivity was observed. The similarity of the conductivity curves for polyacrylates **5b** and **5c** suggest that



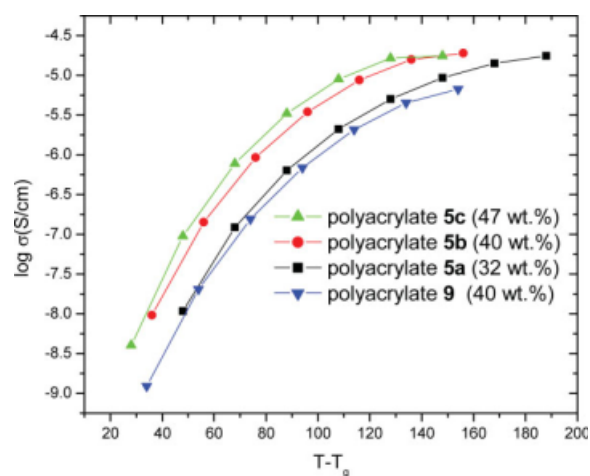
**Figure 2.** Conductivity plot of polyacrylates containing different triazole contents.

there is an interplay of segmental mobility and charge carrier density. The decrease in segmental mobility, as evidenced by the higher  $T_g$  of **5c** versus **5b**, is apparently being offset by the increase in the number of protogenic groups per repeat unit. The influence of the spacer length between the protogenic group and the polymer backbone can be clearly seen when comparing the conductivities of polyacrylate **9** which are approximately 0.5 and 2 orders of magnitude lower than that of polyacrylate **5a** at  $200^\circ\text{C}$  and  $80^\circ\text{C}$ , respectively. A decrease in conductivity is observed when the spacer length is reduced. The similar dependence of conductivity on spacer length has also been observed for oligomers and polymers containing nitrogen-based heterocycles.<sup>11,12,14</sup>

Conductivity in polyelectrolytes as a function of temperature does not follow Arrhenius behavior, but can be described by a Vogel-Tamman-Fulcher (VTF) equation.<sup>28</sup>

$$\sigma = \sigma_0 \exp[-B/(T - T_0)] \quad (1)$$

Because the conductivity ( $\sigma$ ) is, in part, governed by the free volume conformational changes,<sup>29</sup> it is expected that  $\log(\sigma)$  versus  $T - T_g$  curves would converge given a constant protogenic charge carrier density. The normalized conductivity versus  $T - T_g$  plot is shown in Figure 3. The similarity in shape of the curves suggests that all of these polymers have the same proton transport mechanism.<sup>15</sup> The effect of charge carrier reduction in the system was clearly observed when the wt % of triazole was decreased from 47 to 32, while the spacer length was fixed.



**Figure 3.** Conductivity versus  $T - T_g$  plot of the polyacrylates.

One would expect that the conductivity curves of **5b** and **9** would converge given almost identical triazole content (40 wt.%) and  $T_g$  (44 versus 46 °C) in a normalized plot; however, that was not the case. The conductivity of polyacrylate **9** was lower than that of polyacrylate **5b**, and was even lower than that of polyacrylate **5a** (32 wt % with one triazole per repeat unit). These observations suggest that besides segmental mobility and charge carrier density, there is at least one more factor that influences proton conductivity. Similar to the previous work in our group on terpolymers of 1*H*-1,2,3-triazole containing polyacrylate and poly(ethylene glycol)methyl ether acrylate,<sup>17</sup> the chemical composition of the polymer, that is, the presence of oxygen atoms, may have an effect on proton transport. In addition, the branching structure of polyacrylate **5b** could possibly provide a more closely packed heterocycle network, leading to a more continuous hydrogen pathway for proton transport. Further studies on the details of proton transport mechanism of these polymers are in progress.

## CONCLUSIONS

A series of polyacrylates containing a different number of 1*H*-1,2,3-triazole pendants have been successfully synthesized and characterized. The polymers are completely amorphous and thermally stable up to approximately 200 °C. The proton conductivity is predominately governed by two competing factors: segmental mobility and charge carrier density of the protogenic side-groups. Introduction of more than one triazole per repeat unit did not result in an increase in conductivity as it was offset by the accompanying increase in  $T_g$ . Furthermore, a correlation between side-chain spacer length and proton conductivity was shown.

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