**Thermal, Mechanical and Conductive Properties of Imidazolium-Containing Thiol-ene
Poly(Ionic Liquid) Networks.**

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Abstract

A series of imidazolium-based bis(trifluoromethylsulfonyl)imide [NTf₂] poly(ionic liquid)s (PILs) were prepared by conducting the solventless thiol-ene ‘click’ photopolymerization of bisallylimidazolium [NTf₂] and pentaerythritol tetrakis(3-mercaptopropionate) (PTMP). The thiol:ene molar ratio was varied in order to examine changes in the thermal, mechanical and conductive properties of the resulting polymer networks. The 1.0:2.0 thiol-ene PIL network exhibited the highest glass transition temperature (T_g of -5.0 °C) and storage modulus (E' of 9.24 MPa at 100 °C) values. Temperature-dependent ionic conductivities were found to rely on both the T_g /crosslink density as well as the IL content, with the highest ionic conductivity observed for the 1.0:3.0 thiol-ene PIL network (1.42×10^{-5} S/cm at 25 °C). Application of Vogel-Fulcher-Tammann and Williams-Landel-Ferry theories revealed the impact of both T_g /crosslink density and free ion concentration on temperature-dependent conductivity data, and indicated lower free volumes and fragilities for the thiol-ene networks relative to other non-network PILs.

1. Introduction

Thiol-ene ‘click’ photopolymerization represents a robust, solventless, user-friendly, rapidly curing platform for the preparation of homogeneous polymer networks, the mechanism of which involves the step-growth radical reaction between a multi-functional thiol and an ene [1-5]. A high degree of flexibility has been observed with respect to the thermal and mechanical properties of the resulting networks due to the large number of thiol crosslinkers and ene monomers available (commercially and synthetically). As a result, thiol-ene photopolymerization chemistry has been employed in a number of different applications, recent examples of which include nanoprint/soft imprint lithography [6-8], electrospun fibers and nonwovens [9,10], gas barrier and transport membranes[11-14] and lithium ion batteries [15].

One research area where thiol-ene photochemistry has yet to be exploited is in the development of polymerizable ionic liquids or poly(ionic liquid)s (PIL)s. PILs allow for the cationic or anionic center of an ionic liquid (IL) to be constrained within the repeating unit of a polymer chain through the incorporation of a polymerizable group(s). PILs are advantageous in that they combine the unique physical, electrochemical and thermal characteristics of ILs with the thermal and mechanical properties of various macromolecular architectures. As a result, research in PILs (especially cationic PILs) and their applications has increased exponentially over the last decade and several recent reviews have highlighted applications in electroactive and energy devices [16-21]. PILs have many advantages over the use of free ILs in electroactive devices, including enhanced stability, reduced leaching issues and improved mechanical stability. Additionally, PILs act as single-ion conductors since only the counteranion (or countercation) is mobile. Despite these benefits, a constant observed drawback of PILs is that anchoring the IL group causes a restriction in ion mobility, leading to a decrease in ionic

conductivity. New structural variations are constantly being explored in order to improve upon this shortcoming, leading to a better understanding of the relationship between structure, morphology and ion-transport.

PILs that contain the imidazolium cation, in particular those derived from vinyl- or (meth)acryloyl-substituted imidazolium salts, have provided the greatest versatility in terms of synthesis and applications [22-35]. Some of the highest ionic conductivities have been observed when the imidazolium group has been placed pendant at the end of a long chain, coupled with a large, non-coordinating anion such as bis(trifluoromethylsulfonyl)imide [NTf₂]. For example, Long et al. reported the morphology and ionic conductivity of a series of alkyl-substituted imidazolium-based PILs and found that larger counteranions led to depressed glass transition temperature (T_g) values and increased conductivities [26,29]. More recently, modifications of the structural architecture of imidazolium-containing chain-growth polymers have been reported, either by employing pendant ethyleneoxy or long alkyl chains to increase flexibility and improve ion mobility [28,32] or by synthesizing block or triblock copolymers, where microphase separation between the PIL block and the non-ionic block(s) creates conductive microchannels [31,35].

Step-growth PIL architectures have been explored to a far lesser extent. In 2012, Gibson et al. reported on a series of linear imidazolium-containing polyesters where imidazolium-containing diols were mixed with diacid chlorides [36]. Several semicrystalline polyesters that resulted from this work exhibited high conductivities (up to 3.0×10^{-5} S/cm at 25 °C) and good mechanical stabilities. Long et al. discussed the use of imidazolium and phosphonium hydroxy-terminated IL monomers in the preparation of segmented polyurethanes for electroactive applications [37,38] while Drockemuller et al. explored CuAAC ‘click’ cyclization as a method

to gain access to 1,2,3-triazolium-containing polymers with alkyl and ethyleneoxy spacers (conductivities up to 1.0×10^{-5} S/cm at 25 °C) [39-41].

We recently reported several series of covalently crosslinked imidazolium- and 1,2,4-triazolium-containing polyester networks prepared by Michael addition step-growth polymerization [42-44]. Incorporation of flexible chains and/or bulky, non-coordinating counteranions such as [NTf₂] led to a decrease in the T_g and the rubbery plateau modulus (E') and an increase in thermal stability. Despite the development of these interesting PIL networks, the synthesis and purification of the IL-containing acetoacetate monomers was found to be extremely tedious. Additionally, the polymerizations required the use of solvent due to the incompatibility of the acetoacetate and acrylate monomers, leading to long curing cycles (up to one week). As a result, thiol-ene “click” photopolymerization was targeted as a more robust, rapidly-curing, alternative method for the formation of covalently crosslinked, PIL networks. To date, only one report has utilized this chemistry as a way to incorporate a 1,4-di(vinylimidazolium)butane bisbromide monomer into a polymer network for the purposes of studying the material’s anti-corrosion properties [45]. In this manuscript, the preparation of a series of imidazolium-containing polymer networks using thiol-ene photochemistry is discussed. In all of these PILs, the [NTf₂] counteranion was chosen due to its hydrophobic nature and tendency to provide enhanced ionic conductivities [18-21,46]. The thermal, mechanical and conductive properties of the resulting PILs were measured as a function of the thiol:ene molar ratio.

2. Experimental

2.1 Materials

All chemicals were purchased from Sigma-Aldrich or Acros Organics and were used as received without further purification. Chemicals used in this study included allyl imidazole (97 %), allyl bromide (99 %), acetonitrile (ACS grade), lithium bis(trifluoromethylsulfonyl)imide (LiNTf₂, 99 %), 2,2-dimethoxy-2-phenyl-acetophenone (DMPA, 99%), and pentaerythritol tetrakis(3-mercaptopropionate) (PTMP, > 95%). 1,3-Diallylimidazolium bromide **1** was prepared following a published procedure [47]. An ELGA Purelab[®] Ultra filtration device produced ultrapure water having a resistivity of 18 MΩ-cm.

2.2 Monomer Characterization

¹H and ¹³C NMR spectra were obtained on a JEOL-ECS 400 MHz spectrometer and chemical shift values reported below were referenced to residual solvent signals (CDCl₃: ¹H, 7.26 ppm; ¹³C, 77.16 ppm). NMR spectra for monomer **2** are included in the Supporting Information. Elemental analyses were completed by Atlantic Microlab, Inc.

2.3 Preparation of 1,3-diallylimidazolium bis(trifluoromethylsulfonyl)imide [NTf₂] **2**

1,3-Diallylimidazolium bromide **1** (5.00 g, 21.8 mmol) was dissolved in DI water (50 mL). To this stirred solution at RT was added a solution of lithium bis(trifluoromethylsulfonyl)imide (6.58 g, 22.9 mmol) in DI water (50 mL). The resulting mixture was stirred at RT overnight, and then chloroform (50 mL) was added. The organic phase was separated, washed with DI water (3 x 25 mL), and the volatiles were removed under reduced pressure, affording a light yellow oil (8.91 g, 95 %). ¹H NMR (CDCl₃): δ 8.74 (s, 1 H), 7.29 (s, 2 H), 5.95 (m, 2 H), 5.47 (m, 4 H), 4.77 (d, 4 H, *J* = 6.4 Hz); ¹³C NMR (CDCl₃): δ 135.7,

129.2, 123.4, 122.4, 119.9 (q, $J = 321$ Hz, $-\text{CF}_3$), 52.4. Anal. calculated for $\text{C}_{11}\text{H}_{13}\text{F}_6\text{N}_3\text{O}_4\text{S}_2$, C 30.77, H 3.05, N 9.79; found, C 30.80, H 2.92, N 9.81.

2.4 Preparation of Thiol-Ene Networks

The UV curing of thiol-ene networks was conducted at various thiol:ene molar ratios (1.0:1.0, 1.0:1.5, 1.0:2.0, 1.0:2.5, 1.0:3.0) following previously published procedures [6,48,49]. As an example, the polymer network employing the 1.0:2.0 thiol:ene molar ratio was prepared by mixing bisallylimidazolium $[\text{NTf}_2]$ **2** (0.88 g, 2.05 mmol) with PTMP (0.50 g, 1.02 mmol) and 1 wt % of the photoinitiator DMPA (13 mg). The mixture was shaken by hand until a homogenous solution was obtained. The solution was then placed into a TeflonTM mold so as to achieve a film thickness of ~ 0.7 mm. The sample was exposed for 10 minutes to broadband ultraviolet radiation from a 100 W (8500 lumen) E17 metal halide high-intensity discharge lamp (Osram Sylvania, Wilmington MA) whose glass outer envelope had been removed. This was followed by thermal treatment in a vacuum oven (60 °C, < 0.01 mm Hg) for 48 hours prior to any polymer analysis to remove residual moisture. Duplicate specimens at each thiol:ene molar ratio were produced.

2.5 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded on a PerkinElmer Spectrum TwoTM FT-IR in transmission mode. The Perkin Elmer Spectrum 10TM software was used to follow the desired peaks at 1 cm^{-1} resolution using 32 scans. Thiol (2570 cm^{-1}) and double bond (1630 cm^{-1}) signals were monitored from multiple FTIR spectra taken for each thiol-ene network specimen: (a) before UV curing (i.e. monomer mixture), (b) after UV curing and (c) after thermal treatment in the vacuum oven (48 hrs, 60 °C, < 0.01 mm Hg). Functional group conversions were determined from the peak areas (normalized to another peak area unaffected by photopolymerization) using the

following equation: degree of conversion = $(A_o - A_t)/A_o$ where A_o and A_t refer to the normalized peak area before polymerization occurred (A_o) and at a given time t (A_t), respectively. The error in peak area measurements was determined to be less than $\pm 3\%$.

2.6 Thermal Analysis

The glass transition temperature (T_g) for each thermally treated thiol-ene network specimen was determined using a TA Instruments Q200 differential scanning calorimeter, calibrated with an indium standard. Experiments were completed under a 50 mL/min flow of dry nitrogen. Each sample (4-8 mg) was placed into a hermetically sealed aluminum pan and first equilibrated at $-90\text{ }^{\circ}\text{C}$, followed by heating to $150\text{ }^{\circ}\text{C}$ at a rate of $3\text{ }^{\circ}\text{C}/\text{min}$. T_g values were determined from the second heating event using the half extrapolated tangents method in the Universal Analysis software. Variability in T_g was found to be less than $\pm 1.5\text{ }^{\circ}\text{C}$. The T_g width was determined from the difference between the onset and endset temperatures.

A TA Instruments Q500 thermogravimetric analyzer was used to determine the thermal stability (T_{onset} and $T_{\text{d}5\%}$) for each thermally treated thiol-ene network specimen. A sample (5-10 mg) was placed in a platinum pan and heated from 30 to $1000\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C}/\text{min}$ under a flow of dry nitrogen ($40\text{ mL}/\text{min}$). Onset of thermal decomposition (T_{onset}) was determined from the intersection of the tangents of the beginning and sloped portions of the TGA curve. $T_{\text{d}5\%}$ was determined as the temperature at which 5% weight loss was observed. The reproducibility of the resulting T_{onset} and $T_{\text{d}5\%}$ was found to give an average error of less than $\pm 1.3\text{ }^{\circ}\text{C}$.

2.7 Mechanical Analysis

A TA Instruments Q800 dynamic mechanical analyzer was used to determine the mechanical properties of the thiol-ene networks after thermal treatment. Specimens of $\sim 0.7\text{ mm}$ thickness were cut using a razor blade to dimensions of approximately $10\text{ mm} \times 5\text{ mm}$.

Temperature ramp studies were completed on each thiol-ene network specimen using the film/tension clamp from -90 to 200 °C at 5 °C/min under a dry nitrogen environment at a constant strain and frequency (1 Hz). All experimental data reported here are from the second heating event for all polymer network specimens. The storage modulus (E') values were measured at 100 °C in the rubbery plateau region and represent an average of two specimens at each thiol:ene molar ratio. T_g values were determined as the apex of the $\tan \delta$ peak and the T_g width was defined as the full width at half-maximum of the $\tan \delta$ peak.

2.8 Conductivity Testing

Impedance spectroscopy was conducted using a Metrohm Autolab 302N potentiostat with a 4-electrode in-plane cell (BT-112 Conductivity Cell, Scribner Associates, Inc.). The cell was placed into an aluminum cased chamber (built in-house, Figure S3) and the temperature was controlled using a Tempco[®] mica strip heater (Type B), coupled with a variable voltage source (Staco Energy[®]). The alternating voltage setpoint of the potentiostat was set to 200 mV and the frequency was varied from 0.1 Hz to 1.0 MHz. Two specimens at each thiol:ene molar ratio were tested. Since the relative humidity over the course of each experiment was not controlled (measured at 20-36 %), each specimen were tested at three different time intervals after thermal treatment ($t = 0$ h, 48 h and 7 d; left at ambient conditions in-between readings) in order to determine the reproducibility of the impedance data. Each reported value was the result of six measurements performed on each specimen at 25 °C, followed by increments of 10 °C from 30 to 150 °C.

In a typical experiment, the sample was allowed to equilibrate at each temperature until three consecutive frequency sweeps resulted in constant impedance spectra (typically 30-60 min of equilibration). The resistance was calculated from the x-intercept of the Nyquist plot in the

Autolab Nova software suite and subsequently converted to conductivity using $\sigma = L/AR$ where L is the length between the inner electrodes, A is the area between the electrodes and R is the measured resistance. The overall RSD (relative standard deviation) across all measurements was determined to be less than 0.8 %. Tables of $\log \sigma$ values for each specimen at each experiment time are provided in the Supplementary Data section.

3. Results and Discussion

3.1 Monomer and Thiol-ene Network Synthesis

The allyl group was targeted as the active ene functionality due to its high reactivity and propagation rate in thiol-ene photopolymerizations [1]. Coupling of commercially available 1-allylimidazole with allyl bromide was completed following a previously published procedure (Scheme 1), resulting in 1,3-diallylimidazolium bromide **1** [47]. Anion exchange with lithium bis(trifluoromethylsulfonyl)imide (LiNTf₂) then led to the targeted 1,3-diallylimidazolium [NTf₂] **2**. Characterization and purity of monomer **2** was determined by ¹H and ¹³C NMR spectroscopy (Figures S1-S2) and elemental analysis. The residual bromide concentration in monomer **2** was found to be < 0.01 % w/w, as determined by ion chromatography [50].

*Scheme 1: Preparation of 1,3-Bisallylimidazolium [NTf₂] **2***

Thiol-ene networks at various molar ratios (1.0:1.0, 1.0:1.5, 1.0:2.0, 1.0:2.5, 1.0:3.0) were prepared in duplicate by photopolymerizing the appropriate mixtures of 1,3-

diallylimidazolium [NTf₂] **2** and the tetra-functional thiol PTMP with 1 wt % of the photoinitiator DMPA (Scheme 2). All thiol-ene photopolymerizations were completed by exposing the monomer mixture to UV irradiation for 10 minutes in a TeflonTM mold. The UV cured samples were then thermally treated in a vacuum oven for 48 hours (< 0.01 mm Hg, 60 °C) prior to polymer analysis to ensure removal of any residual moisture. The resulting thiol-ene PIL networks were found to be insoluble in a variety of solvents (acetone, acetonitrile, methanol, DMF, DMSO, H₂O).

*Scheme 2: Photoinitiated Thiol-Ene Polymerization between PIL **2** and PTMP*

The extent of crosslinking was monitored by FTIR spectroscopy after UV curing and thermal treatment. The extent of curing was determined by monitoring the reduction of the peak intensities located at 2570 cm⁻¹ (S-H stretching) and at 1647 cm⁻¹ (C=C stretching). By comparing the difference in peak areas of the starting monomer mixture, after UV curing and after thermal exposure, % conversions were determined. Table 1 summarizes the data acquired as a result of the FTIR experiments. It was concluded from this data that the networks were sufficiently crosslinked after UV irradiation and that thermal treatment did not appear to induce

further polymerization as the functional group conversions were found to be unchanged. It is also worth noting that, for the 1.0:3.0 thiol:ene network, a higher than expected conversion of ene was observed, possibly due to polymerization between ene groups, although further analysis would be necessary to support this hypothesis.

Table 1: Thiol and Ene Conversion from FTIR Studies

Thiol:ene ratio	Specimen	Thiol Conversion UV only	Thiol Conversion 48 hrs vac 60 °C	Ene Conversion UV only	Ene Conversion 48 hrs vac 60 °C
1:1	A	58 %	59 %	100 %	100 %
1:1	B	56 %	57 %	100 %	100 %
1:1.5	A	77 %	77 %	100 %	100 %
1:1.5	B	76 %	77 %	100 %	100 %
1:2	A	98 %	98 %	100 %	100 %
1:2	B	96 %	96 %	100 %	100 %
1:2.5	A	95 %	96 %	88 %	89 %
1:2.5	B	97 %	98 %	92 %	93 %
1:3	A	96 %	96 %	74 %	72 %
1:3	B	96 %	96 %	75 %	76 %

3.2 Gel Fraction Analysis

Gel fraction analysis via 24 h soxhlet extraction (CH_2Cl_2) was performed in order to assess the effectiveness of monomer incorporation into the thiol-ene networks (Table 2) [51]. All networks exhibited a gel fraction of greater than 80 % with a maximum gel fraction of 96.4 % observed for the 1.0:2.0 thiol:ene network. The lowest gel fractions were found to occur with higher concentrations of ene, suggesting the presence of dangling end groups, free oligomeric/polymer chains and/or unincorporated sol. ^1H NMR spectroscopic analysis of the

extracts did not indicate the presence of any unreacted 1,3-diallylimidazolium [NTf₂] **2** or PTMP.

Table 2: Gel Fraction and Thermal Data for Thiol-Ene Networks

thiol:ene molar ratio	Gel Fraction	DSC T_g (°C)	TGA T_{onset} (°C)	TGA $T_{\text{d5\%}}$ (°C)
1.0:1.0	91.5 ± 1.5 %	-22.7	355	344
1.0:1.5	93.5 ± 2.5 %	-8.9	357	353
1.0:2.0	96.4 ± 1.5 %	-5.0	353	346
1.0:2.5	88.1 ± 0.9 %	-20.4	364	350
1.0:3.0	80.1 ± 2.0 %	-31.7	359	349

3.3 Thermal Properties of Thiol-Ene Networks

DSC was employed to characterize the T_g values of the thermally treated thiol-ene networks (Figure 1, Table 2). The T_g values reported represent an average of the 2nd heating of two specimens at each thiol:ene molar ratio. All T_g values were found to be below room temperature, a common characteristic of thiol-ene networks, due to the flexible thioether linkages [52]. The overall highest T_g value was observed for the highly crosslinked, stoichiometric 1.0:2.0 thiol-ene polymer network (-5.0 °C). As the ene concentration was reduced (towards the 1.0:1.0 thiol:ene network) the T_g was found to decrease, presumably due to an increase in segmental/chain length between crosslink points, although unreacted thiol groups could also act to plasticize the network. When excess ene was present, a more drastic reduction in T_g was observed, in particular with the ‘extreme’ 1.0:3.0 thiol:ene network (-31.7 °C). It is assumed that the presence of dangling ene endgroups, which effectively plasticize the network, is the primary cause for this drop in T_g . There is also the possibility that, if homopolymerization of ene groups

and/or the formation of soluble, non-covalently crosslinked oligomeric/polymeric chains is occurring (as suggested from the FTIR ene conversion data), such reactions should lead to a more flexible system, decreasing the crosslink density and suppressing the T_g .

Figure 1: DSC Overlay for Thiol:Ene Polymer Networks.

The thermal degradation (T_{onset} and $T_{\text{d5\%}}$) of the thiol-ene networks was determined using TGA, the results of which indicated that all of the networks had similar T_{onset} (> 350 °C) and $T_{\text{d5\%}}$ (> 340 °C) values (Table 2). The thermal stabilities of the polymer networks were found to be slightly higher than the precursor monomer 1,3-diallylimidazolium [NTf₂] **2** (T_{onset} of 335 °C; $T_{\text{d5\%}}$ of 325 °C).

3.4 Mechanical Properties of Thiol-Ene Networks

Dynamic mechanical analysis (DMA) was used to characterize the mechanical properties of the imidazolium-containing thiol-ene networks. Important network properties such as storage

modulus (E'), apparent crosslink density (ν_c) and $\tan \delta$ T_g were determined at a constant strain (frequency = 1 Hz) from the second heating over a temperature range of -90 to 150 °C, averaged from two specimens at each thiol:ene molar ratio (Table 3). The highest E' value (Figure 2) was observed for the stoichiometric 1.0:2.0 thiol-ene network (9.39 MPa at 100 °C) while the ‘extreme’ 1.0:3.0 thiol-ene network exhibited the lowest modulus (1.56 MPa at 100 °C). As with the trends observed for T_g , the reduced E' value for the 1.0:1.0 thiol:ene system is attributed to longer chain lengths between crosslink points. The lower E' value where excess ene is employed (in particular, the ‘extreme’ 1.0:3.0 thiol:ene network) is primarily attributed to dangling, ene endgroups, resulting in a plasticization effect, although it remains possible that unresolved curing/propagation mechanisms are at work, resulting in the presence of soluble, non-covalently crosslinked oligomeric/polymeric chains, as suggested by the combination of high ene conversion (~ 75 % by FTIR) and low gel fraction (80 %).

Table 3: Mechanical Properties of Thiol-Ene Networks

thiol:ene molar ratio	E' @ 100 °C (MPa)	$\nu_c \times 10^{-4}$ (mol/cm ³)	$\tan \delta$ max T_g (°C)	width of glass transition (T_g)	
				$\tan \delta$ max (°C)	DSC (°C)
1.0:1.0	4.00 ± 0.08	4.30 ± 0.09	-3.1 ± 0.7	25.9 ± 3.8	6.5 ± 0.3
1.0:1.5	8.32 ± 0.40	8.94 ± 0.43	1.1 ± 1.0	13.6 ± 0.6	7.1 ± 0.3
1.0:2.0	9.24 ± 0.32	9.93 ± 0.34	4.4 ± 0.5	12.1 ± 0.4	6.9 ± 0.4
1.0:2.5	3.21 ± 0.17	3.45 ± 0.18	-10.5 ± 0.4	13.2 ± 0.2	7.4 ± 0.1
1.0:3.0	1.58 ± 0.07	1.70 ± 0.08	-24.5 ± 0.2	17.6 ± 0.7	9.8 ± 0.2

Dynamic strain measurements indicated that the thiol-ene networks exhibited ideal elastic behavior across the amplitude limits of the DMA instrument (0.1 to 200 μm at a frequency of 1 Hz). Thus, apparent crosslink density (ν_c) was calculated from the rubbery plateau region of the storage modulus (E') curve above the T_g from rubber elasticity theory:

$$\nu_c = E'/3RT \quad (1)$$

where E' is the storage modulus at a temperature above the T_g (Pa), R is the gas constant (8.314 J·mol/K) and T is the temperature (K) [53]. From a thiol:ene molar ratio of 1.0:1.0, ν_c was observed to increase with increasing ene concentration up to a molar ratio of 1.0:2.0, where the highest value ($9.93 \times 10^{-4} \text{ mol/cm}^3$) was obtained, followed by a gradual decrease with further addition of ene (Table 3). The higher gel fraction, modulus and T_g values observed for the 1.0:2.0 network are attributed to this relatively high crosslink density.

Figure 2: DMA Storage Modulus (E') Comparison with Variable Thiol:Ene Molar Ratio

Glass transition (T_g) values were determined from the maximum of the $\tan \delta$ curve for each thiol-ene network, the observed trend of which was analogous to data obtained from DSC

(Figure 3; Table 3). $\tan \delta$ max T_g values were all found to be higher (6-19 °C) than the T_g values obtained from DSC, however this is not surprising due to the differences in timescales between the two experiments in combination with the increased sensitivity of the DMA. The highest $\tan \delta$ T_g value was observed for the 1.0:2.0 thiol-ene network with a decrease in T_g in either direction with a change in ene concentration. A correlation between crosslink density and the widths of the $\tan \delta$ curves was clearly evident in the thiol-ene networks studied here (Table 3) and the presence of sharp $\tan \delta$ and DSC T_g transitions has been used as evidence to support the high degree of homogeneity in thiol-ene polymer networks [1,2,49]. The sharpest $\tan \delta$ peaks (smallest $\tan \delta$ T_g widths) were observed for the polymers with the highest crosslink density (1.0:1.5, 1.0:2.0 and 1.0:2.5 thiol:ene molar ratios), indicating that these networks exhibit a relatively high degree of network homogeneity. Wider $\tan \delta$ T_g widths were found for the ‘extreme’ 1.0:1.0 and 1.0:3.0 thiol:ene systems, indicating some degree of network heterogeneity. As previously discussed, these ‘extreme’ systems likely exhibit combinations of longer distances between crosslink points, coupled with unreacted, dangling end groups, the result of which could lead to variable microdomains. Analysis of the DSC curves indicated that all of the T_g widths were similar in magnitude and relatively sharp (Table 3).

Figure 3: DMA Tan Delta Curves for Thiol:Ene Polymer Networks

3.5 Ionic Conductivities of Thiol-Ene Networks

Impedance spectroscopy was used to probe the influence of the thiol:ene molar ratio on the ionic conductivities of the resulting networks. Figure 4 shows the ionic conductivities of these networks and represents an average of six readings for each thiol:ene molar ratio, across two specimens, at 25 °C followed by 10 °C increments from 30 to 150 °C. Since humidity could not be controlled during these experiments (measured at 20-36 %), each sample was tested at three different time intervals after thermal treatment (0 h, 47 h and 7 d, left exposed to ambient conditions between each set of measurements) to determine the reproducibility of the conductivity measurements. The relative standard deviation across all six measurements was determined to be less than 0.8 %.

Figure 4: Ionic Conductivities of Thiol-Ene Networks.

Ionic conductivity is primarily a function of two factors: free ion concentrations and ion mobility. In PILs, the former is impacted by the amount of incorporated IL as well as the presence of ion pairing/aggregation, while the latter is influenced by fluidity (or flexibility, which is correlated to T_g /crosslink density, as well as gel fraction), and steric barriers to ion motion like ion size and chain packing (i.e., space limitations). Therefore, it is not surprising that the temperature-dependent conductivities of the thiol-ene networks were significantly lower than “free” 1,3-diallylimidazolium [NTf₂] **2** (6.76×10^{-2} S/cm at 25 °C, Figure S4) due to a severe decline in imidazolium mobility upon incorporation into the polymer backbone (i.e., the PILs are single-ion conductors) and reduced fluidity in the polymer relative to “free” IL. Ionic conductivities of the PILs were observed to increase in the following order with respect to the molar ratio of ene: $3.0 > 2.5 > 1.0 > 1.5 > 2.0$. Since this trend is not the same as with T_g , and PIL conductivity generally is highly T_g dependent, Figure 5 was constructed to compare ionic conductivities normalized with T_g [54]. After normalization, the curves do not collapse onto one another, clearly reinforcing that T_g is not the only factor which affects conductivity and ion

transport. In fact, the observed increase in the normalized conductivity curves correlates with an increase in the imidazolium/ion content of the networks, i.e., $3.0 > 2.5 > 2.0 > 1.5 > 1.0$.

Figure 5: Ionic Conductivities of Thiol-Ene Networks versus T_g/T .

These results support the idea that the relationship between ionic conductivity and network structure depends on both the concentration of ionic groups and T_g (crosslink density and polymer flexibility). For instance, even though the 1.0:1.0 thiol:ene network contains the lowest IL content, the system is not highly crosslinked and therefore polymer chain relaxation, an important requirement for ionic conductivity, is more easily attainable. Consequently, the ionic conductivity for 1.0:1.0 is higher than other, more highly crosslinked systems (1.0:1.5 and 1.0:2.0) despite these latter systems containing a higher concentration of ionic groups. On the other hand, even though the 1.0:1.0 and 1.0:2.5 networks have similar T_g values, the conductivity of the 1.0:2.5 network is nearly double that of the 1.0:1.0 due to a much larger mol % of IL present in the former (Table 4). The highest ionic conductivity was observed at a 1.0:3.0 thiol:ene molar ratio (1.42×10^{-5} S/cm at 25 °C) where a large amount of network flexibility exists in combination with the highest mol % IL. It is also possible, due to the relatively lower

gel fractions of the 1.0:3.0 and 1.0:2.5 networks (80 and 88 %, respectively), that the presence of non-covalently crosslinked oligomeric/polymeric materials, as discussed above, could enhance conductivity through increased ion mobilities in these systems. Overall, the ionic conductivities observed for these thiol-ene networks are comparable to and, in several cases, are improvements over other non-network imidazolium-containing PILs over the same temperature range [21,27,30-33,36,37,46].

In addition to the structural relationships noted above, the differences in ionic conductivities among networks appear to be decreasing with increasing temperature, suggesting that changes in T_g and crosslink density become less influential at higher temperatures (with ionic conductivity potentially becoming more dependent upon free ion concentration). So, additional insight into PIL network behavior was obtained by fitting temperature-dependent conductivities to both the Vogel-Fulcher-Tammann (VFT) and Williams-Landel-Ferry (WLF) equations. The application of these theories has been discussed at length (references 27, 32, 33, 41, 55-58, and Supplementary data). Both 3-parameter and 2-parameter VFT fitting [27] were performed; since results were consistent across both fittings and were identical to WLF results (discussed below) only values obtained from 3-parameter fitting are shown in Table 4.

Table 4: Parameters obtained by fitting temperature-dependent conductivity data to the Vogel-Fulcher-Tammann equation.

thiol:ene molar ratio	T_g (K)	mol % IL	$\sigma_{25\text{ }^\circ\text{C}}$ (S/cm)	σ_o (S/cm)	B (K)	T_o (K)	D
1.0:1.0	250.2	40.4	1.46×10^{-6}	0.38	1377	187.6	7.3
1.0:1.5	264.3	48.6	4.10×10^{-7}	0.92	1637	186.2	8.8
1.0:2.0	268.2	53.9	1.86×10^{-7}	0.79	1527	197.3	7.7
1.0:2.5	252.8	57.8	2.49×10^{-6}	1.23	1505	183.5	8.2
1.0:3.0	241.5	60.6	1.42×10^{-5}	1.96	1555	166.8	9.3

The VFT parameter σ_0 is defined as the high-temperature (i.e., as $T \rightarrow \infty$, assuming no degradation) conductivity limit. Consistent with the trend observed for T_g -normalized conductivities (Figure 5), values of σ_0 increase as the mol % of IL in the polymer increases. It therefore appears that, at higher temperatures, the more significant factor controlling conductivity is free ion concentration, while mobility-limiting factors such as polymer chain motion and steric barriers due to the presence of crosslink points are relatively less important. The overall values of σ_0 for the thiol:ene polymers are comparable to or greater than values that have been reported from other imidazolium-containing PILs (with typical values of 0.01-0.5 S/cm) [27,33,56] and in some cases are comparable to the best values obtained for 1,2,3-triazolium-containing PILs (0.15-2 S/cm) [40,41,59-61].

The Vogel temperature, T_0 , defines the low-temperature limit of the conductivity curves, and is the temperature where ion mobility approaches zero and polymer relaxation time extrapolates to infinity [27,57]. Historically, a relationship between T_0 and T_g has been asserted, i.e., $T_0 = T_g - 50$ K, though it is well-known that this relationship is often invalid due to the “decoupling” of polymer chain motion from ion mobility (decoupling is described in more detail, below) [40]. For the thiol:ene polymers described herein, T_0 values were found to be 63-78 K lower than T_g , which coincides with the range of 10-77 K below T_g that has been observed with previously reported PILs [27,32,33,40,41,55,56]. Furthermore, the overall trend for T_0 values directly follows that observed with T_g and crosslink density. Notably, an increase in the ionic conductivities of the PIL networks at 25 °C ($\sigma_{25\text{ °C}}$), which is 30-56 K higher than the range of measured T_g values, is also observed as T_0 , T_g , and crosslink density decrease, the same trend noted above for the overall non-normalized conductivity data. The latter observation highlights

the relative importance of mobility-related factors in ionic conductivity at lower temperatures. Hence, VFT parameters are consistent with the proposal that, in the low temperature regime, conductivities depend strongly on polymer chain dynamics and its impact on free ion mobility, while mobility restrictions are reduced at higher temperatures yielding conductivities that rely primarily on total free ion content. Such a crossover from “ T_g -controlled” behavior to “ion concentration-controlled” behavior has been observed in the past with homologous polymers that varied in the relative amounts of incorporated IL monomer (though it should be noted that those PILs possessed very different architectures than the thiol-ene polymers described herein) [56].

Aside from illuminating polymer features’ impacts on conductivity, VFT and WLF fits can reveal a number of other characteristics of polymer behavior. The VFT fitting parameter, B , can be used to calculate D , which is commonly named the “strength” parameter. D is inversely related to dynamic fragility, m , and together these parameters indicate the degree to which relaxation or transport properties of polymers deviate from Arrhenius behavior [28,55,56,58,62]. Correspondingly, D and m express how rapidly such properties change as T approaches T_g . In addition, strength/fragility measurements are important for determining to what extent ion mobility and polymer chain motions are decoupled [62]. In general, decoupling of polymer motion from conductivity has been defined by the difference in time scales or activation energies for polymer motion versus free ion motion [62,63], which, in single-ion conductors, corresponds to the degree of correlation between cation and anion motion. In other words, the extent of decoupling refers to the relative probabilities of a viscous flow event (polymer chain motion) and free ion motion occurring, with the latter expected to occur with a much greater probability [64]. Nonetheless, smaller values of D and larger values of m correspond to less Arrhenius-like behavior and more decoupling of conductivity from chain dynamics [56]. Data for the thiol:ene

polymers reveal D values of 7.3-9.3, which is at the upper end of the range typically reported for imidazolium-containing PILs (~3.5-9.5, although in a couple of instances, values as high as 12.5 have been reported) [28,32,33,55,56]. This result would seem to indicate a degree of chain mobility-ion transport coupling in the thiol:ene polymers that is stronger than in many other imidazolium PILs. This idea is explored further in the following discussion of dynamic fragility values.

The fitting parameters and subsequent calculated results obtained by applying WLF theory are provided in Table 5. While WLF theory is mathematically equivalent to VFT theory, WLF fitting relies on the determination of two parameters, C_1^g and C_2^g . The WLF parameters have been ascribed physical meanings with C_1^g expressing the number of decades change in relaxation time (i.e., dynamic range) as polymers pass from high temperature to T_g , and C_2^g being a parameter related to fragility of glass formation [57]. In addition, a number of properties can be directly calculated from these parameters, including: fractional free volume (f) at T_g , thermal expansion of fractional free volume (α) at T_g , apparent activation energy (E_g) at T_g , and dynamic fragility (m), all of which are discussed below [27,58]. Further details on such calculations can be found in the Supplementary data section.

Table 5: Parameters obtained by fitting temperature-dependent conductivity data to the Williams-Landel-Ferry equation.

thiol:ene molar ratio	C_1^g	C_2^g (K)	$f(T_g)$	$\alpha(T_g)$	E_g (kJ/mol)	m
1.0:1.0	9.42	66.9	0.046	6.9×10^{-4}	169.2	35.3
1.0:1.5	9.10	80.7	0.048	5.9×10^{-4}	150.9	29.8
1.0:2.0	9.34	72.2	0.047	6.4×10^{-4}	178.1	34.7
1.0:2.5	9.44	68.9	0.046	6.7×10^{-4}	167.6	34.6
1.0:3.0	9.21	67.0	0.047	7.0×10^{-4}	153.5	33.2

The values of C_1^g and C_2^g obtained for the thiol:ene polymers are consistent with values (7.5-13.4 and 39-168 K, respectively) that have been reported for other imidazolium-containing PILs [27,32]. “Universal” values of $C_1^g = 17.44$ and $C_2^g = 51.6$ K have been established by combining data from a large number of uncharged polymers into a single master regression [27], though it has been suggested that, since the polymers used were all relatively flexible and weakly interacting, the “illusion” of universality is not surprising [57]. Nonetheless, the thiol:ene polymers yielded WLF fitting parameters that clearly deviate from the “universal” values for uncharged polymers. Such a deviation has been observed with other IL-containing polymers, and was rationalized to be due to the interactions of ionic groups in the polymer chains, as well as a high free ion concentration [27].

Values of $f(T_g)$, $\alpha(T_g)$, E_g , and m for PILs have been reported sparsely in the literature. In one study of PILs containing pendant imidazolium groups [27], $f(T_g)$ values of 0.05-0.057 were reported, which are twice that of the “universal” value of 0.025 reported for uncharged polymers, which was once again related to free ion concentration and ionic group interactions. In the same paper, values of $3-4 \times 10^{-4}$ were calculated for $\alpha(T_g)$. With the thiol:ene polymers, a $f(T_g)$ range of

0.046-0.048, which is slightly less than double the “universal” value, and $\alpha(T_g)$ values of $6-7 \times 10^{-4}$ were obtained. One reason for the differences in the $f(T_g)$ and $\alpha(T_g)$ values of the thiol-ene PIL networks versus the previously-reported PILs is due to the placement of the imidazolium group in the main polymer chain (rather than as a pendant) group, which could affect factors such as chain packing and ion aggregation. Additionally, only one counteranion was employed in the present study, while 4 different anions were used in the earlier work. Thus, some of the observed differences may be attributable to variations in counteranion sizes and imidazolium-counteranion pairing.

Dynamic fragility values (m) calculated from WLF parameters were found to be between 30 and 35, while ranges of 83-115 and 57-79 have been reported for other imidazolium PILs [28,55]. The relatively low values of fragility for thiol:ene polymers are consistent with strength parameters (D) that are on the high side of the range typically observed for imidazolium PILs, as noted above. Taken together, m and D indicate that temperature-dependent ion transport behavior of these thiol:ene PIL networks is more Arrhenius-like (i.e., less curvature as $T \rightarrow T_g$), and more coupled with chain mobility, than most imidazolium-containing PILs [57]. Such observed behavior is likely due to the same polymer structural characteristics used to explain differences with other parameters, specifically the presence of the imidazolium group in the main polymer backbone and the prevalence of a covalently cross-linked network in the thiol:enes.

In the past, m has been identified as a “ T_g -normalized” activation energy and E_g , the apparent activation energy at T_g , has been proposed as an alternative parameter for evaluating polymer dynamics [58]. The thiol:ene PIL networks have E_g values of 151-178 kJ/mol. While few, if any, PIL studies have included discussions of such a parameter, the values obtained for the thiol:ene systems seem reasonable given some reports of Arrhenius activation energies

between 23 and 144 kJ/mol for ion transport in imidazolium PILs in the glassy state [32,33]. In addition, an activation energy of 170 kJ/mol has been reported for a single imidazolium PIL that displayed Arrhenius behavior across all studied temperatures (including above T_g) [33].

4. Conclusions

Thiol-ene ‘click’ photopolymerization represents a robust, rapidly curing platform for the preparation of homogeneous polymer networks. Despite the user-friendly nature of this reaction, it has yet to be fully utilized in the preparation of poly(ionic liquid)s (PILs). As a result, we report the preparation and properties of a series of novel imidazolium-containing polymer networks using thiol-ene ‘click’ photochemistry. The extent of thiol-ene polymerization was monitored by FTIR spectroscopy and DSC, and it was determined that crosslinking was sufficiently complete after UV irradiation.

The thermal, mechanical and conductive properties of the networks were measured and correlations were made with respect to crosslink density and IL content. The highest T_g value and crosslink density were observed for the thiol-ene network which employed the stoichiometric 1.0:2.0 thiol:ene molar ratio. These values were found to decrease with an excess of thiol or ene concentration as a direct result of a decrease in crosslink density. All of the thiol-ene polymer networks exhibited good thermal stability ($T_{d5\%} > 340$ °C). Impedance spectroscopy revealed that the ionic conductivities of the resulting thiol-ene networks were dependent upon the T_g /crosslink density as well as the imidazolium content. The thiol-ene network which employed the 1.0:3.0 thiol:ene molar ratio was observed to have the highest ionic conductivity (1.42×10^{-5} S/cm at 25 °C) due to the highest level of IL content and network flexibility.

All parameters determined from VFT and WLF fitting of conductivity data deviate from what has been obtained for uncharged polymers but are consistently within the range of what has been reported for other imidazolium-containing PILs. Trends among the VFT fitting parameters T_o and σ_o reveal that thiol-ene PIL conductivity is governed primarily by T_g /crosslink density at lower temperature, with a crossover to %IL-controlled conductivity at higher temperature. Fragilities and free volumes calculated from WLF fitting parameters are generally smaller than observed with most PILs, which is likely due to the placement of the imidazolium within the polymer and the prevalence of cross-linking in the material. This observation may also point to reduced ionic aggregation in the thiol-ene networks relative to other PILs, though this possibility would clearly require further study.

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Appendix A. Supplementary Data

^1H and ^{13}C NMR spectra (Figures S1-S2), log conductivity data for all thiol-ene polymer network specimens at three different time intervals (Tables S1-S5), a snapshot of the apparatus used to determine thiol-ene film ionic conductivities (Figure S3) and the ionic conductivity curve

for 1,3-diallylimidazolium [NTf₂] **2** (Figure S4). A description of the VFT and WLF conductivity curve fittings as well as fitted ionic conductivity curves (Figures S5 and S6) are included.

References

- [1] C. E. Hoyle, T. Y. Lee, T. Roper. *J. Polym. Sci. A, Polym. Chem.* 42 (21) (2004) 5301-5338.
- [2] C. E. Hoyle, C. N. Bowman. *Angew. Chem. Int. Ed.* 49 (9) (2010) 1540-1573.
- [3] A. B. Lowe. *Polym. Chem.* 1 (2010) 17-36.
- [4] C. E. Hoyle, A. B. Lowe, C. N. Bowman. *Chem. Soc. Rev.* 39 (4) (2010) 1355-1387.
- [5] A. B. Lowe. *Polym. Chem.* 5 (2014) 4820-4870.
- [6] L. M. Campos, I. Meinel, R.G. Guino, M. Schierhorn, N. Gupta, G. D. Stucky, C. J. Hawker. *Adv. Mater.* 20 (19) (2008) 3728-3733.
- [7] J. F. Ashley, N. B. Cramer, R. H. Cramer, C. N. Bowman. *Lab Chip* 11 (16) (2011) 2772-2778.
- [8] H. Lin, X. Wan, X. Jiang, Q. Wang, J. Yin. *J. Mater. Chem.* 22 (2012) 2616-2623.
- [9] K. Shanmuganathan, R. K. Sankhagowit, P. Iyer, C. J. Ellison. *Chem. Mater.* 23 (2011) 4726-732.
- [10] K. Shanmuganathan, S. M. Elliot, A. P. Lane, C. J. Ellison. *ACS Appl. Mater. Interfaces* 6 (16) (2014) 14259-14265.
- [11] L. Kwisnek, S. Nazarenko, C. E. Hoyle. *Macromolecules* 42 (18) (2009) 7031-7041.
- [12] L. Kwisnek, M. Kaushik, C. E. Hoyle, S. Nazarenko. *Macromolecules* 43 (8) (2010) 3859-3867.
- [13] L. Kwisnek, S. R. Heinz, J. S. Wiggins, S. Nazarenko. *J. Membrane Sci.* 369 (2) (2011) 429-436.
- [14] L. Kwisnek, J. Goetz, K. P. Meyers, S. R. Heinz, J. S. Wiggins, S. Nazarenko. *Macromolecules* 47 (10) (2014) 3243-3253.
- [15] C. N. Walker, C. Versek, M. Touminen, G. N. Tew. *ACS Macro. Lett.* 1 (2012) 737-741.

- [16] M. D. Green, T. E. Long. *Polym. Rev.* 49 (4) (2009) 291-314.
- [17] O. Green, S. Grubjesic, S. Lee. *Polym. Rev.* 49 (4) (2009) 339-360.
- [18] J. Yuan, D. Mecerreyes, M. Antonetti. *Prog. Polym. Sci.* 38 (7) (2013) 1009-1036.
- [19] J. Yuan, M. Antonetti. *Polymer* 52 (7) (2011) 1469-1482.
- [20] D. Mecerreyes. *Prog. Polym. Sci.* 36 (12) (2011) 1629-1648.
- [21] A. S. Shaplov, R. Marcilla, D. Mecerreyes. *Electrochimica Acta* 175 (2015) 18-34.
- [22] H. Ohno, M. Yoshizawa, W. Ogihara. *Electrochimica Acta* 50 (2004) 255-261.
- [23] S. Washiro, M. Yoshizawa, H. Nakajima, H. Ohno. *Polymer* 45 (5) 1577-1782.
- [24] H. Nakajima, H. Ohno. *Polymer* 46 (25) (2005) 11499-11504.
- [25] H. Chen, J. Choi, D. Salas-de la Cruz, K. I. Winey, Y. A. Elabd. *Macromolecules* 42 (13) (2009) 4809-4816.
- [26] M. D. Green, D. Sala-de la Cruz, Y. Ye, J. M. Layman, Y. A. Elabd, K. I. Winey, T. E. Long. *Macromol. Chem. Phys.* 212 (23) (2011) 2522-2528.
- [27] Y. Ye, Y. A. Elabd. *Polymer* 52 (5) (2011) 1309-1317.
- [28] U. H. Choi, M. Lee, S. Wang, W. Liu, K. I. Winey, H. W. Gibson, R. H. Colby. *Macromolecules* 45 (9) (2012) 3974-3985.
- [29] D. Salas-de la Cruz, M. D. Green, Y. Ye, Y. A. Elabd, T. E. Long, K. I. Winey. *Polym. Phys.* 50 (5) (2012) 338-346.
- [30] Y. Ye, J. Choi, K. I. Winey, Y. A. Elabd. *Macromolecules* 45 (17) (2012) 7027-7035.
- [31] J. Choi, Y. Ye, Y. A. Elabd, K. I. Winey. *Macromolecules* 46 (13) (2013) 5290-5300.
- [32] U. H. Choi, Y. Ye, D. Salas-de la Cruz, W. Liu, K. I. Winey, Y. A. Elabd, J. Runt, R. H. Colby. *Macromolecules* 47 (2) (2014) 777-790.
- [33] C. Jangu, J. H. Wang, D. Wang, S. Sharick, J. R. Heflin, K. I. Winey, R. H. Colby, T. E. Long. *Macromol. Chem. Phys.* 215 (13) (2014) 1319-1331.
- [34] K. M. Meek, S. Sharick, Y. Ye, K. I. Winey, Y. A. Elabd. *Macromolecules* 48 (14) (2015) 4850-4862.
- [35] M. D. Green, D. Wang, S. T. Hemp, J. Choi, K. I. Winey, J. R. Heflin, T. E. Long. *Polymer* 53 (17) (2012) 3677-3686.

- [36] M. Lee, U. H. Choi, D. Salas-de la Cruz, A. Mittal, K. I. Winey, R. H. Colby, H. W. Gibson. *Adv. Funct. Mater.* 21 (4) (2011) 708-717.
- [37] R. Gao, M. Zhang, S. Wang, R. B. Moore, R. H. Colby, T. E. Long. *Macromol. Chem. Phys.* 214 (9) (2013) 1027-1036.
- [38] S. R. Williams, W. Wang, K. I. Winey, T. E. Long. *Macromolecules* 41 (23) (2008) 9071-9079.
- [39] R. P. Dmitrov, S. Beghdadi, A. Serghei, E. J. Drockenmuller, *Polym. Sci. A. Polym. Chem.* 51 (2013) 34-38.
- [40] B. P. Mudraboyina, M. M. Obadia, I. Allaoua, R. Sood, A. Serghei, E. Drockenmuller. *Chem. Mater.* 26 (4) (2014) 1720-1726.
- [41] G. Collait-Dangus, M. M. Obadia, Y. S. Vygodskii, A. Serghei, A. S. Shaplov, E. Drockenmuller. *Polym. Chem.* 6 (23) (2015) 4299-4308.
- [42] S. Kim, K. M. Miller. *Polymer* 53 (25) (2012) 5666-5674.
- [43] C. P. Whittington, L. A. Daily, K. M. Miller, *Polymer* 55 (16) (2014) 3320-3329.
- [44] A. T. De La Hoz, K. M. Miller. *Polymer* 72 (2015) 1-9.
- [45] M. Taghavikish, S. Subianto, N. K. Dutta, N. R. Choudhury. *ACS Appl. Mater. Interfaces* 7 (31) (2015) 17298-17306.
- [46] A. S. Shaplov, E. I. Lozinskaya, D. O. Ponkratov, I. A. Malyshkina, F. Vida, P. H. Aubert, O. V. Okatova, G. M. Pavlov, L. I. Komarova, C. Wandrey, Y. S. Vygodskii. *Electrochimica Acta* 57 (2011) 74-90.
- [47] M. Toure, O. Chuzel, J. Parrain. *J. Am. Chem. Soc.* 134 (43) (2012) 17892-17895.
- [48] L. A. Link, A. T. Lonnecker, K. Hearon, C. A. Maher, J. E. Raymond, K. L. Wooley. 6 (20) (2014) 17370-17375.
- [49] G. Yang, S. L. Kristufek, L. A. Link, K. L. Wooley, M. L. Robertson. *Macromolecules* 48 (23) (2015) 8418-8427.
- [50] C. Villagran, M. Deetlefs, W. R. Pitner, C. Hardacre. *Anal. Chem.* 76 (7) (2004) 2118-2123.
- [51] B.D. Mather, K.M. Miller, T.E. Long. *Macromol Chem Phys* 207 (2006) 1324-1333.
- [52] Q. Li, H. Zhou, D. A. Wicks, C. E. Hoyle. *J. Polym. Sci. Part A: Polym. Chem.* 45 (22) (2007) 5103-5111.
- [53] P. J. Flory, *Principles of Polymer Chemistry* Cornell University Press, Ithaca, 1953

- [54] K. Fukumoto, M. Yoshizawa, H. Ohno. *J. Am. Chem. Soc.* 127 (8) (2005) 2398-2399.
- [55] U. H. Choi, L. R. Middleton, M. Soccio, C. F. Buitrago, B. S. Aitken, H. Masser, K. B. Wagener, K. I. Winey, J. Runt. *Macromolecules* 48 (2) (2015) 410-420.
- [56] C. M. Evans, G. E. Sanoja, B. C. Popere, R. A. Segalman. *Macromolecules* 49 (1) (2016) 395-404.
- [57] J. Dudowicz, J. F. Douglas, K. F. Freed. *J. Chem. Phys.* 142 (1) (2015) 014905.
- [58] Q. Qin, G. B. McKenna. *J. Non-Cryst. Solids* 352 (28) (2006) 2977-2985.
- [59] I. Abdelhedi-Miladi, M. M. Obadia, I. Allaoua, A. Serghei, H. B. Rondhane, E. Drockenmuller. *Macromol. Chem. Phys.* 215 (22) (2014) 2229-2236.
- [60] M. M. Obadia, G. Colliat-Dangus, A. Debuigne, A. Serghei, C. Detrembleur, E. Drockenmuller. *Chem. Commun.* 51 (16) (2015) 3332-3335.
- [61] M. M. Obadia, B. P. Mudraboyina, I. Allaoua, A. Haddane, D. Montarnal, A. Serghei, E. Drockenmuller. *Macromol. Rapid Commun.* 35 (8) (2014) 794-800.
- [62] T. K. L. Nguyen, M. M. Obadia, A. Serghei, S. Levi, J. Duchet-Rumeau, E. Drockenmuller. *Macromol. Rapid Commun.* (2016) DOI: 10.1002/marc.201600018.
- [63] Z. Wonarowska, J. Knapik, J. Jacquernin, S. Berdzinski, V. Strehmel, J. R. Sangoro, M. Paluch. *Macromolecules* 48 (23) (2015) 8660-8666.
- [64] W. Xu, E. J. Cooper, C. A. Angell. *J. Phys. Chem. B* 107 (25) (2003) 6170-6178.
- [65] M. Videa, C. A. Angell. *J. Phys. Chem. B* 103 (20) (1999) 4185-4190.

Table of Contents Graphic

Thermal, Mechanical and Conductive Properties of Imidazolium-Containing Thiol-ene Poly(Ionic Liquid) Networks.

Taylor C. Rhoades, James C. Wistrom, R. Daniel Johnson and Kevin M. Miller*